Abstract-Thermionic Vacuum Arc (TVA) is a new technology for thin film deposition. This technology has been supplied great advantages to growth thin films like compact, low roughness, nanostructures, homogeneities, adhesive, high deposition rate etc. A lot of materials were used for thin films production and characterization. TVA technology is gives ability to growth pure thin films and alloys thin films. Biggest application of TVA is thin films of high melting point materials like C, W, Mo, Nb, Ta, Re, B etc. Also, TVA cans ability to growth thin films for photovoltaic applications and optoelectronic materials.

TVA is a new technology for pure thin film deposition. TVA has different properties of other vacuum thin films technologies. Some differences and advantages of TVA are summarized in following [1-2];

- not need a buffer gas and gas mixing for ignition the plasma,
- thin films produces with high energetic ions,
- high refractivity for metallic thin films,
- plastic and texture were coated,
- low melting materials as polymers can be coated,
- optical devices as mirror, lenses can be coated with refractory materials,
- in-situ and ex-situ deposition will be realized this technique with any deformations,
- semiconductor, insulator, refractory materials and dielectric thin films can be growth in amorphous and crystal structure,

Produced thin films are in high purity, compact, homogeneous, nanostructures, high adherence, low roughness, low contamination, low stress, high deposition rate and etc [1-2].

Experimental arrangement of TVA was shown in Figure 1.

![Figure 1. Experimental arrangement](image1)

TVA has double electrodes. Cathode is a special electron gun which changeable to desire options. Anode is made from refractor materials like wolfram, Molybdenum, Tantalum and Carbon. Voltage-current graph of pure carbon plasma was shown in Figure 2. Pure carbon plasmas were generated with filament currents of 56 A and 70 A. As soon as generated a plasma in vacuum chamber, applied voltages were drop suddenly.

![Figure 2. Voltage-currents graphs of pure carbon plasma](image2)

SEM and TEM images of DLC (Diamond Like Carbon) thin films were shown in fig.3, respectively.

![Figure 3. (a) SEM, (b) TEM images of DLC thin films.](image3)

Fig.4 AFM images of DLC thin film

![Figure 4. is AFM images of DLC thin film.](image4)

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Optical properties of AlN Thin Films Deposited by RF Reactive Sputtering

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Abstract—Optical properties of deposited AlN thin films were investigated by measuring the transmittance spectra. Transparencies of the deposited AlN films at x=0.4 and 0.3 shown highest transparency concentrations were exhibit approximately ~100% in weak absorption and near visible and near infrared regions. Additionally, XRD and AFM measurements were investigated.

Aluminum nitride (AlN) thin films with wurzite hexagonal structure have received great interest because of its excellent physical properties like thermal conductivity (3.2 W/mK), chemical stability, high hardness, high acoustic velocity, large electromechanical coupling coefficient and a wide band gap (5.8-6.2 eV). AlN thin films are promising candidate for electronic material for thermal dissipation, dielectric and passivation layers, surface acoustic wave (SAW) devices and photoelectric devices [1-14]. For these applications, AlN thin films deposition and characterization are very important. As an optical material, it is important to understand its fundamental optical properties. But, the optical constants of AlN thin film are still unclear [1, 10-13].

These methods were shown the optical parameters like transmittances, absorbance, reflection, reflection index, extinction coefficient, bang bap, reel dielectric; imaginary dielectric constants were determined by using Uv-Vis spectrophotometers (200-1100nm). Transmittance values are deposited AlN thin films at x=0.4 and 0.3 (x value corresponds the nitrogen concentrations of Ar-N2 mixed gas plasma) were shown in fig.1 where these values were compared with transparency of reference glass slide (RGS) in fig.1.

As can be seen from fig.1, transmittance spectra of deposited thin films is higher than the reference glass slides (RGS) in near infrared region. Incident lights is describing following:

\[ A + T + R + S = 1 \]

According to the relation, A+R+S is very lower. That is, any loss were not seen to our measurements in near infrared region. This properties is most important parameter of infrared telescope, thermal camera and night-vision system and detectors. Refractive index is define following equations;

\[ n = n_o + iK \]

where, \( n_o \) is a reel part of refractive index. \( K \) is the extinction coefficient of deposited thin films. According to our measurements, \( n_o \) was lower from 1.40 and extinction coefficient is approximately 0.17. deposited thin films refractive index lower from the RGS, which this properties is most wanted properties of optical coatings. Additionally K value is proportional to transparency.

AFM images of deposited AlN thin films was seen in Figure 2.

Figure 1. Transmittance spectra of x=0.4, 0.3 and RGS

Figure 2. AFM image of deposited AlN thin films (given in example)

Rms roughness of the thin films decreased from 60.20 nm to 12.50 nm. Grain size of deposited thin films were approximately 260nm.

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The interaction of C_{60} with solvent molecules
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Abstract—Carbon nanopeapods are the best examples of how the empty space inside the carbon nanotubes can be used for obtaining new hybrid systems with new physical and chemical properties. Since the walls of the carbon nanotubes are inert and robust, these nanometer-sized cylindrical systems are the smallest test tubes. Recently, guest molecules were successfully encapsulated inside the carbon nanotubes using wet-chemistry reactions instead of earlier gas-phase formation methods. These new in-solution methods bring new questions about the detailed formation mechanism, and the purity of the final products. In order to gain insight about the in-solution encapsulation of C_{60} molecules inside the carbon nanotubes, we have investigated the interaction of the carbon nanotubes and C_{60} molecules with solvent molecules. The relative adsorption energies are used to propose a microscopic understanding for the in-solution encapsulation process, and the stability of the carbon nanopeapods.

The hollow core of a carbon nanotube[1,2] provide a one dimensional nanometer-scale container with chemically inert and robust walls. This inner space could be filled with other molecules to obtain hybrid nanostructures with desired physical and chemical properties. As one of the most prominent example of such a hybrid system, carbon nanopeapods [3] are formed by the encapsulation of C_{60} molecules inside single wall carbon nanotubes. The earlier attempts of encapsulating guest molecules inside carbon nanotubes involve a gas-phase reaction that required the guest molecule to be stable in gas phase, and evaporating or subliming. Such reactions can occur in solution using wet-chemistry techniques [4]. This broadens the range of molecules that can be encapsulated inside the carbon nanotubes. In addition, a part of a chemical reaction may be initiated inside the carbon nanotube that is otherwise not possible. The success of such reactions depend on the relative interaction strength between the encapsulating molecule and the solvent molecules. The purity of the final product is affected by how the encapsulation process is exactly proceeds [5]. Note that investigating any fullerene solution one encounters the problem of describing cluster formation. Therefore, the interaction between the nanocarbons and the solvent molecules are crucial for microscopic understanding of the encapsulation.

Figure 1: The atomic and electronic structure of a toluene molecule adsorbed on a C60 fullerene. The equilibrium atomic structure is depicted as a ball-and-stick model in the left panel. In the right panel, the electronic density is presented as a color-coded contour plot of the fullerene. The atomic positions of the atoms that are in front of the contour plane are depicted for guide to eye.

Here, we aim to gain insight for understanding the formation of carbon nanopeapods in the solution. Thus, we use density functional theory calculations for the investigations of carbon nanotubes and C_{60} fullerenes with the solvent molecules of toluene, water, and some alcohols. Since our Hamiltonian is based on the electronic structure, we also obtained the modifications in the electronic structure by the solvent contamination.

We perform ab initio structure optimization and total energy calculations using the density functional theory. The exchange-correlation interaction is treated at the local density approximation (LDA) level in the Perdew-Zunger parametrization, as implemented in the SIESTA code. A double-$\zeta$ basis set augmented by polarization orbitals is employed for expanding the wave functions. The interaction between the core and valence electrons were handled by norm-conserving pseudopotentials.

We first obtain the optimized positions for the solvent molecules on the C_{60} fullerene. The atomic structure of a toluene molecule, which is widely used for recovering fullerenes from fullerene soot and for studying various fullerene-containing systems, on a C_{60} fullerene is depicted as a ball-and-stick model in the left panel of Figure 1. Although the optimized atomic structure does not show large structural changes, the interaction between the fullerene and the toluene molecule is apparent in the charge density that is shown in the right panel of Figure 1. The interaction between the toluene and the fullerene is not through a covalent bond. However, there is a considerable charge density overlap between the sub-systems.

The adsorption energies are calculated for solvent molecules of toluene, water, and some alcohols. We find that the adsorption energies for single molecules are of the order of an eV. We compare these energies with the fullerene-fullerene interaction to gain insight about the clustering tendency of fullerenes inside these solvents. The relative strength of fullerene-fullerene, fullerene-nanotube, and fullerene-solvent molecule interaction energies are used to determine the possibility of solvent contamination during the synthesis of carbon nanopeapods in a wet-chemistry reaction. The basis set superposition errors (BSSE) are eliminated by a counter-poise method. Some key parameters for determining the best solvent for an efficient in-solution carbon nanopeapod formation are proposed. The energy gaps are dominated by the energy gap of the C60 fullerene, albeit with small changes. Calculated electronic density of states of a fullerene molecule interacting with solvent molecules are used to determine the impurity levels that appear between the energy levels of a pristine C_{60} fullerene.

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Self-Assembled Molecular Nanowires:
A Test Case for Bioinspired Supramolecular Electronic Elements

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Abstract—We demonstrate a comprehensive study of self-assembled molecular nanowire formations of modified chlorin systems on a range of surfaces. Detailed atomic force microscopy (AFM) studies reveal the formation of well-ordered π-stacked chlorin rod aggregates on highly ordered pyrolytic graphite (HOPG). The advantages of such assemblies over previously reported comparable self-assembled systems are single stack formation and highly robust structural order so that even after weeks the rod-shaped structures are very stable. These structures are presently being characterized using various methods of microscopy and in particular for their electronic properties like conductivity, photoconductivity etc.

The construction of highly ordered supramolecular architectures in which metallochlorin molecules are organized on surfaces across multiple length scales can represent a key issue within the fast-growing field of supramolecular electronics. In this context, self-assembly appears as an attractive and efficient bottom-up approach for the construction of such molecular systems where enhanced electrical properties are sought, as it allows the preparation of complex functional systems through the use of weak, noncovalent interactions. One of the most promising methods for the construction of these supramolecular assemblies relies on the self-organization ability of π-conjugated systems, as demonstrated for the light-harvesting rod-shaped antennae in the chlorosomes of green phototrophic bacteria (Fig. 1) [1-4].

The focus of this study is the construction of highly ordered π-stacks of zinc aminochlorins (Fig. 2, 3) on solid substrate surfaces to achieve bioinspired materials that are of interest as (semi)conductive 1D wires for supramolecular electronics [5-7]. Up to now, the formation of ordered π-stacks of biomimetic zinc chlorins has only been reported by Huber et al. [6]. However, the most significant structural difference for zinc aminochlorins can be easily noticed, the presence of amino functional groups in 31-position instead of hydroxyl group (Fig. 2). The reason of preparation of such compounds is based on that idea, it would form as highly robust, single stack rod structures probably due to the fact that amino ligands coordinate to the central metal more strongly than oxygen ligands [8] (Fig. 2). Thus, even after days the rod-shaped structures would be remaining very stable. This would be one of the important advantages of such metallochlorin assemblies over previously reported comparable chlorins systems. The investigation of well-ordered stacks of zinc aminochlorins was achieved by AFM. A freshly prepared solution of zinc aminochlorins in different solvent mixtures was deposited by a drop-casting or spin-coating technique on HOPG and allowed to evaporate. AFM studies revealed the formation of rod-like structures in different lengths from nanometer to micrometer scales (Fig. 3). The height, width and density of the structures, as expected, being strongly dependent on the concentration of the drop-cast solution and also applied method.

As seen from the images, it is also possible to run across a junction point formations between two aggregate structures (Fig. 3). This result also would be explained the existing of -NH2 functional groups. The difference between the aggregate shapes may be due to hydrogen bond formation between two rod structures that formed by repeated tetramer units of 31-amino functionalized zinc chlorins (Fig. 4). Possibly the 31-NH group forms hydrogen bridges to the 13-keto group and thus can extend dimers to higher aggregates [8].

In conclusion, self-assembled rod structured of semi synthetic zinc chlorins have been prepared by simple solution-processing steps on graphite substrates. The preparation of highly ordered, easy-to-assemble supramolecular nanostructures on graphitic surfaces is extremely promising. These nanostructures would also be electrically characterized by a conductive-AFM technique. The technique may lead to molecular materials with possible applications in the fields of nano-optoelectronics and photovoltaics.

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A Physically Intuitive Model for Nanotube Growth Process
Ali Zerentürk*, Savaş Berber

Abstract — We propose a model for the growth of both carbon and non-carbon nanotubes. Our model is based on the formation of atomic chains before the growth of nanotubes. It is predicted that the existence of a nanotube with formula X,Y, (X,Y = any element) highly depends on the existence of linear atomic chain with the same formula. Furthermore, the analysis of molecular dynamics calculations show that tubular arrangement of chains and the angle between the chains and nanotube growth direction are the other factors that determine the final structure. We seek the possibility of using pre-grown nanotubes as a template for further growth process. In this templating process, we classified the situations for continuing with the same chirality and for changing the chirality. By following the rules of our model, we achieved continuing with the same chirality and changing the chirality for making junctions of armchair and zigzag nanotubes. By applying the determined rules to non-carbon nanotubes, we successfully obtained a boron carbide nanotube and obtained a clear understanding why Si nanotubes do not exist.

Carbon nanotubes are one of the most famous members of nanoworld whose physical and chemical properties changes drastically with the size and the chirality. For technological applications, it is crucial to grow nanotubes with desired size and chirality. This selective growth procedure is probably the most challenging problem of carbon nanotechnology. Namely, the question of “In which growth condition can we have a semiconductor nanotube or a metallic tube, or a nanotube junction?” remains unanswered up to now. Therefore, various researchers have studied the nanotube formation computationally for a better understanding of what really happens during the growth process [1]. The most common method used in molecular dynamics calculations is growing nanotubes atom by atom [2]. However, this method is very expensive in terms of computational sources. Instead, in this study, we proposed a simple, physically intuitive and computationally cheaper method for obtaining a good understanding of the selective growth process, and we carried out some ab initio and Terhov force-field molecular dynamics calculations. In ab initio molecular dynamics calculations, the exchange-correlation interaction is treated at the local density approximation (LDA) level in the Perdew-Zunger parametrization, as implemented in the SIESTA code. A single-ζ basis set is employed for expanding the wave functions. The interaction between the core and valence electrons were handled by norm-conserving pseudopotentials.

Carbon chain molecules are well known to be found in circumstellar atmosphere of carbon-rich stars and due to their elevated temperatures[3]. Furthermore in the laboratory, laser vaporization of graphite leads to the formation of long carbon chains. These two observations inform us that when a carbonaceous structure becomes hot the first thing to happen is the formation of atomic chain molecules. The lifetime of chains is long enough to recognize that it is the first stage in the growth process of sp2 hybridized carbon nanostructures. Therefore, we begun our simulations from already formed atomic chains.

In our proposed model, there are three stages for the nanotube growth. The first stage is the formation of linear atomic chains, and can be controlled by temperature and external electric field. The second stage is tubular arrangement of chains. We think that the catalyst play a role at this stage in real experiments. The third stage is the alignment of chains to the growth direction. This stage can be controlled by an external electric field, and it has a crucial importance in determining the chirality of the nanotubes. For growing armchair nanotubes, the chains must be aligned parallel to the growth direction, while for growing zigzag nanotubes a small misalignment (~10°) from the growth direction is needed. By applying these rules, and by using a pre-grown (5,5) armchair nanotube, we obtained a junction of armchair-zigzag nanotubes in ab initio molecular dynamics calculations, as shown in Figure 1.

The described method in this study is general and applicable to non-carbon nanotubes. It gives a clear insight why silicon nanotubes don’t exist. The reason is that linear atomic chain of silicon is not stable and transform to a structure that is 3 dimensional. On the other hand, boron carbide atomic chain is found to be stable in the linear form, and thus boron carbide nanotube is predicted to exist and to be stable.

In summary, we have shown that the formation of atomic chains highly enhance the growth of nanotubes. Therefore, it is reasonable to think that the atomic chain formation is the first step in the growth process of nanotubes. We classified which initial structure gives which specific nanotubes, and then by considering a suitable external field that can orient the atomic chains to the desired orientation, we determine some growth rules for nanotube growth.

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Photoelectron Diffraction Studies on Different Thickness L10 PtCo Epitaxy Thin Films

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Abstract- L10 PtCo epitaxy thin films were grown on Pt (111) single crystal by magnetron sputtering deposition. The thickness of films varies from 20 Å to 100 Å by 20 Å steps. The crystal structure changes with thickness of the films were determined by photoelectron diffraction.

PtCo equiatomic composition is called L10 phase. L10 phase materials (FePd, FePt, MnAl) have attracted much attention because of large magnetocrystalline anisotropy. Magnetocrystalline anisotropy constant of PtCo with L10 phase is about twenty times larger than that of pure cobalt [1]. PtCo films usually have disordered face centered cubic (FCC) structure. In general, high-temperature annealing above 500 °C is necessary to transform the disordered FCC phase to the L10 phase. The L10 phase materials (CoPt, MnAl, FePd, FePt etc.) have face centered tetragonal crystal (FCT) structure (Figure 1).

Figure 1. The L10 PtCo crystal structure [2]

Photoelectron diffraction (PD) is based on X Ray Photoelectron Spectroscopy (XPS) technique. XPS and PD are very powerful techniques to investigate the fundamental characteristics of the surface such as the composition, the chemical state of electrons on the surface, the structural sites of surface atoms, and the electronic structure of surface layers. PD and XPS give information in the range of nanometer units; therefore these techniques clarify the details of many problems in nanotechnology [3].

In this work, PtCo epitaxy films were prepared at UHV conditions by magnetron sputtering deposition using co-sputtering from two metallic targets of cobalt and platinum. We prepared L10 PtCo film from 20 Å to 100 Å by 20 Å steps on Pt (111) substrate. During deposition the substrate was hold at 700 °C. After growing process, XPS was used to determine sticometries of the films.

The crystal structure of surface layers was determined by Low Energy Electron Diffraction (LEED). LEED gives only surface symmetry of the films that are epitaxy. Figure 2 shows two LEED pictures, the one on the left picture shows the surface symmetry of Pt (111) and the one on the right picture shows the surface symmetry after 100 Å L10 PtCo sequential deposition.

Figure 2. Left: the LEED picture of Pt (111). Right: the LEED picture of 100 Å L10 PtCo.

The LEED results by itself are not enough to prove that structure is epitaxy so we need PD results. For the PD experiment the reference axis is determined by LEED pictures. PD gives not only the surface crystal structure but also crystal structure of 10 nm thickness within surface. In order to modeling experimental PD results, we used Multiple Scattering Calculation of Diffraction (MSCD) program by developed M.A.Van Hove [4].

The experimental XPD results are presented in Figure 3. In this figure, circles denotes the area values at each polar angles for Pt (111) (black color) and average value of both Pt and Co PD results from 100 Å L10 PtCo film (red color). When two graphs are compared one can see the similar behavior for the same polar angles. This results support that grown films are epitaxial on Pt (111). Since MSCD work is still in progress, the theoretical results will not be included here. After MSCD results magnetic properties such as magnetocrystalline anisotropy, total magnetization and magnetic anisotropy will be investigated.

Figure 3. The experimental polar XPD results for Pt (111) (black colour) and 100 Å L10 PtCo film (red colour).

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Abstract-In this study Al thin film layer thickness and existence of Al$_2$O$_3$ layer effects on the carbon nanotubes (CNTs) grown by chemical vapor deposition method was studied. We observe that increasing Al thickness yield CNT with larger diameters and Al$_2$O$_3$ presence provide thicker CNTs. The difference between CNTs diameters obtained with and without Al$_2$O$_3$ layer presence was about 3 nm. Our study suggests that Al$_2$O$_3$ layer do not have to be on the Fe interface to have efficient CNT growth.

For the CNT growth by chemical vapor deposition (CVD) nano-sized catalyst particles are needed. These catalyst particles can be obtained by thermal pre-treatment of thin metallic films [1] or by some chemical synthesis methods [2]. Most widely used catalyst thin film in recent literature is Fe thin film grown on Si/SiO$_2$/Al$_2$O$_3$ structure by various deposition techniques [3]. Other transition metals (TM) such as Co and Ni can also be used with this structure for CNT growth. The role of the oxide buffer in this structure is to prevent slicide formation and to provide a surface for coalescence of metal film to form nanoparticles. On the other hand, if the interaction between TM film and the buffer is too strong nanoparticles cannot form at reasonable pretreatment conditions.

Most of the researchers report that Al$_2$O$_3$ is the critical material which provides well-aligned and high density CNT growth [4]. The role of the Al$_2$O$_3$ buffer layer is not completely known yet. It is to prevent Fe to coalesce easily by providing stronger interaction compare to that with SiO$_2$ alone. This way, the formed catalyst remains small with narrow diameter distribution which leads to dense CNT growth. Some research reports suggest that the Al$_2$O$_3$ provide efficient CNT growth by catalyzing hydrocarbon while presenting ideal support surface [5]. Some other reports question the catalyzing properties of Al$_2$O$_3$ buffer [6] Al has been studied as a buffer for CNT growth in the past. These studies concluded that Al buffer layer prevented the CNT growth [7].

With this study, we investigate the effects of Al and Al/Al$_2$O$_3$ buffer layers and the effect of Al layer thickness on CNT growth by CVD method. We also examine the growth conditions yielding optimized CNT growth on these buffer layers.

First, we obtain a SiO$_2$ layer of about 200 nm thickness on commercially purchased Si (100) wafers by thermal (dry) oxidation for 2 hours at 1000 °C. Then these oxidized films were used to deposit Al films with two different thickness ranges by thermal evaporation. The first one was in the range of 60-70 nm and the other one was in the range of 70-80 nm in thickness. In the other step the film was oxidized again for 2 hours at 500 °C, followed by 1 nm Fe growth by magnetron sputtering technique. Some of the films oxidized using thermal oxidation technique for 2 hours at 500°C, and the others were kept as is without oxidation. CNTs for all types of catalyst films were grown by CVD method at atmospheric pressure and at 750°C temperature under 150 sccm Ar flow. Carbon precursor was ethylene. Ethylene was used at two different flow rates. The other growth parameter was CO$_2$. Experiments were made with and without CO$_2$. For pretreatment process 10 sccm CO$_2$ and for growth 4 sccm CO$_2$ was used. The system was cooled to room temperature under 150 sccm Ar flow after the growth process.

We analyzed our sample thicknesses with a profilometer, and in order to examine the crystal structures of the films we used X-ray diffraction (XRD). We also analyzed the morphology of the samples by scanning electron microscopy (SEM). After growth, as-grown CNTs were also analyzed with SEM. Their average diameter and length determined by SEM pictures.

In this study, firstly, we investigated Al thickness and particle size. After thermal oxidation of Al thin films, the crystallinity and structure of the films were analyzed 0-20 scans and reflectivity measurements, respectively, with XRD. To obtain layer structure and the roughness of the layers the data fitted using x'pert reflectivity program. We found that samples had thin Al$_2$O$_3$ layer of about 1 nm thickness. Studying Al thickness we saw that when Al thickness increased from the range of 60-70 nm to the range of 70-80 nm, the CNTs diameter also increased, and average diameter changed from 22 nm to 32 nm. The SEM image of one of the samples after CNT growth is shown in Fig. 1. The sample was grown over the Fe/Al/SiO$_2$/Si substrate structure for 15 min resulted in dense aligned CNT growth.

Figure 1. SEM picture of (CNT605) CNT grown on Si/SiO2/Al/Fe film. Scale bar: 5 μm.

In summary, we showed that Al gives rise to well-aligned CNT growth. On the other hand, there is an optimal Al thickness for high quality CNT growth; with increasing Al thickness, CNTs diameter also increases.

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AR Coating of Organic Substrates by Thermionic Vacuum Arc Technique (TVA)

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Abstract—Antireflective or anti-reflection (AR) coatings are a type of optical coating applied to the surface of lenses and other optical devices to reduce reflection. This improves the efficiency of the system since less light is lost. In this study, organic substrates were coated with SiO2 and ZrO2 and transmittances were determined by UV-Vis spectrophotometer. Additionally, SEM, EDX, AFM were used for surface morphologies.

Thermionic Vacuum Arc (TVA) system is a new type discharge for pure thin film deposition. This discharge in pure metal vapors can be ignited in any kind of metal vapors including refractory metals. The electrons emitted from the cathode are accelerated toward the anode by the applied voltage across the electrodes, the flux of electrons being concentrated on a small area of the anode surface which becomes a melted metal spot [1-4].

In this work, SiO2, ZrO2 layers were deposited on the organic substrates by TVA.

Figure 1. Transmission of the SiO2 and ZrO2 coated organic substrate

Figure 2. AFM image (3D) of SiO2 coated organic substrate

Figure 3. AFM image (3D) of ZrO2 coated organic substrate

Table 1. EDX measurements of SiO2 coated substrate

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UV spectra, AFM and SEM measurements of SiO2 and ZrO2 coated substrates were analyzed.

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Some Optical Properties of MgF₂ Thin Films Deposited by Thermoionic Vacuum Arc (TVA)

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Abstract—Magnesium Fluoride (MgF₂) is widely used as a material for optical thin film for the wavelength of visible region. MgF₂ thin films were prepared by thermoionic vacuum arc (TVA) on glass substrates. TVA is a new type deposition method using a combination of anodic arc and electron gun system for the synthesis of thin films from solid precursors under vacuum of 10⁻⁵ Torr. In our study, some optical properties of MgF₂ thin films were determined and AFM images were used to determine surface morphology of produced MgF₂ thin films.

Antireflection coatings usually consist of a combination of materials with different refractive indices. An ultra low refractive index is very advantageous when one designs antireflection coating [1]. Magnesium difluoride (MgF₂) has been extensively used as an antireflection coating material due to its high transmittance in a wide wavelength range. Nevertheless, the optical and structural qualities of MgF₂ films still need to be improved [2]. One of the remarkable properties of MgF₂ is that the refractive index of 1.38 is lower than that of other materials [3].

Thermionic Vacuum Arc (TVA) has a simple construction; the filament surrounded by a Wehnelt cylinder and the anode - an adequate crucible containing the material necessary to generate the vapors. At the application of a high dc voltage over the electrodes, the accelerated electrons incident on the anode, heats the anode material which first melts and afterwards starts to boil and evaporate. A steady state concentration of the anode material’s atoms is established in the interelectrode space. At a further increase of the applied high voltage, in vacuum conditions, a bright Thermionic Vacuum Arc (TVA) is established. Practically, any solid material mounted at the anode can be evaporated and transformed to bright plasma. Even intense plasma of he refractory materials is obtained easily. Due to their high melting points, instead of crucible as anode are used rods of refractory materials [4].

In this work, MgF₂ thin films are obtained as a result of heated cathode discharge established in vacuum condition in the vapours of the material to be deposited. Anode, which tungsten crucible filled with MgF₂ pellet, is bombarded by focused thermo-electrons accelerated toward the anode. Due to the incoming energy, MgF₂ pellet starts to evaporate and a discharge is established in the interelectrode space. TVA which is new type of evaporation, ensure high quality films due to the bombardmen with energetic ions of the own material growing layer. Thus, MgF₂ films were obtained on glass substrates at room temperature in a 5.27x10⁻⁵ Torr vacuum.

The optical properties were tested using the Perkin-Elmer UV/VIS Lambda 2S spectrometer. The spectrometer was used to measure the transmission of the films.

Figure 2. Transmittance spectra of produced MgF₂ thin films

Figure 3. Refractive index of produced MgF₂ thin films

Figure 4. AFM images of produced MgF₂ thin films

In summary, antireflection coating MgF₂ thin films were obtained using TVA technique. Some optical properties of deposited MgF₂ films were determined. In addition to, the surface morphologie given to Fig. 4 prove the smoothness of our MgF₂ thin films.

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Deposition of ZnO Thin Films with Reactive Sputter at Different O₂ Concentrations and Determination of Their Some Physical Properties

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Abstract—ZnO thin films were grown on the glass substrate using reactive sputter technique. Different concentrations of O₂ were used and the deposited ZnO thin films were investigated. Thickness and transparency of deposited films were determined using Swanepoel method. Additionally, energy gap of these films was calculated. ZnO thin films of surface morphology were determined with AFM images.

Zinc oxide (ZnO) which is one of the most important binary II–VI semiconductor compounds has a hexagonal wurtzite structure and a natural n-type electrical conductivity [1]. In addition, zinc oxide thin films are very important for solar cells and optoelectronic devices. Because of zinc oxide has a low electrical resistance and high optical transmittance, it is very important and useful material for solar cells that is used to window layers.

In this work, zinc oxide films are deposited by reactive sputtering on glass substrates with different O₂ concentrations. Some physical properties were analyzed for each ZnO films. Thickness and refractive index of deposited films were determined using Swanepoel method. Additionally, energy gap of these films was calculated.

Table 1. Physical parameters of deposited ZnO thin films at different O₂ concentrations

<table>
<thead>
<tr>
<th>%Ar</th>
<th>%O₂</th>
<th>Pressure (Torr)</th>
<th>n (550 nm)</th>
<th>k (550 nm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>%95</td>
<td>%5</td>
<td>2*10⁻¹⁰</td>
<td>1.82</td>
<td>0.094</td>
<td>178 nm</td>
</tr>
<tr>
<td>%90</td>
<td>%10</td>
<td>2*10⁻¹⁰</td>
<td>1.78</td>
<td>0.067</td>
<td>170 nm</td>
</tr>
<tr>
<td>%85</td>
<td>%15</td>
<td>6*10⁻¹⁰</td>
<td>2.63</td>
<td>0.149</td>
<td>260 nm</td>
</tr>
<tr>
<td>%80</td>
<td>%20</td>
<td>6*10⁻¹⁰</td>
<td>2.33</td>
<td>0.152</td>
<td>155 nm</td>
</tr>
<tr>
<td>%70</td>
<td>%30</td>
<td>2*10⁻¹</td>
<td>2.04</td>
<td>0.041</td>
<td>173 nm</td>
</tr>
</tbody>
</table>

The transmittance spectra were obtained via conventional spectrophotometry. The experimental data were collected in the ultraviolet-visible and near-infrared ranges (λ=200-1200 nm), with a step width of 1nm. From the transmittance spectra the refractive index (n(λ)), thickness (t), absorption index (α(λ)), and extinction coefficient (k(λ)) of the films were calculated using the Swanepoel method [2-3], and the optical band gap (Eₜ) was calculated from α(λ) [2-5].

The locations of the interference maximum and minimum are related to the real part n(λ) of the complex refractive index n(λ) = n(λ) + jk(λ) with k(λ) being the extinction coefficient, by the expression [2];

\[ m = \frac{2\pi n(\lambda)}{\lambda} \]  

where m is the interference order, λ the wavelength and t is the film thickness.

The refractive index can be calculated from Tₘ(λ) and Tₘ(λ).

\[ n(\lambda) = \left( \frac{2(\text{T}_\mu(\lambda) - \text{T}_\nu(\lambda))}{\text{T}_\mu(\lambda) + \text{T}_\nu(\lambda)} \right)^{\frac{1}{2}} + \left( \frac{2n(\text{T}_\mu(\lambda) - \text{T}_\nu(\lambda))}{\text{T}_\mu(\lambda) + \text{T}_\nu(\lambda)} \right)^{\frac{1}{2}} - \left( \frac{1}{T_s^2} - 1 \right) \]  

where s is the refractive index of the substrate and Tₛ is the substrate transmittance which is almost a constant in the transparent zone (λ>350 nm).

This study shows that differences between physical properties of deposited ZnO thin films in different concentration.

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Deposition and Characterization of GaAs Thin Films by RF Sputtering in Argon Atmosphere

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Abstract- Gallium arsenide (GaAs) is a compound of the elements gallium and arsenic. It is an important III/V semiconductor, and is used in the manufacture of devices such as microwave frequency integrated circuits, monolithic microwave integrated circuits, infrared light-emitting diodes, laser diodes, solar cells, and optical windows. In this study, GaAs thin films were deposited on glass substrate by using RF sputtering method. Some physical properties of GaAs thin films were analyzed.

A single RF sputtering apparatus can be used to deposit electrically conducting, semiconducting, and insulating coatings. Consequently, RF sputtering has found wide application in the electronics industry. Often several targets are placed within a common vacuum enclosure so that multilayer coatings can be deposited without breaking vacuum [1-2].

GaAs semiconductor thin films were deposited by RF sputtering method at 300 watt and under 5,52x10⁻² torr pressure on glass substrate. The deposition time was 60 minutes and film thickness measured 16,3 nm by Cressington MTM10 thickness monitor.

GaAs semiconductor thin film was analyzed at room temperature by Shimadzu UV-2101 PC UV-Vis Scanning Spectrophotometer. Some optical properties of GaAs thin film was calculated with optical method.

In this study, GaAs thin films were obtained by using RF sputtering in Argon atmosphere. Deposited GaAs thin films have high optical transmission. Additionally, surface morphologies are very smooth.

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Anti-Reflective Coatings of Mineral Lenses with Thermionic Vacuum Arc (TVA) Technique and Investigation of Some Physical Properties

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Abstract-Thermionic Vacuum Arc (TVA) is a new type plasma source which generates pure material plasma. Until today, TVA was used for research activity. First time TVA is used for optical industrial application. In this study, mineral lenses were AR coated by TVA.

Though procedures of dying of the sun glasses has been realized since century of 15, Primary protective coatings, which were named Anti-Reflection (AR) coatings, have been used with various type systems and methods since 1936 [1]. Nowadays, these coatings have been realized using Thermionic Vacuum Arc (TVA) technique in Plasma Physics Laboratories of Art - Science Faculty of Eskisehir Osmangazi University, Turkey.

Thermionic Vacuum Arc (TVA) is a new technology for thin film deposition [2-4]. TVA has been supplied many great advantages to deposited thin films like compact, low roughness, nanostructures, homogeneities, adhesive, high deposition rate, etc [2-4]. A lot of materials were used for thin films production and characterization in this technique. TVA technique gives ability to deposited pure thin films. TVA can ability to growth semiconductor thin films for photovoltaic applications and optoelectronic devices.

Thermionic Vacuum Arc (TVA) is an externally heated cathode arc which can be established in high vacuum condition, in vapors of the anode material. The arc is ignited between a heated cathode provided with a wehnelt cylinder and the anode which is a crucible containing the material to be evaporated.

Generally, spectacle glasses divided to branch such as mineral and organic. Aims of the AR coating are not only increase to the light transmission and contrast, but to decrease of the UV transmission [1].

In this study, we coated the mineral lenses with ZrO₂ and SiO₂ for anti-reflection.

Qualities of the AR coatings are depending on crystal formation of coatings, firstly, surface hardness, diffusion, thickness of the coatings, homogeneity, roughness and refractive index. At the end of this study, we obtained good results above physical phenomena.

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Figure 1. Schematic representation of TVA’s plasma

Figure 2. Transmission (a) and reflection (b) of the SiO₂ coated lenses.

Figure 3. Transmission (a) and reflection (b) of the ZrO₂ coated lenses

Figure 4. AFM images (4000 nm * 4000 nm) of SiO₂ coated lenses

Figure 4. AFM images (700 nm * 700 nm) of ZrO₂ coated lenses

Figure 5 SEM images of SiO₂ (a) and ZrO₂ (b) coated lenses
Metallic and Bimetallic Nanocatalysts for the Economic Synthesis of Decorated Carbon Nanotubes (CNT) for Environmental Applications

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Nanomaterials unit, Faculty of science- Benisuef university-Egypt

Abstract—doped transition metal oxides [9-11]. The reduction of oxides is an important step in developing alloys with specific catalytic, magnetic and electronic properties. It was found that the composition of the alloys is often a key element in optimizing their properties. The mechanism and kinetics of reduction of different ferrites such as ferrites of cobalt, zinc and strontium were investigated [12–15]. The produced nanoalloy or nanocomposites were used as catalyst for decomposition of hydrocarbon for the production of carbon nanotubes for using as a catalyst in CVD.

Carbon nanotubes is a hot topic today attracting scientists, industrialists, journalists, governments, and even a common people alike. Worldwide extensive and intensive researches on the preparation, characterization and applications of carbon nanotubes have been performed in the past decade [1–3]. Since the first observation of carbon nanotubes (CNTs) [4], extensive investigations have been pursued due to their unique physical properties and potential technological applications. CNTs can be synthesized by various methods such as arc discharge [5], laser vaporization [6], and chemical vapor deposition (CVD) [7,8]. The first two methods can produce high-quality nanotubes; however, the disadvantage is the high temperature or complicated device required, which limits scaling-up of their applications. CVD is a simple and cheap method based on the type of catalyst which is mainly a metal or metal oxide. Many investigators studied the physicochemical properties of transition metal oxides nanoparticles for using as a catalyst in CVD.

Although of the great development of studying preparation and characterization of these oxides, a limited number of investigators studied the reduction kinetics and mechanisms of reduction of pure and doped transition metal oxides [9-12]. The reduction of oxides is an important step in developing alloys with specific catalytic, magnetic and electronic properties. It was found that the composition of the alloys is often a key element in optimizing their properties. The produced nanoalloy or nanocomposites were used as catalyst for decomposition of hydrocarbon for the production of carbon nanotubes.

Decoration of the surface of CNTs can improve some new properties of CNTs such as optical and electrical properties. The combination of magnetic nanostructural materials and CNTs possibly resulting in high electronic or magnetic properties is highly attractive for new material development.

Therefore, the objective of this project is to develop a cheaper, effective and simple method for the preparation of CNTs with the modification of their surface structure to improve and establish promising catalytic, electrical, magnetic and mechanical properties for high efficient practical applications.

Figure 1. Undecorated carbon nanotube (up) decorated carbon nanotube (down).

Influence of Al Incorporation on the Structural and Optical Properties of Semiconductor Tin Oxide Film on Glass Substrate by Sol-Gel Technique and Potential Application of Gas Sensors

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Abstract—Undoped and aluminum doped semiconductor tin oxide film on glass substrate were prepared by sol-gel technique. The structural and optical properties of these films have been investigated. The X-ray diffraction result indicates that the SnO$_2$ film has the polycrystalline nature with average grain size of 28 nm. The optical transmittance spectrum indicates the average transmittance higher than 90% in visible region. The optical band gap, Urbach energy and optical constants (refractive index, extinction coefficient, real and imaginary parts of the dielectric constant) of the film were determined.

Tin oxide (SnO$_2$) has been widely used in large scale applications including flat panel displays, solar cells, gas sensing devices due to its special properties including wider band gap, excellent chemical and thermal stability, and natural non-stoichiometry [1–4]. Recently, the performance of SnO$_2$ has been found to improve by using low-dimensional metal-doped SnO$_2$ nanostructures. Various magnetic metal-, transition metal- and rare earth metal-doped SnO$_2$ nanostructures mainly including films and nanoparticles have successfully fabricated, and related diluted magnetic semiconductor properties, high lithium–ion capacity, enhanced gas sensing and humidity sensitive properties, excellent electrocatalytic activity and stability are successfully achieved [5-9]. Among many techniques for preparing SnO$_2$ films, sol-gel process has many advantages such as simple, inexpensive and having large area applications. Although there are many experimental work about metal doped SnO$_2$, there are few report on the optical constants of Al doped SnO$_2$ film [10].

Figure 1 shows the XRD patterns of the undoped and different Al doping ratios of SnO$_2$ films.

In this study, SnO$_2$ and Al-SnO$_2$ films were prepared by sol-gel technique according to previously published procedure [10]. The crystallinity of the SnO$_2$ and Al-SnO$_2$ films was analyzed by XRD method. Figure 1 shows the XRD patterns of the undoped and different Al doping ratios of SnO$_2$ films.

Figure 2 shows SEM images of SnO$_2$ and Al:SnO$_2$ films. As seen in SEM images, the surface quality of the SnO$_2$ film increases with Al doping, because the incorporation of the Al ions gives the regular grain size. The regular grain size causes the more uniform film.

Optical transmittance and reflectance spectra of the SnO$_2$ and Al:SnO$_2$ films were measured in the wavelength range of 325–800 nm by using V–530 JASCO UV/VIS Spectrophotometer. Refractive indices of thin films were measured at selected wavelengths in the VIS region by a high-accuracy Abbe refractometer at room temperature. Refractive indices were used for determining of film thickness. As shown in Figure 3 (a), refractive indices values can saturated after creation level Al-doping of SnO$_2$ film. Optical band gap values would also decreased which means Al doped SnO$_2$ films are become more conductive when Al doping level is increased. Our results open a approach to create a new semiconductor material for the engineering applications especially for gas sensing.

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The Effect of Ru Substitutions on the Structural, Electrical and Optical Properties of Semiconductor Tin Oxide Film Derived by Sol-Gel Method

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3Ege University, Department of Electrical and Electronic Engineering, Bornova, 35100 Izmir-Turkey.

Abstract-In this study, Ru - SnO2 thin films were deposited on glass substrates via sol-gel technique for gas sensor applications. Transparent solutions were prepared from Sn and Ru based precursors. The solutions were deposited on Si(100) and glass substrates by using spin coating technique which provides thin and smooth films. The deposited films were dried at 300°C for 10 min in order to remove hydrous and volatile content, subsequently to remove organic content films were heat treated at 500°C for 5 min and then they were annealed at 600°C for 1 hour to obtain SnO2 based films in air atmosphere. Finally the surface morphology and roughness of the films were determined via AFM (atomic force microscopy) and Profilometer respectively. The phase structure was determined by XRD. The electrical conductivity of the film dependence of temperature was measured to identify the dominant conductivity mechanism. The optical parameters (band gap, refractive index, etc.) of the film were determined by measuring transmittance and reflectance spectrums.

Tin oxide films have been widely used in fields such as resistors, antireflection coatings in solar cells and detection of gases. As sensors they are deployed for detecting low concentrations of toxic and flammable gases like CO, H2, CO2, H2S, NOx, LPG, C2H5OH and C2H6. However, the main drawback is poor selectivity, ageing and humidity induced effects involving grain growth and surface poisoning causes poor reliability [1]. Therefore, many efforts were devoted to improve the performance of this type of sensor in the last decade [2]. Among the metal oxides, SnO2 based semiconductor gas sensors are of great interest. They are commercially available in the form of thick films, thin films or pellets [3, 4]. In addition to the relatively expensive techniques (e.g. RF sputtering [5], electron gun evaporation [6], pulse laser deposition (PLD) [6] and physical vapor deposition (PVD) [7]), sol-gel process [1] has been proposed for the preparation of SnO2 based semiconductor gas sensors. Sol-gel method has several advantages such as; low cost, high surface area, enhanced film thicknesses, etc...

Thin film sensors (the film thickness is typically less than 1 μm) are of interest because of their relatively small size and low power consumption. In accordance to the parameters above, sensing capacity is related to the microstructure and phase structure of the films. By these way small additions of substitution elements to the films affects the microstructure and sensing capacity.

Electronic structure of a semiconductor is directly related to the substitution of elements like Ru, Al and In. Addition of these substitution elements change the Fermi Level of the semiconductor which results a change in the resistivity. Also the difference of the substitution element can cause a chance in the sensed gas or substances [8].

Niranjan et al. [1] in their work reported a simple approach for controlling the sensor performance by modifying the tin oxide matrix with ruthenium oxide. More specifically, tin oxide is anchored with ruthenium to achieve remarkable enhancement towards the hydrocarbon selectivity and sensitivity. The main aim is to control the amount and distribution of ruthenium in the tin oxide matrix so that the misfit regions are distributed at the grain boundaries in such a way so as to obtain very high sensitivity with good selectivity.

In this present study; pure, and Ru substituted SnO2 thin film were deposited on glass substrates by sol-gel method. Si(100) and glass substrates were mechanically cleaned in a specific acid-alcohol medium by using a magnetic stirrer.

Spin coating technique provides nanoscale and smooth films to be deposited. Thus the films were deposited by technique mentioned above, nanoscale structures such as pores and islands can be obtained. The decrease in the pore size of a sensor from micron scale to nanoscale provides high efficiency and selectivity about gas sensing.

In order to deposit thin films onto the glass substrates spin coating technique was employed. The coating regime was represented in Figure 1.

![Figure 1. Spin coating regime of solutions](image-url)

Optical transmittance and reflectance spectra of the SnO2 and Ru:SnO2 films were measured in the wavelength range of 325–800 nm by using V-530 JASCO UV/VIS Spectrophotometer. Based on these data, optical band gap, Urbach energy, refractive index, extinction coefficient, real and imaginary parts of the dielectric constant will be calculated according to well-known formulas [9]. Electrical parameters will also be determined by using conductivity measurement.

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A Nanotube Self-Assembly of A6K in aqueous solution

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Abstract-The self-assembling process is reversible and dynamic since peptide surfactant of A6K (AAAAAAK) is short and simple, numerous individual peptides can be readily self-organized through the weak interactions including hydrogen bonds, ionic bonds, hydrophobic and van der Waals interactions as well as water mediated hydrogen bond formations. Therefore, the dynamic molecular self-assembly behavior of the peptide surfactant A6K that formed nanotubes in aqueous solution was investigated. These peptides self-assemble into very large structures directly when exceeding a particular concentration which is %12. Investigation of the kinetics of formations revealed that the flat sheets underwent rearrangement into nanotubes during the process of self-assembly over time. The structures of this oligopeptide were examined by Small Angle X-Ray Scattering (SAXS) and cryo-TEM techniques. These findings may play an important role not only having implications for the study of controlled and modelled self-assemblies but also for fabrication of a wide range of peptide nanomaterials.

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Electrospinning of Chitosan-PHBV
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Biopolymers can be produced through a variety of mechanisms they can be derived from microbial systems, extracted from higher organisms such as plants, or synthesized chemically from basic biological building blocks. Variety of polymers can be distinguished into eight major classes according to their chemical structures: nucleic acids, polyamides (proteins and poly-(amino acids), polysaccharides, organic polyoxoesters such as poly(hydroxyalkanoic acids), poly(malic acid) and cutin, polythioesters were only reported recently, polyesters with poly-phosphate, polyisopyrenoides, polyphenols [1].

Chitin which is a nitrogen-rich polysaccharide derived from crustaceans, mollusks, insects and fungi; it is the second most abundant organic material after cellulose. Chitosan, a transformed oligosaccharide, is obtained by deacetylation of chitin, the latter being a bio-polymer obtained from crab and shrimp shells. It is a high molecular weight (MW) linear polymer composed of N-acetyl-D-glucosamine (N-acetyl-2-amino-2-deoxy-D-glucopyranose) units linked by \( \alpha-D-(1\rightarrow4) \) bonds. A sharp nomenclature difference between chitin and chitosan based on the degree of N-deacetylation has never been precisely defined; commercial chitosan typically is 85% deacetylated. Defining the molecular weight of chitosan, or any naturally occurring polysaccharide, has historically been difficult. This is true for chitosan in particular because its backbone of \( (1\rightarrow4)-\alpha-D-glucosamine \) residues is randomly acetylated. Additionally, due to purification challenges, all natural polymers experience batch-to-batch variation. Therefore, chitosan is a general term applying to many deacetylated chitins having a variety of optical characteristics, crystallinity, degree of acetylation, impurity content and molecular weights. As a natural polymer, chitosan intrinsically exhibits enticing properties such as biocompatibility, biodegradability, and aqueous adsorption capabilities. These properties make chitosan an ideal polymer for a wide variety of fields and industrial applications including textiles, ophthalmology, paper coatings, medical, agricultural, and food. However, processing chitosan can be challenging due to its tendency to coagulate with proteins at high pH, its insolubility in most solvent systems including water, and its high solution viscosity. Chitosan is known to be soluble in dilute organic acids such as acetic, formic, succinic, lactic, and malic acids [2][3].

The electrospinning technique is a versatile method to spin polymers into continuous fibers with diameters ranging from a few micrometers to a few nanometers. Electrospinning creates seemingly endless ultrafine fibers that collect in a random pattern. These nanofibers can form non-woven textile mats, oriented fibrous bundles and even three-dimensional structured scaffolds, all with large surface areas and high porosity. It is, thus, the most extensively used fabrication method that offers vast opportunities for control of the morphology of the electrospun fibers[3].

Chitosan solution could not be electrospun into ultrafine nanofibers. To overcome the poor electrospinnability of chitosan solutions, it can be blended with another polymer like PVA, PEO, Polyurethane, and etc. In this study, electrospinning of chitosan-PHBV blended system was investigated and the different conditions were analysed to obtain an appropriate nanofibers.

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Effects of Heat Treatment on Microstructure and Magnetic Properties of Electroless CoNiFe–B Thin Film

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Abstract—This paper explains our recent study on fabrication of a uniform and high-performance CoNiFeB soft magnetic thin film for magnetic recording head core applications and the effect of heat treatment on it. Thin film was deposited from borane-based baths on Si. We could synthesize a narrow film with ~45 nm thickness, high saturation magnetic flux density (~2.3 T) and low coercivity (~15.0 Oe). Some new phases created and magnetic properties changed after the heat treatment at 400°C for 60 minutes in Ar.

CoNiFe materials exhibit many of the desirable characteristics for magnetic recording heads because of their low coercivity and their high saturation flux density ($B_{sat}$)[1]. The electroless deposition method is used for fabrication of uniform magnetic films on complex shape of substrate and does not suffer from problems associated with current density distribution [2]. The applied heat treatment in the final stage of EN coating changes its properties such as magnetic properties. We found that the molar ratio of CoSO$_4$/NiSO$_4$ = 2.647 results in most uniform with smallest particulate size than other bath composition [3]. In this paper, electroless CoNiFe-B soft magnetic thin film will be discussed with emphasis on the effect of heat treatment on its microstructure, morphology and magnetic properties.

Silicon wafer was used as substrate material for the deposition of electroless CoNiFe–B coatings in 30s deposition time. The chemical composition of the electroless deposition bath is as follows: 0.0255M CoSO$_4$, 0.0085M NiSO$_4$, 0.143M lactic acid, 0.07M DMAB. The temperature of the bath was maintained at 70 °C. Heat treatment of electroless CoNiFe-B coatings was performed at 400°C for 60 minutes and in argon atmosphere. XRD and VSM analysis were used to characterize the coatings.

![XRD patterns of (a) as-deposited and (b) heat treated electroless CoNiFe-B coatings](image)

Figure 1 presents the XRD patterns of the as-deposited and heat treated electroless CoNiFe–B. Comparison between these XRD pattern concludes that heat treatment not only leads to crystallization of coating, it also change the phase structure and causes formation of some new phases which includes (Co, Ni, Fe)$_3$B and Ni$_3$B. These new phases are formed by compound of metallic elements with boron which is taken in plated film from DMAB as the reducing agent in the coating bath [4]. The thickness of the as-deposited film measured by a Dektak profilometer and found that it is about 45 nm.

![The magnetic hysteresis curves of as-deposits and heat treated coatings](image)

Figure 2. The magnetic hysteresis curves of as-deposited and heat treated coatings

<table>
<thead>
<tr>
<th>Sample</th>
<th>As-deposited</th>
<th>Heat treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_s$ (T)</td>
<td>2.30</td>
<td>2.52</td>
</tr>
<tr>
<td>$M_r$ (T)</td>
<td>0.95</td>
<td>2.01</td>
</tr>
<tr>
<td>$H_c$ (Oe)</td>
<td>15.0</td>
<td>39.1</td>
</tr>
</tbody>
</table>

Magnetization curves of the CoNiFeB films (as-deposited and heat treated) are plotted in Figure 2. The saturation magnetization ($M_s$), the residual magnetization ($M_r$) and coercivity ($H_c$) of the films are tabulated in Table1.

The saturation magnetization and the residual magnetization increase from 2.30 T and 0.95 T to 2.52 T and 2.01 T after heat treatment at 400 °C, respectively. From the XRD results, it is evident that the as-deposit coating was crystallized into new phases after annealing at 400 °C. The formation of the new alloy phases with high magnetization may be the reason of the increase in $M_s$ and $M_r$. The coercivity ($H_c$) is pertinent to the structure of material and many factors such as grain size, crystal structure, stress and surface roughness [4]. As is seen in Fig.2 and Table.1 the coercivity has changed with a complex mechanism and moved up from 15.0 to 39.1 after heat treatment at 400 °C.

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Morphological study of the FeCo magnetic thin film fabricated by EBPVD

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Abstract—The present paper focuses on the synthesis and characterization of a narrow and homogeneous FeCo thin film prepared by electron beam physical vapor deposition (EBPVD). After optimizing the evaporation conditions, a narrow (~50 nm thickness) and uniform film with very fine particulates (~100 nm) which is suitable for magnetic recording head core applications was synthesized.

In recent years, there are growing requests for higher magnetic recording densities [1]. A magnetic recording head is a key device for achieving high-density magnetic recording, with soft magnetic thin films (having a high magnetic flux density (B) and low coercivity (Hc)) being used as core materials. Fe–Co based alloys can be a promising candidate for this purpose because of having a very high saturation magnetic flux density [1]. The present work deals with the synthesis and characterization of the FeCo thin film prepared by electron beam physical vapor deposition (EBPVD). Mechanochemical process [2,3] was used to prepare the FeCo nano-powder which in turn going to be used as a target material for the thin film deposition. Analytical grade hematite (Fe2O3) (MERCK, Gmbh) was mixed with cobalt oxide (Co3O4) (MERCK, Gmbh) at the elemental Fe:Co molar ratio of 2:1. The mixture was milled at 350 rpm having ball to powder weight ratio of 20:1 for 20 hr. The produced Co-ferrite powder was then reduced with hydrogen at 750 °C.

The surface of the powder and the film shown in Figure 1 and 2 were analyzed by EDS. The results of these analyses are given in Table 1. The data tabulated in the table indicates atomic and weight percentages of the elements have changed after EBPVD. This may be related to the nature of the EBPVD process, resulting in a stoichiometry that is different from the initial material [4].

The uniformity and average size of the particles have significant effects on magnetic properties of FeNiCo thin films. The particulate size should be small to favor a low value of Hc for the soft magnetic thin film, and these fine particulates with same crystalline structure should be homogeneously distributed, keeping the value of Hc low [5]. According to the results, a narrow and homogeneous film with fine particulates which is appropriate for magnetic recording head core materials was fabricated.

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Energy of Fullerenes and Nanotubes

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Abstract—By the Hückel theory the energy of a molecule is defined as the sum of absolute values of its eigenvalues. Because of the large number of carbon atoms in the molecular graph of fullerenes and nanotubes, usually it is not possible to compute the energy of these nanomaterials by this theory. In this paper, we present a numerical algorithm, which is useful for solving such problems.

Let $M$ be a matrix. An eigenvector for $M$ is a non-zero vector that is either left unaffected or simply multiplied by a scale factor after the matrix. The eigenvalue of a non-zero eigenvector is the scale factor by which it has been multiplied. In an exact phrase, a real number $\lambda$ is an eigenvalue of $M$ if there is a non-zero vector $X$ such that $MX = \lambda X$.

Suppose $G$ is the molecular graph of a fullerene or a nanotube. The adjacency matrix of $G$ is a $n \times n$ matrix with rows and columns labeled by graph vertices, with a 1 or 0 in position $(i,j)$ according to whether $v_i$ and $v_j$ are adjacent or not. The eigenvalues of a graph are the eigenvalues of its adjacency matrix. The energy of $G$ is defined as the sum of the absolute values of all eigenvalues of $G$. This quantity has a long known chemical application. Recently much work on graph energy appeared also in the mathematical literature.

For the sake of completeness, we mention below some well-known results in this topic which is crucial in our study. We encourage to interested readers to consult mentioned papers and their references.

Theorem 1: The main properties of the energy are as follows:

- $\sqrt{2m + n(2 - n)} \leq E(G) \leq \sqrt{2mn}$.
- If the graph $G$ consists of components $G_1$ and $G_2$, then $E(G) = E(G_1) + E(G_2)$.
- If one component of the graph $G$ is $G_1$ and all other components are isolated vertices, then $E(G) = E(G_1)$.

Theorem 2: $E(G) \leq \sqrt{2mn}$ with equality holding if and only if $G$ is regular of degree 0 or 1.

Theorem 3: Suppose $G$ is a $(n, m)$ graph, then;

$$E(G) \leq \frac{2m}{n} + \sqrt{\left(\frac{n-1}{2}\right) \left(2m - \frac{2m^2}{n}\right)}$$

with equality if and only if $G$ is either a regular graph of degree 0, 1 or $n - 1$, or a non-complete connected strongly regular graph with two non-trivial eigenvalues both having absolute value;

$$\sqrt{\left(2m - \frac{2m}{n}\right)^2 / (n - 1)}$$

Theorem 4: Suppose $G$ is a $(n, m)$ graph then $2\sqrt{m} \leq E(G) \leq 2m$. If $G$ has no isolated vertices, then the equality $E(G) = 2\sqrt{m}$ holds if and only if $G$ is a complete bipartite graph. If $G$ has no isolated vertices, then the equality $E(G) = 2m$ holds if and only if $G$ is regular of degree 1.

Theorem 5: Let $G$ be a graph with $n$ vertices and $m$ edges then

$$\sqrt{2m + n(n-1)\det A^2} \leq E(G) \leq \sqrt{2mn}.$$
Peptide Self-Assembly

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Abstract-The self-assembly of the trifluoroacetate salt of the short peptide (ala6-lys (A6K) in water has been investigated by Cryo-transmission electron microscopy and small angle X-ray scattering. For concentrations below ca. 12 %, the peptide does not self-assemble but forms a molecularly dispersed solution. Above this critical concentration, however, A6K self-assembles into several micrometer long hollow nanotubes, with a monodisperse cross-section radius of 26 nm. Since the peptides carry a positive charge, the nanotubes are charge stabilized. Because of the very large aspect ratio, the tubes form an ordered phase that presumably is nematic and upon increase in concentration goes from closed packed hexagonal to multi-shelled cylinders. Nanotubes are shown to disintegrate upon increase in temperature using SAXS.

Peptide self-assembly structures not only have importance for medical applications [1, 2] due to their biological origin, but also used in different fields [3, 4]. Understanding peptide self-assembly is not only important to design novel materials but also gain insight for disease, which lowers the quality of life and lead to death.

In this study, we demonstrate our results for the extensive study of self-assembly structures of short synthetic oligopeptide A6K in water. In our previous work [5], we studied the self-assembly structures, including the formation of nematic ordering. The self-assembly structures were investigated using cryo-transmission electron microscopy (Cryo-TEM) and small angle X-ray scattering (SAXS). In this part of the work, the studies were extended to higher concentrations of the peptide.

The phase transition from nematic to isotropic phase upon increasing the temperature is also studied for $\phi = 0.11, 0.12$ and $0.13$.

Figure 1. SAXS patterns obtained from $q_{\text{min}}$ to $q_{\text{max}}$

In Figure 1, SAXS patterns obtained at peptide concentrations from $q_{\text{min}}$ to $q_{\text{max}}$, are presented. At lower $\phi$ values, scattering pattern supports the presence of hollow nanotubes whereas at higher $\phi$, the oscillations smear out, although not completely vanish, and at higher q values other oscillations start to build up. This kind of scattering pattern is associated with concentric cylinders. After reaching the hexagonal phase, as $\phi$ increases, nanotubes go through a transition from a single wall to multishell structure. The theoretical model shows the scattering pattern of a system with cylindrical shells, which contain a maximum of 5 shells, each shell has a thickness of 1 nm and the distance between the shells is 3 nm.

In Figure 2, SAXS pattern for $\phi = 0.13$ is shown. In temperature studies with SAXS, it is seen that the form factor for hollow cylinder disappears between 70-75°C. In summary, we have investigated nanotube nematic to hexagonal phase transition upon increase in concentration and nematic to isotropic upon increase of temperature. This simple system lends itself for systematic investigations of peptide self-assembly including e.g. investigation of the effect of counterion on the nanotube formation and investigation of self-assembly of slightly different peptides such as A6R.

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Computing Eccentric Connectivity Index of Some Classes of Fullerenes
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Abstract—The eccentric connectivity index \( \xi(G) \) of a graph \( G \) is defined as \( \xi(G) = \sum_{v \in V(G)} \deg(v)e(v) \). In this talk, we report our latest results on the subject of eccentric connectivity index of some classes of fullerenes.

Fullerenes are molecules in the form of cage-like polyhedra, consisting solely of carbon atoms. The discovery of \( C_{60} \), a buckyball, which has a nanometer-scale hollow spherical structure in 1985 by Kroto and Smalley revealed a new form of existence of carbon element other than graphite, diamond and amorphous carbon. Fullerenes made up entirely of \( n \) carbon atoms and having 12 pentagonal and \( (n/2 - 10) \) hexagonal faces, where \( n \not= 22 \) is a natural number equal or greater than 20.

Let \( G = (V, E) \) be a connected bipartite graph with the vertex set \( V = V(G) \) and the edge set \( E = E(G) \), without loops and multiple edges. Suppose \( u \) and \( v \) are vertices of \( G \). The distance \( d(u, v) \) is defined as the length of a shortest path connecting them. The eccentricity \( e(u) \) is the largest distance between \( u \) and any other vertex \( x \) of \( G \). The maximum eccentricity over all vertices of \( G \) is called the diameter of \( G \) and denoted by \( D(G) \) and the minimum eccentricity among the vertices of \( G \) is called the radius of \( G \) and denoted by \( r(G) \). The set of vertices whose eccentricity is equal to the radius of \( G \) is called the center of \( G \). It is well known that each tree has either one or two vertices in its center. The eccentric connectivity index \( \xi(G) \) of \( G \) is defined as \( \xi(G) = \sum_{v \in V(G)} \deg(v)e(v) \). We encourage the reader to consult papers [10-13] for mathematical properties of this new proposed topological index.

In this section, the eccentric connectivity index of some fullerenes is computed. To do this, we apply an algebraic approach. Let us recall some definitions and notations. An automorphism of a graph \( G \) is a permutation \( g \) of the vertex set \( V(G) \) with the property that, for any vertices \( u \) and \( v \), \( g(u) \) and \( g(v) \) are adjacent if and only if \( u \) is adjacent to \( v \). The set of all automorphisms of \( G \), with the operation of the composition of permutations, is a permutation group on \( V(G) \), denoted by \( \text{Aut}(G) \). The following simple lemma is crucial in this section. Here our notations are standard and mainly taken from [16-22].

Lemma 1 — Suppose \( G \) is a graph, \( A_1, A_2, ... \), are the orbits of \( \text{Aut}(G) \) under its natural action on \( V(G) \) and \( x_i \in A_i, 1 \leq i \leq t \). Then \( \xi(G) = \sum_{i=1}^{t} |A_i|\deg(x_i)e(x_i) \). In particular, if \( G \) is vertex transitive then \( \xi(G) = r(G)|V(G)|e(x) \), for every vertex \( x \).

Figure 1. The Zig-zag Polyhex Nanotube.

Lemma 2 — The molecular graph of a polyhex nanotorus is vertex transitive.

Theorem 3 — \( \xi(T[p,q]) = 3pq^2 \)

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Computing Wiener Polynomials of VC₅C₇[p,q] Nanotube by GAP Program

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Abstract—In this paper, we give a GAP program for computing the Wiener polynomial of any graph. Also we compute the Wiener index, hyper Wiener index and Wiener polynomial of VC₅C₇[p,q] Nanotube by Gap program.

A topological index is a single unique number characteristic of the molecular graph and is mathematically known as the graph invariant. The topological index of a molecule is a non-empirical numerical quantity that quantifies the structure and the branching pattern of the molecule. Usage of topological indices in biology and chemistry began in 1947 when chemist Harold Wiener [1] introduced Wiener index to demonstrate correlations between physicochemical properties of organic compounds and the index of their molecular graphs. The hyper-Wiener index is one of the recently conceived distance-based graph invariants, used as a structure-descriptor for predicting physico–chemical properties of organic compounds. The hyper-Wiener index was invented by Randić (1993) and was eventually extensively studied [2].

Topological indices, namely Wiener index, Randic’s connectivity index based on distances are used to describe the molecular structure of a series of alkylcupferrons used as mineral collectors in the beneficiation of a Canadian uranium ore. There is a linear relation between any of these topological indices and the separation efficiency of the alkylcupferrons considered. The data fit into two separate curves, differentiating the alkylcupferrons into two subclasses, one with rigid rod-like methyl substituents and the other with flexible alkyl substituents. As in the case of Wiener index, connectivity index has also been correlated with physical properties such as density and heat of vaporization. For details on the mathematical properties of the Wiener index see the reviews [3-5].

Let G be a connected graph. The distance between the vertices u and v is denoted by \( d(u,v) \). The Wiener polynomial, the Wiener index and the hyper Wiener index of G are defined as follows.

The Wiener index of G is

\[
W(G) = \sum_{\{u,v\} \subseteq \Gamma(G)} d(u,v)
\]  

(1)

The Wiener polynomial of G is

\[
W(G,x) = \sum_{\{u,v\} \subseteq \Gamma(G)} x^{d(u,v)}
\]  

(2)

The Hyper Wiener index of G is

\[
WW(G) = \sum_{\{u,v\} \subseteq \Gamma(G)} d(u,v) + d(u,v)^2
\]  

(3)

Wiener polynomials were first introduced by Hosoya in [6]. Observe that the degree of the Wiener polynomial is equal to the diameter of G. Also, notice that

\[
W(G) = W'(G,1), \quad WW(G) = W'(G,1) + W''(G,1)
\]  

(4)

In this paper, we give an algorithm for computing the Wiener polynomial of any graph. Also we compute the Wiener index, hyper Wiener index and Wiener polynomial of VC₅C₇[p,q] Nanotube by Gap program.

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Growth and Characterisation of ZnSe Semiconductor Nanowires

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Abstract. The growth and characteristics of wide gap II–VI semiconductor nanowires prepared by the so-called vapour-liquid-solid (VLS) technique was presented. ZnSe nanowires were prepared on Si (111) by using Au as catalyst. Vapor-Liquid-Solid (VLS) process under certain conditions to form the desired nanowires. The as-synthesized products were characterized by SEM and EDX. The SEM analysis of ZnSe nanowires indicated that nanowires grow randomly at angles widely different from the vertical.

Keywords: Nanotechnology; ZnSe nanowires; VLS; Semiconductors; SEM and EDX

1. INTRODUCTION

Nanotechnology is a cutting edge technology and has many potential applications which can be divided into short-term and long-term applications. The short term is to enrich scientific research to develop the characteristics and effectiveness of nano-materials. On the other hand, long term applications is to build nano-devices using atoms and molecules. Nanotechnology is a new branch of engineering, based on the physics of low dimensional structures. This technology increases the ability to design and build devices on an atomic or molecular scale and provides opportunities to develop materials with unique properties. Nanostructured materials are systems in which the physical size in at least one dimension is less than or equal to 100 nm. They are important for both fundamental research applied oriented research since they have the potential to reach far higher device densities compared to traditional material technology. The properties of nanostructures are not only dependent upon dimensionality, but also their physical size.

In semiconducting materials electrons live in a range of define energy level called bands. The conduction band is partially filled band are areas where electrons are missing, known as hole. The advantage of nanotechnology enables much larger surface area hence much more active electrons. The Fermi level (a band gap) are reduced giving advantage to one kind of nanostructured materials is one-dimensional (1D) nanowires. They were first discussed in 1980 [1], for application to high electron mobility channels. An important advantage of 1D nanowires over other low dimensional material is that the nanowires can function as both active device elements and interconnects carrying current to and from devices.

Vapor-Liquid-Solid (VLS) process was established in the 1960’s by Wagner and Ellis [2], later justified thermodynamically and kinetically [3]. It was recently reexamined by Lieber, Yang, and other researchers to generate nanowires and nanorods from a rich variety of inorganic materials [4-14]. A typical VLS process starts with the dissolution of gaseous reactants into nanosized liquid droplets of a catalyst metal, followed by nucleation and growth of single-crystalline rods and then wires. The one-dimensional growth is induced and dictated by the liquid droplets, whose sizes remain essentially unchanged during the entire process of wire growth. Each liquid droplet serves as a virtual template to strictly limit the lateral growth of an individual wire.

In this process, the anisotropic crystal growth is promoted by the presence of the liquid alloy/solid interface. The VLS process has now become a widely applied to explain the growth of various nanowires from a rich variety of pure and doped inorganic materials that include elemental semiconductors (Si, Ge) [4-8], and II–VI semiconductors (ZnS, ZnSe, CdS, CdSe) [15-17].

This work premise deals method with fabrication of ZnSe nanowires using VLS process. Stringent control over the conditions of the ZnSe nanowires were identified. This study should help to identify the conditions suitable for fabricating optimized ZnSe nanowires, and their associated device (transistor) characteristics. In particular, ZnSe is being actively studied as a result of recent success in the fabrication of blue-green light emitting diodes (LED).

2. EXPERIMENTAL DETAILS

The experimental setup used in this work is illustrated in Fig. 1.
ZnO-Nanotubes as Green and Efficient Catalyst in The Three-Component One-Pot Synthesis of 3, 4-Dihydropyrimidinones Under Solvent-Free Conditions

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Abstract - In this study, the catalytic ability of ZnO nanotube in the three-component condensation reaction of different class of aromatic aldehyde, 1,3-dicarbonyl compound, and urea or thiourea was studied. It was proved that this nano tube is an efficient heterogeneous catalyst for the Biginelli condensation reaction and gave 1, 4-Dihydropyridyl compounds in high isolated yield under mild reaction conditions.

3,4-Dihydropyridyl compounds is obtained via probably what is one of the first described multicomponent reactions. Indeed the venerable Biginelli dihydropyrimidine synthesis was discovered by Pietro Biginelli who reported in 1893 on the acid-catalyzed cyclocondensation reaction of ethyl acetooacetate, benzaldehyde, and urea [1]. During more than a century, only few chemists investigated the synthetic utility and scope of the Biginelli reaction and less than 40 reports have appeared in the literature before 1999. The discovery of the potential anticancer activity of monastrol probably is not irrelevant to, or at least coincides with, an outbreak in the interest for the old transformation as more than 350 articles have been published on the Biginelli condensation since 1999.

3,4-Dihydropyridyl compounds are well known as calcium channel modulators and have emerged as one of the most important classes of drugs for the treatment of cardiovascular diseases. Cardiovascular agents such as nifedipine, nicardipine, amlodipine, and other related derivatives are dihydropyridyl compounds, effective in treatment of hypertension. 1,4-Dihydropyridine derivatives possess a variety of biological activities such as vasodilator, bronchodilator, antiatherosclerotic, antitumor, geroprotective, hepatoprotective, and antidiabetic activity. Extensive studies have revealed that these compounds exhibit various medicinal functions such as neuroprotectant, platelet antiaggregatory activity, cerebral antischismic activity in the treatment of Alzheimer’s disease, and chemosensitizer in tumor therapy. These examples clearly indicate the remarkable potential of novel dihydropyridine derivatives as a source of valuable drug candidates [2-3].

Nontoxic and inexpensive environmentally compatible ZnO has been in great interest from wide range of applications in technological fields associated with nanotechnology; it absorbs large fraction of the solar spectrum and light quanta. Furthermore, ZnO is a semiconductor that can be used as a photocatalyst. It is a promising tool to convert the pollutants into the harmless substances in the waste water, directly, which compliances with green chemistry protocol and it is proved that ZnO nanotube enhances the rate and stereoselectivity of chemical reactions [4].

Having the above facts in mind, we now wish to report a green and ecofriendly protocol for the three-component condensation reaction of aldehyde, 1,3-dicarbonyl compound, and urea or thiourea (Figure 1)

ZnO nanotube was easily prepared by the chemical reaction of zinc acetate and KOH in the water and in the presence of poly ethylene glycol. The condensation reaction of different aromatic aldehyde carrying activated and deactivated groups, 1,3-dicarbonyl compound, and urea or thiourea were carried out in the presence of catalytic amounts of ZnO nanotube under solvent free conditions. The three-component condensation reaction were done efficiently and produced the corresponding 3,4-dihydropyrimidin-2-(1H)-ones in high isolated yield. The reaction protocol is simple, is cost-effective, and gives good isolated yield with high purity.

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Studied at the Effect of the Removal of the Barrier Layer Times in Productive Process for Nano-Porous Anodic Alumina Membrane

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Abstract—Nano Alumina Membrane is produced in two levels anodizing by using various type of acidic electrolyte such as sulfuric acid, phosphoric acid and oxalic acid. Holes characterize with hexagonal structure by differ diameters from 40 to 420. Heat and chemical stability also regular formed holes are made the membranes appropriate for using in gas separating process, drug delivery and applicant for fuel cell membrane. Detaching of membrane from aluminum base is most important stage on producing membrane process. In this research, initially, aluminum based layer omit in CuSO4 and HCl. In secondary step, barrier layer at the end of the holes takes away with phosphoric acid solution. Aim of this work is analyzed the effect of time at the barrier layer removal process.

Production of nano material such as polymeric nanowire, metallic nanowire, 3D nanodot, polymeric and metallic nanotube and etc attract many research directions to itself. Nano-porous Aluminum Oxide can provide simple template for deposited and growth the various materials with ordered structure.

New method of two levels anodizing for synthesis porous aluminum oxide with regular structure in oxalic acid is invented by H.Masuda in 1995 [1], after this invention scientist try to find new ways for synthesis this structure with different feature.

H.Masuda reported some holes structure (500 nm) in acid phosphoric electrolyte in 1998 [2], also other same results announce with scientist of Max Planck institute that anodizing had done at different electrolyte. Synthesis of porous aluminum oxide in Sulfuric Acid in different chemical and physical conditions is analyzed by D.Sulka in 2002 [3]. Nano-porous Aluminum oxide has many useful features like [4-7]

1. Hole diagonal dimension controlling.
2. Resist in heat for all heat experiment on materials in holes without any damage on template structure.
3. Have regular holes in these membranes.

All this features make this material appropriate for synthesis of various types of nanowires, nanotubes, nanodots and etc [8-10].

Figure 1. SEM image shows the bottom surface of Alumina Oxide before the barrier layer removing.

Saturated solution of sulfuric copper and percoloric acid uses for dissolving metallic base and at continues diluted solution of phosphoric acid purpose for removing barrier layer and pore opening process.

Surface structure of samples study with Scanning Electron Microscope (SEM) and has found the ideal time for removing barrier layer without destroyed hexagonal columnar structure is 90 minutes.

Figure 2. shows the bottom surface after barrier layer removing with 90 minutes processing times.

Very important point in this study is periodical condition that maybe the results have used for more times examination and technical works.

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**Nafion as Nano-Protons Conductor in Microbial fuel Cell**

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**Abstract**-Nafion, a sulfonated tetrafluorethylene copolymer, consists of a hydrophobic fluorocarbon backbone (–CF2–CF2–) to which hydrophilic sulfonate groups (SO\(^2\)) are attached. The presence of negatively charged sulfonate groups in Nanomembrane brings about the high level of proton conductivity of it. In this research study, *Saccharomyces cerevisia* was used to production of bioelectricity in a two chambered MFC. 9 m² nafion 117 and nafion 112 was selected as a nano membrane to transport produced proton from anode chamber to cathode compartment at ambient temperature and pressure. Initial glucose concentration was 30g/l. The maximum obtained voltage, current and power density for nafion 117 were 668 mV, 60.28 mA/m² and 9.95 mW/m² respectively. The same results for nafion 112 were 670 mV, 150.6 mA/m² and 31.32 mW/m² respectively.

Experimental results showed that the membrane electrode assembly air-cathode MFC could generate electricity using glucose as substrate, and the required electrically active bacteria presented in *Saccharomyces cerevisia*. When glucose was injected into anode chamber, The initial voltage was immediately generated. It is low. Thereafter, the voltage increased because of biological activity, and stabilized at about 570 mV for 2days after incubation Figure 3 show the open circuit voltage curve. The initial voltage was about 300 mV.

In a batch cycle, once MFC stabilized at the maximum steady voltage, the polarization curve was obtained by recording the voltage via varying the external resistance. Maximum power density was determined from the polarization curves was 9 mW/m². In this condition maximum current density and voltage density were 60 mA/m² and 570 mV, respectively. Figure 3 shows the improvement in polarization curve’s result along with MFC performances during time after inoculation.

![Figure 1. Two-chamber MFC used in this experiment](image1)

![Figure 2. Open circuit voltage curve](image2)

![Figure 3. Polarization curve on(1)first day after inoculation (2) the second day after inoculation (3) after obtaining constant open circuit voltage.](image3)
Electrochemical Preparation of Nanostructured Polyaniline Films on Self Assembled Monolayer Modified Electrodes

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Abstract-Polyaniline film was deposited on thiol coated gold (Au) electrode by using cyclic voltammetry and constant potential electrolysis methods. Self-assembled monolayers of 4-Mercapto-1-butanol (MB) and 11-mercaptoundecanoic acid (MUA) were used. UME behaviour was examined in Fe²⁺/³⁺ solution. Polyaniline microelectrode was then used for DNA immobilization. The discrimination of double-stranded DNA (dsDNA) and single-stranded DNA (ssDNA) was performed. The films were also characterized by scanning electron microscopy (SEM).

Ultramicroelectrodes (UMEs) are different from conventional electrodes due to their geometry which results in enhanced mass transfer rate of electroactive species on the surface and rapid response towards small changes in current levels [1-3]. Thus, UMEs have major applications especially in monitoring electrode/electrolyte interfacial processes [4], fabrication of biosensors [5], electronic circuits and microchip reactors [6]. Fabrication of UMEs consists of sealing of metal wires, microbeads of metal particles assembled on the electrodes or chemical vapor deposition [7,8].

However, electrochemical fabrication of UMEs is so different from those techniques and in favor because of easiness and cheapness. In order to achieve this microfabrication process, surface of gold electrode was modified using self-assembled monolayers of alkanethiols in the study. Second step of the fabrication process consisted of depositing conducting polymer Polyaniline (PANI) on the SAM modified surface.

The usage of self-assembled monolayers serves as substrates for the deposition of PANI films. These well-defined organic surfaces provide a means to control the interface at a molecular level. The gate sites within the film which is free of pinhole defects, can act as a platform for the immobilization of 2D surface-confined polymerization of monomers parallel to the surface. Thus, numbers of ultramicroelectrodes could be formed on the electrode surface. Voltammetric behaviour of these electrodes are also different. The resulting current potential curve is sigmoidal in shape because of rapid heterogeneous electron transfer [9].

In this study, in order to check the UME formation, electrochemical behaviour of the deposited films were investigated in Fe²⁺³⁺ solution. UME with MUA modified PANI coated electrode by potential scanning with 20 cycles gave the best response with S shaped structure. Also, immobilization of DNA on these modified electrodes were performed and enhanced electrochemical signals were obtained compared to the results obtained with only polyaniline coated electrodes. Discrimination of double-stranded DNA (dsDNA) and single-stranded DNA (ssDNA) was carried out using UME, sensitively. Surface morphology of this UME examined by SEM showed the homogeneous distribution of nanostructured PANI onto the electrode surface.

Figure 1. SEM images of (a) dsDNA immobilized UME (b) ssDNA immobilized UME.

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Nitrilase Immobilization on Biodegradable Nanofiber Based Poly-3-hydroxybutyrate (PHB) and Polyhydroxybutyrate-co-3-hydroxyvalerate (PHBV)

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Abstract – In this study, it was aimed that poly-3-hydroxybutyrate (PHB), and polyhydroxybutyrate-co-3-hydroxyvalerate (PHBV) known as biodegradable polysters, were prepared nanofiber by electrospinning method and that suitable nanofibers were used as a support material for nitrilase immobilization. Nanofiber/nitrilase complexes could be designed as a membrane in the wastewater treatment.

PHAs are a biodegradable biopolymer which serve as carbon and energy storage for bacteria and become deposited as insoluble granules in the cytoplasm. Most bacteria are produced in conditions of nutrient limitation but where carbon is available in excess [1]. One of the most common PHAs are poly(3-hydroxybutyrate) (PHB) and its copolymer, polyhydroxybutyrate-co-3-hydroxyvalerate but different bacteria use hydroxy fatty acids of varying chain length, generating a range of PHAs. PHAs those are less brittle and more flexible while retaining tensile strength.

Possible PHA application fields are: packaging films, bags and containers, biodegradable carrier, disposable items, starting materials for chiral compounds, surgical pins, sutures, staples, and swabs, wound dressing, bone replacements and plates, blood vessel replacements [3].

Electrospinning is a process capable of fabricating ultrafine fibers with average diameters in the submicrometer to nanometer range. electrospun polymeric fibers which have a large surface area, are good candidates for a wide variety of applications, including filters, composite reinforcements, drug delivery vehicles and tissue-engineered scaffolds [4].

Nitriles are toxic organic compounds contained cyanide, and played an important role in the production of synthetic rubber, textile and plastic industry so that, increasing the use of organic nitriles in the manufacture of synthetic products increases the probability of their occurance in the industrial wastewater. The conventional treatment method of nitriles is alkaline chlorination. Currently, alternative, eco-friendly and cheap methods are researched about the subject and one of these methods can be enzymatic. Through nitrilase, nitriles were transformed to carboxylic acid and ammonia without formation of free amide intermediates. Nitrilase is found in plant, animal, fungi and some prokaryotes and, is used in the treatment of waste contained toxic nitrile and cyanide and in the chemical synthesis for several applications [5].

Biodegradable PHB and PHBV nanofibers by obtained electrosprinning method were prefered for nitrilase immobilization. In the treatment of synthetic wastewater composed of nitrile, nanofiber/nitrilase complexes could be designed as a membrane degraded in the environment and thus, an extra pollutant will not discharge to the nature during the treatment process.

In the study, different concentrations PHB and PHBV polymers were prepared as electrosprun fibers at various conditions. As a consequences, to supply the most proper fibers for nitrilase immobilization, the conditions are 14% PHBV and 19,9% ethanol mixture at 1 ml/hour flow rate, 15 cm collection distance and 30 kV applied electrical potential (Figure 1). Next, to obtain a biopolymer membrane, commercial nitrilase was immobilized on this nanofiber at optimum conditions to treat nitriles compounds in a synthetically concocted wastewater.

During this procedure, nitrilase activity was assayed by spectrophotometric methods.

Figure 1. SEM image of PHBV (14%) nanofiber

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Catalyst based Hydrogen Generation using Composite Metal/Polymer Films

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In this paper, we observed the effect of nanoporous cobalt catalyst/parylene films on hydrogen production from sodium boro-hydride. Poly(chloro-p-xylylene) is coated on silicon wafers using an oblique angle polymerization method which turns into different polymer structures such as columnar, helical, and doughnut-like (pattern) films. To improve cobalt binding on palladium coated polymer surfaces, vapor pyridine treatment is used in addition to aqueous treatment. Cobalt catalyst coated nanostructured films are kept in a sodium borohydride solution and hydrogen is collected for 60 minutes. Our experimental results show that pattern (macro/nano) films produce the highest amount of H₂ (35 ml/cm².h) and helical films have the best reproducibility in H₂ release rate (0.6 ml/cm².h decrease after 3 cycles). Also, vapor pyridine treatment on all films increased the hydrogen production rate.
Binding of Polyethylene Glycol Imidazolium Bromide on Iron Oxide Nanoparticles as a Novel Magnetic Phase Transfer Catalyst and its Application in Azidoalcohol Synthesis

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Abstract-The catalytic activity of polyethylene glycol imidazolium bromide immobilized on iron oxide nanoparticles as a novel magnetic phase transfer catalyst was investigated for the synthesis of azidoalcohol.

Magnetic iron oxide nanoparticles NPs are of great interest for researchers from a broad range of disciplines, including magnetic fluids, data storage, catalysis, and bioapplications [1-2]. Especially, magnetic ferrofluids and data storage are the applied researches that have led to the intergration of magnetic NPs in a myriad of commercial applications. Currently, magnetic NPs are also used in important bioapplications, including magnetic bioseparation and detection of biological entities (cell, protein, nucleic acids, enzyme, bacterial, virus, etc.), clinic diagnosis and therapy (such as MRI (magnetic resonance image) and MFH (magnetic fluid hyperthermia)), targeted drug delivery and biological labels. However, it is crucial to choose the materials for the construction of nanostructure materials and devises with adjustable physical and chemical properties. To this end, magnetic iron oxide NPs became the strong candidates, and the application of small iron oxide NPs in in vitro diagnostics has been practiced for nearly half a century [3]. In the last decade, increased investigations with several types of iron oxides have been carried out in the field of magnetic NPs among which magnetite and maghemite is the very promising and popular candidates since its biocompatibility have already proven.

Surface functionalized magnetic iron oxide nanoparticles (NPs) are a kind of novel functional materials, which have been widely used in the biotechnology and catalysis.

Having the above facts in mind, we now wish to report the preparation of polyethylene glycol imidazolium bromide (Figure 1) and its immobilization on iron oxide nanoparticles (Figure 2). This novel magnetic phase transfer catalyst was easily used as green and efficient catalyst for regioselective ring opening of epoxide by azide anion.

Figure 1.

Figure 2.

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Vitamin B12 Analysis with Carbon Nanotube-Chitosan Modified Disposable Graphite Electrode

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Abstract - A single walled carbon nanotube-chitosan (SWNT-chitosan) modified disposable pencil graphite electrode (PGE) was used in this study for detection of vitamin B12. The characterization of SWNT-chitosan modified PGE was carried out using scanning electron microscopy (SEM). Modified electrodes were used for the voltammetric analysis of Vitamin B12. The quantification of vitamin B12 in pharmaceutical products were also carried out. Our results show that modification of PGE with SWNT/chitosan composite enhances electrochemical signals.

Vitamin B12, also known as cobalamin, is an essential water-soluble vitamin that is commonly found in a variety of foods such as fish, meat, egg and dairy products. Determination of vitamin B12 is important for the quality control tests of drugs, nutrients and serum ingredients. General analysis methods of vitamin B12 are microbiological, chromatographic and spectroscopic methods. Besides these methods, electrochemistry provides simple, time saving and inexpensive routes [1,2].

Nano-structured materials have attracted great attention in recent years in many fields and the development of many new technologies [3,4]. Among them, carbon nanotubes (CNTs) play an important role due to their high electrochemically accessible area, good electronic conductance and strong mechanical, structural properties [5]. Depending on the arrangement of the carbon atoms, the CNTs can be metallic or semiconducting [6]. In electrochemical analysis, as a result of modification of electrodes with CNTs, higher active surface area, thus, enhanced and sensitive electrochemical signals can be obtained.

In this work, we used a SWNT/chitosan modified electrode for analysis of vitamin B12. Cyclic voltammetry (CV) and square wave voltammetry (SWV) was performed for analyses. A signal enhancement was obtained for the reduction of cobalt redox couples in the structure of Vitamin B12 using SWNT-chitosan modified PGE at low potentials due to the catalytic activity of SWNT in the study. The modified electrode was provided quantification of Vitamin B12 in pharmaceutical products giving good recovery results.

The preparation of SWNT-chitosan modified PGE presented here was simple, fast, easy, cheap. The method has novelty and comparability with the studies based on Vitamin B12 analysis in the literature.

Figure 1. The square wave puls voltamagrams of SWNT-chitosan modified electrode after 5μL, 15μL, 25μL, 30μL, 35μL, 40μL vitamin B12 added in pH 2.0 0.1 M phosphate buffer solution.

Figure 2. Relationship between SWNT/chitosan modified electrode and chitosan modified electrode’s reduction peak currents and vitamin B12 concentrations.

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Preparation of Carbon Nanotube-Chitosan Modified Disposable Graphite Electrode

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Abstract - A single walled carbon nanotube-chitosan (SWNT-chitosan) modified disposable pencil graphite electrode (PGE) was prepared in this study for electrochemical analysis. The characterization of the modified electrode was carried out using atomic force microscopy (AFM). The electrochemical behaviour of the obtained electrode was investigated and compared with the electrochemical behaviour of chitosan modified and unmodified PGEs. Our results show that the modification of PGE with SWNT-chitosan enhances electrochemical signals due to good physical and chemical properties of SWNT.

Carbon nanotubes (CNTs) have been a very attractive material for the researches from almost every field. CNTs have interesting electrocatalytic activities due to their size and structure. So they can be used in detection of electroactive compounds in complex analytes due to ability of promoting electron transfer reactions [1,2].

CNTs lead aggregations in solutions due to inter-tubular interactions as van der waals forces, hydrophobic interactions and π-stacking among individual tubes. The use of CNTs as nanomaterial requires that the CNTs have some degree of solubility or dispersity. The dispersion of functionalized CNTs is much better in charged polyelectrolyte solutions like chitosan than the organic and aqueous solutions [3]. Chitosan is a naturally abundant polysaccharide. Its polycationic structure strongly interacts with the relative anionic structure of acid treated CNTs.

In this work, we prepared and characterized a SWNT-chitosan modified electrode. Firstly commercial SWNT was purified with various steps and mixed with chitosan polymer for preparing their composite. Then, PGE was modified with this composite. AFM images show that SWNT-chitosan composite was homogeneously deposited on electrode surfaces.

Prepared electrodes was used in three electrode system as working electrode. With the use of voltammetric analysis, SWNT-chitosan modified electrode was compared with chitosan modified and unmodified electrodes. Electrochemical characterization studies proved the enhanced electrochemical signals in the presence of CNTs.

Figure 2. Cyclic voltograms of unmodified PGE, chitosan modified PGE and SWNT-chitosan modified PGE (1mg/mL SWNT, V: 100mV/s)

This electrode also showed electrocatalytic effect for hydrogen evolution. The preparation of SWNT-chitosan modified PGE presented here was simple, easy and cheap. The further researches on our laboratory will be using this electrodes in the analysis of biomolecules.

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Abstract-A series of CoFe/Cu multilayers were electrodeposited on Ti substrates from the electrolytes containing their metal ions under potentiostatic control. The Cu layer thickness was changed from 0.3 nm to 3.0 nm, while the ferromagnetic CoFe layer thickness was fixed at 4.0 nm. The deposition was carried out in a three-electrode cell at room temperature. The deposition of Cu layers was made at a cathode potential of -0.3 V with respect to saturated calomel electrode (SCE), while the ferromagnetic CoFe layers were deposited at -1.5 V versus SCE. The structural analysis of the films was made using X-ray diffraction (XRD). Magnetoresistance measurements were carried out using the Van der Pauw method at room temperature with magnetic fields up to ±12 kOe. All multilayers exhibited giant magnetoresistance (GMR) and the GMR values were observed to oscillate depending on the Cu layer thickness.

The multilayers exhibiting giant magnetoresistance (GMR) have been one of the most important mechanisms of nanotechnology. The GMR is defined as the large changes in electrical resistance of the ferromagnetic multilayers in the magnetic field. The effect was first observed in Fe/Cr multilayered [1] and Fe/Cr/Fe sandwiched [2] structures grown by molecular beam epitaxy (MBE). In later years, a variety of multilayers with GMR was produced by vacuum techniques such as MBE and sputtering, and non-vacuum techniques such as electrodeposition. Among these, electrodeposition is an inexpensive and simple technique to produce the ferromagnetic nanostructure materials with GMR [3]. Such materials containing iron-group metals (Fe, Co and Ni) are of importance for GMR sensors in hard disk drive (HDD) read/write heads and microelectromechanical systems (MEMS).

CoFe/Cu multilayers were electrodeposited on Ti substrates from the electrolytes containing 0.075M CoSO₄, 0.05 M FeSO₄, 0.05 M CuSO₄, 0.25 M boric acid, 0.01 M sulfamic acid under potentiostatic control. The pH value of the electrolyte was about 2.5. Deposition was carried out in a three electrode cell at room temperature. The deposition of Cu layers was made at a cathode potential of -0.3 V with respect to saturated calomel electrode (SCE) and the CoFe layers were deposited at -1.5 V versus SCE. All films thicknesses were fixed at 3 µm. The Cu layer thickness was changed between 0.3 nm and 3 nm while the CoFe layer thickness was held constant at 4 nm. The structural analysis of the films was made using X-ray diffraction (XRD) with Cu Kα radiation, in the range of 2θ = 40°-100°. Magnetoresistance (MR) measurements were made at room temperature in the magnetic fields of ±12 kOe using the Van der Pauw method. The peaks appeared at 2θ = 44°, 51°, 74° and 90° are the main Bragg peaks of the multilayers, arising from the (111), (200), (220) and (311) planes of the face-centred cubic (fcc) structure respectively, which correspond to the average lattice spacing within the multilayer itself. No satellite peak was detected.

Figure 1 shows that longitudinal magnetoresistance (LMR) and transverse magnetoresistance (TMR) curves of electrodeposited 652[CoFe(4 nm)/Cu(0.6 nm)] multilayer. %MR of this multilayer is up to %6 at ±12 kOe.

It is clearly seen from the Fig. 2 that the GMR oscillates as a function of the Cu layer thickness. The first peak of GMR occurs at a Cu layer thickness of 0.6 nm, the second one at 1.2 nm, and the third one at 2.0 nm. Note that the peak positions appear at each 0.6 nm, that is, the oscillation period is ~0.6 nm. In these peaks, magnetic layers are coupled antiferromagnetically.
Investigation on the Usage of Nano-TiO₂ Modified Electrode for Electrochemical Determination of Trace Amounts of a Basic Dye in Aquoeus Solutions

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Abstract-A novel carbon paste electrode modified with nano-TiO₂ (Ti-MCPE) was developed for the voltammetric determination of trace amounts of basic dye- Setacryl Blue B3 in aqueous solution systems. The electrochemical behaviour of Basic Blue 3 (BB3) at a bare carbon paste electrode (CPE) and nano-TiO₂ modified carbon paste electrode was studied with cyclic voltammetry and square wave voltammetry for the first time.

Dye wastewaters are generated by a wide variety of sources, such as textiles, printing, dyeing and food plants. They are important sources of water pollution and some dyes degradation products may be toxic carcinogens. Moreover, the color produced by minute amounts of organic dyes in water is of great concern because it is aesthetically unpleasant. Therefore, developing a sensitive and a convenient method for the determination of organic dyes are of great importance and interest.

Electroanalytical methods, which allow for the accumulation of analytes on the electrodes through a nonelectrolytic process lead to the development of very sensitive, selective and rapid techniques, such as anodic stripping voltammetry, which has been widely employed for the trace determination of usually inorganic compounds and also some organic compounds [1]. Modified and unmodified carbon paste electrodes are easy to prepare and use, and exhibit good sensitivity and reproducibility for electrochemical determinations of organic and inorganic compounds. Several groups have reported the use of clays in modifying electrodes for determination organic compounds [2,6]. However, electrochemical determination of organic dyes by using nano-TiO₂ modified carbon paste electrode has not been reported.

The objective of the work is to develop a sensitive, selective and convenient electrochemical method for the determination of trace amounts of basic blue 3 by using nano-TiO₂ modified carbon paste electrode. The working electrode Nano-TiO₂ used as a novel modified agent offers the advantages of being simple and easy to prepare. The electrochemical measurements were performed on a Gamry Inst. Reference 600 in a three-electrode system by using cyclic voltammetry and square wave voltammetry. The working electrode was a self-made Ti-MCPE electrode and the reference and counter electrodes were a saturated calomel electrode and a Pt wire, respectively. 0.05 M phosphate buffer (pH=7) solution was used as the supporting electrolyte for BB3 determination. The electrochemical behavior of BB3 of 5x10⁻⁴ mol L⁻¹ in 0.05 M pH=7 phosphate buffer on Ti-MCPE was investigated using cyclic voltammetry (CV) at scan rate 100 mV s⁻¹. An oxidative peak at 0.98 V appeared at the anodic scan, while no responding reductive peaks were observed at the reverse scan. The oxidative peak was examined at different scan rates in the range of 20-800 mV s⁻¹ and different pH solutions in the range of 4-10. The results indicated that the best peak current of BB3 was obtained in pH=7 phosphate buffer solutions at scan rate 100 mV s⁻¹. To evaluated of the analytical parameters, such as the limit of detection (LOD) and the limit of qualification (LOQ) of BB3 at Ti-MCPE was carried out square wave voltammetry method. Under the optimal conditions, square wave voltammometric measurements were performed for different concentrations of BB3. The accumulation step was proceeded at 0V for 120 s while stirring the solution of 500 rpm. The square wave voltammograms were recorded when sweep from 0V to 1.2V after 10 s quiescence. The well-defined stripping peak was appeared at mean potential 0.98V. The stripping peak currents increased proportional to BB3 concentrations. Linear calibration dependency was found in the concentration range of 0.2- 2 μM. LOD and LOQ values were found as 21.72 nM and 72.39 nM, respectively.

The performance of trace amounts of basic dye for determination at a bare carbon paste electrode (CPE) and nano-TiO₂ modified carbon paste electrode was also compared.

Finally, compared with the unmodified carbon paste electrode, Ti-MCPE not only significantly enhances the oxidation peak of BB3 but also lowers oxidation overpotential, suggesting that the Ti-MCPE can remarkably improve the determining sensitivity of BB3.

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Synthesis of TiO$_2$ Coated Self-Cleaning Materials

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Abstract- Self-cleaning materials containing a nanometer scale TiO$_2$ thin film were prepared and tested for antimicrobial properties beside their surface analyses.

Titanium dioxide (TiO$_2$) thin films are widely used in various applications. Most physical, chemical and spraying techniques are used to coat metal and ceramic substrates at high process temperatures. The resulting thin film coated material exhibits photocatalytic properties and degrade organics and dirt on its surface.

In this study, TiO$_2$ nanoparticles were coated on glass (silica or quartz), steel and a ceramic surface using the sol-gel method technique.

Thin films were obtained and surface properties were determined using surface analysis techniques such as SEM, EDX, AT-FTIR, Raman, XRD (Figure 1).

Surface analysis revealed that TiO$_2$ thin films were successfully prepared on various materials and nano particles were clearly determined. Nano particles were mainly of the anatase phase which is the photoactive crystal structure of TiO$_2$. Those materials were tested for antimicrobial properties using e-coli and Candida albicans as model microorganism.

Antibacterial tests also reveal that a TiO$_2$ thin film surface is quite effective for the degradation of studied microorganisms.

Details of the study including antimicrobial properties of produced materials will be presented.

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A Catalytic Separation Method for Removing Ethylene from Oxidative Coupling of Methane Products Via Alkylation of Benzene to Ethyl Benzene on Nanocatalyst

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Abstract- Efficient separation of ethylene or creative ideas in process operation is needed to make the oxidative coupling commercially feasible. Additionally combinations with other reactions have been proposed. Ethylene was successfully converted to the useful chemical intermediate ethyl benzene using nanocatalyst. With this method, in a combined process of oxidative coupling and reforming of methane, which can still be valuable in terms of heat integration of the reactions, methane and ethane present in the feed were not converted and can be used for steam reforming in the proposed reaction concept.

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Amongst various schemes for methane conversion, oxidative coupling to ethylene is a promising process to upgrade natural gas. The limitations of the oxidative coupling have led to development of several alternatives. Efficient separation of ethylene or creative ideas in process operation is needed to make the oxidative coupling commercially feasible. Additionally combinations with other reactions have been proposed. Ethylene was successfully converted to the useful chemical intermediate ethyl benzene using nanocatalyst. With this method, in a combined process of oxidative coupling and reforming of methane, which can still be valuable in terms of heat integration of the reactions, methane and ethane present in the feed were not converted and can be used for steam reforming in the proposed reaction concept.
A Simple Kinetic Model for Oxidative Coupling of Methane over \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta} \) Nanocatalyst

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Abstract- The main goal of this work is discuss about a simplify kinetic for OCM reaction which investigated by power rate law expression of \( \text{C}_2^+ \) (ethane and ethylene) and \( \text{C}_1 \) (CO and \( \text{CO}_2 \)) formation. This method appears to be simple and practical. For this category the intermediates are hindered, instead, the rate of any product formation can be expressed as a function of the reactant concentrations.

Natural gas is composed primarily of methane with minor amounts of paraffin hydrocarbon family, ethane, propane, butanes. Nonhydrocarbon constituents include nitrogen, hydrogen sulfide, carbon dioxide, helium, and water vapor. In order to make an efficient utilization of natural gas, we must consider transforming it into more valuable chemicals. Higher hydrocarbons are more useful for chemical industries. OCM reaction is thermodynamically advantageous in comparison with the direct coupling reaction of methane without oxidant. However, no catalysts could reach the principal criteria for industrial application of OCM. In this work, firstly we discuss about method of preparation of \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta} \) nanocatalyst and it’s characterization and properties. \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta} \) perovskite-type nanocatalyst were synthesized by citric-EDTA (ethylene diamine tetra acetic acid) complexation method. BET surface area of oxide powder after calcination of the gels at 1050 °C calculated from the linear BET plots. The XRD pattern of \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta} \) powders show that pure perovskite crystallinity can be obtained and exhibit the features of the perovskite structure, no secondary phase has been detected. The main goal of this work is discuss about a simplify kinetic for OCM reaction which investigated by power rate law expression of \( \text{C}_2^+ \) (ethane and ethylene) and \( \text{C}_1 \) (CO and \( \text{CO}_2 \)) formation. This method appears to be simple and practical. For this category the intermediates are hindered, instead, the rate of any product formation can be expressed as a function of the reactant concentrations.

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**ZnO-Nanotube as Ecofriendly, Green and Efficient Catalyst in the Protection Reaction**

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**Abstract** - The catalytic ability of ZnO nanotube in the protection of carbonyl groups as phenylhydrazone and 2,4- diphenylhydrazone under solvent free condition was studied. It was proved that ZnO nanotube is an efficient heterogeneous catalyst for protection reaction of aldehydes and ketones and gave the protected products in high isolated yield under mild reaction conditions.

Nontoxic and inexpensive environmentally compatible ZnO has been in great interest from wide range of applications in technological fields associated with nanotechnology; it absorbs large fraction of the solar spectrum and light quanta. Furthermore, ZnO is a semiconductor that can be used as a photocatalyst. It is a promising tool to convert the pollutants into the harmless substances in the waste water, directly, which compliances with green chemistry protocol and it is proved that ZnO nanotube enhances the rate and stereoselectivity of chemical reactions [1-2].

Finding creative ways to reduce hazard and waste has been the goal of many academic labs across the country. In recent history, the trend has been toward "solvent free" methods; because of their high efficiency, environmentally benign conditions and convenient work-up [3].

Phenylhydrazones and 2,4- diphenylhydrazones are very important intermediates in synthetic organic chemistry, in addition to their biological activities they are particularly significant as an antimicrobial agents, vasodilator and antioxidants. Having the above facts in mind, we now wish to report a green and ecofriendly protocol for the protection of carbonyl groups as phenylhydrazones and 2,4-diphenylhydrazones under solvent-free conditions in the presence of catalytic amounts of zinc oxide nanotubes (Figure 1).

![Figure 1](image)

R= alkyl or aryl
R'= alkyl, aryl or hydrogen
Ar= Phenyl or 2,4-dinitrophenyl

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Magnetic Iron Oxide Nanoparticles with Bioactive Coatings for Magnetic Resonance Imaging
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Abstract- Iron oxide magnetic nanoparticles (MNP) offer tremendous potential for magnetic resonance imaging (MRI). Herein, we present synthesis and characterization of functional MNP. These particles are coated with peptides and proteins to introduce biocompatibility, hydrophilicity and targeting. The potential MRI applications of the iron oxide nanoparticles with bioactive coatings are being investigated.

Magnetic Resonance imaging (MRI) is one of the powerful techniques for disease diagnosis due to its non-invasive, 3-D and dynamic monitoring capabilities. Contrast agents (CA) have been used to enhance monitoring capabilities of MRI technique. CA changes T1 or T2 relaxation times of water protons.[1] Gadolinium is the most commonly used CA agent and a high concentration of gadolinium is necessary for sensitive detection.[2] Currently, new contrast agents that are more sensitive and less toxic are being developed for MRI systems. Superparamagnetic iron oxide nanoparticles (SPION) are one of the newly emerged MRI contrast agents, which reveal extraordinary magnetic properties within nanometer size, and are biocompatible and suitable for surface modification.

Here, magnetite nanoparticles were synthesized by thermal decomposition method.[3] Briefly, 2 mmol Fe(acac)3, 6 mmol palmitic acid, 6 mmol hexadecane amine, 10 mmol 1,3-propanol mixed in 20 ml phenyl ether and magnetically stirred under Ar gas for 30 minutes. Then, the solution was first heated up to 200°C for 2 h and later, heated to reflux at 250°C for 1 h. The nanoparticles were characterized by TEM, FT-IR, XRD and DLS. XRD result in figure 1 demonstrates that particles are magnetite. According to DLS result as shown in figure 3, the particles are highly monodisperse and hydrodynamic sizes of the particles are ca. 8-10 nm. TEM results are also in agreement with DLS results (figure 2).

The magnetic nanoparticles are coated with amphiphilic peptides to introduce bioactivity. Peptides are synthesized by solid phase peptide synthesis (SPPS).[4] Peptide was characterized by LC-MS. The peptide in water and the SPION in hexane were mixed in solution and sonicated for 30 minutes. Peptide coated nanoparticles were characterized as well.

We are currently investigating the MR properties and the bioactivity of the nanoparticles.

Figure 1. XRD analysis of the SPION particles.

Figure 2. TEM images of the coated SPION.

Figure 3. DLS results coated SPION.

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Electrochemical Copolymerization and Characterization of (3,4-ethylenedioxythiophene) and (3,4-ethylenedioxythiophene-methanol)

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Abstract-In our study, EDOT (3,4 Ethylenedioxythiophene) and EDTM (3,4 Ethylenedioxythiophene-methanol) were electrochemically copolymerized on single carbon fiber micro electrodes (SCFMEs) with different mole fractions.

Due to its high oxidation potential, thiophene itself is difficult to polymerize electrochemically. The best result are obtained in BF₃·Et₂O medium [1]. However, upon alkyl substitution the monomer oxidation potential is lowered to an easily accessible range, which has resulted in the extensive study of poly(3-methyl thiophene) and other poly(3-alkylthiophenes) [2]. Substitution at the 3- and 4- positions of thiophene prevents the occurrence of α-β and β - β coupling during electropolymerization, yielding more ordered polymers with longer conjugation lengths. Initially, the synthesis of 3,4-disubstituted polythiophenes were carried out with the goal of stabilizing the oxidized form as well as providing solubility and processibility [3].

PEDOT is one of the most interesting polymer because of its environmental stability in the oxidized state combined with its high conductivity [4]. Polymerization of methanol substituted EDOT (EDTM) is a common strategy to create a PEDOT-like material bearing hydroxyl groups which are a convenient point of attachment for a variety of functional groups [5].

Microelectrodes can be used in highly resistive environments; they can work in very small sample volumes and enable the detection of very small amounts of material. Compared with other conducting polymers, little research has been done on the development of biosensors based on poly(3,4-ethylenedioxythiophene) (PEDOT) derivatives, although this material is a promising bio sensor systems [6].

In this study, EDOT(3,4-ethylenedioxythiophene) and methanol substituted EDOT (EDTM) was electrochemically copolymerized on single carbon fiber micro electrodes (SCFMEs) with different mole fractions of EDTM (fEDTM), at the same scan rates in the same potential range and with the same scan numbers via cyclic voltammetry in NaClO₄/ACN electrolyte solution. The copolymer films on SCFMEs were characterized via Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and FTIR-ATR spectrophotometer.

The aim of this work is to achieve the electrochemical copolymerization of EDOT and EDTM, and to show the availability of biosensor applications.

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A New Approach in the Usage of Ligands for the Preparation of Enzyme and Bi-enzyme Electrodes

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Abstract-The aim of this study was to improve functional nanostructured materials for analytical and biomedical applications. Such developments require standardized analytical procedures and reference materials with well-defined nanoscale structures. We investigated properties of newly designed organic materials as potential red-ox mediators in biofuel cell design.

Biosensors, especially based on enzyme-modified electrodes, have received great interest after first demonstration of this concept by Clark in 1962 [1]. These devices have some advantages as being sensitive, highly selective and fast-responding analytical tools, which are used for industrial, environmental and clinical applications [2-4]. However in some cases they are relatively expensive. To overcome this problem recently number of studies has been realized in order to apply some metal (e.g. iron, ruthenium and osmium) in the construction of amperometric biosensors.

In particular, the usage of the complexes in biosensing systems has some advantages but most of these metal complexes are not available commercially and the synthesis of these complexes is very complicated and/or time-consuming. For this reason only a limited number of phenanthroline complexes with osmium and ruthenium have been reported recently [5-7]. To overcome this problem a simple and rapid method for preparation of these complexes would undoubtedly promote screening of new mediators and designing of new biosensors.

This study according to our best knowledge is one of the first demonstration of application 1,10-phenantroline derivatives (PDs) in design of amperometric biosensors. In general, this study is focused on demonstration of some PDs as suitable red-ox mediators for biosensors and biofuel cells. Differently from many other studies, the PDs were not included into structures of metal complexes. Bioelectrochemical responses of PDs and enzyme modified electrodes were studied amperometrically and potentiometrically. The experimental measurement procedure is given in Figure 1.

This study clearly illustrates that some PDs can be applied as redox mediators for oxidases and are suitable for development of biosensors and biofuel cells.

Figure 1. The shematic diagram of our experimental procedure

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Affinity Magnetic Nanoparticle Supported Galactitol Dehydrogenase with NADH Recycling for Enantioselective Reduction Reactions

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Abstract—Rapid immobilization with one pot purification of Galactitol dehydrogenase (GatDH) is achieved using iminodiacetic acid chelated Co²⁺ modified magnetic nanoparticle as a carrier. Formate dehydrogenase from C. methlica was used as a multienzyme for recycling of NADH/NAD⁺ with repeated representative synthesis of (S)-1,2 propanediol followed by chiral GC. The affinity magnetic nanoparticles were characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR), while the purity of GatDH was assayed by SDS-PAGE analysis. The immobilized two-enzyme system, reflecting the pH dependence of its constituent enzymes, had optimal activity at pH 7 and retained up to 70% of its activity after one week of repeated use.

The immobilization of enzymes onto insoluble supports has been a topic of active research in enzyme technology and is an important tool for their application at industrial process, fabrication of a diverse range of functional materials or devices [1]. In the recent years, the nanosized magnetic particles has received increasing attention because of their superparamagnetic properties and easy separability from reaction mixture by the application of a magnetic field [2].

Dehydrogenase represents an important class of enzyme in biotechnological due to their enantioselective oxidative and reductive catalytic properties [3]. The enzyme galactitol dehydrogenase catalyzes the interconversion of polyvalent aliphatic alcohols and polyols to the corresponding ketones and the corresponding (S)-configured alcohols [4]. However for preparative syntheses, catalytic enzymatic recycling of the cofactor NAD⁺/NADH is required. Formate dehydrogenase from Candida boidinii (CboFDH) has been reported to catalyse the oxidation of formate anion to carbon dioxide with concomitant reduction of NAD⁺ to NADH [5]. The micron- or nanoscale particles with divalent metal ions have selectively bind to His (6)-tagged recombinant proteins and combine the advantages of magnetically responsive particles and the metal affinity ligand within enzyme purification and immobilization studies.

Herein we have describe the immobilization of His (6)-tagged GatDH and FDH on affinity magnetic nanoparticle with NAD⁺/NADH recycling with one pot purification of enzyme and repeated representative production of (S)-1,2 propanediol from hydroxyacetone.

First Iron (III) oxide Fe₂O₃ nano particles (7nm, Integran Techno., USA) were modified as reported earlier [6]; the metal ion chelated magnetic nanoparticles was designated as M-SiM. Then M-SiM were characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). In second step His (6)-tagged GatDH and FDH were produced [4, 7]. Immobilization of GatDH and FDH was carried out by using 5 mL M-SiM particles (ca 0.25 g wet weight) which were washed twice with binding buffer (pH 6.5, 100mM Bis-Tris, 300mM NaCl, 25 mM imidazole). The clarified cells crude extract of 15 mL (1 mg/ml) was mixed with nanoparticles for 30 min at 4 C with mild shaking. The GatDH and FDH immobilized M-SiM were washed twice with binding buffer to remove the nonspecifically bound impurities. The protein content was determined with the standard Bradford assay. The immobilized enzyme was checked for its purity by SDS-PAGE analysis. The maximum protein amount that was attached to the resin was estimated as 6 mg g⁻¹ for GatDH and 7 mg g⁻¹ for FDH.

The reactions catalyzed by the immobilized GatDH and FDH system is illustrated in Scheme 1. The combined reactions required repetitive cycling of NAD⁺ and NADH and were followed by measuring the amount of (S)-1,2 propanediol formed. The reaction solutions performed with 200 mg of each M-SiM immobilized GatDH and FDH, 1.5 mM NADH and 0.5 mM NAD with 100 mM hydroxyacetone and 100 mM sodium formate in 40 ml of Bis-Tris buffer (50 mM, containing 1mM MgCl₂ pH 7.0).

Scheme 1. Reaction catalyzed by immobilized GatDH and FDH for NAD⁺/NADH recycling

The both immobilized enzyme stored at 4°C retained activity over a period of four week and was able to reuse many times.

In summary an efficient process for the simultaneous purification and immobilization of His (6)-tagged GatDH and FDH with recycling of NAD⁺/NADH using iminodiacetic acid chelated Co²⁺ modified magnetic for enantioselective representative production of (S)-1,2 propanediol with excellent ee (> 99%) has been presented.

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NanoPharmaceuticals are the pharmaceuticals designed using “Nanoscience & nanotechnology”. Nanoscience is suddenly becoming a big field: in addition to the enabling technologies, scientists have realized the future applications of this research. By convincing political leaders around the world, countries have instituted initiatives to promote nanoscience and nanotechnology in their universities and research institutes. Many scientists are pursuing this research and the rate of discovery has increased dramatically. NanoPharmaceuticals are broadly classified as NanoEngineered Drugs and NanoCarriers. Extensive research effort is going on in application of nanotechnology in therapeutic segments. Due to their size, nanoparticles, can be stronger, lighter and highly soluble, less hygroscopic, or with totally different physicochemical properties. Nano-design of the existing drug molecule might help in increasing their solubility and oral bioavailability; development of different dosage forms (e.g. nano-suspensions for parentals) and in exploring different routes of administrations (e.g. nasal and ophthalmic) to provide patient-friendly preparations. After i.v. administration of particulate drug carrier, they will be cleared from the circulation by spleen and liver depending upon their particle size. It was reported that particles less than 200 nm can escape this physical screening, hence, nanoparticulate carriers might be of great interest. Nanoparticles with hydrophilic surfaces avoid reticuloendothelial system uptake and are long circulating. Nanoparticles which are long circulating might get targeted to tumor tissue by a mechanism known as enhanced permeation and retention. Where in nanoparticles permeate into leaky vascular for a typical tumor tissue, subsequently they will be retained due to the primitive lymphatic system development.

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Thiol-Stabilized CdTe Nanocrystals and Phthalocyanine Photosensitizers: Potential Applications in Photodynamic Therapy

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Abstract- Thiol stabilized CdTe quantum dots (QDs) synthesized in aqueous phase were used as energy donors to tetra substituted aluminum, gallium and indium phthalocyanines through fluorescence resonance energy transfer (FRET). Energy transfer occurred from the QDs to phthalocyanines upon photoexcitation of the QDs. An enhancement in efficiency of energy transfer with the nature of the carboxylic thiol stabilizer on the QDs was observed. As a result of the conjugation between nanoparticles (NP) and the phthalocyanines (Pcs) the photoluminescence efficiency of the Pcs moieties in the conjugates do not strictly follow the quantum yields of the bare phthalocyanines. Study of the photophysics of Pcs in the presence of the QDs revealed a high singlet oxygen quantum yield, hence the possibility of using QDs in combination with phthalocyanines as photosensitizers in photodynamic therapy.

Photodynamic therapy (PDT) in cancer treatment involves the uptake of a photosensitizer by cancer tissue followed by photoirradiation. The use of nanoparticles as carriers of photosensitizers is a very promising approach because these nanomaterials can satisfy all the requirements for an ideal PDT agent [1].

Quantum dots (QDs) are semiconductor nanocrystals which are very attractive because of their small size, photostability and emission tunability compared to conventional dyes. QDs and their molecular conjugates are becoming increasingly important for a wide range of applications in biotechnology and medicine [2]. Metal phthalocyanines (MPcs) have been a focus of attention because they exhibit exclusive properties.

Figure 1. Photodynamic Therapy

In this study we have investigated photophysical and photochemical properties of aluminum, gallium and indium (III) phthalocyanines mixed with CdTe nanocrystals for photodynamic treatment. Aluminum, gallium and indium tetra-polyoxy substituted phthalocyanines were synthesized and characterized according to reported method [3]. CdTe QDs were synthesized from aqueous solution and were stabilized by using water soluble thiol thioglycolic acid. In addition to serving as stabilizer, this thiol capping serve to passivate the surface of the QDs and thereby removing the surface traps which lower the photoluminescence (PL) efficiency of the quantum dots. General trends are described for quantum yields of photodegradation, fluorescence and fluorescence lifetimes as well as singlet oxygen quantum yields of these compounds. Singlet oxygen quantum yields were determined in DMSO using 1,3-diphenylisobenzofuran (DPBF) as a chemical quencher. The disappearance of DPBF was monitored using UV–vis spectrometer. Figure 2 shows the singlet oxygen measurements of AlPc in DMSO.

Figure 2. A typical spectrum for the determination of singlet oxygen quantum yield. This determination was for AlPc in DMSO at a concentration of 1 x10-5 mol.dm-3.

In summary, the interaction of CdTe quantum dots with AlPc, GaPc and InPc derivatives shows that a strong overlap occurs between the emission of the TGA capped QDs and the absorption spectra of these Pc derivatives. The largest fluorescence energy transfer (FRET) was observed for InPc followed by GaPc and then AlPc. The singlet oxygen quantum yields of these Pc derivatives increased in the presence of QDs, hence making the combination of these Pc derivatives and QDs potential candidates for applications as photosensitizers in PDT.

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Antiparkinsonian drug levedopa, \([(-3)-(3,4-
\text{dihydroxyphenyl})-l\text{-alanine}](LD)\) is principally metabolized by an enzymatic reaction (dopa-decarboxylase) to dopamine compensating for the deficiency of dopamine in the brain [1]. Parkinson’s disease is a progressive neurological disorder that occurs when the brain fails to produce enough dopamine. This condition causes tremor, muscle stiffness or rigidity, slowness of movement (bradykinesia) and loss of balance. Dopamine cannot be administered directly because it cannot penetrate the blood–brain barrier. Therefore LD, which can be orally administered, is used to provide a source of dopamine, and is used in the treatment of Parkinson’s disease to provide symptomatic relief to most patients at the initial stages of the disease. However, elevated levels of dopamine also cause adverse reactions such as nausea, vomiting and cardiac arrhythmias [2]. In order to prevent its metabolism by aromatic L-amino acid decarboxylase (AADC) to dopamine in the periphery, LD is routinely administered in combination with an AADC inhibitor such as CD. However, when administered with CD, a considerable amount of LD is converted to 3-O-methyl-levodopa (3-OMD) by peripheral catechol-O-methyltransferase (COMT), and only one-tenth of the administered dose reaches the brain [3]. The rationale behind the use of COMT inhibitors in combination with LD / CD is to (i) increase the LD availability to the brain, while inhibiting the peripheral O-methylation of LD, (ii) improve the transport of LD across the blood–brain barrier, since 3-OMD competes with LD for transport into the brain [4] and (iii) reduce fluctuations in plasma and brain levels of LD, avoiding the exposure of brain dopamine receptors to alternating high and low concentrations of dopamine [5].

Nanostructured materials have aroused dramatic interests and have become an intensive research area for the past decade due to their finite small size, high specific surface area, high porosity, and unique physical/chemical properties. The fascinating properties and functions related to the size effect incur intriguing applications in many fields [6]. Studies of novel materials at the nanometer scale have been the most important and challenging task in the modern material science, which involves nanoparticles, nanowires, nanotubes and their significant roles in medicines, biomedical engineering, environmental applications, and surface science [7]. The nanostructures with large specific surface area could provide an important and feasible platform for catalysis, separation, sorption, sensing and fuel cells.

In the present paper, the use of a novel carbon paste electrode modified by 2,2’-[1,2 butanediylbis (nitriloethylidyne)]-bis-hydroquinone (BBNBH) and and TiO\(_2\) nanoparticles prepared by a simple and rapid method for the determination of LD and CD was described. In the first part of the work, cyclic voltammetry was used to investigate the redox properties of this modified electrode at various scan rates. The apparent charge transfer rate constant, \(k\), and transfer coefficient, \(\alpha\), for electron transfer between BBNBH and TiO\(_2\) nanoparticles paste electrode were calculated. In the second part of the work, the mediated oxidation of LD at the modified electrode was described. It has been found that under optimum condition (pH 8.0) in cyclic voltammetry, the oxidation of LD occurs at a potential about 420 mV less positive than that of an unmodified carbon paste electrode. The values of electron transfer coefficients (\(\alpha\)), catalytic rate constant (\(k\)) and diffusion coefficient (D) were calculated for LD, using electrochemical approaches. Differential pulse voltammetry (DPV) exhibited two linear dynamic ranges and a detection limit (3\(\sigma\)) of 0.2 \(\mu\)M for LD. In the third part of the work, simultaneous determination of LD and CD at the modified electrode was described. Finally, this method was used for the determination of LD in some real samples, using standard addition method.

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Novel Method to Simultaneous and Selective Voltammetric Determination of Norepinephrine, Acetaminophen and Folic Acid Using ZrO$_2$ Nanoparticles Modified Carbon Paste Electrode

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Abstract-A novel ZrO$_2$ nanoparticles modified carbon paste electrode (ZONMCPE) was fabricated, and the electrooxidation of norepinephrine (NE), acetaminophen (AC) and folic acid (FA) and their mixture has been studied using electrochemical methods. The modified electrode displayed strong function for resolving the overlap voltammetric response of NE, AC and FA into three well-defined voltammetric peaks.

Nanotechnology has recently become one of the most exciting fields in sciences. There is currently intense interest in the use of nanoparticles for the fabrication of modified electrodes and a wide range of bioscience applications. Using nanoparticles to modify electrode surface has enhanced the response signal, increased the sensitivity, and showed better reproducibility [1].

The electrochemical determination of biomolecules has been intensively investigated over the past two decades. Among these biomolecules, NE is one of the most important catecholamine neurotransmitters in the central nervous system. Many diseases are related to changes of its concentration, and the determination of NE concentrations in biological systems provides important information on its physiological functions. NE determination is usually executed by high-performance liquid chromatography, gas chromatography, and spectrophotometry. Meanwhile, NE is an electroactive species and can be detected with electrochemical oxidation at various modified electrodes [2].

Acetaminophen or paracetamol (AC) is an antipyretic and analgesic drug widely used, it is an effective and safe analgesic agent used worldwide for the relief of mild to moderate pain associated with headache, backache, arthritis and postoperative pain. It is also used for reduction of fevers of bacterial or viral origin [3]. So it is very important to establish a simple, fast, sensitive and accurate detection method for AC.

Folic acid (pteroylglutamic acid, abbreviated as FA) is a widely distributed vitamin (called vitamin BC, vitamin M, or vitamin B9). It is involved in single carbon transfer reactions in metabolism, and it is the precursor of the active tetrahydrofolic acid coenzyme. It was first discovered in spinach. Folic acid deficiency causes growth weakness in mammals and different kinds of anaemia; it causes a failure to make the purines and thymine required for DNA synthesis. FA is a potential agent for cancer prevention by free radical scavenging and antioxidant activity. FA is made up of the building blocks pterin, p-amino-benzoic acid, and glutamic acid. Folate is the preferred name of folic acid and folic acid derivatives. Electrochemical methods have been used for determination of FA [4].

AC administration is known to increase brain serotonin (5-HT) levels as a result of liver tryptophan-2,3-dioxygenase (TDO) inhibition and 5-HT is known to play a role in NE release in the brain. Also, FA, the synthetic form of the B vitamin folate, works primarily in the brain and nervous system and is necessary for the synthesis of DNA, the production of red and white blood cells and of NE and serotonin in the nervous system. Also, some substances like nonsteroidal anti-inflammatory drugs such as aspirin, ibuprofen and AC can inhibit FA from being absorbed or used by the body. Likewise, when taken for long periods of time, AC and other anti-inflammatory medications can also increase the need for FA. Therefore simultaneous determination of NE, AC and FA is important.

To our knowledge, no study has been reported the using of ZrO$_2$ nanoparticles for modifying carbon paste electrodes, also, no study has been published so far reporting the simultaneous determination of NE, AC and FA by using modified ZrO$_2$ nanoparticles carbon paste electrode or other kinds of carbon electrodes. Thus, here we report the preparation and application of a ZONMCPE as a new kind of carbon electrodes for the first time. The analytical performance of the modified electrode has also been evaluated during NE-quantification in the presence of AC and FA.

Figure 1. SEM of ZrO$_2$ nanoparticles

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Self-assembly and Structure Investigation of Recombinant S-layers Expressed in Yeast
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Abstract—In this work, we investigated the in-vivo and in-situ structures, stability and self-assembly characteristics of genetically engineered surface layer (S-layer) proteins of Bacillus stearothermophilus ATTC 12980 expressed in yeast Saccharomyces cerevisiae BY4741. Our results show that the fusion protein structure is retained under osmotic shock and could be successfully reassembled giving hints about their possible applications in nanobiotechnology.

S-layers are the outermost layers of some gram-negative, gram-positive bacteria and Archaea consisting of protein (or glycoprotein) monomers that form planar self-assembly structures [1]. Subunits can self-assemble in oblique (p2), trimeric (p3), tetragonal (p4), or hexagonal (p6) symmetrical structures [2]. The lattice diameter of such layers ranges from 2.5 nm to 35 nm and array depth varies between 5.0 nm and 70 nm [3]. S-layer arrays are extremely porous (up to 70%) having pores of identical size (2-8 nm range) and morphology [4]. In bacteria, their function encompasses maintenance of cell shape and stiffness; ion traps and molecular filters, virulence factors, adhesion sites for exoenzymes and biomineralization nuclei [5]. S-layers have been used in biotechnology and biomimetics as isoporous ultrafiltration membranes, immobilization matrices for many molecules like enzymes, antibodies, biotin, avidin, vaccine and vaccine derivatives and supporting layers for lipid membranes [6]. In nanotechnology, S-layers have been recrystallized on various solid substrates for microelectronic applications and sensor development technologies [6]. In addition, S-layers can also be used as templates for obtaining regularly distributed nanoparticles [8]. In such applications, patterning of S-layers is important to obtain ultrathin high-resolution resists [7].

In this study, we investigated the structure, self-assembly and metallization capacities of recombinant S-layer proteins expressed in yeast. In this context, S-layer protein (SbsC) of B. stearothermophilus ATTC 12980 fused with eGFP (Enhanced Green Fluorescent Protein) was cloned and expressed in yeast Saccharomyces cerevisiae BY4741. Further, in-vivo, in-situ and in-vitro analyses of the S-layer-eGFP structures were performed. Finally, recrystallization capacity of the fusion protein was studied.

Fluorescence microscopy of live yeast cell showed that SbsC-eGFP fusion protein formed tubular networks in the cells (Fig 1). After enzymatic disruption of the cells these tubular structures were preserved in-situ as shown by fluorescence microscopy (Fig. 1). In order to see if such structures can also be obtained after denaturing the proteins by a chaotropic agent, proteins were monomerized with Guanidine hydrochloride (GuHCl) and subsequently dialyzed. As a result, we observed the successful reassembly of SbsC-eGFP in-vitro by Scanning Electron Microscopy.

In summary, we show that SbsC-eGFP fusion protein expressed in yeast forms tubular structures that exhibit an extraordinary stability and persists osmotic cell disruption. Upon monomerization they retain their ability to reassemble in-vitro.

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Integration of P-glycoprotein, a Membrane Protein, to Artificial Lipid Membranes
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Abstract - The aim of the study was the construction of a new system for in vitro membrane protein research. For this purpose, an artificial lipid membrane was constructed by a three step procedure and the process was monitored and optimized by using of Surface Plasmon Resonance (SPR). The utility of the system was investigated by integration of P-glycoprotein (P-gp), a membrane protein, to the artificial membrane.

Membrane proteins have a wide range of important functions in cell and their malfunction cause a lot of diseases. Therefore, most of the drug-design research focuses on these proteins [1-3]. Multi-drug resistance (MDR) proteins that pump xenobiotics out of cell are examples for membrane proteins. They have lot of members such as MDR1, MDR2, MDR3, etc. and they are related with a number of diseases from diabetes to cancer [4, 5].

In this study, an artificial lipid membrane was constructed to integrate P-gp, one of the important members of MDR1 proteins, in its functional form and the process was optimized/characterized by SPR. Although its primary function is not known [6], P-gp has been reported to have interactions with a variety of drugs from obesity to cancer [7, 8].

In order to construct the artificial membrane, SPR gold slides were firstly activated with 3, 3′-dithiodipropionic acid (N-hydroxy succinimide ester) (DTSP) dissolved in dimethyl sulfoxide (DMSO, 1mM). DTSP has the ability to self-assembled on Au surfaces via its thiol groups. After this gold surface activation step, a spacer molecule, 1,2-distearyl-sn-glycero-3-phosphoethanolamine -N-[amino polyethylene glycol]-2000) (ammonium salt) (DSPE-PEG) was incubated with DTSP covered gold slides. The amino group at the DSPE-PEG reacted with free succinimide groups of DTSP to create the first layer of the membrane (Figure 1). For the final layer, liposomes with or without P-gp were produced and spread over the surface. To prepare the liposomes, a thin lipid film was prepared from phosphatidylcholine dissolved in chloroform (1 mg/ml), then the film was suspended in a buffer solution by vigorous vortexing. In the final stage, the suspension was passed through a lipid-extruder. The steps in membrane construction were schematically presented in Figure 1.

The effect of DSPE-PEG concentration on membrane construction was optimized at different concentrations of DSPE-PEG and a fixed concentration of liposomes in the absence of P-gp. SPR data showed that the amount of DSPE-PEG bound on surface was increased with increasing initial concentration. Liposome spreading was in turn significantly affected by DSPE-PEG amount on the surface and 0.03 and 0.04 mg/ml of DSPE-PEG concentrations were observed to be optimum for bilayer construction. In the second part, P-gp was incorporated into liposomes and the effect of different P-gp concentrations was monitored. High amount of P-gp integrated liposomes showed lower spreading and 10 µl of P-gp integrated liposomes was found to give optimum spreading on 0.03 mg/ml of DSPE-PEG. For further studies, different optimization methods will be used and protein-ligand interactions will be monitored.

![Schematic presentation of layer by layer membrane construction.](image)

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Synthesis of $^{131}$I labeled Diethylstilbestrol (DES) Glucuronide and Conjugated with Magnetic Nanoparticles

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Abstract- We predict that $^{131}$I-DES-G to conjugated magnetic nanoparticles will be valuable for imaging and therapy breast and prostate tumors as a novel radioiodine labeled estrogen radiopharmaceutical.

UDP-glucuronyltransferases (UGTs) are a family of membrane-bound enzymes of the endoplasmic reticulum. They catalyze the glucuronidation of various endogenous and exogenous compounds, converting them into more polar glucuronide derivatives.

In this study, Diethylylstilbestrol (DES)-Glucuronide was enzymatically synthesized. DES is known as a well non-steroidal estrogen with high affinity for the estrogen receptor (ER) [1]. Enzyme UDP-Glucuronosyltransferase rich microsome preparate was prepared from rat livers and was used for enzymatic synthesis. The magnetite iron nanoparticles were prepared to conjugate DES. Firstly magnetic iron oxide nanoparticles were covered with silica. They were then conjugated with amino silane. These were carried out for surface modification[2]. After this application, glutaraldehyde was combined to magnetic particles for conjugation with DES glucuronide. (Des-G) conjugated magnetic nanoparticles were labeled with $^{131}$I [3].

Radioiodinated compounds prepared by oxidative radioiodination procedures were originally developed for labeling proteins and peptides [4]. One of the most commonly used oxidizing agent is 1,3,4,6-tetrachloro-3a,6a-diphenylglycouril with the trade name of iodogen [5]. Quality control studies were established using High Performance Liquid Chromatography (HPLC) and Thin Layer Radio Chromatography (TLRC) methods. Scanning electron microscopy (SEM), Atomic Force Microscope (AFM), X-Ray Diffraction Analyses (XRD) and Vibrating Sample Magnetometer (VSM) data have been used to support the analysis carried out with the susceptibility data.

Glucuronidation yield of DES is 85.43%. HPLC chromatograms showed that there was a single peak for each compound and the retention time was different from each other. Radioiodination yield of $^{131}$I-Des-G was over 95 % according to TLRC results. These results clearly showed that Des-G could be successfully radioiodinated using iodogen as an oxidation agent.

Radiolabeling yield of magnetic nanoparticles conjugated Des-G was found 85.2 %.

AFM results showed that the size of magnetic particles was about 120 nm (as seen in Fig. 1). According to SEM, the particles were monodispers.

Figure 1. AFM of magnetic nanoparticles conjugated DesG.

Figure 2. XRD pattern of magnetite core

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Preparation of Radiolabeled Magnetic Nanoparticles
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Abstract- The aim of this work is to design a new molecule with D-Penicillamine and to be gained magnetic properties to it. Therefore, technetium-99m is being used and magnetic biologic nanoparticles are radiolabeled with this radionuclide. Thus, the complexes having magnetic biologic nanoparticles could be considered for potential use of new imaging agents in nuclear medicine.

Technetium is a suitable radionuclide, and preferred in nuclear medicine mainly for diagnostic applications. Magnetic radioactive nanoparticles have the advantage of being able to deliver high concentrations of radioactivity to the target area, without damaging normal surrounding tissue. It’s thought that these new complexes will find a wide spread field in creation of materials besides medicine.

In this study magnetic nanoparticles, Fe₃O₄, were prepared by the co-precipitation method from ferrous and ferric ion solutions with a molecular ratio of 1:2 and they coated with tetraethyl orthosilicate (TEOS). The obtained silica-coated magnetic particles coated with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS) to prevent the aggregation. After being coated with silica, the AEAPS-treated magnetic silica nanospheres were well-dispersed. Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD) and Vibrating Sample Magnetometer (VSM) analysis of these magnetic nanoparticles were obtained.

According to SEM images show that the average size of silica-coated nanoparticles was in the range of 30-50 nm. The XRD diffraction peaks of the magnetic nanoparticles, (220), (311), (400), (422), (511), and (440) were matched to reference magnetite crystal peaks as seen in figure 1.

Then, obtained magnetic nanoparticles conjugated to D-Penicillamine, an aminoacid derivative, using agents such as glutaraldehyde. In final step these nanoparticles radiolabeled with technetium tricarbonyl core.

Quality control processes were done with Thin Layer Radio Chromatography. These results show that D-Penicillamine conjugated magnetic nanoparticles radiolabeled with Tc-99m in a high yield. Also, protein binding affinities will be determined using cell culture processes to decide its target specificity.

In conclusion, these complexes could be considered a new approach to formation of new imaging agents. This will lead to a new generation of products and a range of applications, while minimizing any potential adverse health impacts.

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**Preparation of Radiolabeled Magnetic Nanoparticles with Guanine**

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**Abstract**- It is aimed to synthesize magnetite nanoparticles (MNPs), surface modification with amino-silane and guanine (Gua) conjugation by the help of glutaraldehyde as a cross-linker. Then magnetite biologic nanoparticles are radiolabeled with tri carbonyl cores of technetium to formation of new imaging agents.

Magnetic nanoparticles have numerous applications in biotechnology and medicine, and they have become important tools for the imaging of prevalent diseases, such as cancer, atherosclerosis, diabetes, and others. Technetium is a suitable radionuclide, and preferred in nuclear medicine mainly for diagnostic applications. Also tri carbonyl cores of technetium are preferred instead of +5 oxidation state of technetium, because of its high stability. Magnetic radioactive nanoparticles have the advantage of being able to deliver high concentrations of radioactivity to the target area, without damaging normal surrounding tissue. It’s thought that these new complexes will find a wide spread field in creation of materials besides medicine.

In this study magnetic nanoparticles, Fe₃O₄, were prepared by the co-precipitation method from ferrous and ferric ion solutions with a molecular ratio of 1:2 and they coated with tetraethyl orthosilicate (TEOS). The obtained silica-coated magnetic particles coated with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS) to prevent the aggregation. After being coated with silica, the AEAPS-treated magnetic silica nanospheres were well-dispersed. Finally Guanine, a DNA bases, was conjugated to the MNPs by the cross-linker of glutaraldehyde. The modified particles were radiolabeled with Tc(I)-tricarbonyl core for magnetically diagnosis of the diseases.

The results obtained by Scanning Electronic Microscopy (SEM) and X-ray Diffraction (XRD) confirmed that the prepared nanoparticles had spherical morphology and the particle size is distributed uniformly in the range of 20–30 nm. The magnetic properties of nanoparticles were examined by a Vibrating Sample Magnetometer (VSM) (Figure 1). Guanine conjugation to the magnetic nanoparticles was confirmed by Fourier Transform Infrared (FTIR). Eventually the labeling yield of guanine conjugated MNPs with Tc(I)-tricarbonyl core were found to be 72 ± 4 %.

In conclusion, these complexes could be considered a new approach to formation of new imaging agents. This will lead to a new generation of products and a range of applications, while minimizing any potential adverse health impacts.

![Figure 1. Magnetization vs. applied magnetic field for silica and amino-silane coated magnetite nanoparticles.](image-url)

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DESIGN OF PHOTOCONTROLLABLE DNA CHIP

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Abstract— We describe the possibility of the photocontrollable DNA hybridization by changing orientation of azobenzene layer on the silicon wafer surface. The self-assembled monolayers (SAMs) containing the switchable 4-[(4-aminophenyl)azo]benzocarbonyl (APABA) chromophore have been formed on to silicon wafer surface using 3-glycidoxypropyltrimethoxysilane (GPTS) linkages. In order to understand and control this reversible photoswitchable mechanism of photoswitchable surface, we have measured water contact angles after UV and visible light irradiation. To prepare a photocontrollable DNA chip, Cy3 labeled amino terminated single stranded oligonucleotides (Cy3-ssDNA-NH₂) were then immobilized onto COOH-terminated photoswitchable surface. Using fluorescence microscopy, the probe ssDNA concentration and the incubation time were investigated. The optimum hybridization conditions were studied with Cy5 labeled complementary DNA (Cy5-ssDNA) using fluorescence microscopy.

DNA has been widely used for developed of new nanomaterials and biosensors because it undergoes highly sequence-specific hybridization and forms a highly regular double-helical structure with suitable flexibility¹. To develop new controllable DNA sensors, stimuli-sensitive materials are able to use due to change certain properties in response to specific external stimuli such as heat or light². Light can be used as a precise stimulus by selecting suitable wavelengths, polarization directions, and intensity, allowing non-contact control. Azobenzene derivatives are typical compounds adapted to prepare such a photoswitchable surface. Indeed, because these compounds undergo photon-driven reversible cis-trans isomerization. It is no surprise that the clean and unique azo photochemistry has been applied to switching biological systems due to the physical and chemical properties of the two isomers are different³⁴. Photo-control of the binding affinity of a transcription factor to its promoter, allowed for, in essence, light-control of gene expression in the organism. These kind of studies suggest that the biological systems can be controlled using light. This allows one to turn a biological process on and off at will, using light⁵⁶.

In this study, a new photocontrollable DNA chip was designed on Si(100) wafer. The photo-controllable substrate was prepared by azobenzene-containing self-assembled monolayers (SAMs) on the Si(100) via chemisorption of 3-glycidoxypropylmethoxysilane (GPTS) and 4-(4'−aminophenylazo)benzoic acid (APABA). Photosensitive APABA was synthesized by using Schünchhütte method and characterized by FTIR, NMR and LC-MS. The azobenzene monolayers were formed on Si(100) surfaces by GPTS linkages. The modified surfaces were characterized by X-ray photoelectron spectroscopy (XPS), contact angle analysis and atomic force microscopy (AFM) techniques. The reversible photoswitching performances of APABA molecules were investigated by UV Spectroscopy in DMSO solution. In order to understand and control this reversible photoswitching mechanism, contact angle measurements were performed by using a variety of liquids after UV and visible light irradiation. These contact angle results were used to calculate the components of the APABA-modified surface energy under UV and visible light with the aid of the Lifshitz–van der Waals/acid–base approach. The total surface energies of photoswitchable surfaces after visible and UV light irradiation were calculated as 37.28 mJ/m² and 36.95 mJ/m², respectively.

To prepare a photo-controllable DNA chip, Cy3 labeled amino-terminated single stranded probe-DNA arrays were then immobilized onto the photoswitchable surface. Using fluorescence microscopy, the probe-DNA concentration and the incubation time were investigated. The optimum hybridization conditions were studied with Cy5 labeled complementary-DNA using fluorescence microscopy. In addition, the photocontrolling of DNA hybridizations onto prepared surfaces were verified by confocal microscopy after vis and UV light irradiation. The percentage hybridization ratios for the on and off state of the DNA chip were calculated as 61% and 5%, respectively.

Scheme 1. Schematic presentation of the photocontrollable DNA sensor.

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**In Vitro Cytotoxic Studies of Polymer Coated Magnetic Nanoparticles for Anti-cancer Drug Delivery**

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**Abstract** - Cytotoxicity of naked magnetic nanoparticles and polymer coated nanoparticles (PLGA and chitosan) are investigated on MCF-7 human breast cancer cell line by XTT cell proliferation assay.

Nanoscale structures and materials hold significant potential for biomedical applications due to their molecular size, high volume-surface ratio and multifunctional characteristics. Magnetic nanoparticles (MNP) have been widely used in areas such as drug delivery, hyperthermia, magnetic resonance imaging, cell separation, immunoassay and detoxification of biological fluids [1-5]. They provide a promising approach in cancer therapy as targeted drug delivery systems which enable reducing the side effects of current treatments on healthy tissues [6,7]. Encapsulation of magnetic nanoparticles overcomes the problem of protein absorption on MNPs and also increases the blood circulation time [5]. PLGA [poly (lactic-co-glycolic acid)] and chitosan are both biodegradable and biocompatible polymers commonly used in drug delivery systems [8].

In the present study, cytotoxic effects of PLGA (PLGA-MNP) and chitosan (C-MNP) encapsulated magnetic nanoparticles and naked magnetic nanoparticles (N-MNP) are analyzed on MCF-7 human breast cancer cell line.

Naked Fe₃O₄ magnetic nanoparticles and core of polymer coated magnetic nanoparticles are synthesized by a modification of the co precipitation method [9].

MCF-7 human breast cancer cells are maintained in RPMI 1640 medium supplemented with 10% (v/v) fetal bovine serum and 1% (w/v) gentamycin in an incubator at 37 °C in a humidified, 5% CO₂ atmosphere.

Cytotoxic analyses of magnetic nanoparticles are confirmed with XTT assay (Biological Industries-Cell Proliferation Kit). 5000 cells per well are seeded in 96 well plates and treated with different concentrations of N-MNP, PLGA-MNP and C-MNP. After incubation for 72 h, XTT reagent is added and spectrophotometric measurements are performed at 500 nm by ELISA microplate reader. Applied highest MNP concentrations are 1000 μg/mL which are diluted horizontally with ½ dilution factor. Measured data of cell control group (cells without MNP) is accepted as the indicator of 100% growth. The viability percentages of cells exposed to MNPs with concentration range of 0-1000 μg/mL are expressed in proportional to the control group.

**Figure 1.** Cell viability of MCF-7 breast cancer cells treated with MNP, PLGA-MNP and C-MNP.

The cytotoxic studies revealed that there is no obvious change in cell viability in the studied concentration range of 0-500 μg/mL of MNPs (either naked or polymer coated). C-MNPs exhibited slightly lower cell viability values. A common increase in the cell viability is observed in this concentration range which needs to be clarified. However, this phenomenon is also observed in the literature [5, 10, 11]. Besides, cell viability is found to reduce by 10-20 % at 1000 μg/mL of MNP concentration. To conclude, it may be argued that prepared nanoparticles do not exhibit toxicity on MCF-7 cells so they may be considered for relevant drug delivery and future biomedical applications.

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Covalent Immobilization of Invertase on PAMAM-Dendrimer Modified Superparamagnetic Iron Oxide Nanoparticles

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Abstract—In the present study, polyamidoamine (PAMAM) dendrimer was synthesized on the surface of superparamagnetite nanoparticles to enhance invertase immobilization. Maximum reaction rate (Vmax) and Michaelis-Menten constant (Km) were determined for the free and immobilized enzymes. Various characteristics of immobilized invertase such as; the temperature activity, thermal stability, operational stability and storage stability were evaluated.

Employment of free enzymes in biotechnological applications is limited due to the their cost and to the impossibility of recovering and separating them from the reaction medium after the enzymatic process. To cope with these difficulties, enzymes were immobilized to obtain a catalyst which is separable from the reaction medium. Furthermore, they endowed with good properties such as resistance to temperature and denaturants, as well as stability longer than their free counterpart [1].

In the present study, preparation of PAMAM dendrimers modified magnetic nanoparticles for invertase immobilization is reported along with a detailed physicochemical evaluation. Phase investigation of the product was performed by XRD and XRD pattern of SPION-PAMAM G-5. Coating and functionalization of SPION with aminosilane and PAMAM were monitored by FT-IR spectroscopy. The FT-IR spectra for uncoated SPION, aminosilane coated SPION (APTMS modified SPION-NH2, G0-SPION) and PAMAM coated SPION (dendrimers modified SPION-PAMAM G5). Morphology and size distribution of SPION was analyzed using TEM.

In summary, APTMS was grafted onto the surface of magnetite nanoparticles which were then used for successive addition of methacrylate and ethylenediamine step by step to form dendritic structure of PAMAM on the superparamagnetic nanoparticle surface[2].

![Figure 1. TEM micrographs (a) dendrimers modified SPION-PAMAM G5 at different magnifications.](image1)

![Figure 2. Modification of magnetic nanoparticle with PAMAM dendrimers for invertase immobilization.](image2)

Dendrimer-modified magnetite nanoparticles with average diameter 9 nm were prepared and characterized by x-ray diffraction, FT-IR, and TEM. It was found that the number of terminal NH2 groups increased from generation SPION-PAMAM G1 through G5, thus increasing the amount of immobilized enzyme by 250% over silane functionalized SPION-G0. After activation with glutaraldehyde invertase was immobilized onto PAMAM modified magnetic nanoparticles. The Michaelis-Menten kinetic constants $K_m$ and $V_{max}$ of the free and immobilized invertase were also determined and revealed that the affinity of invertase to sucrose decreased after immobilization. The properties of the free and immobilized invertase were compared and results indicate that the stability of the immobilized invertase towards temperature, pH and storage was enhanced by immobilization.

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PHOTOPHYSICAL AND COMPUTATIONAL INVESTIGATION OF INTERMOLECULAR PYRENE COMPLEXES WITH PHENOTHIAZINE AND PROMAZINE

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Abstract—This study concerns photophysical interactions between pyrene (Py), a polyaromatic hydrocarbon, and two drug molecules, phenothiazine (Pheno) and its derivative promazine (Prom). Particularly, phenothiazine–pyrene and promazine–pyrene systems, dissolved in methycyclohexane, dichloromethane, tetrahydrofuran and acetonitrile, have been characterized by both computationally and spectroscopically. The ground state thermodynamic stabilities of intermolecular charge transfer complexes between these molecules were determined with DFT functionals and their vertical singlet–singlet transitions were calculated and characterized employing TD-DFT methods. The S0 → S1 transitions with transition wavelengths of ±484 nm for [phenol–py] and ±252 nm for [prom–py] are pure CT transitions from donor to acceptor molecules occurring between HOMO – LUMO of the complexes. Excitation energies of TDDFT calculations are in accordance with those obtained from the fluorescence spectroscopy.

Pyrene and its derivatives are polyaromatic hydrocarbons which cause environmental pollution (i.e. petroleum wastes). They can also enter the human body by various ways and may interact with some biologically important molecules. Some drugs (i.e. promazine and paracetamol) have aromatic structures consisting of π-electron systems. Phenothiazine is an aromatic molecule which contains π-electrons. Its derivatives are a pharmacologically important class of heterocycles, known as pharmacophores in sedatives, antidepressant agents, etc. Promazine and fluphenazine (phenothiazine derivatives) are frequently used with psychotic patients in psychiatric practice. Phenothiazine and promazine act as good electron donors and they can function as a charge transfer or electron transfer donor at drug receptor sites. This is consistent with the observation of the formation of charge transfer complexes of phenothiazine and its derivatives with a variety of acceptor compounds [1]. Determining molecular complexation and their geometries are among the most important tasks in biological systems [2].

In this study, the intermolecular interactions between the pyrene (as acceptor) and phenothiazine, promazine (as donors) were investigated by using UV-Vis and fluorescence methods. The fluorescence intensities have decreased depending on the increasing concentration of phenothiazine and promazine. Fluorescence quenching rate constants for phenothiazine–pyrene and promazine–pyrene systems have been calculated from Stern-Volmer equation as $\tau_{0} = 10^{10}$ M$^{-1}$s$^{-1}$. These results support the conclusion that the rate constants for Pheno-Py and Prom-Py are diffusion controlled.

In addition, possible complex formations between these compounds in the ground state have been investigated by utilizing computational quantum chemical methods. In particular, all the geometries were optimized and characterized using DFT-PBE1PBE method as implemented in Gaussian 98 program suite [3]. Single point TD-DFT calculations for determining vertical excitation energies of the complexes were also performed utilizing their ground state DFT geometries.

The computational studies resulted in that the pyrene-phenothiazine and pyrene-promazine complexes have thermodynamic stabilities at the ground state in gas phase. Moreover, the TD-DFT calculations revealed that the S0→S1 transitions for all complexes are pure charge transfer transitions from donor to acceptor molecules between HOMO–LUMO of the complexes.

<table>
<thead>
<tr>
<th>Species</th>
<th>$E_{\text{exc}}^\text{exp}$ (eV)</th>
<th>$E_{\text{exc}}^\text{theo}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pheno-Py</td>
<td>2.87</td>
<td>2.77</td>
</tr>
<tr>
<td>Prom-Py</td>
<td>2.91</td>
<td>2.98</td>
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</table>

Excitation energies ($E_{\text{exc}}^\text{theo}$) obtained by TDDFT calculations are in accordance with the data gained by the fluorescence spectroscopy, as well. Finally, it is found that the phenothiazine-pyrene complex is energetically more easily attainable than promazine-pyrene complex.

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Application of Nanoparticles in Diagnosis and Treatment of Cancer

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Abstract—One of the ultimate goals of nanomedicine is to create medically useful nanodevices that can function inside the body. Among the newly developed nanomedicine and nanodevices such as quantum dots, nanowires, nanotubes, nanocantilevers, and nanopores, nanoshells and nanoparticles are the most promising applications for various cancer treatments[2].

Cancer is on the increase in the developing world as well as in the industrial world. The latest world cancer statistics report that the number of new cancer cases will increase to more than 15 million in 2020[3]. Human cancer is a complex disease caused by genetic instability and accumulation of multiple molecular alterations[4]. Most current anticancer agents do not greatly differentiate between cancerous and normal cells, leading to systemic toxicity and adverse effects. In addition, cancer is often diagnosed and treated too late, when the cancer cells have already invaded and metastasized into other parts of the body. Cancer nanotechnology is emerging as a new field of interdisciplinary research, cutting across the disciplines of biology, chemistry, engineering, and medicine, and is expected to lead to major advances in cancer detection, diagnosis, and treatment.

Nanoparticles and their use in drug delivery is a far more effective antitumor method than conventional chemotherapy[5].

Biomarkers or biomolecule markers include altered or mutant genes, RNAs, proteins, carbohydrates, lipids, and small metabolite molecules, and their altered expressions that are correlated with a biological behavior or a clinical outcome[6]. Biomarker harvesting is an underutilized application of nanoparticle technology and is likely to undergo substantial growth. Functional polymer coated nanoparticles can be used for quick detection of biomarkers and DNA separation[7].

The best way to increase the efficacy and reduce the toxicity of a cancer drug is to direct the drug to its target and maintain its concentration at the site for a sufficient time for therapeutic action to take effect[2]. Novel therapeutic strategies include the development of targeted transport vehicles allowing drug delivery to specific cells or cell structures[1]. The efficiency of drug delivery to various parts of the body is directly affected by particle size. Nanostructure mediated drug delivery, a key technology for the realization of nanomedicine, has the potential to enhance drug bioavailability, improve the timed release of drug molecules, and enable precision drug targeting[2].

Generally, polymers that are used for preparation of nanoparticles fall into two major categories: natural polymers and synthetic polymers. A number of natural polymers such as heparin, dextran, albumin, gelatine, alginate, collagen, and chitosan have been intensively investigated. Synthetic polymers including polyethylene glycol (PEG), polyglutamic acid (PGA), polylactic acid (PLA), polycaprolactone (PCL) and N-(2-hydroxypropyl)-methacrylamide copolymer (HPMA) have been exploited as well. The drug can be loaded into polymeric nanoparticles by physical entrapment or by chemical conjugation[8].

Liposomes are self-assembling spherical particles with a membrane composed of phospholipid bilayers. Drug delivery systems based on unmodified liposomes are limited by their short blood circulation time[8].

Liposomes are the archetypal, simplest form of a nanovector. They use the overexpression of fenestrations in cancer neovascularure to increase drug concentration at tumor sites. Liposome-encapsulated formulations of doxorubicin were approved 10 years ago for the treatment of Kaposi’s sarcoma, and are now used against breast cancer and refractory ovarian cancer. Liposomes continue to be refined and applied to more cancer indications; they are only the first in an ever-growing number of nanovectors under development for novel, more efficacious drug-delivery modalities[9].

Colloidal gold nanoparticles are another attractive platform for cancer diagnosis and therapy. Gold nanoparticles have been used as contrast agents in vitro based on their ability to scatter visible light[6]. Gold nanorod can generate heat when it is radiated by a near infra-red (IR) laser (wavelength > 650 nm). At this range, the laser is relatively safe to the tissue and organs[8].

Iron oxide nanoparticles have been clinically used as imaging agents for MRI. One unique advantage of iron oxide nanoparticle delivery systems is that they can be delivered in a targeted manner to a desired region by applying an external magnetic field[8].

Nanotechnologies promise to extend the limits of current molecular diagnostics and enable point-of-care diagnosis, integration of diagnostics with therapeutics, and development of personalized medicine. Nanomedicine promises to play an important role in the future development of diagnostic and therapeutic methods[7]. Anticancer nanoparticulate technology is being developed with the goal to minimize side effects for nanoparticle treatments by relying on nanoparticles that are perfectly engineered to attack cancer in a decisive manner with healthy tissues suffering no undesirable consequences at the initial stages of cancer cell development. Nanoparticles will likely serve as the norm rather than an exception in the majority of all areas of future conventional cancer treatments[5].

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**Tissue Distribution of a Nanoparticle Containing Quercetin in Mic**

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**Abstract**—Quercetin is a plant-derived flavonoid which is ubiquitous in our daily diet, specially in tea, onion, red wine and apple. Because of its health-promoting effects, quercetin is recognized as a drug. It exhibits anticarcinogenic, antioxidant, antiviral, antibacterial and anti-inflammatory effects. It is used as a drug for cardiovascular diseases. Quercetin is also attractive as a neuroprotective drug to reduce anxiety. In spite of all these beneficial effects and frequent presence in dairy diet, it has little absorption in intestine after digestion. To enhance its absorption, a biodegradable polymer was designed and made that could deliver the drug into the body. Applying this nanoparticle improves the absorption of the drug tremendously, reduces the side effects and targets the drug to the specific sites. In the present study, in order to assess the efficient concentration and tissue distribution of the drug quercetin, a group of mice will be chosen. A variety of drug concentrations will be administered both orally and intravenously. Then in different intervals the critical organs such as liver, kidney, brain, digestive organs and testis will be purified and analysis of quercetin will be performed by HPLC.

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Synthesis of Biodegradable Polyurethane Nanocomposite Based on Chitin

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Abstract— In this study Biodegradable polyurethane nanocomposites (B-PUN) were synthesized as bioabsorbable suture by in situ polymerization. Different percentage of organically modified nanoclay (cloisite® 30B) (1, 3, 5 wt %) were used to evaluate the influence of nanoclay on rate of nanocomposites’ biodegradability. Incorporation of chitin as biopolymer and chain extender improved biodegradation rate. We characterized B-PUNs by X-ray diffraction (XRD) and measured in vitro degradation rate and hydrophilicity of nanocomposites.

For decades, polyurethanes have been a biomaterial of choice for many applications because of their biocompatibility and excellent mechanical properties [1].Biodegradable polyurethane is generally achieved by the incorporation of labile moieties susceptible to hydrolysis in the polymer chain. The most common method of introducing these hydrolysable linkages into PUs has been the incorporation of hydrolysable soft segments such as poly (ε-caprolactone) into the backbone. The degradation rate of PCL-based PU is very slow in most cases. On the other hand, the introduction of a polysaccharide chain extender such as chitin can accelerate the degradation rate [2]. Nanoclay enhances the mechanical properties and hydrolytic degradation of nanocomposites [3]. absorbable sutures should maintain their mechanical property until it is no longer needed and then be absorbed and excreted by the body, leaving no trace [4].

In this study B-PUNs were synthesized by using toluene diisocyanate (TDI), poly (ε-caprolactone) (PCL), chitin and 1,4–butane diol (BDO) with mass ratio 50:50 as chain extenders with the same molar ratio PCL/TDI/Chitin: BDO (50:50) 1:3:1:1 and different percentage of C30B (0, 1, 3, 5 wt %). The --NCO terminated prepolymer was first prepared by reaction of PCL and TDI at 100 °C for 1.5 h, in a four-necked reaction kettle. The dried C30B stirred by NMP Solvent for 12 h to swell completely then was Ultrasonicated at 20 kHz for 30 min. The sonicated nanoclay was mixed by solution of chitin [mixture of NMP and dimethyl sulfoxide (DMSO) with ratio of 2:1, treated chitin] and BDO. The combination of chitin/BDO/nanoclay was mixed with the prepolymer in reactor at 600 rpm for 3 min. The synthesized nanocomposite was then casted into Teflon plate to form uniform sheet of 2-3 thickness, then placed in a hot air circulating oven at 100 °C and cured for 24.

The state of dispersion of nanoclay particles in synthesized samples was analyzed using WAXD patterns; cloisite® 30B was exfoliated in samples B-PUN-1 and B-PUN-3. By increasing the amount of C30B, we have found poor dispersion in nanocomposites (B-PUN-5). The degradation of suture in body occurs in two stages, first hydrolytic degradation of hydrolysable soft segments (PCL) and second enzymatic attack in chitin. In general chitin was degraded by enzymatic hydrolysis; one of the most effective catalysts for the hydrolysis may be lysozyme, which is known to be ubiquitous in the body [5]. In vitro degradation of B-PUNs was measured by recording the samples’ weight loss over time in PBS buffer solution at 37 °C to evaluate hydrolytic degradations, we found that the rate of biodegradation of samples increased with increasing content of nanoclay, because of the less phase separated morphology of B-PUNs compare to pure polyurethane.

Since the surface properties of biomaterials are influential on tissue response when implanted, the static water contact angle of nanocomposites were measured at 25 °C with the conventional sessile drop method. The values of contact angle decreased by increasing the percentage of nanoclay in synthesized samples; this means an improvement on hydrophilicity surface morphology. It is well known that any increase in crystallinity of polymer ultimately results in decreasing hydrophilic characterization of the polymers. Chitin itself crystalline polysaccharide and its affinity with water is negligible; therefore incorporation of chitin in polyurethane backbone due to decreases hydrophilicity of Pu/chitin [6]. Dispersed nanoclay platelets reduced the crystallinity of polymer [7] than could be improving the hydrophilicity of Pu/chitin biopolymer by reducing crystallinity.

In summary, in this work we synthesis a novel biodegradable nanocomposites with different proportions of nanoclay and modified the surface morphology of nanocomposites to use as bioabsorbable suture.

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Synthesis of Magnetic Nanoparticles as a Targeting System for Drug Delivery
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Abstract- Iron oxide (Fe3O4) magnetic nanoparticles are synthesized by coprecipitation of iron (II), iron (III) salts and ammonium hydroxide at 90 °C. To prevent agglomeration of nanoparticles, oleic acid is added to the solution. After synthesis, products are identified with Transmission Electron Microscopy (TEM), Fourier Transform Infrared (FTIR) Spectroscopy and X-Ray Diffraction (XRD) analysis.

Magnetic nanoparticles are beneficial for a variety of scientific and technological applications such as contrast agents in magnetic resonance imaging (MRI), hyperthermic cancer treatment, targeted drug delivery and tissue repair [1,2]. All of these applications require that the nanoparticles have high magnetization properties and a narrow particle size distribution (smaller than 100 nm) with uniform physical and chemical properties [3]. The synthesis of nanoparticles with small size and homogeneity have been intensively studied for iron oxide magnetic nanoparticles (maghemite or magnetite). Complex processes are required to classify the particles with adequate size [4]. Many studies have been carried out for the synthesis of magnetite nanoparticles such as microemulsions, co-precipitation, laser pyrolysis, sol-gel, thermal decomposition etc. Direct decomposition of iron precursors or decomposition of iron precursors followed by oxidation in organic solvents in the presence of surfactants can produce high-quality monodisperse iron oxide crystals [5]. However, this process usually requires relatively high temperature, high boiling point solvents, some of which are toxic and expensive. Whereas the wet chemical routes to magnetic nanoparticles are simpler, more tractable and more uniform. The most common method for synthesis of magnetite nanoparticles is by coprecipitation from a solution of Fe (II) and Fe(III) salts in an adequate ratio and using a proper base such as alkali metal hydroxides. The chemical reaction of Fe3O4 precipitation is given below.

Fe2+ + 2Fe3+ + 8OH− → Fe3O4 + 4H2O

One of the significant problems of this process is agglomeration of the nanoparticles. In order to prevent agglomeration, surfactants are needed. Oleic acid is often used as a surfactant to enclose and/or to make the magnetite particles hydrophobic. Oleic acid has higher affinity to the surface of particles compared to other surfactants [6].

In this study, magnetite nanoparticles are synthesized by using coprecipitation method with some modifications [6]. Synthesis method consists of two steps. First step is preparation of magnetite nanoparticles, second is covering process of particles with surfactant.

Ammonium hydroxide is added to iron salt solution under vigorous mixing at 90°C. After magnetic decantation, magnetite nanoparticles are washed with water to drop pH of the solution. After washing, magnetite particles are divided into two parts. First one is dispersed in water. Then oleic acid is added to the colloid suspension as a surfactant under mechanical stirring. The second part is added to hexane-oleylamine-oleic acid mixture. Then, ultrasonication is applied to the mixture. Nanoparticles are characterized with XRD, TEM, FTIR. When TEM results of two different methods are compared, it is observed that the second method involving hexane solution overcomes the problem of agglomeration (Figure 1). These magnetic nanoparticles are going to be used for drug delivery and targeting after further modifications.

Figure 1. TEM micrograph of synthesized Fe3O4 nanoparticles by co-precipitation (a) after mechanical stirring (b) after ultrasonication.

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Preparation of PLGA and Chitosan-modified PLGA Coated Magnetite Nanoparticles
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Abstract- In this study, iron oxide (Fe₃O₄) magnetic nanoparticles are synthesized with coprecipitation method. Emulsion evaporation is used for preparation of polymer coated magnetite nanoparticles. Poly(lactide-co-glycolide) (PLGA) and Chitosan-modified PLGA are used in the preparation and are characterized. Morphology, size and zeta potential of nanoparticles are examined. The magnetite entrapment efficiency is determined.

During the last two decades, biodegradable magnetic materials gained importance in biomedical and bioengineering research such as targeting drug delivery, tissue engineering, cancer treatment, magnetic resonance imaging (MRI) contrast agents etc. [1,2]. For drug delivery and targeting applications, the magnetic carriers should have a certain size distribution to avoid rapid uptake by reticuloendothelial system (RES) and coated with biocompatible hydrophilic materials to form a stable aqueous dispersion at physiological pH 7.4 [3]. Therefore, coating of magnetic nanoparticles with biocompatible polymers has gained much attention and have been extensively studied. Some of these biocompatible, biodegradable and non-toxic polymers such as poly(lactide-co-glycolide) (PLGA), poly(lactic acid) (PLA), poly(glycolic acid) (PGA), dextran and chitosan have been approved by FDA (US Food and Drug Administration) for human therapeutic uses [4].

There are several processes to prepare magnetic polymeric nanoparticles. The most common methods are emulsion techniques [5]. The emulsion evaporation technique is one of the oldest methods. It has been also used to entrap drugs. If the magnetic polymeric nanoparticles are designed properly, they could be used to increase the effectiveness and to reduce the systemic adverse effects of anticancer drugs.

In the present study, a single emulsion evaporation method for encapsulation of surface modified magnetite with oleic acid is used. According to the emulsion evaporation technique, these oleic acid coated magnetite nanoparticles were dispersed into an organic phase. The PLGA and magnetite containing dispersion is emulsified into an aqueous phase containing poly(vinyl alcohol) (PVA) to prevent agglomeration of PLGA nanoparticles. For surface modification of PLGA nanoparticles, Chitosan is used as an encapsulation shell due to its polycationic property.

The characteristics of polymeric nanoparticles, including composition, morphology, size distribution, zeta potential, magnetic properties and magnetite entrapment efficiency in different conditions are investigated. As seen from the figure, SEM images indicate that the composite sub-micron particles are nearly spherical. The particles sizes and zeta potential of the nanoparticles are measured for both PLGA and Chitosan-modified PLGA. The magnetite entrapment efficiency of particles are also determined.

Figure 1. SEM micrograph of (a) PLGA coated magnetite nanoparticles, (b) Chitosan-modified PLGA coated magnetite nanoparticles.

A.Y. thank to TUBITAK-BIDEB for partial support.

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Extra-cellular Metabolites Probing Utilizing Composite Silver Nanoparticles and Surface-Enhanced Raman Spectroscopy

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Abstract-Composite anionic (citrate-stabilized) and cationic (CTAB-stabilized) silver nanoparticles were modified with ethylene oxide–propylene oxide block copolymers (Pluronics). The modification increases sensitivity of SERS detection of aromatic compounds due to promotion of analyte adsorption of the surface of the probe. Modified nanoparticles were applied for SERS monitoring of metabolites released from living human cells which presumably correspond to energetic molecules.

Living mammalian cells excrete a number of compounds into surrounding media, e.g. signaling and energetic metabolites, drugs, structural proteins. Secreted metabolites are useful markers of cell metabolic activity and apoptosis. The sensitive analysis of cell metabolites is of particular interest in cellular biology and toxicology studies.

Surface–Enhanced Raman Spectroscopy (SERS) is a powerful technique which is of great potential for living cell analysis. Modified noble metal nanoparticles are commonly used as SERS probes for the analysis of different biomolecules.

Recently, we modified colloid silver nanoparticles with ethylene oxide–propylene oxide block copolymers (Pluronic) [1]. We found that Pluronics form a thin amphiphilic layer at the surface of silver nanoparticles which prevents their aggregation and promotes the adsorption of some aromatic compounds on the surface of the probe. This results in significant SERS signal enhancement (up to $10^7$ in comparison with unmodified nanoparticles) which was observed for rhodamine 6G, doxorubicin, purine bases and aromatic amino acids. The modification with Pluronics can also increase biocompatibility of nanoparticles and promote their penetration through cellular membranes.

For SERS analysis noble metal nanoparticles are commonly introduced into living cells to probe their components [2]. Living cells are very complex matrix making it difficult to identify SERS spectra arose from low and high molecular cell components [3].

Alternatively, as we demonstrate here, the nanoparticles can be used to probe the media surrounding the cells. In this study different adhered human cells were cultured under standard conditions. The cells were harvested and transferred into the buffer solution allowing them to release the metabolites. The viability of the cells was verified by trypan blue exclusion assay. In order to analyze cell metabolites released, Pluronic-modified silver nanoparticles were mixed with buffer solution and spotted onto SERS slide. As an example, the Figure shows SERS spectrum of metabolites of vascular smooth muscle cells.

![Figure 1. SERS spectra of metabolites of vascular smooth muscle cells (VSMC) on silver nanoparticles modified with Pluronic F127 (830 nm excitation).](image)

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Detection of Protease Activity Using Gold Nanorods

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Abstract—In order to obtain a sensitive and rapid analysis method for the detection of protease activity, we developed a method based on surface-enhanced Raman spectroscopy (SERS) with Raman labeled nanoparticles. At the end of the study we educed the limit of detection (LOD) and limit of quantification (LOQ) values of the method as 0.43 and 1.30 mU/mL, respectively.

Enzymes are biochemical catalysers and responsible most of the reactions in the living cell. The enzymes which have proteolytic activity are known as proteases and they are the most dominant group of enzyme that have significant roles for system functions of living. So detection of protease activity is crucial like initial step cancer screening [1]. Proteases are very important in food processing and quality control as well as in medicine for diagnostical or therapeutical applications [1,2]. These enzymes have both desirable and undesirable effects on foods [3-5]. For example, proteolytic reactions are essential biocatalyzers in cheese making, where as the uncontrolled hydrolysis of casein is not desirable due to cheese defects [5]. In addition, exogenous or endogenous origin proteases can also cause unpleasant flavours and odours in milk [6]. Due to the crucial role of protease, it is important to determine the proteolytic activity. In this research, a new method has been studied to determine the protease activity.

In this method, surface-enhanced Raman spectroscopy (SERS) was used with Raman labeled nanoparticles for the detection of protease. For labeling nanoparticles 5,5′-Dithio-bis (2-nitrobenzoic acid), DTNB, was used. The underlying reason is, not only the NO2 stretch at 1326 cm⁻¹ but also for the property of constituting SAM on the nanoparticle surface. NO2 stretch at 1326 cm⁻¹ was pursued as Raman label. Assay platform is composed of gold coated glass surface, self-assembled monolayer (SAM), substrate, and Raman labeled rod shaped nanoparticles.

Figure 1. Shows the SERS spectra of the assay platform before and after the enzyme.

The calibration curve was obtained by pursuing the SERS intensity at 1326 cm⁻¹ versus protease activity. Within the 0.135 to 1350 mU/mL of the enzyme concentration, the relationship between SERS signal intensity and enzyme concentration was described. Observed change was linear up to 2 mU/mL enzyme concentration.

Figure 2. Shows the correlation between the enzyme concentration and SERS intensity.

This developed method was compared with azocasein method for the commercial enzyme preparate rennet, which is used for the cheese making process. The results were within the acceptable range (± 5.0%).

This method has superiorities for the quantification of protease activity with minimum analysis time, minimum sample preparation stage, and low detection limit. Also this method has a flexibility to be use in different enzyme activity determinations only by changing the substrate.

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CdSe$_x$Te$_{1-x}$ Colloidal Nanocrystals Induced Regulation of Gene Expression and Cycle Arrest in Lung Cells

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Abstract- Nanocrystals taken with respiration are responsible for the damage of airway epithelial cells and have implicated in malign transformation of lung cells. Related with this, alterations of cell viability and cycle distribution of normal (BEAS2B) and malign lung cells (A549), and expressional changes of survival related target genes stimulated by CdSe$_x$Te$_{1-x}$ nanocrystals were investigated.

CdSe$_x$Te$_{1-x}$ nanocrystals find applications in biology and medicine as imaging agents. It is essential to study toxicity and biological response of cells to the nanoparticles to ensure their utilization in biomedical and biotechnological applications [1].

CdSe$_x$Te$_{1-x}$ nanocrystals with size of 5.0 nm synthesized in our laboratory were used in this work. BEAS2B normal bronchial epithelial and A549 lung adenocarcinoma cell lines were used. Images of nanoparticles internalized within cells were collected by confocal microscopy. Viability was assayed with MTT test and cycle analysis was performed with flow cytometry by propidium iodide staining of cells. Quantitative PCR was used to identify expression of Bax, Bcl2, Bcl XL, p53 and cyclinD1 genes.

Nanocrystal signals in A549 and BEAS2B cells were detected in cytoplasmic endosomes with incubation at 1.0 µg/ml concentration. Viability of cells was decreased with time and nanocrystal dose dependent manner in both cell lines.

Flow cytometry analysis indicated that A549 cells were arrested in G1 phase of cell cycle associated with decreased S phase cell counts whereas BEAS2B cells in G2 phase. Quantitative PCR results showed a significant reduction in expression of Bcl2, Bcl XL and p53 genes in both cell lines. Bax and cyclinD1 gene expressions, correlated with cycle distribution results, was reduced in A549 cells but increased in BEAS2B cells.

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CdSe$_x$Te$_{1-x}$ nanocrystals were internalized by A549 and BEAS2B cells, and were displayed toxic effects. By regulating survival and cycle related genes associated with normal or malign feature of lung cells differentially, nanocrystals mediate cycle arrest. These effects of semiconductor nanoparticles would have imply a significant involvement in growth modulation of cancer cells.

Figure 1. Cell viability assay for the lung cells

Figure 2. Gene expression analysis for the lung cells incubated with 50 µg/ml of nanocrystals for 24h.
A Biosensor for Aflatoxin B₁ Based on Acetylcholinesterase Inhibition on Self-Assembled Monolayer

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Abstract—A new electrochemical biosensor for aflatoxin based on acetylcholinesterase (AChE) inhibition by Aflatoxin B₁ is proposed. The AChE and Choline Oxidase (ChO) are two enzymes that covalently immobilized to the mercapto-carboxylic acid (Au-MPA SAM) self-assembled monolayer on the gold electrode. The molecular dimension distance between two immobilized enzymes on Au-MPA SAM results in concentrated choline, the product of AChE, in the ChO nano-environment and at the same time electron transfer from reduced ChO to PBQ and PBQ to the Au-electrode surface would be improve. The data are presented and discussed from which a new method is proposed for AFB₁ determination based on the chronoamperometry and electrochemical impedance spectroscopy (EIS) measurements.

With recent advances in nanotechnology, electrochemical biosensors, in combination with nanomaterials have become simple, efficient tools to measure the concentration of analytes and the response time functions of target biomolecules to the drugs or the toxic reagents [1]. Aflatoxin B₁ (AFB₁) is a highly toxic and carcinogenic metabolite produced by certain Aspergillus species on agricultural commodities [2]. There are limited analytical methods available for the determination of aflatoxins such as high-performance liquid chromatography (HPLC) [3], thin layer chromatography [4], gas chromatography and capillary electrophoresis [5]. However, these techniques require expensive equipment as well as complicated and time-consuming solvent cleanup steps. Recently, some novel concepts to overcome these obstacles have been suggested. A promising alternative approach involves the use of enzyme-linked immunoassay (ELISA) [6]. While they have often demonstrated the required sensitivity and acceptable specificity, these assays need specific antibodies and, indirectly, the use of animals in order to produce these “receptors” [7]. To respond to these various issues, enzymatic methods have shown promise in some cases, as an alternative to classical methods, to achieve faster and simpler detection of some environmental and physiological species. In a recent study, Cometa et al. [8] analyzed the inhibition of acetylcholinesterase (AChE) by AFB₁, a key enzyme in the transmission of nerve impulses. The AFB₁ inhibition on AChE extracted from mouse brain was studied and the implications in terms of kinetic mechanism and toxicity discussed. New study [7] was shown that AFB₁ inhibits the AChE from electric cell. On the basis of this effect, a method to quantify AFB₁ by measuring the decrease in enzyme activity, determined using Ellman’s spectrophotometric method.

In this work, AChE and Cholinoxidase (ChO) are immobilized on the gold Mercapto-propionic acid self-assembled monolayer (Au-MPA SAM) as a working electrode (Fig. 1).

We first studied the formation of a surface with carboxylic acid functional groups that in molecular dimension close to the electrode surface. Then the surface carboxylic acid functional groups are activated by some activator agents to link with amine groups of a few enzyme amino acids to form amide bonds and by the way the enzymes were immobilized covalently, close to the gold surface. After biosensor fabrication, the electrochemical cell was set up, and in the deoxygenated buffer solution (pH 7.0, I=0.1 M) acetylcholine, choline, and PBQ was added. The AChE inhibition by AFB₁ is detected in electrode surface using ChO enzyme and Parabenzoxquinone (PBQ) as an electron mediator. These results suggest that the fabricated biezynmotic self-assembled monolayer biosensor can be successfully used for the electrochemical determination of AFB₁, in real samples.

The data are presented and discussed from which a new method is proposed for AFB₁ determination based on the chronoamperometry and electrochemical impedance spectroscopy (EIS) measurements.

In summary, we showed that two enzymes immobilized on the Au-MPA SAM electrode can act as biosensor that measure AFB₁ at low levels. The residual enzyme activity was measured using a choline oxidase amperometric or impedimetric biosensor coupled with the AChE enzyme reaction in solution.

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Figure 1. Schematic illustration of the immobilization of AChE and ChO on gold electrode using a SAM of MPA and EDC-NHS as coupling agents for AFB₁ determination. The final product is Hydroquinone, which is measured at the Au modified electrode at an applied potential of +0.3 V vs. Ag/AgCl by Chronoamperometry and EIS.
**Fate of Oligonucleotide and Dye Modified Multifunctional Gold Nanoparticles in Living Cells**

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**Abstract** - The use of nanoparticles in medicine is increasingly becoming important. A number of nanoparticles and their derivatives are synthesized and used for delivery and cellular and biomedical imaging. In this study, the gold nanoparticles (AuNPs) modified with Rhodamine 6G (R6G) and oligonucleotides are synthesized and their toxicity, cellular uptake and destination of these newly modified AuNPs are explored.

AuNPs are good candidates for cellular and biomedical imagining and non-viral gene and drug delivery [1]. There is also a possibility of using modified nanoparticles as drug candidates [2]. It is known that in the presence of the AuNPs the efficiency of certain drugs increases to cure the targeted diseases [3]. There are a number of modified AuNPs and their applications in the literature [4]. However, there are many unknowns with their effects on living systems and their destinations upon entry to a living cell. Since there are many biomolecules and ligands can be chemically attached to the AuNPs, their effects on living systems must be clearly understood. The molecules attached to the AuNPs mostly govern their behavior and destination in the living cell.

Rhodamine B (RB) is a routinely used dye molecule to stain mitochondrion cell membrane. Since the delivery of certain molecules to mitochondrion is critically important, we explored whether Rhodamine 6G (another dye molecule) modified AuNPs can be directed to this organelle or not. Upon success of this approach, the drug molecules can be easily attached to the AuNPs and delivered with great precision. In order to serve the goal, first R6G and second oligonucleotide and R6G modified AuNPs were synthesized and their toxicity, cellular uptake studies, and their destination in a living cell are investigated.

In this study, the AuNPs modified with Rhodamine 6G (R6G) and oligonucleotides are synthesized and their toxicity, cellular uptake and destination of these new modified AuNPs are explored. It was found that R6G modified AuNPs could not enter the cell due to their hydrophobic surface properties. The attachment of 12 base-long nucleotides improved the cellular uptake and the dispersion of nanoparticles in the cytosol.

 Au nanoparticles

Rhodamine 6G

Oligonucleotide

Au nanoparticles & both dye and thiolated ssDNA modified GNP

We first studied entrance of the gold nanoparticles into the cells which were only modified with R6G. It was observed that after the R6G modification, the AuNPs became hydrophobic which prevented them from entering into the cells and caused nanoparticle accumulation outside of the cells.

Second, besides the R6G modification, oligonucleotides were also added for the AuNP modification. It was observed that both the dye and DNA modified AuNPs could enter the cells. A 12 base-long DNA oligonucleotide was used and it was observed that the oligonucleotide modification enhanced the dispersion of nanoparticles in the cytosol.

Finally, we investigated the localization of the dye and DNA modified AuNPs in the cells. RB was used as a dye to stain the mitochondria. We looked for any interaction between the mitochondria and modified AuNPs.

In summary, due to the fact that only certain size of AuNP clusters can be observed spontaneously, we can not visualize individual AuNPs or very small aggregates of them. Thus, fluorescence imaging of AuNPs by surface modifications as modifying them with a dye or both dye and oligonucleotide is an effective way to gain information about their destinations in the cell and their influence upon the cell. First, it is observed that modified AuNPs have no toxic effect on the cells but their morphologies change after treatment. Latter, when AuNPs are modified with only a dye (R6G), their modified form, DAuNPs, do not enter the cell due to the excessive aggregation. However, when AuNPs are modified with both dye (R6G) and oligonucleotide (thiolated ssDNA), their modified form, DOAuNPs, enter the cell easily. Nevertheless, we do not yet know the destination and localizations of these DDAuNPs in the cells. Investigations are continuing.

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Self Assembly of Silver Nanoparticles with Proteins by Influence of Hydrophobic Tip

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Abstract–Surface-enhanced Raman scattering (SERS) has the ability to detect down to single molecule. Therefore, it might be used for the detection of biological macromolecules with the desired sensitivity. The protein detection and identification have further gained importance with the development of proteomics. However, reproducible SERS spectra cannot be acquired from proteins due to the several reasons such as possessing different shape, size and charge properties, which determines the mode of interaction with the noble metal nanoparticles and surfaces. In this study, we demonstrate that the assembly of silver nanoparticles (AgNPs) with proteins can provide a new way for the successful SERS spectra acquisition. The simplicity and the effectiveness of the approach offer new opportunities for protein analysis.

Surface-enhanced Raman scattering (SERS) is such a powerful technique that detailed molecular information can be obtained from chemical and biological structures [1, 2, 3]. The potential of the technique for the analysis of biological molecules and structures increasingly gaining importance [4,5]. Among the biological macromolecules, proteins are most vital groups of molecules with great diversity and functionality. Therefore, new approaches for their characterization, detection and identification are always pursued. SERS as a promising technique can be utilized for the goal. However, proteins dried with colloids cannot yield reproducible SERS spectra. Thus, new assays for the detection of protein using colloidal AgNPs have been studied [6,7]. However, these reported assays are far from being universal detection techniques and they work only for certain group of proteins.

In our study, the AgNPs and globular protein molecules were assembled on surfaces without disturbing their 3D conformation. For this, the concentrated (8x) AgNPs were mixed with proteins to achieve a final concentration of 100.0, 50.0, 5.0 and 0.5 μg/ml. A 1μl of this mixture was spotted on CaF2 surfaces and a hydrophobic tip was touched into the droplet. Since AgNPs and protein were prepared in distilled water, hydrophobic force pushed them away from hydrophobic tip. This force resulted with the formation of layers around tip (Figure 1b).

The SERS spectra obtained from the control drop and layers of hydrophobic tip touched droplet are presented in Figure 2. While there are only two peaks appearing on the SERS spectra obtained from regular droplet of Human Serum Albumin (HSA), several peaks are seen on the SERS spectra from the touched-tip drying droplet. The formation of several layers on the light microscope image (figure 1 b) is visible. This indicates that AgNPs and protein molecules are forming self-assembled structures that position the protein molecules to the close proximity of AgNPs with proper orientation.

The assembly of several protein molecules with varying size, shape and charge properties is demonstrated and the SERS spectra were acquired. The results indicate that this simple method can be used for the protein detection and identification.

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Convective Assembly of Bacteria and Yeast Mixture for Surface-Enhanced Raman Scattering

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Abstract-In this work, we showed that application of convective assembly of microorganism mixtures for SERS would provide us well ordered structure, separation of microorganisms based on their size and mass, and in turn, SERS spectra of having better quality and reproducibility than that of simple mixing. The use of acquired SERS spectra from mixture of yeast and bacteria for separation and identification is demonstrated.

Microorganisms reside almost everywhere including human body and their fast identification is an important task since many serious and even fatal medical conditions result from bacterial and fungal infection. Many techniques have been developed over the years to identify microorganisms [1] and among these techniques Surface Enhanced Raman Spectroscopy (SERS) is one of the most promising ones due to its speed, versatility, and minimum sample preparation step [2].

The convective assembly is a technique in which a controlled assembly of two-dimensional (2D) or three-dimensional (3D) structures from nano- and micro-particles can be prepared. It was reported that this proper and controlled assembly made the SERS spectra acquired from the samples prepared with this technique having better quality and improved reproducibility [3].

In this work, we demonstrated superiority of convective assembly approach over simple mixing for identification using bacteria and yeast mixtures in varying ratios. A 72 μl of silver colloid prepared with the method reported by Lee and Miesel [4] was mixed with yeast (Candida albicans) and bacteria (E. coli). 5 μl of it was transferred onto a slide, and for convective assembly, 40 μl of it was spotted at the junction of two slides and the velocity of the bottom stage was set to 1.0 μm/s.

From SEM images, it was observed that there were three distinct regions on the slide onto which convective assembly was applied. Initially, some bacteria deposited onto slide which also contained relatively small amount of yeast, and then, deposition of a mixture of bacteria and yeast followed. Lastly, third region contained only bacteria. The width of the third region varied with the initially spotted amount of bacteria. AgNPs were also sedimenting, therefore it was in highest amount in the middle region and that situation directly affected SERS measurements acquired from the three regions.

Regarding SERS measurements, it was observed that because silver colloid was just depositing, a weak intensity of the spectra was obtained from the first region. Intensity of the middle region was quite good and contained SERS peaks of both bacteria and yeast, and weakest spectra was of the third region due to decreased amount of AgNPs. In addition, as a comparison, it can be easily seen on the figure 1 that SERS spectra of the middle region were better than that of the droplet spotted onto glass slide regarding both intensities and bands.

In summary, we showed that with the power of convective assembly not only on proper stacking and assembling of 2D and 3D structures but also on separating these particles regarding their size, mass, charge, and so on, it can be used for identification and discrimination of microorganisms.

Figure 1. Comparison of SERS spectrum of bacteria and yeast mixture prepared with two methods.

Figure 2. SEM images: (A) Initial region; (B) End region

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Viability and DNA Damage of Human Cells upon Exposure to Gold and Silver Nanoparticles with Different Size and Surface Properties

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Abstract-The use of nanoparticles (NPs) is extensively investigated for cancer therapy, gene delivery, cellular/biomedical imaging and sensing. However, their adverse effects on living systems are not clearly understood. Cancer and healthy cells are treated with two different sizes of Au and Ag nanoparticles (AuNPs and AgNPs) for a greater understanding of the relationship between size and surface chemistry effect of noble metal NPs on their cytotoxicity and DNA damage. The results demonstrate that the surface properties and size of NPs have a critical role for the cytotoxicity and cellular DNA damage.

Nanoparticles (NPs) have been used in physics, chemistry and biological sciences in applications such as imaging and sensing due to their unique tunable properties [1]. They can also be used for cancer therapy without any damage to the healthy surrounding cells. The possibilities to prepare NPs with different physicochemical properties have triggered a remarkable progression in nanotechnology [2]. AuNPs are generally used for biological studies; however, AgNPs are not used due to their size and surface property based toxicity [3]. The cytotoxicity of the NPs can be reduced based on their surface modification. It is known that the surface modification and size of the nanoparticles have a great role for the cellular uptake and cytotoxicity [2].

In this study, we comparatively investigated the size and surface chemistry impact of AuNPs and AgNPs with different size and surface chemistry on cytotoxicity and cellular DNA damage in cancer and noncancer cells. The outcome of this study can be important for the efforts to utilize these NPs for gene delivery and other therapeutic uses [4-7]. The synthesized AuNPs and AgNPs were treated with model cells; human dermal fibroblast and lung cancer cells (A549) cells.

Increasing the concentration of NPs to 100.0 μg/mL significantly influences the cell viability for all types of NPs. The cytotoxic effect of small size AuNPs and AgNPs to human cells was more extensive than large size AuNPs and AgNPs. For instance, 13 nm AuNPs were more toxic than 50 nm AuNPs and small size AgNPs has more pronounced toxic effect than large size AgNPs. On the other hand, AgNPs had more cytotoxic effect than AuNPs of the same size. The synthesized AgNPs with gallic acid behave more toxic while other NPs show toxicity to a lesser extent. The highest cytotoxicity was 7 nm silver nanoparticles which synthesized with gallic acid in cancer cells and noncancer cells. A 25 μg/mL lactose modified AgNPs increase the cancer cell viability when compared to other NPs with different surface chemistry.

The DNA damage upon exposure to NPs was investigated using comet assay. The concentration-dependent damage to DNA was assessed after exposing the cells with NPs. The comet assay of NPs treated cells exhibited concentration dependent increase in tail momentum (Figure 1B) as compared to untreated cells (Figure 1A), which indicated the level of the damage.

The length of the tail increases with the extent of DNA damage. The extent of DNA damage was much higher in lung cancer cells with respect to human dermal fibroblasts.

Figure 1. Comet analysis: untreated (A) and 29 nm Ag-NPs (synthesized with gallic acid) treated (B) cancer cells stained by SYBR green (conc. 50 μg/mL).

Our results demonstrate that surface modification was successful for improving cytotoxicity and cellular DNA damage. Furthermore, small size of NPs has more potential to cause cytotoxicity and DNA damage with respect to large NPs. The mechanism of DNA damage and the influence of the size and surface chemistry on apoptosis and gene expression are currently under investigation in our laboratories. The further information on the subject will provide important clues for the assessment of the NPs concerning their therapeutic applications.

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Benzoylformate Decarboxylase Immobilized on Magnetic Solid Support

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Abstract—Histidine tagged recombinant Benzoylformate Decarboxylase (BFD) was immobilized to surface modified magnetic particles for affinity ligand binding. First, the Co2+-NTA functionalized γ-Fe2O3 nanoparticles were employed for one-pot purification-immobilization steps. It was shown by SDS-page analysis that the magnetic nanoparticles were eligible for selective binding of HIS-tagged BFD. Loading capacity of the resin was determined by standard Bradford protein assay. Cell free extract of E. coli BL21(DE3)pLysS containing HIS-tagged BFD was incubated with resin and after excessive washing, protein was eluted and quantification of protein was performed. Maximum protein amount that has been attached to resin was estimated as 4.31 mg BFD/g resin. Enzyme-magnetic resin heterocatalyst system was highly responsive to magnetic field, where the slurry could be clarified in 30 second by using a regular magnet Histidine tagged recombinant benzoylformate decarboxylase was immobilized to surface modified magnetic particles for affinity ligand binding.

Magnetic particles of iron oxides (magnetite and maghemite) are widely used in many applications in the fields of biotechnology and biomedicine [1-3]. Many of the particles used in the separation technology are superparamagnetic [4]. It is necessary to modify the surfaces of magnetic particles in order to obtain a functionalized product which can be used in magnetic bioseparations. Functionalization of magnetic nanoparticles for the separation and purification of specific biomolecules is based on the immobilization of the required affinity ligand on the surface of magnetic particles.

Benzoylformate decarboxylase (BFD) is a TPP dependent carboligating enzyme that has been used for many applications for synthesis of pharmaceutically important compounds with a wide range of substrate spectrum [5]. Carboligation activity of BFD was described in Pseudomonas putita first and since then BFD is used as an efficient catalyst for the enantioselective formation of α-hydroxyketones and (R)-benzoin [6]. BFD enzyme has characterized and cloned to an over expressing E. coli with histidine tagging. Immobilized metal affinity chromatography (IMAC) purification of benzaldehyde lyase (BAL), another TPP depending carboligating enzymes have been reported previously [7,8]. However to our knowledge, purification studies associated to BFD have not been reported yet.

The aim of this study is to prepare surface modified magnetic γ-Fe2O3-silica nanocomposite particles suitable for the IMAC purification and immobilization of recombinant 6Xhistidine tagged BFD enzyme. First, γ-Fe2O3-silica nanocomposite particles were prepared using a sol-gel technique, and then their surfaces were modified by the condensation 3-Glycidoxypropyltrimethoxysilane (GPTMS) technique, and then their surfaces were modified by the nanocomposite particles were investigated. The surface modified γ-Fe2O3-silica nanocomposites were characterized using vibrating sample magnetometry (VSM), thermal analysis and X-ray diffraction techniques (XRD).

Thus prepared resin exhibited superparamagnetic property and good responsiveness in a magnetic field, besides it is easily dispersible in aqueous medium. The adsorption capacity of the resin for BFD was found as (4.31 ± 0.33 mg BFD/g resin). The capacity did not show variation at least after four successive usage of the same resin. Figure1 shows Immobilization benzoylformate decarboxylase.

The favorable properties of the γ-Fe2O3-silica-GPTMS-NTA-Co2+ magnetic affinity support in adsorption capacity, stability in protein adsorption, and magnetic properties revealed that the resin would be applicable in rapid and selective one pot purification and immobilization of histidine tagged recombinant BFD enzyme.

Figure1. Immobilization benzoylformate decarboxylase

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In this study we have investigated photophysical and photochemical properties of aluminum, gallium and indium (III) phthalocyanines mixed with CdTe nanocrystals for photodynamic treatment. Aluminum, gallium and indium tetra-polyoxy substituted phthalocyanines were synthesized and characterized according to reported method [3]. CdTe QDs were synthesized from aqueous solution and were stabilized by using water soluble thiol thioglycolic acid. In addition to serving as stabilizer, this thiol capping serve to passivate the surface of the QDs and thereby removing the surface traps which lower the photoluminescence (PL) efficiency of the quantum dots. General trends are described for quantum yields of photodegradation, fluorescence and fluorescence lifetimes as well as singlet oxygen quantum yields of these compounds. Singlet oxygen quantum yields were determined in DMSO using 1,3-diphenylisobenzofuran (DPBF) as a chemical quencher. The disappearance of DPBF was monitored using UV–vis spectrometer. Figure 2 shows the singlet oxygen measurements of AlPc in DMSO.

Figure 1. Photodynamic Theraapy

In summary, the interaction of CdTe quantum dots with AlPc, GaPc and InPc derivatives shows that a strong overlap occurs between the emission of the TGA capped QDs and the absorption spectra of these Pc derivatives. The largest fluorescence energy transfer (FRET) was observed for InPc followed by GaPc and then AlPc. The singlet oxygen quantum yields of these Pc derivatives increased in the presence of QDs, hence making the combination of these Pc derivatives and QDs potential candidates for applications as photosensitizers in PDT.

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Plasma Treated Electrospun Nanofiber Modified Quartz Crystal Microbalance Surfaces Intended For Biosensor Applications
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Abstract-In the scope of this study, we aimed to increase QCM based sensor performance by aligned electrospun nanofibers. We investigated to modify QCM sensor’s surface with a highly oriented nanofiber films. Plasma polymerization technique used to create specific groups on these surfaces. It makes these surfaces excellent candidates for sensor applications.

Quartz crystal microbalances (QCMs) are one of a broad class of acoustic wave (AW) techniques that have been applied to detect small mass uptake when used as microsensors [1].

Sensor performance such as sensitivity, selectivity, and time response is largely influenced by the properties of the sensing films. QCM is highly sensitive to mass changes in the presence of a coating that interacts with the target. In the literature, QCM sensor surfaces modified by different materials such as zeolites, fullerene C60, chiral materials, carbon graphites, ITO films, and oligonucleotides intended for different applications [2]. In this study we aimed to coat QCM surfaces with Polyvinyl alcohol (PVA) nanofibers. PVA is an important polymer that widely used in coatings due to its excellent chemical and physical properties such as non toxicity, processability, good chemical resistance, wide range of crystallinity, good film formation capacity, complete biodegradability and high crystal modulus etc. [3]

Electrospinning is a novel technique for surface modification. Electrospun fibers deposits as nonwoven mats, have a diameter range of 200-500 nm. Electrospun fibers with controllable membrane thickness, fine structures, diversity of materials and large specific surface are expected to be an ideal candidate as the structure of sensing materials.

Plasma polymerization technique is an elegant method for generating functional polymer surfaces. Surface modification by low pressure plasma treatment illustrates many important advantages over other techniques, such as environmental safety, uniformity and reproducibility, diversity of reagent gases, and selective modification with minimization of bulk property change [4]

To investigate the effects of some of the key process parameters to the fiber diameter, we conducted electrospinning at different conditions. The parameters studied were concentration, capillary-screen distance, electric potential at the tip, flow rate and the collector effect. Different concentrations (10-15 wt %) of PVA (Polyvinyl alcohol) solutions were prepared. Using different voltages (15-25 kV), capillary-screen distances (10-20 cm), flow rates, we found the most available conditions to produce nanometer scaled fibers. Later SEM (Scanning Electron Microscopy) was performed for characterization.

We discussed gold stripes’ electrical field effect on the electrospun nanofibers [5]. QCMs are modified to gain highest surface to volume ratio.

Following modification of QCM surfaces by electrospinning method, plasma polymerization technique used for creating specific groups on those surfaces. Low pressure cold plasmas are emerging and promising technologies for modification of nanofiber films. In this process, Ethylenediamine (EDA) was used to form functional amine groups on nanofiber based surfaces.

Bovine Serum Albumin (BSA) was chosen as a target protein in the sensing experiments. The results of sensing experiments indicate that the nanofiber modified sensors showed much higher sensitivity and quicker responses to target molecules. Our results open a new approach to highly sensitive biosensors by plasma treated electrospun nanofiber modified QCM surfaces.

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Antibacterial activity of ZnO nanoparticle suspensions on gram-positive and gram-negative bacteria

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Abstract— We determine the antimicrobial activity of ZnO nanoparticles against gram negative and gram positive bacteria with respect of particle size, concentration and time. The results show that gram negative bacteria are more resistant to ZnO nanoparticles than gram positive bacteria and the antibacterial activity of ZnO nanoparticles increase with decreasing particle size and increasing concentrations. This effect is time dependent and take effect gradually.

Nanoparticles are a special group of materials with unique features and extensive applications in diverse fields [1]. Nanoparticles display completely different properties in comparison with their bulk size which is mainly related to the increased specific surface area and high reactivity of nano size materials [2]. The considerable antimicrobial activities of inorganic metal oxide nanoparticles such as ZnO, MgO, TiO2, SiO2 and their selective toxicity to biological systems suggest their potential application as therapeutics, diagnostics, surgical devices and nanomedicine based antimicrobial agents [3, 4, 5, 6, and 7]. The advantages of using these inorganic oxides nanoparticles as antimicrobial agents are their greater effectiveness especially on resistant strains of microbial pathogens, less toxicity and heat resistance. In addition they provide mineral elements essential to human cells and even small amounts of them exhibit strong activity [2, 8, 9]. Among metal oxide nanoparticles, ZnO nanoparticles as one of the multifunctional inorganic nanoparticles has many significant features such as chemical and physical stability, high catalysis activity, effective antibacterial activity as well as intensive ultraviolet and infrared adsorption with broad range of applications as semiconductors, sensors, transparent electrodes, solar cells, etc. [1,10]. In addition ZnO nanoparticles have the potential to impact many aspects of food and agricultural systems because of its antimicrobial efficacy [11]. Some data suggest the selective toxicity of the ZnO nanoparticles toward cancer cells [12].

The aim of the present study is to determine the antimicrobial activity of ZnO nanoparticles against gram-negative and gram-positive bacteria Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus) were used as test microorganisms. The effects of particle size and concentration on the antibacterial activity of ZnO nanoparticles was studied using bacteriological tests such as disc and well diffusion agar methods, Minimum Inhibitory Concentration (MIC) and Minimum Bactericidal Concentration (MBC). These tests were performed in nutrient broth and nutrient agar following standard methods. In addition the effect of different concentrations of ZnO nanoparticles on the growth of E. coli and S. aureus was measured with respect of time.

At the first the antibacterial activity of ZnO nanoparticles was tested by the disc and well diffusion agar methods. We used different ZnO nanoparticle concentrations between 0.195 mg/ml to 10 mg/ml in disks and wells. The results showed that ZnO nanoparticles have antibacterial inhibition zone of 29 mm and 19 mm at the concentration of 10 mg/ml against E. coli and S. aureus respectively. There was no inhibition zone at concentration less than 0.039 mg/ml for S. aureus and 0.312 mg/ml for E. coli.

We next examined the MIC and MBC for tested bacteria. The Minimum inhibitory concentration was determined using seven different concentrations of ZnO nanoparticles including 16, 8, 4, 2, 1, 0.5 and 0.25 mg/ml. The MIC value for E. coli and S. aureus was 1 mg/ml and 0.5 mg/ml respectively. The results of time-dependent antibacterial activity of ZnO nanoparticles showed that colony forming unit (cfu) of the tested bacteria for each concentration decreased gradually during 72 h, whereas colony formation of control solution remained uncountable. It was found that ZnO bulk powder showed no significant antibacterial activity and the antibacterial activity of ZnO nanoparticles increased with decreasing particle size and increasing powder concentration. Based on the results obtained from MIC, MBC, disc and well agar diffusion methods, it can be suggested that in comparison with gram-positive bacteria, the growth of gram-negative bacteria is inhibited at higher concentrations of ZnO nanoparticles which could be related to differences in cell wall structure, cell physiology, metabolism or degree of contact.

We thank Dr. Gholamreza Amiri for preparing ZnO nanoparticles for this study.

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Electrochemical monitoring of DNA hybridization by magnetic particles based sensor technology

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Abstract—An indicator-based and indicator-free magnetic assays connected with a disposable pencil graphite electrode (PGE) were successfully developed, and also compared for the electrochemical detection of DNA hybridization. The oxidation signals of echinomycin (ECHI) and electroactive DNA bases, guanine and adenine, respectively were monitored in the presence of DNA hybridization by using differential pulse voltammetry (DPV) technique. The detection limits (S/N = 3) of the magnetic assays based on indicator or indicator-free were found in nM concentration level of target using disposable sensor technology with good reproducibility.

The development of advanced biological sensor systems could impact significantly the areas of genomics, proteomics, biomedical diagnostics and drug discovery [1,2]. Recent advances in biosensors based on nucleic acid have led to the development of genosensor technology for gene sequence analysis and for nucleic acid ligand binding studies [3-5].

The electrochemical nucleic acid sensor system based on magnetic particles [6-11], labeling with an enzyme [8], using label-free system [7,9,11] or combining with metal nanoparticles [6,10], enables the sequence specific detection of DNA hybridization observed in low detection limits resulting from efficient magnetic separation.

A biomagnetic assay of DNA sequences related to breast-cancer gene (BRCA1) was reported based on label-free detection [7]. Coupling the label-free guanine detection with the efficient magnetic isolation of the hybrid as using biotinylated inosine-substituted probes, streptavidin-coated magnetic beads with potentiometric stripping analysis (PSA) measurements at a renewable graphite pencil electrode.

In this study, an indicator-based and indicator-free magnetic assays connected with a disposable graphite sensor (pencil graphite electrode, PGE) were successfully developed, and also compared for the electrochemical detection of DNA hybridization. The changes at the oxidation signals of echinomycin (ECHI) and electroactive DNA bases, guanine and adenine, respectively were monitored in the presence of DNA hybridization by using differential pulse voltammetry (DPV) technique. The selectivity of these magnetic assays for DNA hybridization was also checked in the presence of single base mismatch and noncomplementary DNA sequences. There have not been yet any reports about both indicator-based and indicator-free magnetic assays connected with disposable sensor system by measuring the oxidation signals of ECHI, guanine and adenine in the same measurement scale.

The reported magnetic assays based on indicator-based and indicator-free methods connected with a disposable graphite sensor (PGE) were successfully developed for the electrochemical detection of DNA hybridization. There have not yet been any reports of both indicator-based and indicator-free magnetic assays connected with a disposable sensor system through measurement of the oxidation signal of indicator ECHI with the signals of DNA bases, guanine and adenine, in the same measurement scale. Easier, quicker and more sensitive detection scheme for DNA hybridization based on magnetic assay was explored herein in comparison to the traditional techniques reported earlier in the literature [5,12], in which several external indicators [Co(phen)3]3+, methylene blue, meldola’s blue have been applied by using advanced surface modification or regeneration schemes. The use of PGE brings the other advantage to our assay with a better reproducibility; such as, being cheaper, easy to use (single-use) and portable, which are crucial properties of devices for DNA chip technology contrary to other transducers; such as, gold electrode and hanging mercury drop electrode. A.E. acknowledges the financial support from TUBITAK (Project no.106S181). H.K. acknowledge a scholarship from PhD students obtained from TUBITAK.

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Formulation of Nano Drug Delivery Systems

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Abstracts- We aimed to show the advantages, disadvantages and possible applications of the different formulations in nano drug delivery systems.

Nanotechnology by manipulation of characteristics of materials such as polymers and fabrication of nanostructures is able to provide superior drug delivery systems for better management and treatment of diseases. The nanostructures employed as drug delivery systems have multiple advantages which make them superior to conventional delivery systems [1].

Nanoparticles and other colloidal drug delivery systems modify the kinetics, body distribution and drug release of an associated drug. Other effects are tissue or cell specific targeting of drugs and the reduction of unwanted side effects by a controlled release [2].

Micelles in which the most commonly used amphiphilic block copolymer is “Pluronic” a ternary copolymer of poly (ethylene glycol) and poly (propylene oxide). Multifunctional micelles can be prepared throught conjugation of targeting ligands (e.g., folic acid, RGD peptide, antibodies, RNA aptamer and carbohydrates like glucose, lactose, etc.) to their shell aiming to induce specific targeting and uptake by the cells. Liposomes are forms of vehicle that consist either of many, few or just one phospholipid bilayers. Polar drugs can be encapsulated in the lipid core, whereas amphiphilic and lipophilic molecules can be solubilized within the phospholipid bilayer. Dendrimers consist of a central core, branching units and terminal functional groups [3]. Nanoparticles (including nanospheres and nanocapsules) are stable, solid, organic or inorganic particles, with sizes in the range of 10-1000nm. Nanoparticles tend to be accumulated in tumors, inflammatory and infectious sites by virtue of the enhanced permeability and retention (EPR) effect on the vasculature [4]. Solid lipid nanoparticles (SLN) with lipids which are in solid state at room and body temperature were prepared and stabilized with emulsifier, nanometer size particles [5]. SLN generally solid lipids, emulsifiers and water are formed. Lipid broad term means are used, and triglycerides (tristearin, etc.), partial gliceridleri (Imwitor, etc.), oil acids (stearic acid), steroids (cholesterol) and candles (setil palmitate,etc.) contains [6].

<table>
<thead>
<tr>
<th>DRUG DELIVERY SYSTEMS</th>
<th>CONTENT</th>
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<tr>
<td>Micelles</td>
<td>Amphiphilic block copolymer</td>
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<tr>
<td>Liposomes</td>
<td>Phospholipid bilayers</td>
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<tr>
<td>Dendrimers</td>
<td>Central core, branching units and terminal functional groups</td>
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<tr>
<td>Nanoparticles</td>
<td>Nanospheres, nanocapsules and solid, organic or inorganic molecule</td>
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<tr>
<td>Solid Lipid Nanoparticle(SLN)</td>
<td>Triglycerides, partial gliceridleri, oil acids, steroids and candles</td>
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Table 1. Content of drug delivery systems

In this study, advantages and disadvantages of implementation and preparation methods of drug delivery systems used in diagnosis and treatment of various disease have been evaluated.

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Use of Nanocarrier Systems in Cancer Therapy

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Abstracts-In this study, we supposed to show that how the drug delivery systems can be used for cancer treatments and what the possible future applications could be.

Cancer is the abnormal growth of cells in our bodies that can lead to death [1]. Because of high death rate associated with cancer and the serious side effects of chemotherapy and radiation therapy, many cancer patients seek for alternative methods of treatment [2]. The newer approaches to cancer treatment not only support the conventional chemotherapy and radiotherapy but also prevent damage to normal tissues and prevent drug resistance [3].

Nanoparticles are designed as multifunctional diagnostic and therapeutic devices. For pharmaceutical purposes and more specifically for cancer drug delivery and cancer imaging various carrier types have been developed [4]. This resulted in the development of various nanocarriers such as polymeric nanoparticles, carbon nanotubes, liposomes, solid lipid nanoparticles, magnetic nanoparticles, nanoshells, nanocapsules, and dendrimers for targeting tumor sites to enable its molecular imaging [5]. The use of nanoparticles as drug delivery vehicles for anticancer therapeutics has great potential to revolutionise the future of cancer therapy [6]. As drug delivery systems, nanoparticle widely investigated because of many advantages such as smaller size, controlled drug release potential, targeting ability, enhancement of therapeutic efficacy and reduction of toxicity [7].

The effects of drug carrier systems which have been prepared using different active ingredients on cancer cells have been theoretically investigated in this study.

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Advantage and Disadvantage in Drug Delivery Systems

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Abstracts- We aimed to compare different nanoparticles in drug delivery systems. We also tired to show the advantages and disadvantages of the preparation methods of these systems.

Nanotechnology, systems-devices manufactured at the molecular level, is a multidisciplinary scientific field undergoing explosive development. A part of this field is the development of nanoscaled drug delivery devices [1]. Nanotechnology advances in drug delivery deal with the development of synthetic nanometer sized targeted delivery systems for therapeutic agents of increased complexity, and biologically active drug products [2].

Nanomedicine is defined as the application of nanotechnology to achieve breakthroughs in healthcare. The development of drug delivery systems has improved the therapeutic and toxicological properties of existing chemotherapies and facilitated the implementation of new ones [3].

Currently used drug delivery systems, such as liposomes, micelles, nanoemulsions, polymeric nanoparticles and many others demonstrate a broad variety of useful properties [4].

The successful implementation of nanoparticles for drug delivery depends on their ability to penetrate through several anatomical barriers, sustained release of their contents and their stability in the nanometer size. However, the scarcity of safe polymers with regulatory approval and their high cost have limited the widespread application of nanoparticles to clinical medicine [5].

To overcome this limitation the drawbacks associated to the traditional colloidal systems [6], such as emulsions, liposomes and polymeric nanoparticles, solid lipid nanoparticles (SLN®) and nanostructured lipid carriers (NLC®) were developed [7]. The main difference between SLN and NLC is the fact that the concept of these latter is performed by nanostructuring the lipid matrix, in order to increase the drug loading and to prevent its leakage, giving more flexibility for modulation of drug release.

A. Liposome  B. Miceles

C. Nanoparticle  D. Solid Lipid Nanoparticle

Figure 1. Various nanostructures used in drug delivery systems.

In this study diagnosis and treatment of various diseases with different drug carrier systems have been examined. Furthermore, advantages and disadvantages of the preparation and implementation stages of drug formulations, as well as their detection systems have been compared each other.

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Binding of antibodies to Concanavalin A-modified Magnetic Chitosan Nanoparticles

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Abstract—Binding of human immunoglobulin-G (IgG) from aqueous solutions and human plasma to concanavalin A (Con A) immobilized magnetic chitosan nanoparticles has been studied. Well-dispersed suspension of magnetic chitosan nanoparticles were produced by co-precipitation method. The carbonyl groups of chitosan nanoparticles were opened by EDC activation. Then, Con A was immobilized by covalent binding onto the nanoparticles. Loading ratio of Con A was 70 mg/g. The maximum IgG adsorption on the Con A-magnetic chitosan nanoparticles was observed at pH 7.4 from aqueous solutions. Adsorption ratio of IgG was 63 mg/g from aqueous solutions. Desorption ratio was >95% of adsorbed IgG which was achieved with 2.0 M NaCl.

Magnetic nanoparticles (NPs) have considerable interests because of their great potential applications in magnetic fluids, catalysis, biotechnology/biomedicine, magnetic resonance imaging (MRI), magnetic recording devices, and environmental remediation [1]. Particularly, magnetite (\(Fe_3O_4\)) has recently received more attention due to their potential applications in nanobiotechnology such as using both as a tag for sensing and imaging, and as an active agent for antitumor therapy [2,3]. However, for high performance in function-specific biological applications, magnetic NPs (\(Fe_3O_4\)) should be spherical, biocompatible, superparamagnetic and have narrow size distributions and large surface areas (for maximal protein or enzyme binding), high magnetic saturation to provide maximum signal, and good dispersion in liquid media.

Due to the hydrophobic surfaces and large surface area to volume ratio of the iron oxide nanoparticles during the applications, they tend to form agglomeration. Magnetic nanoparticles can be modified by using a biocompatible polymer as coating to overcome these problems [4,5].

Chitosan, 1-4,2-amino,-2-deoxy-b-Dglucan, is a partially deacetylated derivative of chitin, and is a large polymer of crystalline polysaccharide. It has a polycationic carbohydrate structure. So chitosan has been widely used in the fields of medicine, pharmacy and biotechnology [6]. Magnetic separation is relatively rapid and easy, requiring a simple apparatus composed of centrifugal separation [7].

Lectins have been extensively used to purify glycoproteins. This work explores the performance of Concanavalin A (Con A) using their affinity to human antibody IgG. Immunoglobulin G (IgG) is the most important type of antibodies in the immune system and more than half amount of the antibodies belongs to IgG. It widely presents in the serum and tissue fluid [8].

In our study, well-dispersed suspension of magnetic chitosan nanoparticles were produced by co-precipitation method from the aqueous solutions of FeCl\(_2\)H\(_2\)O and FeCl\(_3\)\cdot6H\(_2\)O using NH\(_3\) solution as a coprecipitant. Characterization of the nanoparticles were done by using scanning electron microscopy (SEM), FTIR, electron spin resonance (ESR) and vibrating sample magnetometer (VSM) measurements. Con A molecules were covalently bound to the nanoparticles by using Con A as an affinity ligand. IgG adsorption on Con A modified magnetic chitosan nanoparticles from aqueous solutions containing different amounts of IgG at different nanoparticle size and nanoparticle amounts. Elution of IgG and regeneration of nanoparticles were also tested.
Our motivation is to prepare neuronal growth stimulation on the surface modified biodegradable polymeric surfaces for artificial neural Networks. C and C+N ion implantations have been held by using Metal-Vapour Vacuum Arc (MEVVA) ion implantation technique. Samples were implanted with a fluence of $10^{15}$ ion/cm$^2$ and extraction voltage of 30 kV. In vitro neural cell culture studies have been carried out with model cell lines (PC12 and Kelly) to show that C and C+N ion implantation can stimulate the neural growth on biodegradable polymeric surfaces for biomedical and bioelectronics applications. Scanning electron microscopy (SEM) was used to examine the cell attachments on the surface.

Chitosan, PLA, PDLG and PCL samples are prepared by solvent casting method with different solutions in %3-5. Assymetric membrane is prepared with immersion precipitation method with chloroform and distilled water. All samples were C and C+N ion implanted with the dose of $10^{16}$ cm$^{-2}$, 1 pps. frequency and 20kV. Voltage.

Cell attachment studies have been done with the:

**Cell Line:** CRL 2754 Human Neuroblastoma

**Cell density:** $8.4 \times 10^6$ ml.

**Incubation temp.** 37°C for 2 hours.

Contact angle measurements refers to surface structure is changed after ion implantation and with this dose of energy hydrophilic Chitosan and PCL surfaces have became hydrophobic while same trend is not valid for PDLG surfaces. They expressed hydrophilic properties after both C and C+N ion implantation. On the other hand asymmetric PLA samples represent more hydrophobic properties after C and C+N implantation.

![Figure 1](image)

Figure 1. In the figure it can be clearly seen that neural cell attachment properties of the biodegradable surfaces are all improved after C and C+N implantation except Assymetric PLA samples. This important advantage brings the further possibilities on any application for cell attachment studies on ion implanted polymeric surfaces.
Neural Cell Attachment Studies on C and N Ion Implanted Biodegradable Polymers

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Abstract— In this work, we used metal-gas ion implantation technique to determine the best condition with this technique for neural guidance on biodegradable surfaces. As a polymer, we used lactic derivative Poly L-Lactide (PL), Poly -DL- Lactide Glycolide (PDLG), Poly Caprolactone (PCL) polymers and chitosan. Our motivation is to prepare neuronal growth stimulation on the biodegradable polymeric surfaces for artificial neural networks. Ag and C ion implantations have been held by using Metal-Vapour Vacuum Arc (MEVVA) ion implantation technique. Samples were implanted with a fluence of 1015 ion/cm2 and extraction voltage of 30 kV. Fourier Transform Infra Red and Raman Spectroscopy techniques were used for surface studies. In vitro neural cell culture studies have been carried out with model cell lines (PC12 and Kelly) to demonstrate that Ag and C ion implantation can stimulate the neural growth on biodegradable polymeric surfaces for biomedical and bioelectronics applications. Scanning electron microscopy (SEM) was used to demonstrate the cell attachments on the surfaces.

Bio-active surfaces are continuously being investigated for a wide range of applications. The ability to engineer and control the interactions of cells with biomaterials is critical for fundamental cell biology studies, medical implants, and functional biomaterial scaffolds for tissue engineering, as well as for the development of cell integrated biochips used in neural-cell sensors and “lab-on-a-chip” bioanalytical systems. Physicochemical parameters such as hydrophobicity, surface charge, molecular and elemental composition, and roughness are known to affect cell adhesion. The controlled attachment of desired cell populations in precisely engineered geometries will enable production of truly bioactive systems with a broad spectrum of applications [1].

The primary goal of this work is to develop a versatile precise process for neuronal growth stimulation on the biodegradable polymeric surfaces. For this aim we used ion implantation technique which is a surface modification process with ions are injected into the near-surface region of a substrate. Ion implantation was carried out using a vacuum-arc ion source Mevva-based system that has been fully described elsewhere [2-6]. In this facility, a high current, energetic metal ion beam is formed by a vacuum-arc ion source and used to implant high energy ions. The source is operated in a repetitively pulsed mode, with pulse length 250µ s and pulse repetition rate a few pulses per second. The metal ion species can be any of the solid metal elements as well as metallic compounds and alloys. Implantation is done in a broad-beam mode, without magnetic analysis of charge-to-mass components, and the ion trajectories are line-of-sight from ion source to substrate. For the present work, the implants were done at a relatively low energy 30 keV, with doses from 1015 cm-2 with C and N. As a polymer, we used lactic derivative Poly L Lactide (PL), Poly -DL- Lactide Glycolide (PDLG), Poly Caprolactone (PCL) polymers and chitosan.

In vitro neural cell culture studies have been carried out with model cell line (PC12) to demonstrate that C and N ion implantation can stimulate the neural growth on biodegradable polymeric surfaces for biomedical and bioelectronic applications. Scanning electron microscopy (SEM) was used to demonstrate the cell attachments on the surface.

Contact angle measurements and spectral analysis refers to surface structure is changed after ion implantation and with this dose of energy hydrophilic Chitosan and PCL surfaces have become hydrophobic while same trend is not valid for PDLG surfaces after C and C+N implantation. This important advantage brings the further possibilities on any application for cell attachment studies of ion implanted polymeric surfaces

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Figure 1. FTIR spectra of biodegradable polymers after ion implantation

Figure 2. PC12 Cell culture with C and C-N implanted PLA
Preparation of Superparamagnetic TNF α Nanotraps Using ANADOLUCA Crosslinking Method

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Abstract-In this study, a synthesis method for preparation of superparamagnetic TNF α nanotraps have been reported using bis(2-2’-bipyridyl) bis(MATyr)-ruthenium(II) as photosensitive chelate monomer. This study is an application of AmiNoAcid (monomer) Decorated and Light Underpinning Conjugation Approach (ANADOLUCA) method. This method provides a strategy for the preparation of photosensitive ruthenium based aminoacid monomers and hapten, aminoacid monomer-protein cross-linking on micro and nano-structures.

Nanomaterials are ideal probe candidates because of their (i) small size (1-100 nm) and correspondingly large surface-to-volume ratio, (ii) chemically tailorable physical properties, (iii) unusual target binding properties, and (iv) overall structural robustness. In addition, super paramagnetic nanoparticles (SPN) have a unique property due to magnetically separable their low toxicity [1]. Therefore, SPN have used many applications [2]. At this point in time, the use of nanobio-conjugates for life sciences and biotechnology applications are the fastest moving fields of nanobiotechnology. By employing different conjugation technologies they can not only be rendered biocompatible, but also, to fulfill tasks. To achieve this goal, different monomeric or polymeric coatings are applied to provide biocompatibility and additional bioconjugation (also for multivalent interaction) for targeting those particular drugs which prevent the disease spreading and other applications [3].

This study is an application ANADOLUCA method [4]. In this method, the photosensitive, covalent and cross-linking conjugation methods based on aminoacid and ruthenium-chelate based monomers provides accurately antibody orientation, preventing denaturation during bonding and after bonding. Indeed, they provide efficiency of bounded proteins as well as many uses such as reusable enzymes, reusable separation solid phase systems based affinity chromatography, theranostics, nanoprotein carrier, receptor targeted nanocargoes, manageable imaging and detection technologies.

In this present study, we have synthesized superparamagnetic TNF α nanotraps, using bis(2-2’-bipyridyl) bis(MATyr)-ruthenium(II)photosensitive chelate (MATyr-Ru(bipy)-MATyr) as monomer and used for TNF α separation. As it is known, TNF is a protein group which has studied in cancer researches recently [5]. TNF α is found in very low level in blood serum. Therefore, determination and separation of TNF α is very difficult. Until today, some techniques such as ELISA [6], radioimmunoassay [7], fluorescence immunoassay [8], chemiluminesence assay [9], solid-phase capture with radiolabel and MALDI-MS detection [10] have used for this purpose.

For preparing of superparamagnetic TNF α nanotraps, firstly, 3-(4-hydroxyphenyl)-2-[(2-methylacryloyl)aminopropanoic acid (methylacryloyl tyrosine, MATyr), was synthesized according to previously published method [11]. And then, bis(2-2’-bipyridyl)bis(MATyr)-ruthenium(II) was synthesized as photosensitive crosslinking monomer. Finally, anti TNF α antibody conjugated SPNs were synthesized and characterized. The study includes preparation procedures, characterization data and TNF α separation with TNF α nanotraps. The last step (TNF α-superparamagnetic TNF α nanotraps interaction) was investigated by fluorimetry. The association constant (Ka) for the specific interaction between the TNF α and superparamagnetic TNF α nanotraps itself was determined by Scatchard’s plots. The Ka for the binding of TNF α to superparamagnetic TNF α nanotraps is 9.0×10^7 M^-1. The value of Ka suggest that affinity of the binding sites is very durable as well as biological receptors (10^7–10^9).

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References:
Tubulin Separation by Anti Tubulin Antibody Conjugated Quantum Dots
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Abstract-In this present study, anti tubulin antibody conjugated quantum dots have synthesized using MATyr-Ru(bipy)r2-MATrp as monomer and have used for tubulin recognition. This study is an application of AmiNoAcid (monomer) Decorated and Light Underpinning Conjugation Approach (ANADOLUCA) method. The photosensitive aminoacid monomer linkers can react via chemically and biocompatible to a lot of different micro and nano-surface and then to the protein when they act as a single-step cross-linking reaction using irradiation. The photosensitive conjugation based on click biochemistry can be carried out at mild conditions, independent of pH and temperature, without affecting conformation and function of protein.

The most commonly used conjugation chemistry for protein and peptide immobilization is covalent attachment via primary amino groups onto a carboxy-modified nanosurface following activation with N-ethyl-N'-dimethylaminopropyl-carbodiimide (EDC) and N-hydroxysuccinimide (NHS). However, while applicable for many proteins and peptides, these very acidic isoelectric points (pI < 4.0) will not be electrostatically concentrated into the matrix which is essential for effective covalent immobilization [1]. Immobilization can be defined as the attachment of biomolecules to a surface resulting in reduction or loss of mobility. In some cases, immobilization may lead to partial or complete loss of protein activity, due to random orientation and structural deformation. Oriented immobilization of active proteins are good steric accessibilities of active binding sites and increased stability [2].

The present invention appertains to the preparation of photosensitive amino acid monomer and oligomers, protein conjugating method (ANADOLUCA- AmiNoAcid (monomer) Decorated and Light Underpinning Conjugation Approach) [3], and their use in life sciences and biotechnology. The photosensitive, covalent and cross-linking conjugation methods based on aminoacid and ruthenium-chelate based monomers to provide accurately antibody orientation, preventing denaturation during bonding and after bonding. Indeed they provide efficiency of bounded proteins as well as many uses such as reusable enzymes, theranostics, nanoprotein carrier, receptor targeted nanocargoes and detection technologies.

In this present study, as an example for using of ANADOLUCA method, anti tubulin antibody conjugated quantum dots have synthesized using MATyr-Ru(bipy)r2-MATrp as monomer and have used for tubulin recognition.

In experimental procedure, firstly 3-(4-hydroxyphenyl)-2-[(2-methylacryloyl)amino]propanoic acid (methylacyloyl tyrosine, MATyr) and N-[1-(1H-Indol-3-ylmethyl)-2-oxo- propyl]-2-methylacrylamide (methylacyloyl tryptophan, MATrp) were prepared according to previously published method [4] by us. Then, Bis (2-2’-bipyridyl) MATyr-MATrp-ruthenium(II) (MATyr-Ru(bipy)r2-MATrp) was synthesized as photosensitive crosslinking monomer. Finally, anti tubulin antibody conjugated QDs were synthesized and characterized. The study includes preparation procedures, characterization data and tubulin separation from cell cocktail. Tubulin recognition by anti tubulin antibody conjugated QDs were investigated by flourimetry.

Figure 1. Emission changing of QDs interaction with cell fraction at 650 nm for room temperature and for 0 °C

In conclusion, we have developed a method for the preparation of photosensitive ruthenium based aminoacid monomers and haptons, aminoacid monomer-protein cross-linking using photosesitation and conjugation approach (ANADOLUCA) on quantum-dots by ruthenium-chelate based monomers. We have prepared tubulin recognition systems by means of conjugation of anti tubulin antibody onto QDs. This QDs are useful for the separation of tubulin and can be used 10 times without significant decrease in their capacities.

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Cell Uptake of Magnetic Nanoparticles Conjugated $^{131}I$-Uracil Glucuronide

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Abstract-The surface-modified magnetic nanoparticles were immobilized with uracil glucuronide derivatives and then labeled with I-131 in this study. The morphology, structure and composition of the magnetic particles were examined by SEM and XRD. SEM analyses showed that the particles size were 40-60 nm. Labeling yields were found 91.2% for uracil glucuronid immobilized magnetic particles. In the cell culture studies, incorporations of $^{131}I$-Uracil Glucuronide conjugated magnetic nanoparticles were examined on adenocarcinoma cells.

Magnetic nanoparticles (MNPs) have been explored for various biomedical applications that include their use in cell labeling/cell separation [1], magnetofection to facilitate gene delivery [2], as contrast agents for magnetic resonance imaging (MRI) [3], to induce local hyperthermia in response to an external alternating magnetic field to selectively destroy cancer cells [4], and as a magnetically targeted carrier system in drug delivery applications [5]. Although several magnetic materials are under investigation, iron oxide is the most commonly used magnetic material because of its biodegradable nature, biocompatibility, and its superparamagnetic effects on MRI contrast. Several attempts have been made to use MNPs for drug delivery while retaining their inherent magnetic and imaging properties. Such magnetic drug delivery has the key advantage that it allows very concentrated drug doses to be delivered to a target tissue while minimizing the exposure of healthy tissues to the side effects from highly toxic drugs.

In this study, enzyme UDP-glucuronyl transpherase was prepared from Hutu-80 cells and used for enzymatic synthesis of uracil glucuronide. Two different glucuronide derivatives were obtained and the total reaction yield was obtained to be 92.95±2.4 (n=4). Glucuronid ligands which were defined as uracil-N-glucuronide (UNG) and uracil-O-glucuronide (UOG) were analyzed by high-performance liquid chromatography-mass spectrometry (HPLC-MS).

Figure 1. SEM of magnetite silica nanoparticles

Magnetic nanoparticles coated with silica and silane were synthesized and characterized by electron microscopic methods (SEM) and crystal structure analysis (XRD). The particles size were 40-60 nm. After surface modification with an amino silane coupling agent, N-[3-(trimethoxysilyl) propyl]-ethylenediamine (SG-Si900), uracil (U), uracil-O-glucuronide (UOG) and uracil-N-glucuronide (UNG) were covalently linked to the amine group using glutaraldehyde as cross-linker. The magnetic nanoparticles were then radiolabeled with $^{131}I$. Labeling yield was 91.2% for uracil glucuronide conjugated silanated magnetic particles.

Figure 2. XRD pattern of magnetite core

Hutu, Caco and Detroit cell lines were used in the cell culture studies. The experiments were performed six times for each experimental condition.

Figure 3. Incorporations of $^{131}I$ labeled samples on cell lines

I-131 labeled UOG had the highest incorporation ratio for all cells compared UNG and other labeled components. There was a statistically significant between adenocarcinoma cells for incorporation ratio of UOG. Applying magnetic field incorporation rates are increasing for all components and differences are decreasing between them. Results show that I-131 labeled glucuroni de conjugated nanoparticles promise in imaging and therapy and further research should be done in preclinical stages.

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**Preparation, Characterization, and In-Vitro Biocompatibility Study of Bacterial Poly(hydroxybutyrate-co-hdroxyvalerate) (PHBV) Nanofibers Scaffolds**


**Abstract**

PHBV, a copolymer of microbial polyester, is one of the most promising materials for tissue engineering. In this study, we produced Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) using Alcaligenes eutrophus DSM 545 strain. Nanofibrous scaffolds were fabricated through electrospinning and characterized of nanofibrous scaffold by using scanning electron microscopy (SEM).

**Polyhydroxyalkanoates (PHAs)** are a family of polyesters synthesized by microorganisms through the fermentation of carbon substrates. PHAs are emerging as a class of biodegradable polymers for applications in tissue engineering due to their reasonable biocompatibility, adjustable mechanical properties, and controllable biodegradability [1]. PHBV can be used for biomedical applications because of its biocompatibility and non-toxicity to living tissues [2-4]. Recently, a variety of techniques have been developed for nano- or submicron fiber fabrication, including phase separation [5, 6], electrospinning [7], and self-assembly [8]. Among them, electrospinning provides a straightforward way to fabricate fibrous scaffolds with nano-sized diameter fibers, which mimic the structure of natural extracellular matrix (ECM) [9].

In the present study PHBV was produced by a fed-batch culture of *Alcaligenes eutrophus* DSM 545 strain using sucrose syrup as carbon source. Cultivation of bacteria consisted of two stages: in the first stage, bacteria were grown in nitrogen-rich medium which contained 10 g/l glucose, 2 g/l yeast extract, 2 g/l pepton, 1 g/l K2HPO4, 1 g/l KH2PO4, 1 g/l (NH4)2SO4, 0.05 g/l MgSO4, 7H2O.

The bacteria were harvested by centrifugation and washed in order to remove residual nitrogen. In the second stage, cells were cultivated in a synthetic medium containing: 20 g sucrose, 1.5 g/l KH2PO4, 3 g/l Na2HPO4, 0.2 g/l MgSO4, 7H2O, 0.01 g/l CaCl2.2H2O, 30 g/l sodium propionate and trace element solution: 2 g/l FeSO4. 7H2O, 0.3 g/l H3PO4, 0.2 g/l CoCl2.6H2O, 0.03 g/l ZnSO4.7H2O, 0.03 g/l MnCl2.4H2O, 0.03 g/l (NH4)6 Mo7O24.4H2O, 0.03 g/l NiSO4.7H2O, 0.01 g/l CuSO4.5H2O. The organism was cultivated under rotational agitation at 150 rpm and 30 °C for 48 h in a 500 ml Erlenmeyer flask containing 200 mL of media. After fermentation, bacterial PHBV purified using hypochlorite solution. We characterized purified PHBV by Fourier Transform Infrared (FTIR), these results indicate that high purity bacterial PHBV polymer was obtained. (Figure 1) Biodegradable and biocompatible poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) copolymer of microbial polyester, was fabricated as a nanofibrous mat by electrospinning from chloroform (CHCl3)/ethanol polymer solutions.

**Figure 1.** FTIR spectrum of commercial and bacterial Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV)

The electrospinning conditions such as the polymer concentration, solvent composition, and applied voltage were optimized in order to get smooth and nano-sized fibers. Systems parameters obtained %65 polymer concentration, 17 kV, 15 cm, 20 ml/h as concentration, voltage, flow rate, the distance between the tip of the syringe and collector. Three-dimensional interconnected fibrous network were observed in these matrices with average fiber diameters of 700-800 nm. To assay the biocompatibility of electrospun fibers, cellular behavior on the nanofibrous scaffolds, protein absorption, platelet adhesion, were also investigated. The results show that mouse fibroblast cell line (L929) proliferated well on or within the nanofiber. The results indicate that a bacterial PHBV nanofiber matrix may be a better candidate for tissue engineering in biomedical applications such as scaffolds.

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Micro-Nano Structuring to Improve Surface Wettability for Cell Culturing
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Abstract- Hydrophilicity of bio-medical materials is most important factor to growing of different kind of cells. Due to this feature many of the researchers are developing material surfaces for body implants and cell culturing by changing the surface morphology. Even if there is more way to modification, lasers are still mostly chosen sources because of their unique specifications for these applications. In this work we create micro/nano structures on to the our bio-compatible Al/Al2O3 core/shell nanowires to increasing the hydrophilicity.

Lasers are well known sources for surface treatment because of their pulsed option. surface treatment of materials got interest in recent years especially in bio-medical. For the growing of cells, they need convenient surfaces. Many of the methods can be found in literature for surface treatment. Acid, Ion etching and lithography are another ways to modify surfaces [1, 2, 3].

Laser surface modification is fast and repeatable technique for every kind of application. Depend on the optics in used and different mask shapes; it is possible to create different structures on the surfaces as line, dot or others. Pulse duration of the laser is another affect for the structuring as well. With short pulses it is possible to create precisely controlled structures [4].

In this work a nano-second Q-switched Nd:YAG laser had been used to modify the 1D Al/Al2O3 core/shell nanowires coated on surfaces which are produced by CVD technique. These nanowires deposited on to the glass samples with 12mm diameter and 0.7mm thickness. They cleaned by acetone and then placed on to a graphite holder to get the optimum heating conductivity. At 600 º C under vacuum we got the structures [5]. (Figure 1)

Figure 1. Image of High Density Al/Al2O3 core/shell nanowires. They show chaotic distribution. At the corner 12mm glass samples is shown.

This is known that hydrophilicity of bio-medical material surfaces is quite important for Neuron and fibroblast cells growth [5,6]. Therefore we structured our Al/Al2O3 nanowires coated surfaces with second harmonic of nano-second Nd:YAG laser. To perform the periodic structures we used a micro lens array. This micro lens has spherical shape and pitch of this array is 150um and the focal length is 6.7mm. The opportunity of this lens is to create more than four thousand structures with one laser shot. During the experiment depending on our experience we applied 3 shots with optimum power to survive the nano structures. With this technique it is easy to control the surface structuring by shifting the translation stage and the focal point of the micro lens array. In that current work we perform 3 different matrixes with 150um*150um, 75um*75um and 75um*150um pitch. And each structure has diameter around 30um. Figure 2 shows the wetting angle of samples.

Figure 2. Wetting angles of laser treated nanowires coating with different periods. At the corner SEM image of periodic structures (75um*75um)

In the first step of that experiment our structures show that decreasing the pitch of the structures in x and y axis causes increasing of hydrophilicity. And the most important advantage of this work, during the treatment, surface chemistry doesn’t change. This feature gives us opportunity to control the cell growing.

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[3] Seiji Ban, Yukari Iwaya, Hiroshi Kono, Hideo Sato, dental materials 2 2 ( 2 0 0 6 ) 1115–1120
Abstract- A compact, inexpensive, and low-powered detection system based on a proven optical biosensing modality, the Spectral Reflectance Imaging Biosensor (SRIB), is designed for detection of several infectious pathogens simultaneously in order to meet the challenging needs of global health diagnostics. Work showing virus detection in serum and clinically sensitive levels of detection on the laboratory SRIB is shown along with the design and preliminary experiments of the compact, portable SRIB.

Infectious diseases such as malaria and HIV constitute major global health problems causing a combined 4 million deaths per year. Malaria, the leading cause of mortality in children under the age of 5 in Africa, comprises 10% of the country’s disease burden of health services and costs Africa about USS 12 billion in lost production per year.[1] Currently, rapid diagnostic tests (RDTs) which differentiate between different infectious diseases do not exist. The development of a portable detection system based on a proven optical biosensing modality, the SRIB, is designed to test for several infectious pathogens simultaneously to meet the challenging needs of global health diagnostics.

The SRIB is an optical biosensor reviewed by Nature Biotech as one of the most promising new label-free (no fluorescent/chemical labeling) biosensing platforms.[2][3] In our device, an immunoassay microarray with specific biomarker probes for viruses, toxins, pathogenic DNA, and antigen proteins is spotted on a bi-layered Si/SiO2 substrate. Each sample costs less than a dollar to manufacture and can be customized to screen for a particular set of pathogens. LEDs, at specified wavelengths, are used to illuminate the surface causing reflection from both interfaces of the bi-layered substrate resulting in an interference image. Based on the wavelength dependent signature captured for each pixel, the surface accumulation due to any specific biomolecular binding interactions can be determined. The SRIB detection principle has published data showing that even small amounts of target biomolecular binding events can be detected and quantified with high sensitivity and specificity.[3]

In summary, our laboratory systems have shown capable of virus detection in serum as well as clinically sensitive levels of hepatitis detection. With the flexibility offered by our surface functionalitation, the compact, low-cost SRIB has the capability to detect a wide array of pathogens concurrently using a quantitative label-free method in order to meet the the needs of the global health community. This work is supported by the Smart Lighting Engineering Research Center and the NSF.

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Figure 1. LED SRIB detection system showing illumination, reflection, and recording by camera. The substrate is highlighted showing the varying reflection interferences, which manifest as intensity differences as a result of biological material accumulation.

With recent success of clinically relevant Hepatitis detection as well as virus detection in serum, the SRIB and our LED-based prototypes allows us to venture into the realm of clinical infectious disease diagnostics by pursuing the use of new probes and searching for targets within bodily fluids. Our surface functionalization gives us the wide flexibility to immobilize protein antigens, antibodies, complementary DNA strands, and cellular receptors for viruses, dependent only on the disease we are interested in screening. This scenario is essential for multiplex, high throughput diagnosis of a variety of infectious diseases in a single test.

Our poster will present the following:
- Demonstration of clinically sensitive hepatitis detection as well as virus experiments in serum on the laboratory SRIB
- Design of a low-cost, low-power, and compact SRIB platform for point-of-care use
- Preliminary experiments showing binding detection using the compact SRIB

This compact, low cost design will provide the basis for future work in replicating the clinical sensitivity seen on the laboratory device. Antigens, secretory antibodies (IgA), and primary adaptive antibodies (IgM) that can easily be derived from saliva or blood samples will be tested for infection with the compact device. Furthermore, we wish to perform assays combining the pathogens listed before with many more, including tuberculosis, sexually transmitted infections, and poliovirus to develop highly multiplexed assays.
Controlled Delivery of Antisense Oligonucleotides by Self-assembled Peptide Amphiphile Nanofibers

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Abstract- Antisense oligodeoxynucleotides are complementary to target mRNA sequences down-regulate target mRNA’s expression specifically. Herein, peptide amphiphile molecules are used to form nanofibers upon introduction of oligonucleotides through electrostatic interactions. Hydrogels that are composed of three-dimensional networks of peptide nanofibers and oligonucleotides were formed for slow release of oligonucleotides. The potential impact of the oligonucleotide release against cancer cells is being studied.

Antisense oligodeoxynucleotides are chemically modified single-stranded DNA fragments of twenty or fewer bases in length. They can be used in antisense therapy that has important advantages such as gene-target specificity and reduced side-effects [1]. Controlled release of oligonucleotides is desired in order to increase stability and efficacy of the oligonucleotides. To achieve a sustained release and to increase pharmacological activity of oligonucleotides, non-viral biodegradable delivery systems are preferred [2].

Amphiphilic peptides which contain a hydrophobic tail and hydrophilic, functional peptide head group can form nanostructures through non-covalent interactions. Depending on pH and electrolyte concentration, peptide amphiphiles self-assemble into nanofibers which form a 3-D network that result in hydrogel formation [3, 4]. Electrostatic interactions between negatively charged DNA and cationic amphiphilic peptides resulted in gel formation [5].

Peptides are synthesized by solid phase peptide synthesis (SPPS) [6]. The hydrogel formed by peptide amphiphile and oligonucleotides were characterized by LC-MS, circular dichroism, SEM (Figure 1) and rheology. These measurements demonstrated gel formation with nanofibrous network.

![Figure 1](image1.jpg)

Figure 1. SEM image of 3-D network of the hydrogel formed by peptide amphiphile and oligonucleotides.

Oligonucleotide release assay was carried out over a period of 6 days. Sustained release of DNA from peptide amphiphile network was observed. The majority of the oligonucleotides (80–90%) was released by 6 days (Figure 2).

![Figure 2](image2.jpg)

Figure 2. Release profile of oligonucleotide from hydrogel formed by peptide amphiphile and oligonucleotides.

Currently, we are working on effect of these oligonucleotides on cancer cells along with peptide amphiphiles as a drug delivery system.

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Nanotechnology in Biomedical Applications

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Abstract— Nanotechnology is the ability to measure, design, and manipulate at the atomic, molecular and supramolecular levels on a scale of about 1 to 100 nm in an effort to understand, create, and use material structures, devices, and systems with fundamentally new properties and functions attributable to their small structures[1]. In this respect we can built the objects to atom by atom specifications by the ability of nanotechnology. Therefore nanotechnology will make possible very big range of new products. On the other hand those products will be also inexpensive and clear products. As the industrial perspective it can be concluded that nanotechnology affects almost all of the industrial sectors (i.e., energy, electronic, communication, textile etc) due to its mentioned advantages. One of the most important application fields of nanotechnology is about the medicine and health sciences as biomedical applications. Biomedical applications of nanotechnology consists of the nanoscale principles and techniques to understanding and transforming the biomaterials and biosystems for medical purposes such as drug and gene delivery-controlled release systems, molecular imaging and diagnostics, cardiac therapy, dental care, orthopedics, tissue engineering applications and targeted cancer and/or gene therapies[2].

Biomedical applications of nanotechnology or using the nanotechnological approaches to maintain and improve human health at the molecular scale can be called as “nanomedicine”. The main goal of nanomedicine is to diagnose as accurately and early as fast as possible and to treat as effectively as possible without side effects, and to evaluate the efficacy of treatment noninvasively by using the nanotechnological approaches.

Mainly nanotechnological approaches in biomedical sciences can be categorized as diagnosis and treatment or therapy. Different types of nanomaterials and/or nanoplatforms can be used in both of these approaches such as nanoparticles, nanofibres, nanopores, nanowires, magnetic nanoparticles, metallic nanoparticles and quantum dots as QDots, dendrimers, nanotubes (i.e., carbon nanotubes, CNTs and peptide-protein nanotubes) etc.

System design and production by using mentioned nanoplatforms for diagnosis and therapy in biomedical applications can be categorized into three main sections such as nanocolloidal systems, surface modifications of biomaterials at molecular level and nanodevices.

One of the primary objectives of this investigation was to explore applications of nanomaterials to develop intelligent systems to treat complex diseases and enhance health-related quality of life (HRQL) index[2].

On the other hand biomedical applications of nanotechnology can be summarized as time-controlled and targeted release of drug regimen/gene delivery; diagnostic imaging; molecular diagnostics; bio-molecular detection; cardiac therapy; tissue engineering and nerve regeneration; dental care; orthopedics; ophthalmology; artificial tissues/organs; and antibacterial/ antimicrobial surfaces of biomaterials.

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Complexation of Salbutamol (Active Ingredient of Asthma Drug) With Iron
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Abstract-Dopamine has a significant role in the proper function of central nervous system which is responsible of body movements. Dopamine is a strong chelator of Fe, which is the most essential element in the all living systems. The stability of complex is evaluated by the formation constant values using a computational graphical program. Present study will explore interesting aspects about the interaction of dopamine and its analogous molecules with iron.

Asthma is a wide speared disease all over the world. Extensive work is carried for drug development to treat this disease. Ventolin is used for this purpose. It is an effective drug. Its active ingredient is Salbutamol Sulphate, which is a bronchodilator. Salbutamol Sulphate, (C13H21NO3)2.H2SO4 is [1,1 – (Dimethylthethyl) amino]methyl]-4-hydroxy-1,3-benzenedimethanol. Due to its oxygen & nitrogen donor sites, it has been assumed that it may interact with metals present in the biological system, and therefore disturb the metals equilibrium and imbalance the metabolism.

Since iron is the most important metal, the complexation of Salbutamol ion with Ferrous & Ferric ions is studied. The Stoichiometry of complex, effect of pH and formation constants of the complex is investigated. Salbutamol formed a purple colored complex with iron having maximum absorbance at 550nm. The results showed a 1:3 complex formation at pH 3.5 in format buffer at 30 °C.

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Synthesis of Ag Nanoparticles and Investigations of Their Antibacterial Activity in the Polymer Composite Coatings

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Abstract - As nanotechnology can overcome the limitations of size and nanomaterials can be improved for better efficiency to achieve different applications, silver (Ag) has been synthesized in nanosize in this study by a reduction method. By adding them to a polymer matrix (polyurethane dye) with different loading levels and coating glass substrates with those polymer composites, different types of coated samples are obtained. Then obtained samples were characterized by XRD, FTIR, SEM-EDS, AFM and Scrat tests. The antibacterial activity against Escherichia coli (E. coli) and Staphylococcus aureus (S. Aureus) has been studied applying the so-called in vitro test. The bactericidal activity for the above bacteria cells was estimated by zone of inhibition on the nutrient agar plates. It was concluded that Ag nano particles shows an antibacterial activity as a coating material.

Antibacterial and antimicrobial materials/systems are becoming increasingly important not only in the hospital and healthcare environments, but also for laboratory, home, marine and some industrial applications. Materials and systems are being developed to prevent the build up, spread and transfer of harmful bacteria and viruses, as well as actively disabling them [1].

Ag has been used as an anti-bacterial agent by civilizations throughout the world for thousands of years. It was employed as a germicide and antibiotic long before the development of modern pharmaceuticals [2]. Unlike antibiotics, which are useful only to bacteria, Ag is effective to other microorganisms such as anaerobic bacteria, viruses, yeasts, and fungus too. Ag works for destroying the enzymes of those microorganisms for disabling them. So, those microorganisms are not able to improve any resistance to silver, because it attacks their food source, but not them directly [3]. The exact mechanism of action of Ag on the microbes is still not known but the possible mechanism of action of metallic, ionic and nanoparticle silvers have been suggested according to the morphological and structural changes found in the bacterial cells [4]. Nevertheless in general, the antimicrobial activity of the silver can be explained by the following reaction (Figure 1) [5].

In this study, the antimictobial effects of the Ag has been investigated. Ag has been synthesized in nanosize by a reduction method (approx. 40 nm in size). Polyurethane paint composites were prepared by adding Ag nanoparticles at different ratio into the polyurethane matrix. By concentrating the composite matrix with Ag nanoparticles, each coated sample of different concentration was used to see the concentration dependence of Ag nanoparticles' antibacterial effects. Ag-loaded coating specimens in size of 2.4×2.4 mm were prepared as mentioned above to investigate its antibacterial activity. Osteotoxicity of the Ag-loaded polymer coatings was evaluated by in vitro cell culturing test. Two different bacteria, Gram-positive S. aureus (ATCC 6538P) and Gram-negative E. coli (ATCC 8739), were used for testing the antibacterial activity of coating films. The antibacterial activity of Ag-loaded polymer coatings was examined using the zone of inhibition (ZOI) [15]. Totaly 19 samples were prepared in agar plaets. One of them is shown in Figure 2. This was % 1 Ag nanoparticles having coating. Zone of inhibition can be clearly seen that this material is a very good antibacterial material. In summary we synthesize Ag nanoparticles and they exhibited very good antibacterial property as a coating material in a dye material.

Figure 1. Antimicrobial activity of Ag [5]

In summary we synthesize Ag nanoparticles and they exhibited very good antibacterial property as a coating material in a dye material.

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Humidity Sensing Properties of Chitosan by using Quartz Crystal Microbalance

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Abstract — The humidity adsorption kinetics of the chitosan films was investigated by quartz crystal microbalance (QCM) technique. The Langmuir model was used to determine the adsorption rates and Gibbs free energy for various relative humidities between 11% and 97%. Our reproducible experimental results show that chitosan films have a great potential for humidity sensing applications at room temperature operations.

Humidity measurements play an important role in concerns environmental fields, such as medical or domestic applications for human comfort, industrial uses, agriculture, automobiles, textiles, etc. To sense humidity, a sensor using adsorption and absorption of water by quartz has already been studied [1,3]; the apparent mass was modified and so was the resonant frequency. To increase the sensitivity of such device, a hygroscopic material has been laid on the quartz and the mass was sharply modified by humidity of ambient air. In this direction we explored the chitosan is sensing relative humidity. Chitosan, poly [β-(1-4)-linked-2-amino-2-deoxy-D-glucose], is the N-deacetylated product of chitin, which is a major component of arthropod and crustacean shells such as lobsters, crabs, shrimps, and cuttlefishes[2].

In the structure of chitosan (Figure 1), there are functional groups for example; amino group, at two different positions hydroxyl groups which are, as known, good hydrogen bond donor and acceptor groups. Figure 1 represent chemical formula of chitosan.

Figure 1: Chemical formula of chitosan.

The humidity response is depending on molecular structure of chitosan. Under humid condition, between water and chitosan molecules, the hydrogen bond might be formed due to having such groups as given in figure 2. This absorption property of chitosan molecule makes it applicable as a humidity sensor.

In this work, we have investigated the humidity sensing capability of Chitosan molecules using quartz crystal microbalance (QCM) method. In order to show humidity sensing properties, chitosan was prepared in acetic acid solution and was applied on the surface of quartz crystal by drop-coating technique. The Resistance, QCM, and AFM techniques were used to for the characterization.

Figure 2: Possible sites on a chitosan molecule to form H bonds.

The relationship between the surface adsorption kinetics and frequency shift (Δf) of QCM can be expressed as following:

\[
\frac{d\Delta f}{dt} = (\Delta f_{\text{max}} - \Delta f)k_aC - k_d\Delta f
\]

where \( \Delta f \) and \( \Delta f_{\text{max}} \) are the QCM resonance frequency shifts, \( k_a \) and \( k_d \) are the adsorption and desorption rate constants, \( C \) is the concentration of water molecules in air, \( t \) is the time [3].

Figure 3: QCM frequency shifts for adsorption and desorption cycles between 11% and 97% RH (a) and various RH values as a function of time (b), RH dependence of the frequency shifts (c) and the fit to the dynamic Langmuir model (d).

We have observed the adsorption and desorption processes to be reversible with the relaxation time 0.718546 s. To explained the response of the humidity sensor, it was used dynamic Langmuir model. The average values of adsorption and desorption rates between 11% RH (concentration of 1.060E-04 M) and 97% RH (concentration of 9.310E-04 M) were calculated as 69.4 M⁻¹ s⁻¹ and 5.328E-03 s⁻¹ respectively. The equilibrium constant and average Gibbs free energy of three humidity adsorption and desorption cycles were obtained as 1.303E+04 and -9.475 kJ/mol, respectively.

During adsorption process the frequency shift decreases with increasing RH and goes to near saturation values. This reproducible experimental results show that chitosan films have a great potential for humidity sensing applications for room temperature operations.

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A Self-reporting Biosensing Platform based on Novel Synthetic Proteins

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Abstract—Novel synthetic recombinant sensor proteins have been created to detect analytes in solution, in a rapid single-step noncompetitive homogenous assay process, based on modulating the Förster resonance energy transfer (FRET) property of the sensor proteins upon binding to their targets. The diversity of sensor-target interactions that we have demonstrated in this study points to a potentially universal applicability of the biosensing concept.

In this study, we report a new sensor protein design that allows efficient FRET-based noncompetitive homogeneous assays of potentially a broad range of target molecules. Noncompetitive assays are generally more sensitive than competitive assays [1]. Furthermore, non-competitive assays do not require labeled target analogues that add complexity and cost and may not be readily available. The sensor proteins reported in this study comprise a protein scaffold inserted by genetic fusion between two fluorescent protein variants that form a FRET pair, such that the FRET pair is in close proximity to enable FRET. A specific target-capturing element is incorporated into the sensor scaffold at strategic locations. We postulated that binding of the target to the target-capturing element creates a steric effect to alter the distance and/or orientation, or potentially the non-bulk refractive index [2] between the FRET pair, leading to changes in FRET property of the sensor.

In the sensor reported here, a mutated maltose binding protein (MBP) is used as the protein scaffold which is sandwiched between a cyan fluorescent protein variant and a yellow fluorescent protein variant. In the current work, selected amino acid residues of MBP were mutated to cysteine to allow site specific chemical conjugation with thiol-reactive target-capturing elements.

Initially enhanced cyan fluorescent protein (ECFP) and enhanced yellow fluorescent protein (EYFP) were used as the FRET pair, and position MBP-Q49 was selected for cysteine-substitution, since it is located between the N- and C- terminus of the MBP protein and exposed on the protein surface, which would allow efficient conjugation. As a proof-of-concept for the new sensor technology, we initially selected biotin as the target-capturing element, by conjugating maleimide PEO2-biotin to the sensor protein scaffold, for detecting a goat anti-biotin antibody Fab fragment. As a result, the FRET ratio of the biotinylated sensor protein decreased in response to increased concentrations of anti-biotin Fab antibody before reaching saturation at high Fab concentrations.

The sensor was further improved by optimizing the fluorescent labels. The ECFP and EYFP in the initial sensor were replaced by CyPet and YPet, an engineered CFP/YFP pair optimized for FRET assays [2]. As a result, the maximum change in the normalized and un-normalized FRET ratio was increased by 2-fold and 5-fold, respectively, hence generating a much more sensitive biosensor. To study the effect of the conjugation site of the target-capturing element, instead of MBP-Q49, we created three other sensor proteins containing MBP-E45C, A52C, and S73C mutation, respectively, while using CyPet/YPet as the FRET pair. These sensor proteins were conjugated with maleimide PEO2-biotin and analyzed for FRET in response to anti-biotin Fab. The best performance was seen with the two sensors bearing respectively the MBP-S73C and the MBP-A52C mutation, giving a maximum reduction in the normalized FRET ratio by 32% for the former (from a FRET ratio of 5.3 at zero Fab conc.) and 30% for the latter (from a FRET ratio of 5.2 at zero Fab conc.).

Upon the initial verification of the sensor concept using biotin as a model target-capturing element, we then demonstrated the proposed sensor protein technology platform for detecting an oligo-histidine (His) peptide-tagged recombinant protein and an anti-FLAG peptide antibody. Further work is underway to examine the molecular mechanism underlying the signal change, and to further validate the concept with different targets and target-capturing moieties, including peptides genetically fused to the sensor scaffold. Some part of this work was previously published by us [3].

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PCL/Collagen Nanofibers FOR Tissue Regeneration

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Abstract- In this study, polycaprolactone (PCL)/collagen (COL) nanofibrous matrices were fabricated by electrospinning process in two different nanofiber construction i.e. random and aligned. The electrospinning conditions and matrice properties were determined for their possible use in nerve and skin tissue engineering applications.

Tissue engineering aims to repair or regenerate the functions of damaged tissue by using cells and synthetic functional components called scaffolds. Scaffolds made of nanofibers play a key role in the success of tissue engineering by providing a structural support for the cells to accommodate and guiding their growth in the three-dimensional space into a specific tissue. Although there are variety of nanofiber fabrication methods such as phase separation, template synthesis and etc. [1], electrospinning have come forefront with its versatility, flexibility and ease of fiber production. Basically, a high voltage electric field is applied to produce electrically charged jets from polymer solution or melts, which on drying by means of evaporation of the solvent produce nanofibers. The highly charged fibers are field directed towards the oppositely charged collector, which can be a flat surface or a rotating drum, to collect the fibers.

The goal of this study was to produce random and aligned nanofibrous scaffolds for tissue engineering applications. For this purpose, we aimed to fabricate polycaprolactone (PCL) and PCL-blended collagen (PCL/COL) nanofibrous scaffolds by electrospinning process. PCL and PCL/COL were dissolved in dichloromethane/dimethylformamide (DCM/DMF; 50:50 v/v) and hexafluoro-iso-propanol (HFIP), respectively [2, 3]. Then, high voltage was applied to fabricate nanofibrous scaffolds. Optimization of electrospinning was done by changing the applied voltage and solution feed rate for both random and aligned scaffolds. Nanofiber alignment was investigated by changing the rotation rates from 2000 to 2500 rpm.

It was reported that well alignment can be achieved at lower solution feed rates [4], therefore aligned PCL nanofibers were obtained at 3 mL/h by keeping other parameters constant. Production parameters of PCL/COL nanofibers were identical with random nanofibers. Progressive increase in fiber orientation was observed as the rotation rate increased from 2000 to 2250 rpm, however, further increasing did not significant effect on orientation anymore (data not shown).

Chemical and thermal characterization of nanofibrous scaffolds were done by ATR-IR and TGA. The results obtained from ATR-IR confirmed the chemical structures of both PCL and PCL/COL scaffolds. Although both random and aligned PCL nanofibrous scaffolds were hydrophobic (contact angle: 131±4°), the presence of collagen significantly improved the water affinity (contact angle: 0°) and water uptake capacity.

According to these results, random and aligned PCL/COL nanofibrous scaffolds may have the potential to be applied in wound dressing and nerve tissue engineering applications.

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Photophysical and Computational Investigation of Intermolecular Hydroxypyrene Complexes with Phenothiazine and Promazine

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Abstract- In this study, phenothiazine-hydroxypyrene and promazine-hydroxypyrene (methylcyclohexane, tetrahydrofuran, dichloromethane and acetonitrile) intermolecular charge transfer complexes have been studied by spectroscopically and computationally. Experimental excitation energies obtained from UV-Vis and fluorescence spectra of these complexes were characterized by TD-DFT calculations, which revealed that these transitions are \( S_0 \rightarrow S_1 \) charge transfer transitions occurring from donors (phenothiazine and promazine) to acceptor (hydroxypyrene).

Most polyaromatic hydrocarbon (PAH) derivatives are considered as risk chemicals [1]. These chemicals have been shown to have major mutagenic and carcinogenic activity [2]. Because of the carcinogenic activity of these compounds, they also affect the human health. And it is very important to know their interactions with biologically important molecules. Hydroxypyrene (pyOH) is one of the polyaromatic hydrocarbon derivatives which is harmful for health [1]. The carcinogenic activities of hydroxypyrene are based on its role as acceptor of the \( \pi \) - electronic excitation energy.

Phenothiazine (pheno) and its derivative promazine (prom) are pharmaceutically important class of heterocycles, known as pharmacophores in sedatives, tranquilizers, anti-epileptics, anti-tuberculosis antipyretics, anti-tumour agents [3]. On the other hand, phenothiazine and promazine contain \( \pi \) - systems and they can form donor-acceptor interactions with hydroxypyrene in the excited state. In this study, possible exciplex formations between hydroxypyrene (as an acceptor) and phenothiazine and promazine (as donors) have been investigated in terms of stable geometries, dipole moments, bimolecular fluorescence quenching constants and thermodynamic stabilities.

In experimental part, UV-Vis and fluorescence spectra of the complexes have been taken in several solvents having different polarity. In particular, methylcyclohexane, tetrahydrofuran, dichloromethane and acetonitrile (in the order of increasing polarity) were used as solvents.

According to experimental results, it is observed that the fluorescence intensity of acceptor (pyOH) decreases with the increasing concentration of donor (pheno). This quenching can be explained by the exciplex formation between the pyOH and pheno.

In computational part, the ground state geometries obtained from DFT-PBE1PBE functionals[4]. TD-DFT calculations were also performed at the ground state DFT geometries for determining excitation energies.

### Table 1. \( S_0 \rightarrow S_1 \) Excitation Energies for the Systems Studied

<table>
<thead>
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<th>( E_{\text{exc}}^{\text{exp}}(eV) )</th>
<th>( E_{\text{exc}}^{\text{theo}}(eV) )</th>
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<tbody>
<tr>
<td>pheno-pyOH</td>
<td>3.2219</td>
<td>3.4299</td>
</tr>
<tr>
<td>prom-pyOH</td>
<td>3.2052</td>
<td>3.4663</td>
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The computational studies indicated that the pheno-pyOH and prom-pyOH, complexes have thermodynamic stabilities at the ground state in gas phase. Moreover, the TD-DFT calculations revealed that the \( S_0 \rightarrow S_1 \) transitions for all complexes are charge transfer transitions from donor to acceptor molecules. As seen from the Table1, excitation energy values (\( E_{\text{exc}} \)) obtained from the fluorescence spectroscopy are well agree with those calculated by TD-DFT.

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STM for Imaging tRNA

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Abstract- tRNA molecules compose a small percentage of cellular RNA. Their advanced three dimensional structures make them easily recognized in a complex mixture of RNA molecules. We were able to image single tRNA molecules by STM with serial dilution and analysis of total cellular RNA obtained from leukemia cells. This may have facilitate the analysis of conformation of tRNA and its interactions with regulatory molecules.

STM is a powerful imaging tool for the examination of biomolecules as it has the capacity to resolve molecular structures in atomic detail. The possibility of operating STM under ambient conditions allows the preservation of the three dimensional shape [1]. tRNA plays an important role in decoding the genetic information. Therefore, image analysis of these molecules may be useful in understanding its structural and functional properties as well as its interactions with other regulatory molecules [2].

We were able to obtain the STM image of tRNA. The image was in accordance with the structural information about tRNA molecule such as the clover leaf conformation and having three distinct loops.

Cells were separated by density gradient. Cytosolic RNA was isolated by detergent treatment followed by organic separation (3) Samples were diluted in ultrapure water at nanomolar concentrations and applied to gold coated mica. STM was operated at atmospheric pressure with bias voltage of 300-400 mV and the tunneling current was < 10 pA.

The image obtained by using STM demonstrates the characteristic structural features of tRNA. The average thickness of double stranded parts of the molecule was 26 0Å which is in accordance with x-ray findings.

It is concluded that the three dimensional structure of tRNA was conserved during the imaging process. Furthermore, the STM images obtained by using different samples have all demonstrated the same characteristic features. Therefore, STM may be a useful method for the analysis of tRNA conformation in media having having different ionic compositions and it may also facilitate the visual detection of tRNA-biomolecule interactions.

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Figure 1. STM image of tRNA molecule matched with the theoretical structure and dimensions.
Effect of Hydrodynamic Bubbly Cavitation on Lysozyme Structure
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Abstract- The effect of hydrodynamic cavitation on lysozyme structure was investigated. Lysozyme solutions were exposed to bubbles emerging from microtubes of inner diameter ~147 µm under bubble cavitating conditions. After the exposure for different times, biophysical methods were used to reveal the effect of hydrodynamic cavitation on lysozyme solutions. Circular dichroism spectropolarimetry and dynamic light scattering measurements showed that secondary structure content and hydrodynamic radius of lysozyme was changed upon cavitation. This study proves that hydrodynamic bubble cavitation could result in structural changes in lysozyme structures after the exposure for sufficient time.

Hydrodynamic cavitation describes a promising alternative method to ultrasonic cavitation for the treatment of certain pathological conditions. Unlike ultrasonic cavitation, which is characterized by a relatively large cavitation volume and fairly uniform spatial power distribution, hydrodynamic cavitation permits the more focused and higher-power cavitation of a specific target in a very localized region. As such, the merit of this technique is currently being investigated to potentially treat conditions such as kidney stones and prostate diseases. Indeed, the potentially destructive effects of hydrodynamic cavitation at the cellular level have been recently established [1] but no work exists to characterize the potential harm that might ensue at still smaller length-scales such as that of the protein. To date, a handful of work related to extended sonication times has established definite structural and chemical changes in proteins [2, 3]. In this seminal work, lysozyme was subjected to hydrodynamic cavitation under in vitro conditions. Various experimental parameters such as buffer composition, cavitation time, cavitation power and cavitation range were assessed to better appreciate the rules that might govern protein disruption inside living systems.

Hydrodynamic cavitation is initiated with local static pressure reduction below a critical value in microscale. For this, a sudden reduction in local pressure is introduced by a microprobe, which is a plain microchannel of inner diameter of 147 µm. The tests were conducted by applying different inlet pressure values at the inlet of a microprobe of length 1.5 cm (7-10 atm). The outlet pressure was set constant to 1 atm, and the outlet of the microprobe was exposed to the ambient. Increasing inlet pressure values were applied during the tests until bubbly cavitating flow pattern is observed. In our experiments, Lysozyme was subjected to hydrodynamic cavitation for 5 to 17 minutes at a pressure of ~170 psi. Lysozyme solutions were prepared in pH 8.0 potassium phosphate / KCl or pH 4.8 sodium-acetate / KCl buffer. Protein concentration was determined spectrophotometrically using lysozyme extinction coefficient 2.64 (cm¹ mg/ml¹). Our results show that 5 and 10 minutes of hydrodynamic cavitation do not alter lysozyme structure while 13 to 15 minutes long exposures to cavitation do result in a change in the hydrodynamic radius of lysozyme molecules accompanied with a change in secondary structure.

The homogeneity/monodispersity of lysozyme solutions are altered after 15 and 17 minutes of cavitation at pH 8.0 (Fig.1). Control and 5, 10 and 13 minutes cavitated samples consist of particles with diameter around 3.7-3.8 nm independent of concentration. On the other hand, the newly formed particles after 15 minutes have diameters of ~3.0-3.3 nm. Circular dichroism spectroscopy analyses show that the secondary structure of lysozyme is also slightly altered upon cavitation (Table 1). Protein molecular mass is not changed upon cavitation as shown by SDS-PAGE analysis.

Ultrasonic cavitation was shown to cause changes in lysozyme secondary structure after 10 minutes [3]. Our results show that hydrodynamic cavitation also induces protein structure change after a comparable time. Thus, these results prove that hydrodynamic cavitation could be a cost effective and energy efficient alternative to ultrasonic cavitation. In similar lines, the use of hydrodynamic cavitation in biomedical/biophysical applications would provide a strong alternative to ultrasonic cavitation due to the elimination of use of high frequency ultrasound.

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The Effect of Surface Nanotopography on Neural Stem Cell Alignment

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Abstract—Surface topography is one of the main parameters used to control the design of biomedical devices, implants, high throughput cell-arrays, and basic cell biology. Square millimeter sized arrays of nanopillars of up to 900 nm height, 200 nm diameter and a pillar-to-pillar distance of 1 μm to 10 μm were produced. The effect of these nanopillars on neural stem cells (NSCs) was studied in vitro and the cell attachment, alignment, and morphology were analyzed. NSCs were aligned along the ridge-like structures formed by nanopillars. Cells in their natural environment are surrounded by and are in interaction with nanostructures, when contacting with other cells or with the extracellular matrix (ECM) that is formed by biomolecules configured in a variety of geometrical arrangements and forms (nanopores, nanofibers, nanogrooves, nanoposts). Fabricated nanotopography can also influence cell morphology, guidance, adhesion, migration, proliferation, and cytoskeletal organization [1]. This ability to control orientation of cells can be very useful in biomaterial and tissue engineering applications in order to create more advanced products.

It has recently been shown that nanotopography can have strong effects on a range of cell types [2]. Since the nerve cells in native tissue are either unidirectionally aligned or form networks, patterning of scaffold surfaces has been used extensively to study and control the interactions of various neuronal cell types with surfaces [3].

The aim of the present study was to investigate the influence of well defined nanoscale structures, nanopillars, on the behavior of NSC in order to gain insight into the mechanism of nanotopographical guidance.

Nanopillars were produced on a silicon wafer by e-beam lithography, chromium deposition and lift-off followed by reactive ion etching. From this template a negative replica of polydimethylsiloxane (PDMS) was cast. The final replica was produced by solvent casting of a 2% solution of poly(L-D,L-lactic acid) (P(L-D,L-LA) on PDMS templates. Films were examined by SEM and AFM. Mouse NSCs were cultured in the growth medium of (DMEM)/F12 containing human transferrin, bovine insulin, chemically defined lipids, sodium selenite, streptomycin/penicillin and a supplement of epidermal growth factor. The cells were seeded on polymeric films with adsorbed fibronectin. The fixed cells were stained with FITC labelled Phalloidin and propidium iodide (PI) in order to investigate the orientation of the cells using fluorescence microscopy. They were examined with SEM to determine their location on the field patterned with nanopillars.

Figure 1: AFM micrograph of nanopillars on PLLA film

Figure 2: Fluorescence micrographs of FITC-Phalloidin (for cytoskeleton) and PI (for nuclei) stained NSCs on the nanopillar patterns (x20, scale bar: 100 μm). Nanopillars orientations are shown with arrows.

Figure 3: SEM micrographs of aligned NSCs on patterned regions on the P(L-D,L-LA) films.

AFM studies showed that nanopillar patterns of the template was successfully reproduced on the P(L-D,L-LA) films with PDMS replica serving as the intermediary template (Figure 1). In Figure 2 the nuclear and cytoskeletal orientation of NSCs showed that the cells were positioned and elongated on the nanopillar-based patterned areas controlled by the distance between the nanopillars; the cells followed the pillars separated by shorter distances. This tendency was also supported by SEM (Figure 3). Moreover, mouse NSCs were localized between the ridge-like structures (900 nm in height) formed by nanopillars. However, these cells were randomly oriented on the fields of symmetrically distributed nanopillars (data not shown).

In conclusion, the results on size and type of organization of nanopillars on cell alignment suggest that the cells are able to sense relative distances on such small topograph.

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Immobilization of immunoglobulin G in a highly oriented manner on a protein-A terminated multilayer system

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Abstract — In this contribution, we have developed a novel multilayer system -polymer additive and protein A terminated- on a silicon wafer surface for oriented immobilization of immunoglobulin G (IgG) molecule. Our results showed that specific binding proteins such as protein A must be used for construction highly reproducible and sensitive immunosensors.

Immobilization of proteins at surfaces is of great importance in number of applications, including surface-based biosensors [1-3] and biomedical devices such as implants [4,5]. For biosensing applications, the chemical properties of self-assembled monolayers (SAMs) must be tailored such that the surface presents functional groups which specifically bind to proteins of interest while rejecting all other proteins.

In this work, we have fabricated a multilayer system consisting of 3-glycidoxypropyldimethylmethoxy silane (GPDS), poly(dimethylsiloxane) bis 3-aminopropyl terminated (PDMS) and protein-A on a silicon wafer surface for oriented immobilization of immunoglobulin G (IgG) as presented in Fig 1.

Figure 1. Schematic representation of the designed multilayer system

The multilayer system with a different component in each layer was characterized by ellipsometry, contact-angle goniometer, grazing angle attenuated total reflectance-Fourier transform infrared spectroscopy (GATR-FTIR), x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and fluorescence microscopy. It was found that the PDMS film about 4.6 nm thick is produced on the GPDS-monolayer by the chemical reaction between the amine groups at end of PDMS chain and the epoxy groups of GPDS molecules. By introducing the PDMS chains, the hydrophilic GPDS-monolayer becomes more hydrophobic with a water contact angle to be about 74°. Study of the time dependence of film formation shows that the adsorption of GPDS-monolayer is fast, whereas at least 16 h is needed to generate the homogeneous PDMS film. Protein-A is then bound to the PDMS layer and used to capture IgG. It was shown that the existence of protein-A in the multilayer system has a strong influence on the binding properties of IgG not only in the efficiency of binding, but also in its specificity. The multilayer system with protein-A has the potential to be further developed into an efficient immunoassay protein chip.

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Characterizations of Immobilized Rocket Catalase on Chitosan Particles
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Abstract- Catalase from rocket plant was immobilized on the chitosan particles. Free catalase and immobilized catalase on chitosan particles were characterized by determining the optimum temperature, optimum pH, thermal stability, storage stability and kinetic parameters. It was determined that optimum temperature for free catalase and immobilized catalase on chitosan film is 25 °C, and optimum pH is 7.0. It was found as Km 19.22 mM, Vmax 10042 μmole/min mg protein for free catalase, Km 22.67 mM, Vmax 1522 μmole/min mg protein for immobilized catalase on chitosan. It was observed that there was a big difference between Vmax value of the free catalase and Vmax value of immobilized catalase on chitosan film whereas there were minor changes in the value of Km for free catalase and immobilized catalase. It was found that storage stability at 4°C for immobilized catalase is greater than free catalase.

The application of native enzymes biochemical, biotechnological, textile and food industrial fields is not always useful and optimal. Enzymes are often immobilized onto or into solid supports to increase their thermo stability, operational stability, and recover. Many methods are available for enzyme immobilization. The various methods devised for enzyme immobilization may be subdivided into two general classes: chemical methods, where covalent bonds are formed with the enzyme, and physical methods, where weak interactions between support and enzyme exist. Of the many carriers that have been considered and studied for immobilizing enzymes, organic or inorganic, natural or synthetic, chitin and chitosan are of interest in that they offer the above characteristics. Chitin and chitosan are natural polyaminosaccharides. Chitosan, (1→4)-2-amino-2-deoxy-β-D-glucan, a derivative of chitin, (1→4)-2-acetamido-2-deoxy-β-D-glucan, is chemically prepared by N-deacetylation of the latter. In addition, chitosan appears economically attractive since chitin is the abundant natural polymer next to cellulose [1].

Catalase (EC 1.11.1.6) is a heme containing metalloenzyme which decomposes hydrogen peroxide to water and oxygen has been used in industry for a long time. Immobilized catalase has useful applications in various industrial fields in removal of hydrogen peroxide used as oxidizing, bleaching or sterilizing agent and in the analytical field as a component of hydrogen peroxide. With immobilized enzymes, improved stability, reusability, continuous operation, possibility of better control of reactions, high purity and product yields and hence, more favorable economic factors can be expected [2].

In this work, we investigate immobilization of rocket catalase on chitosan particles and to find kinetic parameters, thermal stability and storage stability for immobilized catalase. Catalase was chosen because of its broad industrial using.

We first extracted catalase from rocket plant (Eruca Sativa) with pH 7.0 phosphate buffer. The mixture was filtered and centrifuged (5000 g). The activity of catalase was determined spectrophotometrically by direct measurement of the decrease in the absorbance of hydrogen peroxide at 240 nm due to its decomposition by the enzyme. After the rocked catalase was characterized, chitosan particles were prepared. Chitosan was dissolved in 2.0% (v/v) acetic acid. 0.75 mg/ml TPP (sodium polyphosphate) was dropped into a beaker. Chitosan particles were stably stored in distilled water. The characterized rocket catalase was mixed with phosphate buffer containing 1.0 mg chitosan particles. Immobilization time was 15 min at room temperature. Then the immobilized enzyme was gotten after the mixture was centrifuged (5000 g) and dried. Then the immobilized catalase was characterized with different concentrations of hydrogen peroxide. The optimum pH, temperature and storage stability for immobilized and free enzyme were kinetically characterized.

In summary, we showed that rocket catalase was kinetically characterized and immobilized in to chitosan particles successfully. The optimal temperature of the immobilized enzyme was 35 °C. The free and immobilized enzyme exhibited maximal activity at pH 6.5. K_m value of the immobilized rocket catalase was 22.67 mM, higher than that of the free rocket catalase 19.22 mM. What's more, the immobilized enzyme exhibited remarkably improved stability properties to various parameters, such as temperature, reuse, and storage time. Thus chitosan particles were suitable for an immobilized rocket catalase carrier.

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Toxicity Effect of ZnO Particles with Different Size and Shape

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Abstract—ZnO nanoparticles are widely used in commercial and industrial applications ZnO. But there is toxicological risk to use ZnO nanoparticles. Our results show that different size and shape ZnO particles toxicity in lower doses is so low. According to exposure time and concentration, toxicity of ZnO particles getting higher.

Nanotechnology is one of the fastest growing sectors of the high-tech economy. In recent times, there are more than 1000 nanomaterials products that are used in commercial, medical and personal applications [1,2]. Engineered nanomaterials with dimension of 100 nm or less provide novel applications in electronics, healthcare, cosmetic technologies and engineering industries [1,2,3]. ZnO nanoparticles are widely used in cosmetic applications [2,4]. Although nanomaterials have high properties, problems like toxicity will come with together. Being without toxicological data on nanomaterials makes it difficult to determine if there is a risk associated with nanomaterials exposure [1,2].

In this study, we have studied adverse effects of nanomaterials with in vitro methods. Cytotoxic effects of ZnO metal oxide particles were investigated with MTT (mitochondrial activity) test which is accepted as indicator of mitochondrial activity and NR (lysosomal activity) test which is accepted as cytotoxicity or cell viability following exposure to toxic substances on V79 379A (Chinese Hamster lung cells). Three ZnO materials that are used have different shapes and dimensions.

We have two exposure times (4 and 24 hours). According to MTT and NR results three ZnO particles have the cytotoxicity effects dependent on times and concentrations. NRU results are different from the MTT results. Because, the results that are measured with different methods will be different [5]. According to 4 hours results, toxicity is so low But, 24 hours exposure results is so high. After 40 μg/ml concentrations all three particles, toxicity is getting higher. Lysosomes are more affected by the ZnO particles than mitochondria. Figure 1 is an example of 4 hours exposure time cytotoxicity data of the 100 nm ZnO nanoparticles with MTT test.

In summary, we showed that ZnO nanoparticles have cytotoxic effects depending on the increasing concentrations and time. Toxicity data generated in this study can potentially be used to evaluate human current risk of nanomaterials. Future studies should be focused on investigating the potential risk or nanomaterials to human health at the microscopic cellular level by practising suitable microscopic techniques to show general mechanisms of toxicity and characterising exposure to nanomaterials.

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**Antioxidant Enzyme Carrier Polymeric Nanoparticles Against Oxidative Stress**

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**Abstract**—Oxidative stress induced by reactive oxygen species including H₂O₂ plays a key role in many cardiovascular and pulmonary diseases. The current study describes encapsulation of catalase (an antioxidant enzyme which dissociates H₂O₂ into water and oxygen) into polymeric nanoparticles composed of PLGA-b-PEG copolymers. Catalase carrier polymeric nanoparticles prepared in this study exerted H₂O₂ degrading activity and afforded a potent protection against oxidative stress.

Vascular oxidative stress is a condition involved in many cardiovascular and pulmonary diseases [1]. Oxidative stress is often initiated and spreaded by overproduction of reactive oxygen species such as hydrogen peroxide (H₂O₂) and their conversion to potent oxidants. Detoxification (degredation) of H₂O₂ is supposed to be an important therapeutic goal and antioxidant enzymes are candidate drugs for this aim [2]. However, inactivation by inhibitors and proteases and inadequate delivery limit the effectiveness and use of therapeutic enzymes. In order to improve the delivery of therapeutic enzymes, they can be encapsulated within polymeric nanocarriers. However, loading of such large protein molecules into nanoparticles without loss of activity of the therapeutic enzyme is the main challenge of polymeric nanocarrier encapsulation.

In this study, we prepared therapeutic enzyme carrier nanoparticles from poly(lactic-co-glycolic acid)-block-polyethylene glycol copolymer (PLGA-b-PEG) for delivery of catalase, a hydrogen peroxide detoxifying enzyme (Figure 1). First, PLGA-b-PEG copolymer with a terminal carboxylic acid group was synthesized by using PLGA-COOH and NH₂-PEG-COOH. PLGA-COOH was preactivated by l-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) and N-hydroxysuccinimide (NHS) and then reacted with NH₂-PEG-COOH. Second, therapeutic enzyme encapsulated nanoparticles were prepared by using the w/o/w double emulsion method as described previously [3,4].

![Figure 1. Schematic representation of the synthesis of PLGA-PEG-COOH copolymer and the encapsulation of catalase by the double emulsion solvent evaporation method.](image)

By using this system, catalase was encapsulated within pegylated PLGA nanoparticles (350 nm ± 15.6 nm, n= 5) with protected enzyme activity. The hydrophilic PEG groups on the surface can resist uptake by tissue macrophages and can get rid of systemic clearance. Additionally they facilitate the presentation of the carboxylic acid groups on the surface which can be functionalized with a targeting molecule for a targeted delivery.

The activity of loaded catalase was determined by the direct monitoring A₂₄₂ nm absorbance of H₂O₂ by using a standart catalase assay. A representative kinetic data obtained in catalase activity assays (Figure 2) showed that catalase loaded nanoparticles represented an H₂O₂ degrading activity.

The decrease in absorbance of H₂O₂ represented the protected enzymatic activity of the internalized catalase which exerted its effect without release from the nanoparticle, due to degradation of H₂O₂ diffusing through the polymer shell. Therapeutic efficacy, toxicity and cellular uptake of nanoparticles will be evaluated by ongoing experiments.

![Figure 2. A representative kinetic data obtained in catalase activity assays](image)

As a result the nanoparticles generated by using this system can protect the cells from the toxic effects of H₂O₂ and afford a potent protection against oxidative stress. Furthermore, the components of the nanoparticles were biodegradable, biocompatible and also approved by the Food and Drug Administration (FDA). The FDA approved components facilitate the translation of these nanoparticles into clinical practice.

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Application of Gold Coated Iron Oxide Nanoparticles for in vitro Plasmid DNA Transfection

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Abstract-The aim of this study is to synthesize gold coated iron oxide nanoparticles due to their unique optical and magnetic properties and potential applications in biological separation systems. Iron oxide nanoparticles were coated with gold film (Fe₃O₄ - Au) forming a typical core–shell structure. Applications of these nanoparticles for diverse biomedical applications including Plasmid DNA transfection is under investigation.

Magnetic nanoparticles consisting of magnetite (Fe₃O₄) or maghemite (γ-Fe₂O₃) have been thoroughly studied due to their widespread biomedical applications. Magnetic particles possess unique features that are not present in other materials used for medical applications. Each medical application requires materials with different magnetic properties; thermal, chemical, and colloidal stabilities; magnetic characteristics, and particle morphology. All materials used for these applications must, obviously, be non-toxic. Superparamagnetic iron oxide nanoparticles have been functionalized with many different biological ligands for interaction with human cancer cells. The range of biomedical applications of magnetic nanoparticles depends on their stability in solutions at various physiological pHs and the degree to which their surfaces may be chemically functionalized. Surface modifications of magnetic nanoparticles with different stabilizers including organic and inorganic molecules affect their stability, magnetization and, therefore, biomedical applications. [1].

In order to add new properties (inertness, protection of the magnetic core against oxidation), an external inert shell such as Au has been widely attempted. The unique Au surface is safe in both animals and humans, and exhibit an absorption band in the visible region due to its surface plasmon phenomenon, allowing the colorimetry of biomolecules with high-selectivity. Moreover, the Au coating renders sites for strong binding with various proteins (e.g. enzyme, biotin and so on) through their mercapto groups. Thus, magnetic nanoparticles covered with an Au shell would provide all the characteristics of the Au element suitable for biomedical application and deliver magnetic properties to be utilized for further manipulation with an external magnetic [2].

Nonviral gene delivery into cells is a key tool for gene therapy. Several kinds of gene carriers, e.g., cationic liposomes, polymers and oligopeptides, have been reported. Although the nonviral technique circumvents some of the problems occurring with the viral method, such as endogeneous recombination, oncogenic effects and unexpected immune response, the limited efficiency and short duration of transgene expression are major obstacles to the application of nonviral systems to gene therapy. Recently, the use of inorganic nanoparticles such as amino-modified silica nanoparticles and cationic gold nanoparticles was reported. The special character of the nanoparticles differs from that of organic gene carrier molecules, and they are expected to be a novel base material for the next generation of functional gene carriers [3].

Gold nanoparticles have the advantages of easy preparation and the possibility of chemical modification of the surface, which requires skilled organic synthesis in the case of round gene carrier compounds. In this study, we investigated the preparation of gold coated iron oxide nanoparticles modified with cationic groups and examined the DNA-binding ability and transfection efficiency of these nanoparticles into cultivated cells.

The Fe₃O₄ nanoparticles (cores) were prepared by coprecipitation of Fe(II) and Fe(III) chlorides (FeII/FeIII ratio of 0.5) in an alkaline solution. To obtain oxidized Fe₃O₄ nanoparticles, the precipitate was first washed in 0.01 M HNO₃. The particles were then dissolved in 0.01 M HNO₃ and heated at 80–90 °C with stirring until the color of solution became brown. Au-shell coating was performed by reduction of Au⁺ on the surface of Fe oxide using a modification of Brown and Natan’s boiling citrate seeding procedure [4].

These gold coated iron oxide nanoparticles that were separated only by a magnet show a surface plasmon peak at 528 nm while a surface plasmon peak at 520 nm was observed from a solution containing both gold coated iron oxide nanoparticles and pure gold nanoparticles. The obtained gold coated iron oxide nanoparticles were characterized by UV–vis spectroscopy and Zeta-Sizer. The magnetic properties of these particles were characterized with vibrating sample magnetometer (VSM). The biological applications of Au–Fe oxide nanoparticles take advantages of the Au surface and strong magnetic properties of the nanoparticles.

Transfection efficiency of the cationic gold coated iron oxide nanoparticles into HeLa cells with the plasmid DNA are under investigation.

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SPR Enhanced TIRE Applications of Gold Nanospheres and Nanorods

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Abstract- In this report, gold nanoparticles of different sizes and shapes (nanodot and nanorods) have synthesized due to their unique optical properties and potential applications in bio and medical systems. Self-assembled monolayer (SAM) formations of 3-mercaptopropyltriethoxysilane (MPTS) molecules on glass surface (BK7) have investigated by changing dipping time and solution concentrations. Nanoparticles (AuNPs) have immobilized onto modified glass surfaces and these surfaces were used as surface plasmon resonance enhanced total internal reflection ellipsometric sensors (SPRe-TIRE) and performed as sensitive optic nucleic acid sensors. TIRE shows high sensitivity for low concentration of assembled layers adsorbed on surface due to surface plasmon resonance effects. The data, expressed in ellipsometric values as in angles (ω and Δ) and recorded during the interaction of Mycobacterium Gordonae (GOR).

Applications of these nanoparticles for diverse biomedical studies including array systems are under investigation.

The metallic nanoparticles have been providing new opportunities for biological research methods and biosensing applications because of their unique optical and mechanical properties. Among them, gold nanoparticles (AuNPs) are most popular because they have excellent stability, good biocompatibility, low-cost availability, and well-established surface chemistry for modification with biomolecules [1-4].

Nowadays, there is an increasing interest in developing biosensor systems which can detect, in a fast and selective way, various substances at very low concentrations due to affinity interactions. Ellipsometry is an optical technique that based on reflection for thin film and surface characterization.

The aim of this study is to produce gold nanoparticles and use as an optic DNA biosensor for different probe and target concentrations.

Gold spherical nanoparticles (AuNPs) were prepared by sodium citrate reduction of HAuCl₄·3H₂O. Gold nanoparticles of average diameters between 20 and 150 nm were synthesized by varying the ratio of HAuCl₄·3H₂O concentration to sodium citrate concentration. Gold nanorods were produced by means of a seed mediated growth approach in the presence of AgNO₃, which consists of synthesis of small diameter seed particles and subsequent growth of these nanoparticles into nanorods by addition to gold salt solution containing cetyltrimethylammonium bromide (CTAB) in the presence of ascorbic acid. Average length (200 nm-1μm) and aspect ratio (~2~~30) of the nanorods were synthesized. The obtained colloids were characterized by UV–vis spectroscopy, atomic force microscopy (AFM) and Zetasizer.

The study on nanoparticles is undertaken in order to investigate the immobilization of modified AuNPs onto the self-assembled monolayers of MPTS. Glass surface (BK7) has chosen for these experiments that is an optically transparent substrate on account of its possible applications in refractometric analysis.

The sensor response for interaction of GOR target had equilibrium at 300 minutes and reported ellipsometric data were 2.622 ±0.019, 2.787 ±0.032, 3.22 ±0.073, 3.45 ±0.070 Delta for 0.25, 0.50, 1.0 and 2.0 μM targets. SPRe-TIRE based nucleic acid sensor of two types of nanoparticles was applied to stimulate plasmon resonance on TIRE surface and performed successfully with a detection limit of 0.25 μM target.

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Polymeric Nanocapsules in Nanotechnology

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Abstracts: We tried to locate polymeric nanocapsule in nanotechnology and treatment.

Nanotechnology (NT) is related to the production and use of materials with engineered properties at the atomic or molecular scale [1]. Nanotechnology can be applied in almost every area such as electronic, magnetic, optical, information technology, development materials and biomedicine. Because of their small size, nanoscale devices can communicate with biomolecules on both the surface and inside cells [2].

Nanomaterials are usually defined as materials that have at least one dimension smaller than 100 nanometers [3]. Nanomaterials may have different chemical, physical, electrical and biological properties [4]. Nanocapsules are submicronscopic container which are composed of an oily or aqueous core. And this oily or aqueous core is surrounded by a thin, permeable polymer membrane nearly various to tens of nanometers thick [5]. Nanocapsules can be involved in many function in various ways. Nanocapsules can be produced as monodisperse particles with exactly defined biochemical, electrical, optical, and magnetic features [6].

Nanocapsules have a wide range of applications including drug delivery, encapsulation, and imaging [7]. A good deal of physical and chemical methods have been improved for the preparation of polymeric nanocapsules [8]. Such as template synthesis self-assembly, emulsion polymerization and core removal of dendrimers [7]. Biodegradable polymeric nanoparticles have been run for potential drug delivery devices. Because they have ability to circulate for a prolonged period time target a definite organ, as carriers of DNA in gene therapy and also they have ability to deliver proteins, peptides and genes [9].

In this review, we have tried to locate polymeric nanocapsules in emerging nanotechnology. We aimed to explain compose of nanocapsules and their applications.

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Encapsulation of Atorvastatin in Polysorbate-80 Coated Polymeric Nanoparticles
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Abstract—Previously it was reported that nanoparticles with polysorbate-80 coating are able to penetrate through blood-brain barrier after i.v. administration. The objective of this study was to develop polysorbate-80 coated and atorvastatin encapsulated poly(lactic-co-glycolic acid)-block-poly(ethylene glycol), (PLGA-b-PEG) nanoparticles and to investigate the relative advantages of polysorbate coating on NPs for neurological disorders. The particle size analysis indicated a unimodal particle size distribution in sorbate coated NPs, with a mean diameter of 162 nm. ATR were efficiently encapsulated in nanoparticles.

Polymeric nanoparticles (NPs) are used in drug delivery systems because of their superior abilities like; penetrating through biological barriers (i.e. such as blood brain barrier), transporting the cargo molecules to their targets more precisely, delivering the drugs that have solubility problems without any issues, getting eliminated from the body after its work has done, lowering the toxicity risk of drug at other regions of the body [1].

Statins are known as lipid lowering drugs but they also have neuroprotective effects and can be used against neurological disorders like Alzheimer’s disease, stroke, Parkinson’s disease and multiple sclerosis. These drug molecules are promoting the release of neurotrophic factors, increasing neurogenesis and synaptogenesis, activating neuroprotective enzymes, increasing nitric oxide production and improving vascular function. However, statins are contra-indicated for patients having liver diseases and have side effects like muscle ache and gastro intestinal symptoms (GIS). These systemic side effects can be avoided by delivering these drugs with nanoparticle formulations and target them to specific regions [2]. Atorvastatin (ATR) is a synthetic one among statins and widely being used by hyperlipidemic patients.

In this study, we developed polysorbate-80 coated and atorvastatin encapsulated poly(lactic-co-glycolic acid)-block-poly(ethylene glycol) (PLGA-b-PEG) nanoparticles by modified version of nanoprecipitation method [3] for neurological disorders (Figure 1). It is expected that PLGA-b-PEG polymer that is composed of two bio-compatible blocks (PLGA) and PEG) can circulate through the body for longer period of times by getting over the elimination process of biocompatible blocks

The mean particle diameter was determined by Zetasizer (Malvern) and morphology and size was confirmed by Atomic Force Microscopy (AFM). The ATR entrapment efficiency was determined with HPLC method. ATR loaded nanoparticles were found to have average diameters of 132 nm (Figure 2) with 93 % drug loading. Polysorbate coating increased the average diameter of NPs up to 162 nm.

It was observed that increasing polymer concentration significantly increased nanoparticle diameter. On the other hand loading efficiency was increased slightly (Table 1). Increasing concentration of PEG from 5 % to 15 % (w/w) in polymer composition decreased the nanoparticles’ diameter slightly and improved the drug loading up to 93 % (Table 2).

Cellular uptake of formulated nanoparticles will be examined with fluorescent labeling and in-vivo performance of NPs will be evaluated by further experiments.

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Protein Adsorption on Cholesterol Incorporated Langmuir-Blodgett Phospholipid-Emulsifier Monolayers

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Abstract- Effect of cholesterol on the intermolecular forces between lipid molecules and the emulsifier was studied. DSPC (1,2-dipalmitoyl-sn-glycerol-3-phosphocholine) and PEGR₄₀ (Polyoxyethylene glycol) stearate were used as the main lipid component and the emulsifier, respectively. Langmuir-Blodgett (LB) technique was employed to obtain monolayers on alkanethiol assembled gold surfaces. The condensing effect of cholesterol as well as the protein adsorption capacities were investigated by both the topography and roughness analysis obtained by the atomic force microscopy (AFM).

Cholesterol is one of the main constituents of all cell membranes where they are required to establish membrane permeability and fluidity. Previous studies have shown that the structural order of the phospholipid hydrocarbon chains of cell membranes have been increased by addition of cholesterol [1]. Moreover, LB film of DPPC and cholesterol mixed monolayers at the air/water interface has shown that cholesterol has a considerable condensing effect [1]. Figure 1 shows the chemical structure of these components. The condensing effect increases the packing density and homogeneity of the monolayer. Moreover, it plays an important role in the formation of vesicles, such as microbubbles, micelles, for controlled and targeted drug delivery [1,2,4].

In this study, two types of mixtures have been prepared for investigation of the effect of cholesterol. One of the mixtures was composed of DSPC, PEGR₄₀, and cholesterol with a mixing ratio of 0.77:0.09:0.14, respectively. The other mixture contained only 80% DSPC and 20% PEGR₄₀ (8:2). The monolayer formation of these films was applied onto the alkanethiol treated gold surfaces. The aim of this treatment was to allow the hydrocarbon tails of the amphiphiles attach on the substrate and expose the hydrophilic head groups outer the surface for roughness analysis. AFM was employed for both the topography measurements and roughness analysis.

Figure 2 shows the topographies of the mixtures at the 5 μm scale, indicating that 0.77:0.09:0.14 DSPC-PEGR₄₀-cholesterol monolayer coated in the pure water has more homogeneous structure than the monolayer coated without cholesterol under the same conditions. This is in well agreement with the literature [3].

The roughness analysis (Figure 2) also supported the smoothness of the monolayers with the root mean square (rms) values. While the rms of 8:2 DSPC-PEGR₄₀ monolayer is 6.38 nm, the rms of 0.77:0.09:0.14 DSPC-PEGR₄₀-cholesterol monolayer on thiol assembled gold layer.

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Generation and Engineering Antibodies to Potently Neutralize Botulinum Neurotoxins A and B.

Botulinum neurotoxin (BoNT), the most poisonous substance known, causes naturally occurring disease – botulism. It has been classified as a Category A toxin that has been classified within seven serotypes, designated A-G. Sequence variability occurs in BoNT variant strains (subtypes), which significantly alters antibody binding properties. The diversity within serotypes and their subtypes causes surface variability that makes the generation of cross reactive antibodies difficult at best. We constructed nine immune human antibody libraries to develop recombinant monoclonal antibodies (mAb) based antitoxin to treat botulism resulting from BoNT/A, B subtypes. Gene diversity antibody libraries displayed on the yeast surface were sorted for BoNT serotypes binding by fluorescent activated cell sorter (FACS), and a panel of lead antibodies cross-reactive with the different BoNT/A and B subtypes were isolated. The mAb epitopes were mapped by displaying the three functional domains of BoNT/A and B (binding domain-HC, translocation domain- HN, light chain/ zinc endopeptidase-LC) on the surface of yeast. Cross reactivity of antibodies were broadened while increasing the affinities of antibodies by yeast display. Combination of three affinity maturated monoclonal antibodies completely protecting mice against challenge with a 0.5ug of antibody combination with 40,000 mouse LD50 for both BoNT/A and B serotype. BoNT/A mAb combinations have been produced for phase2 analysis to treat type A botulism.

Keywords: human antibody library, antibody affinity maturation, FACS, Surface Plasmon Resonance, Biacore, yeast display, molecular evolution, botulinum neurotoxin, single chain Fv.
Evaluation of Angiogenic Properties of Ag$^{+}$ Ion Doped Calcium Phosphate Based Ceramic Nano-powder

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Abstract - The aim of the study was to investigate the cytotoxic and angiogenic effects of Ag$^{+}$ ion doped calcium phosphate based ceramic nano-powder. Ag$^{+}$ ion content of powders showed a concentration related cytotoxicity characteristics and didn’t have any significant effects on basal angiogenesis.

As an important component in the development of nanotechnology; nanoparticles and biomaterials which play an important role replacing human organs, tissues and modifying their functions, have been extensively explored for possible modern medical applications (1,2,3). Ceramic composites and scaffolds are popular implant materials in the field of dentistry, orthopedics and plastic surgery (4,5). Moreover, biomaterials are extensively used as critical components in tissue engineering and drug delivery systems aimed at inducing therapeutic angiogenesis (6,7,8). All of this requirements show that an ideal biomaterial candidate must be antimicrobial, has biocompatibility and contains low toxicity. The aim of the study was to investigate the cytotoxic and angiogenic effects of Ag$^{+}$ ion doped calcium phosphate based ceramic nano-powder. The cytotoxicity of 10 mg/ml and 100 mg/ml concentrations of the test compounds was evaluated on HUVEC (Human Umbilical Vein Endothelial Cells) utilizing MTT assay at 24 and 48 hours. Besides angiogenic properties of same doses were demonstrated by tube forming assay. Ag$^{+}$ ion content of powders showed a concentration related cytotoxicity characteristics. Furthermore, angiogenic effects of Ag$^{+}$ ion doped calcium phosphate based inorganic powder on HUVEC were observed. Especially at 10 mg/ml concentration of antibacterial ceramic powders showed non-toxic and angiogenic effects.

Figure 1. Cytotoxic effects of all test compounds at 10 μg/ml on HUVEC cells.

Figure 2. Cytotoxic effects of all test compounds at 100 μg/ml on HUVEC cells.

Figure 3. Angiogenic effects of the highest dose compound on HUVEC cells. a) Control, b) 35-A 10 μg/ml, c) 35-A 100 μg/ml.

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Investigation of Copper Ion-Peptide Interaction Mechanisms in Biological Systems by Using the MXCXXC Motif of The Atx1 Protein in Model Organism Saccharomyces Cerevisiae by Molecular Modelling

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Abstract - We investigate the interactions and binding properties of the MXCXXC peptide motif of the Atx1 protein in Saccharomyces Cerevisiae with Cu(I) and Cu(II) ions. We have replaced the “X” residues with selected six amino acids and tried observe the effect(s) of mutations on the interactions by the help of computational tools. The results indicate that peptides may have selective binding affinities towards Cu(I) and Cu(II) ions upon sequence change. This may be a very important tool for developing new systems for applications in biomanotechnology.

Some metals are essential for living organisms. Copper, as an essential metal, participates in many protein structures for their functionality and it is transported by copper chaperones inside the cell to the right locations [1]. Atx1, a copper chaperone in Saccharomyces cerevisiae, transports copper ions to Ccc2 protein which brings the ion to Golgi [2]. Atx1 has a conserved MXCXXC motif that is also conserved in Atx1-like proteins in many organisms, to bind copper ions, where M is Methionine, C is Cysteine, and “X” is any amino acid. It is assumed that the copper ion binding nature of this motif is independent of the X residues [3].

The aim of this study is to investigate the copper binding mechanism of MXCXXC motif with respect to different amino acids used for “X” residues by computational analysis. Because of the large increase in the total number of structures to be studied six selected natural amino acids, Alanine (A), Glycine (G), Threonine (T), Valine (V), Serine (S) and Cysteine (C) are used in all possible combinations in the MXCXXC motif instead of X residues. Since this motif is located somewhere in the middle of a long peptide chain, acetate groups have been added to the terminal groups to resemble the actual structure of the peptide in the real system. Most stable structures of the peptides from the conformational analysis are chosen for modeling the interactions with the two types of copper ions, copper(I) and copper(II). At least nine locations are defined on peptides for binding of the copper ions which can increase depending on the used “X”. For each interaction, first one copper(I) is located to one of these positions, and then two copper(I) are located to two different positions; the same procedure will be used for copper(II) ions. Primary calculations for the conformational analysis and interactions of the peptides will be carried out with molecular mechanics using the CHARMM22 force-field as implemented in HyperChem [4]. The calculations will be repeated with quantum mechanics by using the Density Functional Theory methods (DFT) methods implemented in Gaussian series of programs [5].

All interactions occur in solution in biological systems. In order to have a correct understanding of the peptide-metal ion interactions, calculations in solution are very important. In addition to the calculations in gas phase (vacuum), solvent effects will be investigated by the help of PCM models. Unfortunately, PCM models are inadequate to investigate the solute-solvent interactions properly. Therefore, these calculations will be carried out with Molecular Dynamics (by using Discovery Studio software) which allows adding solvent molecules directly to the studied systems.

The detailed information gained in this study on the mechanism of peptide-metal interactions will provide useful data that can be used in many fields of health, biotechnology and biomanotechnology.

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Development of Carbon Nanotube Modified Biosensors for Electrochemical DNA and Protein Detection

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Abstract—Here in we describe label free carbon nanotube (CNT) modified electrochemical biosensors for rapid detection of point mutations and aptamer – protein interaction. For this purpose screen printed graphite electrodes were modified with MWCNTs. DNA and aptamer sequences were immobilized onto modified surfaces via adsorption or carbodiimide chemistry. Voltammetric guanine oxidation signal and electrochemical impedance spectrometry (EIS) were used as signal techniques.

Electrochemical DNA biosensors, based on electrochemical transduction of hybridization events, have great promise for the task of pharmaceutical, clinical, environmental and forensic applications. Such devices couple the high specificity of DNA hybridization reactions with the high sensitivity, low cost and portability of electrochemical transducers. The electrochemical biosensors can be assembled to a miniaturized array known as DNA chips [1 - 4].

Recently there has been a considerable interest in developing a DNA electrochemical biosensor for safe and rapid applications in genetic analysis as alternative to conventional methods. The development of electrochemical genosensors holds great promise for detecting inherited and microbiological diseases in connection with clinical analysis. High sensitivity of such devices, coupled to their compatibility with modern microfabrication technologies, portability, low-cost and minimal power requirements make them excellent candidates for molecular diagnosis [5-6].

Aptamers are short single-stranded DNA or RNA sequences which have high specific affinity in binding protein targets. Aptamer based studies represent a novel modern and a strategic approach in bioanalytical analysis for specific protein detection. Due to their high stability, chemical simplicity, and easy applicability, they can be used as alternative captures to antibodies. Thereby, aptamer applications hold a great promise for biosensing of protein, and for developing protein arrays [7-8].

Aptamer based protein detection and DNA based hybridization and point mutation detection studies were performed in this work. MWCNT modified screen printed surfaces were used as sensor surface for label free detection. Aptamer sequence was immobilized onto MWCNT modified SCPEs via carboximide chemistry and protein recognition was monitored by EIS responses in the presence of 5mM [Fe(CN)\textsubscript{6}]\textsuperscript{3-/4-}.

21 mer inosine substitute DNA probe sequence was immobilized onto MWCNT modified SCPEs by adsorption. Point mutation and hybridization was monitored by voltammetric transduction of guanine oxidation.

This study represents an alternative electrochemical biosensor for rapid and label free detection of DNA and proteins with interest for future applications.

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Molecular Dynamics Simulations of A Phospholipid Membrane
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Abstract- Molecular dynamics simulations play important roles in providing insight into the properties of membranes. Most of experimental and computational studies have performed on model systems consisting of a single phospholipid. In this study we perform simulations on a phospholipid membrane by using some parameters.

Biological membranes consist largely of phospholipids molecules and are considerably complex systems in the sense of both structure and their dynamical properties. The properties of a biological membrane are governed by the detailed composition of the bilayer which contains various lipid types.

Experimental methods such as spectroscopic and calorimetric techniques play important roles in highlighting and investigating the properties of biological membranes and the interactions of biological membranes with different molecules [1-4]. In addition to experimental methods, computational and theoretical modeling methods are widely used as tools for studying the structure and dynamics of lipid bilayer membranes. In these methods, due to the complexity of natural membranes, the large majority of studies have used pure or binary lipid mixtures as membrane models [5].

Simulation studies of simplified systems have been necessary and have increased our understanding of the properties of biological membranes.

Recently molecular dynamics simulations have been increasingly used to investigate the molecular-level interactions of lipid membranes and different molecules. In addition, molecular dynamics simulations are used as an important tool for investigating atomistic details of phospholipid membrane properties. In principle molecular dynamics simulations can provide an atomic-scale picture of membrane structure that complements and assist in the interpretation of experimental results [6].

Molecular dynamics simulations of lipid bilayers vary in different respects which can be grouped into different macroscopic boundary conditions (different ensembles) and different microscopic interaction parameters (force fields). Moreover more technical parameters, such as cutoffs in the microscopic interactions or step size and time widow of the simulations can vary.

In the last few years many reports of molecular dynamics simulations of lipids have appeared in the literature. For example, Hofsaß et al. have investigated the interaction of phospholipids bilayers with cholesterol [7], Pandit et al. performed molecular dynamics simulations of a dipalmitoylphosphatidylcholine (DPPC) bilayer with NaCl [8], Smodyrev and Berkowitz studied molecular dynamics simulation of DPPC bilayer in dimethylsulfoxide [9].

In this study we have used one of zwitterionic phospholipids such as DPPC, dimyristoylphosphatidylcholine (DMPC) in our molecular dynamics simulations. Among the phospholipids, phosphatidylcholines (PCs), popularly called lecithins, are one of the most common constituents of biological membranes. Model membranes composed of phosphatidylcholines are the most widely studied.

All molecular dynamics simulations and analyses were performed with GROMACS v4.0. An initial phospholipid molecule was created in Spartan 08 for windows.

We calculated the order parameter for each of the hydrocarbon tails separately. We also determined the density profiles of lipid bilayer.

This study will make us inform about the physical properties of membranes.

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**Colorimetrik Determination of Cysteine With Glutathione Capped Silver Nanoparticles**

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Abstract—Glutathione modified silver nanoparticles (GSH-Ag NPs) were prepared in aqueous solution by reduction of silver nitrate using sodium borohydride as reducing agent and GSH as capping agent. The GSH-Ag NPs provided a simple and rapid determination of cysteine (Cys) in the presence of Ni\(^{2+}\). Ni\(^{2+}\) ions can bind with both the GSH-Ag NPs and Cys molecule through metal-ligand interactions.

GSH is a tripeptide (γ-Glu-Cys-Gly) that contains a –SH group and has been utilized for the stabilization of silver nanoparticles (Ag NPs) through chemisorption [1]. There are also other functional groups such as –NH\(_2\) and –COOH which have affinity to the metal ions. Ni\(^{2+}\) is an essential element which can form complex with amino acids, peptides, phosphates and biotic ligand models. Colorimetric sensors are gaining increased attention due to required minimal instrumentation and simplicity, rapidity [2]. Metal nanoparticles have great interest because of the color changes which dependent on size and shape of the particle, adsorbed species etc. [3].

![Figure 1. GSH modified silver nanoparticle](image1)

In this work, we present determination of Cys amino acid in neutral aqueous solution using GSH-Ag NPs (Fig. 1) in the presence of Ni\(^{2+}\) ions. Interaction of the GSH-Ag NPs with an amino acid is comparatively weak. However in the presence of metal ions can interact both the GSH-Ag NPs and Cys. We have shown that the interaction of GSH-Ag NPs with Cys in the presence of Ni\(^{2+}\) resulting in changes in color and absorption properties.

Silver nanoparticles were prepared according to reported method [4] by the reduction of silver nitrate with sodium borohydride producing vivid yellow colored solution. After stirring 5 minutes aqueous solution of the GSH was added dropwise to solution. FTIR spectra (Fig. 2) show us the characteristic absorption peaks for –SH at 2523 cm\(^{-1}\) as found in pure GSH has disappeared in GSH-Ag NPs.

![Figure 2. FTIR spectra of (a) GSH and (b) GSH-Ag NPs](image2)

This suggests that GSH is modified onto the surface of Ag NPs via the thiol group. Figure 3 shows UV-Vis spectra of the water solutions of GSH-Ag NPs in the presence of different amino acids and Ni\(^{2+}\).

![Figure 3. The UV-Vis spectra of GSH-Ag NPs in the presence of different amino acids and Ni\(^{2+}\), GSH-Ag NPs and Ag NPs](image3)

The UV-Vis spectra indicate the absorption spectrum changes of solution while in the presence of Cys with GSH-Ag NPs because of the GSH-Ag NPs and Cys molecule through metal-ligand interactions via Ni\(^{2+}\) ions. In conclusion we have demonstrated a new method for selective determination of cysteine based on glutathione functionalized silver nanoparticles in the presence of Ni\(^{2+}\) ions.

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AFM and Kelvin Probe Study of Emulsifier Incorporated Phospholipids

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Abstract- Monolayers of DSPC (1,2-dipalmitoyl-sn-glycerol-3-phosphocholine) and PEG40St (Polyoxymethylene glycol) stearate at different compositions (9:1 and 8:2) were analyzed with atomic force microscopy (AFM) in the Kelvin Probe (KP) mode. The effects of the composition and the medium on compactness of the monolayer were investigated. Contrasting agents for ultrasound comprise micron sized of gas (microbubbles) stabilized by a shell of biocompatible material. These agents alter the scattering character of the blood under ultrasound, creating contrast with respect to the imaged tissue [1]. Microbubbles are administrated to the patient during imaging and are expected to recirculate in the blood stream until the imaging is complete. Viability of the microbubbles in the systemic circulation is closely related to the shell structure. In this study, DSPC and PEG40St are used as the main constituents of the microbubbles. A mixture of DSPC/PEG40St at predetermined compositions was spread at air-water interface and transferred to a substrate for atomic force microscope imaging using Langmuir-Blodgett (LB) film method. Mainly, DSPC/PEG40St mixtures at compositions of 9:1 and 8:2 were analyzed both in pure water and phosphate buffer saline at 110 mM (PBS). Monolayers showed more homogeneous and compact behavior in buffer solution compared to pure water for both compositions. Additionally, the 8:2 mixed monolayers indicated more homogeneous structure both in the pure water and buffer solution in comparison to 9:1 mixed one.

Contrast agents for ultrasound comprise micron sized of gas (microbubbles) stabilized by a shell of biocompatible material. These agents alter the scattering character of the blood under ultrasound, creating contrast with respect to the imaged tissue [1]. Microbubbles are administrated to the patient during imaging and are expected to recirculate in the blood stream until the imaging is complete. Viability of the microbubbles in the systemic circulation is closely related to the shell structure. In this study, DSPC and PEG40St are used as the main constituents of the microbubbles. A mixture of DSPC/PEG40St at predetermined compositions was spread at air-water interface and transferred to a substrate for atomic force microscope imaging using Langmuir-Blodgett (LB) film method. Mainly, DSPC/PEG40St mixtures at compositions of 9:1 and 8:2 were analyzed both in pure water and phosphate buffer saline at 110 mM (PBS). Monolayers showed more homogeneous and compact behavior in buffer solution compared to pure water for both compositions. Additionally, the 8:2 mixed monolayers indicated more homogeneous structure both in the pure water and buffer solution in comparison to 9:1 mixed one.

As shown in Figure 1, this comparison was also performed with the bare gold monolayer as reference monolayer in order to evaluate the differences between surface potential values. Figure 2 shows the height profile along the scan and surface potential measurement of 8:2 DSPC/PEG40St mixture coated films both in pure water and PBS. The characterization of the Langmuir-Blodgett (LB) films with AFM in Kelvin Probe mode shows that 8:2 mixed monolayer in buffer solution have higher surface potential values than 9:1 mixed one both in pure water and PBS (data not shown).

The surface potentials have been measured as 0.030184 V for bare gold substrate, 0.4894 V and 0.43 V for the 8:2 DSPC/PEG40St monolayer in pure water and PBS, respectively. Surface roughnesses have been measured as 0.544479 nm for bare gold substrate, 0.903692 nm and 4.41735 nm for 8:2 DSPC/PEG40St monolayer in pure water and PBS, respectively.

According to these investigations of emulsifier incorporated phospholipids, we surmise that the increase in homogeneity and the surface potential of the monolayers may be resulting from intermolecular interactions between the molecules forming the monolayer and the medium. The effect of the medium on the molecular interactions and the compactness of the monolayer will also be tested on microbubble formation.

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Quantum Dots in Heisenberg Model
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Abstract—We used Heisenberg model in quantum dots containing unlimited number of electrons subjected to an external magnetic field \(B\) in \(z\)-direction. We have used spin wave theory (SWT) with this model on QDS to calculate their physical properties such as ground state energy, excitation energies and lattice magnetization. SWT was used because for several reasons. First of all we can easily formulate the mathematical expressions of the physical quantities. Secondly we can run them in any PC and get results in a relatively short time comparing with other numerical studies. And SWT is believed to be accurate in the case of ferromagnetic systems.

Extensive attention was paid in the past decade toward Nano technology in both theoretical as well as experimental branches. This technology deals with tiny material of size ranging between 1 to 10 nm. At this level materials show different behavior of that of bulk ones [1]. This different behavior gave these material wonderful characteristics, amazing and vast applications in several fields. The reason behind this behavior is due to two reasons: the ratio of the surface to the volume and secondly due to Heisenberg uncertainty principle [2].

Quantum dots (QD) also referred to as artificial atoms are one of these nano materials. They are made from several semiconductor material such as: Cadmium Selenide (CdSe). Also QDs were made from Zinc Sulfide (ZnS) and Zinc Selenide (ZnSe) [3, 4]. Semiconductors are considered as founding stone in manufacturing most of electrical instruments because of their electrical properties. They do have many applications and used in almost all of electrical devices such as light emitting diodes, personal computers and others.

As mentioned above QDs are of size ranges from 1 –10 nm. Each QD may contain in it from a single electron to several thousand up. They do consist of two parts: the core which is made of a semiconductor material such as CdSe, and a shell which is also a semiconductor like ZnS. For some other applications a coating for QDs is made from polymers to prevent leakage of toxic materials into them and helps QDs to dissolve in water. The coating also makes them very useful in several biological applications. Beside their quantum confinements, quantum dots have another advantage regarding their size. The flexibility of QD size allows researchers to grow and manufacture it in several ways. This gives QD the wide range of life applications.

These properties and wide application of quantum dots attracted attention of many researchers (both experimentalists as well as theorists). Experimentally several compounds of QDs were under study and investigation such as Gallium arsenide (GaAs) which is used in supercomputers and in making logic gates [5]. It is well-known by theorists that these ferromagnetic quantum dots can be described by Heisenberg model.

\[
H = \sum_{i,j}^{N} J_{ij} S_i \cdot S_j + \mu g \beta B \sum_{i,j}^{N} (S_i^z - S_j^z)
\]

We used linear spin wave theory LSWT to investigate QDs described by Heisenberg Hamiltonian and calculated ground state energy, excitation energies and magnetization. We applied Heisenberg Hamiltonian to QDs containing unlimited number of electrons and subjected to an external magnetic field \(B\). Linear Spin wave theory is applied to the system followed by Holtsin-Primakoff transformation and Bogoliubov transformation to get the diagonal Hamiltonian. Mathematical expressions of the physical quantities are then computed.

Ground state energy \(E_g\) increases with increasing the external magnetic field \(B\). This increase took the form as \(E_g \sim (B)^{1/2}\). A point of transition from a singlet to a triplet state at \(B \sim 1\) T was observed in agreement with previous studies.

Excitation spectrum of the QD – like other ferromagnets - is gapless at momentum \(K = 0\) in the absence of external magnetic field \(B = 0\) T. But a gap appears in the spectrum and increases linearly with \(B\) as soon as the magnetic field is switched on. This linear behavior differs before and after the transition point \(B \sim 1\) T.

Finally magnetization curve shows an increase to a saturated value with \(B\) as expected- since the magnetic field forces the spins to align in its direction. This increase goes as \(M \sim (B)^{0.1}\). We also observe a transition point around \(B \sim 1\) T.

Still many efforts have to be done in studying QDs to clear and understand all of their characteristics to make them more applicable. We hope that we contributed to these investigations in making QDs a little bit more clear.

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Synthesis and Magnetic Properties of Bipyridine Based Polyimides- NiFe$_2$O$_4$ Nanocomposites

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Abstract—Polyimide films in which magnetic nanoparticles are uniformly distributed are prepared. Novel hybrid polyimide composites are structurally elucidated by means of SEM, XRD and thermal analytical techniques, magnetic properties are measured by VSM.

Magnetic nanoparticles are of great interest for researchers from a wide range of disciplines, including magnetic fluids, catalysis, biotechnology/biomedicine, magnetic resonance imaging, data storage, and environmental remediation. However, an unavoidable problem associated with particles in size range is their intrinsic instability over longer periods of time. Such small particles tend to form agglomerates to reduce the energy associated with the high surface area to volume ratio of the nanosized particles. Polymers are often employed to passivate the surface of the nanoparticles during or after the synthesis to avoid agglomeration.

Aromatic polyimides are well-known as highly heat resistant materials and have been widely used in many applications such as electronics, coatings, composite materials, and membranes. Recently, polyimide magnetic nanocomposites have generated tremendous attraction, and they have become one of the most active and promising research areas.

In this study, NiFe$_2$O$_4$-polyimide hybrid nanocomposites were prepared by imidization and blending. The required ratios of NiFe$_2$O$_4$ nanoparticle and various bipyridine bearing polyimide were mixed using N-methyl-2-pyrrolidone (NMP) as aprotic solvent. The prepared polyimide-NiFe$_2$O$_4$ nanocomposite films were characterized for their structure, morphology, and thermal behavior employing Fourier transform infrared spectroscopy, scanning electron micrograph, X-ray diffraction and thermal analysis (DTA/TGA/DSC) techniques. These studies showed the homogenous dispersion of NiFe$_2$O$_4$ in the polyimide matrix. Magnetic properties of polyimide-NiFe$_2$O$_4$ nanocomposites were measured at 5-300K temperature range by vibrating sample magnetometer. Figure 1 shows the magnetic hysteresis loop at 5 K for the different weight percentage compositions.

Figure 1. M-H loops of polyimide-NiFe$_2$O$_4$ nanocomposite

In Figure 2, the synthesis of the polyimide is demonstrated. PI-NiFe$_2$O$_3$ composites were prepared with different weight percentages of NiFe$_2$O$_3$ (1, 5, and 10). The details of the method are as follows: 0.01 mole of 4.4’ dianimobipyridine and 0.01 mole of benzophenone tetracarboxylic dianhydride in 15 mL of dimethyl acetamide gave viscous gel of 17.4% poly (amic acid), which was used for the experiment. Different weight percent of NiFe$_2$O$_3$ (1, 5, and 10 wt %) were sonicated for an hour and were added to the weighed poly(amic acid), and the suspension was stirred for 2 h at room temperature under the flow of nitrogen. The composite films were then cast from the suspension placed on a glass plate kept in humid free chamber. The films henceforth are called as PI-NiFe$_2$O$_3$ films, with their weight ratios mentioned.

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Preparation of Polyimide/Silica Nanocomposites with Low Dielectric Constant

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Abstract—In this study, the new polymer–silica hybrid materials were prepared based on the organo-soluble polyimides of five various dianhydrides and diamines. 3-Aminopropyl trimethoxysilane (APS) was used to increase the intrachain chemical bonding and interchain hydrogen bonding between the polyimide and silica moieties, respectively. The chemical interaction would significantly affect the morphologies and properties of the prepared films. The produced polyimide-silica nanocomposites were investigated by X-ray diffraction analysis (XRD), scanning electron microscope (SEM) and thermal analysis techniques. Capacitances were determined with a HP4294A at a frequency between 1 kHz and 1 MHz. The dielectric constants of the resultant nanocomposites are lower due to the increased free volume and fewer polar Si-O-Si groups.

Organic–inorganic hybrid materials have been recognized as a new class of advanced materials because of the versatile approaches on synthesis, processing, and tunable properties [1,2]. The size of the inorganic segment in the hybrid materials could be controlled by the synthetic method (e.g. reverse micelles) or by the combination of synthesis and processing. Recently, several applications of hybrid materials in optoelectronic devices have been reported, including thin film transistors, solar cells, light-emitting diodes, optical waveguides, low dielectric constant materials, and high refractive index thin films[3]. However, the thermal and mechanical properties are required to be enhanced if high temperature processing or integrating with other inorganic materials is required. One possible solution is to prepare polyimide–silica hybrid materials. There were several classes of polyimide–silica hybrid materials reported in the literature [4], which show improved thermal stability and mechanical strength in comparison with their parent polyimides. One of the primary problems for preparing the hybrid materials is the phase separation between the organic and inorganic moieties. To overcome the phase separation of polyimide and inorganic oxide, the approach of either short chain polyimide segment, coupling agents [4], or the combination of both approaches were used to enhance the compatibility by increasing the density of coupling sites [5]. Among them polyimide (PI)–silica nanocomposites attracted much interest as packaging materials and in membrane technology [2] due to the excellent thermal stability of polyimide, its chemical resistance, its mechanical properties and its high selectivity for separation of gas mixtures[3]. Less attention has been paid to the potential of such nanocomposites as low dielectric permittivity $\varepsilon$ materials, which could replace PI in microelectronics applications, the relative high values of intrinsic $\varepsilon$ of silica (3.8 – 4.0 at room temperature against values in the range 2.6 – 3.2 for PI[3]) being probably the reason for that. However, $\varepsilon$ values lower than 3.0 have been reported for PI-based nanocomposites at relatively high filler contents[4]. The incorporation of inorganic materials like silica is a promising approach to enhance the thermal and low dielectric properties of polyimide.

In this study, new polymer–silica hybrid materials were prepared based on organo-soluble polyimides from various dianhydrides and two type diamines developed. A dianhydride end-capped polyimides were obtained first and then reacted with 3-aminopropyl trimethoxysilane (APS). The molecular structure and morphology of the prepared polyimide–silica hybrid films were characterized by FTIR, SEM, and x-ray. The thermal, dielectric, and physical properties of the prepared hybrid films were studied and correlated with the molecular structure.

Figure 1. SEM imagine of PI–silica composite.

A series of new polymer–silica hybrid materials was successfully prepared through the intrachain coupling by 3-aminopropyl trimethoxysilane (APS). The prepared hybrid films were homogeneous and thermally stable. The thermal properties of the organo-soluble polyimides were significantly enhanced by only hybridizing 6.30–7.99 wt% of silica. Silica particles with diameter of around 30–50 nm were observed in the hybrid films by scanning electron microscopy. The flame retardance, decomposition temperature and glass transition temperature of the film increased with increasing silica content.

Figure 2. Dielectric constants of PI–silica composites with different loadings of nickelocene in polymer (1–10%).

The dielectric constants of the resultant nanocomposites are lower due to the increased free volume and fewer polar Si-O-Si groups.

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The Calculation of the Local Density of States and the Thickness of Incompressible Strips of 2DEG with Green’s Function Technique

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Abstract—We have calculated the local density of states (LDOS) under strong magnetic and different electric fields within Green function techniques for a quantum Hall system. We have investigated the quantum motion of electrons under the influence of crossed static magnetic and the electric fields and then the overlap of adjacent Landau Levels. We showed that electric field effect in quantum Hall systems raises the same effect with the one of disorder. We have demonstrated, the changing of the thickness of incompressible strips (IS) at the Hall systems leads the important effects on the local density of states.

For the last decades, there have been a considerable pickup of interest in the electronic properties of nanometric-scale metal and semiconductor structures [1]. Integer quantum Hall effect (IQHE) is one of the most important discoveries of condensed matter physics, that is usually explained by disorder, extended and localized states or edge states [2].

Many experiments have been performed to understand the features of the two-dimensional electron systems (2DEGs) [4,5,6,7]. The local density of states is a very interesting quantity which is experimentally accessible via spatial scanning tunneling spectroscopy (STS) [5,6,7].

We consider a two dimensional electron gas (2DEG) in the x-y plane and a strong magnetic field in z what is the direction of electric field vector and perpendicular electric field. We deal the orthogonal magnetic and electric fields to create the Hall configurations. This system can be considered as quantum Hall system. The most convenient way to calculate to the density of states is the use Green’s function method [8].

Green’s functions can be written as

\[ G(r, r', E) = \frac{1}{\hbar} \int d\tau e^{iE\tau} K(r, \tau | r', 0) \]

where \( K(r, \tau | r', 0) \) is a quantum propagator which represents the possible amplitude for a particle at transition from point \( r \) to \( r' \) and at the time \( \tau \). By using the definition of density of states function one can write density of states \( n(r, E) \) [9] in terms of Green's function as

\[ n(E) = -\frac{1}{\pi} \text{Im}[G(r, r : E)] \]

A potential gradient is the rate of potential change with respect to the local displacement changing. Then in accordance with electrostatic this electrostatic potential energy is \( \Delta V = \varepsilon \Delta x \) where \( \Delta V = \hbar \omega_L \).

Figure 1., shows that the local density of states overlapping in the case of 34 nm wide of incompressible strip. As a result the adjacent Landau levels overlap. Blade overlap on Landau levels, eliminates the quantization of energy. Thus, the quantum Hall effect disappears.

Figure 1. Two-dimensional density of states \( n(E) \) (in units of \( eB / 2 \pi \hbar \omega_L \)) for a magnetic field \( B=5T \) and electric field \( 2000V/m \).

In summary, we have analyzed the relation between the local density of states and the different electric field amplitudes. We conclude that the Landau Levels become broader as the electric field increases. We have seen that the calculated electric field effect in quantum Hall systems with disorder effect raises the similar results. Our calculations show that in the case of 34 nm incompressible strip wide the local density of states start to overlap. We have demonstrated, a change in the thickness of incompressible strips will lead to important changes in the local density of states.

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Nonequilibrium Electronic Transport Properties of Graphene Nanodevices

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Abstract — We study the electronic transport properties of graphene which consists of monolayer, bilayer and multilayer graphene sheets. We experimentally investigate current-voltage (I-V) characteristics to determine the dependence of carrier mobility of single and bilayer graphene on the current density and temperature.

Graphene is a two dimensional crystal with one atomic thick layer of sp² bonded carbon atoms packed in honeycomb lattice structure [1]. Graphene has attracted great attention because of its excellent mechanical as well as electronic properties since its discovery [2]. Its charge carriers behave like relativistic particles with an effective speed of light ($v_F \sim 10^6$ m/s) described by Dirac equation. Hence charge carriers are called Dirac fermions. Transport measurements show that graphene has a remarkably high carrier mobilities. Mobilities of both electrons and holes exceed $15,000$ cm² V⁻¹ s⁻¹ even under ambient conditions. [1-2-3]

In this work we study the dependence of carrier mobility of single and bilayer graphene on the current density and temperature. Devices were fabricated on mechanically exfoliated graphene. Single layer bilayer of few layer graphene sheets are transferred on to SiOx. Raman Spectroscopy are used to identify the numbers of graphene sheets [Figure 1]. Devices are patterned by optical lithography and electron beam lithography dry etching and contacts are made by Cr/Au deposition. Measurements are done in a temperature range of 4.2 K – 300 K. The results provide information on how carrier scattering mechanisms vary with the number of layers.

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Energy Spectrum of Carriers in Kane-Type Semiconductors in Magnetic Field of Constant Direction With Hyperbolic Depending Variation Perpendicular To The Field.

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Abstract- We calculated energy spectrum and wave functions of carriers in two-dimensional A^3B^4 and A^2B^6 type semiconductors in magnetic field of constant direction with hyperbolic depending variation perpendicular to the field.

A two-dimensional (2D) electron gas in a magnetic field has proved to be an extremely rich subject for theoretical and experimental investigation [1]. For example, considerable effort has been devoted to the study of the integral and fractional quantum Hall effects, transport properties, and edge states [2]. The response of a 2D electron gas to a spatially an inhomogeneous magnetic field had been the subject of considerable interest in recent years [3]. In [4], are found compact analytical solutions for the energy eigenvalues orthonormalized eigenfunctions, and the gradient B drift velocity including the spin for a single electron in the quasi-2D case in a magnetic field B of constant direction with arbitrarily strong exponentially depending variation perpendicular to the field direction.

Exact analytical solutions for the bound states of a graphene Dirac electron in various magnetic fields with translational symmetry were obtained in [1]. The behavior of the discrete spectrum, probability and current densities was discussed [5].

Electron transport properties of magnetic well nanostructures have attracted considerable attention in this study, using a three-band Kane model including the conduction band, light and spin-orbital hole bands, the energy spectrum of carriers are calculated in the 2D semiconductors in a magnetic field B of constant direction with hyperbolic depending variation perpendicular to the field.

In Fig.1 the electron spectrum of low-lying electron states in the InSb type semiconductors as a function of the wave number k for different quantum number (n) has been presented. It’s clear from the figure that energy spectrum of electrons decreases in a parabolic way.

Figure1: Energy spectrum of electrons as a function of wave number k for InSb. Here E+ and E- are the electron energy for spin +z and –z directions, respectively.

owing to the advance in the micro fabrication technique and potential applications to electronic devices in the recent years [6].

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Abstract—Ni_{x}Zn_{1-x}Fe_{2}O_{4} (x=0, 0.05 and 0.1) nanoparticles have been synthesized by the sol-gel technique using Zn, Ni and Fe based alkoxide. Ni_{x}Zn_{1-x}Fe_{2}O_{4} nanoparticles, annealed at various temperature and time, were examined the doping ratio and temperature effects on magnetic properties. The phase and the crystal structure of the NiZnFeO nanoparticles were characterized using 20-0 x-ray diffraction. Magnetic measurements were performed with a Quantum Design PPMS. The structural and the magnetic properties of the NiZnFeO nanoparticles are presented.

Ferrites, which are ferrimagnetic oxides emerged as one of the important magnetic materials because of their high electrical resistivity, low eddy current losses and appropriate dielectric loss and hence find vast technological applications over a wide range of frequencies [1]. They belong to a large class of compounds which have spinel structure. The spinel unit cell consist of a close-packed cubic array of 32 oxygen anions, 16 Fe^{3+} ions 8 Fe^{2+} ions. Total 24 metal cations are distributed among eight tetrahedral interstices and sixteen octahedral interstices [2,3].

The goals of the present work are to investigate characterization, doping ratio, and temperature effects on magnetic properties of the Ni_{x}Zn_{1-x}Fe_{2}O_{4} nanoparticles using sol-gel technique.

Ni_{x}Zn_{1-x}Fe_{2}O_{4} solution was prepared by sol-gel synthesis using Zn, Ni and Fe precursor which were dissolved into solvent and chelating agents. They were all mixed with a magnetic stirrer for 12 hours at room temperature until clear, homogeneous and stable solution was obtained. Container cover was opened and they were rotated to remove the solvent at room temperature using magnetic stirrer. They were preheated at various temperatures (300-400 °C) for 10 min. After that the powders were ground and post annealed at various temperatures (800-950 °C) and time (10-300) min under air in a box furnace.

For the measurements of magnetic properties, a Quantum Design physical property measurement system (PPMS) was employed. The applied field dependence of magnetization of Ni_{x}Zn_{1-x}Fe_{2}O_{4} nanoparticles were recorded by using a VSM magnetometer at 300 and 9 K. Figure 1a and 1b show the magnetization hysteresis loop of the Ni_{x}Zn_{1-x}Fe_{2}O_{4} for x-concentration of 0, 0.05 and 0.1, as a function of magnetic field at 300 and 9 K. The saturation magnetization of the Ni_{0.05}Zn_{0.95}Fe_{2}O_{4} is about 35 emu/gr and hysteresis loop serves a clear field shift of ~60 Oe at room temperature.

In summary, Ni_{x}Zn_{1-x}Fe_{2}O_{4} (x=0, 0.05 and 0.1) nanoparticles were prepared by the sol-gel technique. The results of PPMS measurements bring out that coercivity and the magnetization of Ni_{x}Zn_{1-x}Fe_{2}O_{4} nanoparticles increase with the decrease temperature. Also, the coercivity and the magnetization decrease with the increase Zn ratio.

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Energy Band Structure of Graphene under Uniaxial Strain
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Abstract—As oppose to the literature, we propose that uniaxial strain is never able to open a band gap in the single layer graphene. We obtained energy-band structures for several different uniaxially strained graphane structures by using tight-binding method including the second nearest neighbor interactions. Since the $\sigma$ bands cross the Fermi level, there is no band gap opening in graphene due to an applied strain.

The structures like carbon nanotubes, graphite, diamond, fullerenes, and graphene made up of carbon atoms have been drawing a huge attention by the scientists. Among these, graphene has a basics position in order to understand the behaviors of other carbon based materials [1]. Both with its mechanical properties [2] and the electronic properties [3, 4] graphene provide a unique field of research. The combination of these main properties can be observed by investigating the electronic structure of graphene by subjecting it to an applied stress. Recent works on the strained single layer graphene suggest that it is possible to obtain a band gap opening by applying an amount of ~24% uniaxial strain. [5, 6] In addition, it is reported that the band gap increment is directly proportional to the increment of the applied strain.

In this study, we first tried to obtain band gap opening as a result of applied strain to the system by using tight method. Although it is a simple approach, it provides us the changes in energy-band structures with respect to the applied strain. Rather than stress, we introduced strain into the calculations as a tunable parameter as it was done in some other studies [5]. As measured for the graphite [7], we used Poisson ratio to be 0.165. Due to the strain, the positions of the atoms change and as a result of this, the geometry of the reciprocal space changes, too. Also the interaction parameters should be scaled with respect to the applied strain. In Ref.5, it is clear that, the only bands under consideration are $\sigma$ bands originating from $p_z$ orbitals which are calculated by tight binding method with only first nearest neighbor interactions. We carried our calculations one step further by considering the second nearest neighbor interactions.

As it can be seen in Fig 1, there is a slight band opening at the high symmetry point M. The bold lines were calculated from the energy expression provided in Ref. 5 which is considering just the $p_z$ orbitals and only the first nearest neighbor interactions. The increment on the band gap opening with respect to the strain can be seen in Fig. 1. The inset is taken from Ref.5, and the main graph is the result of our calculations based on the separations of the $\sigma$ bands.

![Fig.1 The opening of $\sigma$ bands as a function of applied strain. The inset shows the so called “band gap” as a function of applied strain as presented in Ref.5](image1)

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Effect of Exchange Bias on Magnetic Anisotropies in Fe/CoO Bilayers
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Abstract- We report on the structural and magnetic properties of exchange-biased CoO/Fe bilayers. The electron spin resonance (ESR) spectra of bilayers have been studied as a function of temperature at X-band frequency. Temperature dependence of the magnetic anisotropies and the corresponding theoretical simulation are shown and discussed for varying Fe thicknesses.

Exchange bias (EB), also known as unidirectional anisotropy, refers to a shift of the ferromagnetic (F) hysteresis loop to positive or negative values when a F system is in contact with an antiferromagnetic (AF) system. The exchange bias can be set by cooling through Néel temperature (T_N) of the AF system in the presence of an applied magnetic field [1]. AF materials, such as CoO, magnetically order below their T_N with the zero net moment. However, at the interface with a FM, there are localized net moments (Figure 1) CoO has extensively been used as an antiferromagnet in exchange-biased bilayers and multilayers. The main physical advantages of the choice of CoO as a AF are the easily accessible Néel temperature, which is close to room temperature, the strong anisotropy and the simple crystal structure, which recommend it both for experimental as well as for theoretical studies [2].

Figure 1. Schematic diagram of the spin configurations of a FM–AF couple after the field cooling procedure T< T_N.

The exchange bias effect is essential for the development of spin valves, tunneling devices and for read heads of hard drives and magnetic random access memories [3]. For these applications a predictable, robust, and tunable exchange bias effect is required [4].

Recently, there have been studies on Co/CoO [5-7] and Fe/CoO [2,4,8] bilayers. In these studies, they have been focused on various aspects of exchange bias. However there is no low temperature ESR study, except our recent experimental and theoretical work on Fe/CoO system for only one Fe thickness [9]. Therefore, in this study, we have investigated the magnetic properties of Fe/CoO bilayers at low temperatures by using FMR technique as a function of Fe thickness. The magnetic parameters, such as magnetization, magnetic anisotropy and magnetodynamics have been deduced as a function of temperature by fitting the experimental data.

The samples were grown on MgO (100) substrates by using ion beam sputtering technique. Before sputtering, a base pressure of ~10^-9 mbar was provided and the substrate was etched for 20 seconds with Ar. Then the FM Fe layer was grown on the top of the substrate with a pressure of 4.4×10^-3 mbar. Finally, AF CoO layer was deposited with a pressure of ~10^-4 mbar. The thickness of Fe layer was varied between 5nm and 30nm and the thickness of CoO was chosen as 10nm. The thickness of both layers has been checked by x-ray reflectivity measurements.

The electron spin resonance (ESR) spectra of bilayer, in terms of temperature and angle dependence, were carried out by using a commercial Bruker EMX spectrometer operating at X-band frequency. The setup also allows us to cool samples down to liquid He (LHe) temperatures. FMR experiments have been carried out at RT and low temperatures (below T_N) for both in plane and out of plane geometries.

The experimental data show that the Fe layer has a cubic symmetry at room temperature with an easy axis along [011] direction. After field cooling down to 4.2 K magnetic anisotropies dramatically changes depending on field cooling direction. In order to explain these features we have developed a theoretical model which nicely fits the experimental data. The possible origins for a low blocking temperature of CoO are also discussed.

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**Abstract**—We have studied the spatial distributions of thermodynamic and hydrodynamic variables such as current density and temperature, in a two dimensional electron system under integer quantized Hall effect conditions. By using the charge and energy conservation equations, we have investigated the spatial variation of the electron temperature in local equilibrium. We observed that the electron temperature has an important role in the large current regime where the breakdown of the quantum Hall effect (QHE) takes place. It is shown that spatial distribution of electron temperature causes a certain change in the current density distribution.

Quantum Hall effects (QHE’s) are remarkable phenomena observed at two-dimensional electron systems (2DESs), where the diagonal conductivity \( \sigma_{xx} \) vanishes in the low current regime while the Hall conductivity \( \sigma_{xy} \) is quantized to integer multiples of \( e^2/h \), where \( e \) is the unit charge and \( h \) is the Plank’s constant [1, 2, 3]. With increasing the current up to a critical value, \( \sigma_{xx} \) increases by several orders of magnitude within a narrow range of the current and the QHE breakdown [4, 5, 6, 7]. The model that deals with this phenomena is the hot electron model. It is proposed in this model that the electron heating is responsible for the increase of \( \sigma_{xx} \) at the breakdown, that is, electron temperature \( T_e \) is the key variable in determining \( \sigma_{xx} \) [8, 9, 10].

In this work, we investigate spatial dependence of the electron temperature in quantum Hall systems (QHS) considering compressible and incompressible strips [11]. To study spatial distributions of the electron temperature, we employ a theory of thermodynamics in QHS, which is described by equations of conservation with electron number and thermal flux densities.

We consider a 2DES in the xy plane which is subject to a perpendicular magnetic field \( B=0(0,B) \). Two dimensional electrons are confined by the potential due to ionized impurities which are distributed uniformly in the xy plane. Energy distribution of these electrons is described by the Fermi distribution function

\[
f(\epsilon, \mu_{ec}, T_e) = \frac{1}{1+\exp((\epsilon - \mu_{ec})/k_B T_e)}
\]

where \( T_e \) is the electron temperature and \( \mu_{ec} \) is the electrochemical potential.

There are two equations of conservation in this model of QHS. One describes the conservation of the electron number, the other describes the conservation of the energy. The equation of electron number conservation is given by

\[
\frac{\partial n}{\partial t} = -\nabla \cdot J_n
\]

with the electron density \( n \) and the number flux density \( J_n \).

The equation of energy conservation is given by

\[
\frac{\partial \epsilon}{\partial t} = -\nabla \cdot J_\epsilon - P_L
\]

with the energy density \( \epsilon \), the energy flux density \( J_\epsilon \) and the energy loss \( P_L \) due to the heat transfer between electrons and phonons. Then the flux densities are given by

\[
\begin{align*}
J_{nx} &= -L_{xx}^{11} \nabla_x \epsilon_{ec} + L_{xx}^{11} \nabla_y \epsilon - L_{xx}^{12} T_e^{-1} \nabla_x T_e \\
J_{qx} &= -L_{xx}^{21} \nabla_x \mu_{ec} + K_{xx}^{21} \nabla_y \epsilon - L_{xx}^{22} T_e^{-1} \nabla_x T_e \\
J_{qy} &= -K_{xx}^{21} \nabla_y \epsilon - L_{xx}^{21} \nabla_y \mu_{ec} - L_{xx}^{22} T_e^{-1} \nabla_y T_e
\end{align*}
\]

with \( \epsilon_{ec} \) being the electrochemical potential [10, 13].

To summarize: spatial distributions of the electron temperature are obtained by solving equations of electron number conservation and energy conservation as well as Poisson’s equation self consistently in QHS [14, 15]. We have observed that the deviation of the electron temperature shows spatially oscillating behavior which is closely related to the thermal flux in the \( y \) direction.

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Application of Orbital-Free Energy Functional to Quantum Dots
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Abstract—We calculate the total energy of a semiconductor quantum dot (QD) which is defined by metallic gates, etching and trench gates. In our calculation we used a recently developed energy functional called "orbital free functional energy (OFEF)". We have compared the Thomas Fermi and two dimensional-local density approximation (2D-LDA) calculations with OFEF for rectangular quantum slab (QS) and have found that the result is consistent with the local-density approximation yielding better agreement than the Thomas-Fermi approximation.

Two dimensional (2D) electronic systems have attracted vast interest since the beginning of the rapid developments of nanotechnology. Applications to 2D quantum dots (QD’s) and rectangular quantum slabs (QS’s) represent basic components of nanoelectronics. Density Functional Theory (DFT) with two dimensional-local density approximation (2D-LDA) is a standard method for the electronic structure calculation of the semiconductor QD’s. The exchange and the correlation functionals in many body systems are the most critical point of 2D-LDA with DFT. Therefore new investigations in both exchange [1] and correlations [2, 3] of 2D density functionals have been remarkable studies. Although LDA gives good results for many systems, total density is the sole input variable instead of electronic orbitals. The number of electrons treated numerically is limited since Kohn-Sham (KS) scheme in DFT requires the computation of single particle KS orbital for the kinetic energy [4].

However an alternative theory, called orbital free DFT [5, 6, 7] is more convenient than traditional DFT in this respect. This approach is more complicated in construction of an accurate energy functional especially for three dimensional (3D) systems. An important example of free orbital DFT is the Thomas-Fermi approximation (TFA) that has been analyzed in 2D and applied successfully in the electronic structure calculation [8].

The standard TF approximation for total energy is given by

$$E[\rho] = T_{TF}[\rho] + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r'} \frac{\rho(\mathbf{r}) \rho(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} + \int d\mathbf{r} \rho(\mathbf{r}) V_{ext}(\mathbf{r}).$$

Since the electron-electron interactions have been treated only classically, there is an important deficiency in Thomas-Fermi energy functional. Therefore in limited particle and low density regime, performance of this method is an open question because the lack of the quantum mechanical effects (exchange and correlation) [4].

In order to improve TF approximation, a nonempirical, orbital-free density functional for the total energy of interacting electrons is derived. The orbital free density functional for the total energy of interacting electrons in two dimensions is defined as [4],

$$E[\rho] = T_{TF}[\rho] + \frac{\pi}{2} \sqrt{\frac{N - 1}{2}} \int d\mathbf{r} \rho^{3/2}(\mathbf{r}) + \int d\mathbf{r} \rho(\mathbf{r}) V_{ext}(\mathbf{r}).$$

This functional is numerically very efficient due to its orbital free form and in the calculating the Hartree integral.

In our study, we have obtained the density of QD systems from 3D Poisson Equation. Then the obtained density is applied on QD which is defined with metallic gates, etching and trench gates, to calculate the energy of the system by using the orbital free functional developed recently [4].

According to our first results, this new functional works quite well in many electrons systems in the limit of low density. Our future aim is to apply this method to quantum point contacts and to investigate their transport properties.

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Magnetic resonance studies of colloidal wüstite/metal ferrite core/shell nanocrystals

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Abstract—We present the results of ferromagnetic magnetic resonance experiments on bimagnetic nanocubes and nanospheres, consisting of an antiferromagnetic (AFM) ferrous oxide core and a ferrimagnetic (FIM) Mn and Co ferrite shell. We determined the effective magnetic anisotropy up to 600 K and show that it exceeds that of the bulk material. We show also the effects of exchange coupling between the AFM core and the FIM shell and determine the unidirectional exchange field.

Nanometer sized metal ferrites are promising materials for magnetic storage devices as well as magnetic resonance imaging. In this work we study the magnetic properties of monodisperse, colloidal nanocrystals (NCs) with use of the magnetic resonance technique, which is a powerful tool to investigate not only single crystals but also ensembles of nanocrystals. In a randomly oriented system of non-interacting particles, however, instead of a narrow, angularly dependent Lorentzian resonance absorption line a non-uniformly broadened, isotropic line is observed, with a linewidth corresponding to $2H_A$ where $H_A$ is the internal anisotropy field of the nanocrystal. In addition, the resonance is shifted towards lower magnetic fields by the amount of $H_A$. In the NC system studied here, $H_A$ is a sum of the magneto-crystalline, shape-, surface-, interface-, and strain- related anisotropy fields.

The NCs investigated were obtained in a one pot reaction, (the details of the synthesis are given in [1]) and consist of an antiferromagnetic (AFM) ferrous oxide (wüstite, FeO) core and a ferrimagnetic (FIM) metal ferrite (MeFe$_2$O$_4$, Me=Mn, Co) shell. For the purpose of the experiments a thin layer of nanocrystals was deposited on silica glass. The imposed additional shape anisotropy, related to the dipole coupling between the NCs, allows us to measure simultaneously the anisotropy contained in the linewidth and the resonance field shift, as well as the magnetization of the layer. The magnetization, derived from the directly measured depolarization field, is automatically in units of magnetic moment per volume and does not depend on the number of NCs investigated. This is a great advantage over SQUID, where determination of volume or weight of multiphase systems is difficult.

We detect only the ferromagnetic resonance (FMR) mode related to the net magnetic moment of the FIM phase (FIM and AFM exchange resonances occur at frequencies exceeding that of the X-band spectrometer used). Typical results, obtained for 15-nm sized FeO/Mn Fe$_2$O$_4$ cubes, are shown in the figure. It can be seen that the magnetization and the FMR signal intensity increase with temperature up to the Neel transition at ~150 K (a), which is related to pinning of the spins near the FIM/AFM interface. The Neel temperature, however, is slightly lower than that of bulk FeO (198 K). In contrast, the internal effective anisotropy field turns out to be considerably higher than the magnetocrystalline anisotropy of bulk Mn ferrite (b), which shows the significant contribution of surface and interface anisotropies. Below 150 K effects of randomly oriented exchange anisotropies are visible. When the NCs are cooled through the Neel transition in an applied magnetic field, $H_0$, a shift of the resonance position is detected for the spectra recorded with $H$ parallel and antiparallel to $H_0$, as shown in the inset.

In summary, we studied bimagnetic wüstite/metal ferrite core/shell nanocubes and nanospheres with use of ferromagnetic resonance and determined the effective magnetic anisotropy as well as the exchange field. The research leading to these results has received funding from the European Community’s 7th Framework Programme ([FP7/2007-2013] under grant agreement n°215368, the Austrian Nanoinitiative (project NSI), and from ÖAD, GMe and FWF, all Vienna.

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Double Heterostructure Selection and the Application in Quantum Conductors for the Investigation of the Development of Quantum Dot Lasers and their Advantages

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Abstract-In this work, by using program of Gain for choosing double hetero-structure and program of Waveguide that calculate the needed parameters for designing Quantum Lasers; choosing of double hetero-structure and the application of Quantum Conductures are realised with seven materials and its priority of Quantum dot lasers on other Quantum Lasers are observed.

By using Gain computer program; for each material systems, input parameters, output parameters, band calculations, choosing of materials, conduction band, valance band and weak hole bands for energy values, confinement factors, efficiency culations, threshold current density $J_{th}$ and calculations for slope of efficiency are able to carried out [1-6].

The outputs handed from calculations and suitable number of Quantum wells, slope of efficiency (%), threshold current density $J_{th}$ (A/cm²), threshold current $I_{th}$ (mA) and band offset values for each materials are handed one by one and it is ensured the determination of pick values of efficiency of materials.

Investigation of Thickness Dependent Magnetic Anisotropies in FeCo Alloys

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Abstract. The magnetic anisotropies of FeCo thin film structures were studied with ferromagnetic resonance technique as a function of film thickness. We investigated the change of magnetic properties with increasing thickness of the epitaxial FeCo thin films as well as reported the results of ferromagnetic resonance (FMR) measurement of these films grown on the MgO single-crystal substrate.

With the discovery of perpendicular magnetic anisotropy in rare earth-transition metal (RE-TM) alloys in the 1970s, research and development for high performance magnetic materials have mainly concentrated on rare earth and transition metal element based compounds. Experimentally, the phenomenon of the transition from out-of-plane to in-plane magnetization that is called spin reorientation transition (SRT) has been investigated in several ultra-thin films (such as permalloy, Fe, Co thin films) with changing film thickness. The technique of ferromagnetic resonance (FMR) has made a lot of contribution to the understanding of the magnetic behavior in ultra-thin films [1,2].

Recently, the structural and magnetic properties of FeCo thin films, grown on MgO single-crystalline substrates, have been studied [3]. They investigated the dependence of magnetic properties on the direction of MgO substrate with a fixed thickness of FeCo about 20 nm. However, there is no report on detailed magnetic anisotropies of this system up to now.

Therefore, in this study, we have investigated the magnetic anisotropies of FeCo alloy thin films at room temperature by using FMR technique as a function of FeCo thickness.

The samples were grown on MgO (100) substrates by using ion beam sputtering technique. Before sputtering, a base pressure of ~10⁻⁹ mbar was provided and the substrate was etched for 20 seconds with Ar. Then the FeCo layer was grown on the top of the substrate with a pressure of 4.4×10⁻⁴ mbar. Finally, Al₂O₃ layer was deposited with a pressure of ~1×10⁻³ mbar. The thickness of Fe layer was varied between 0.5nm and 30nm and the thickness of Al₂O₃ was chosen as 20nm. The thickness of both layers has been checked by x-ray reflectivity measurements. The structural properties of the samples were characterized by small and high angle x-ray diffraction (XRD). The magnetic properties are investigated by using vibrating sample magnetometry (VSM) and ferromagnetic resonance (FMR) techniques in a temperature 300 °K.

FMR measurements were taken for both in-plane and out-of-plane geometries. Figure shows resonance fields as a function of in-plane angle for the sample with a FeCo thickness of 1nm. It is clear from the figure that the FeCo layer has a cubic symmetry with an easy axis along [010] direction of MgO substrate. It is also important to note that the easy axis is rotated by 45 degrees for thicker FeCo films and oriented along [011] direction of MgO. The magnetic parameters, such as magnetization, magnetic anisotropy and magneto dynamics have been deduced as a function of thickness by fitting the experimental data.

In summary, the alternation of magnetic anisotropies depending on thickness of the epitaxial FeCo thin films, which have been grown on the MgO single-crystalline substrates by using ion beam sputtering technique, are studied and ferromagnetic resonance (FMR) investigations of magnetocrystalline anisotropy in FeCo films are presented.

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X-ray Photoelectron Spectroscopic Investigation of Photoactive Materials under both Electrical and Optical Stimuli

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Abstract — Various p- and n-type HF-cleaned Si without and with thermally grown oxide and ultra-thin spin-coated PMMA layers are investigated under electrical and optical stimuli by using XPS.

The electrical and optical properties of high-end technologic devices such as photovoltaics, photonics, optoelectronics, sensors, etc, become more crucial due to required a dramatic reduction on the size of such devices to reach a faster processing power with lower energy consumption. Moreover, the thickness of the semiconductor layer in device has already been downsized to a few tens of atomic layers, so that differentiated properties at the interfaces between different types of junctions have become more pronounced. In this work we deal with a similar problem for trying to distinguish between surface photovoltage and photoinduced conductivity developed in less than ca. 5 nm oxide layer and/or at interface between the oxide layer and its Si substrate.

We have recently developed a technique for recording the changes in the positions of the XPS peaks in response to different forms of electrical stimuli for probing dynamics of charging/discharging processes of thin dielectric films, which we have named as Dynamic XPS. [1-3] Modulation of the electrical signals in the forms of square, sinusoidal and triangular waves at different frequencies enables us to extract some dielectric properties such as effective resistance, and capacitance values in a chemically resolved fashion. This makes XPS more powerful technique for characterizing today’s demanded nano or optoelectronic devices. [1-6]

![Figure 1. Grounded XPS spectrum of (a) Au4f peak of pure Au metal, Si2p peaks of p-type Si (b), n-type Si (c), and n-type SiO2/Si samples (d). While black spectra are recorded without illumination or labeled as “Laser OFF” mode, red spectra are recorded under a 405nm laser (180 mW) illumination or labeled as “Laser ON” mode.](image)

Earlier work, we had also introduced photoillumination as an additional form of the stimuli and investigated the combined optical + electrical responses of semiconductive n- and p-type Si with thermally grown ca. 5 nm thermal oxide layer, as well as CdS and CdSe films. [6] The present contribution is a continuation of our earlier work, where we try to distinguish between two important photo processes.

As shown in Figure 1a, grounded spectra of Au4f peak of Au metal has no measurable shift upon illumination with a 405 nm laser (180 mW, and in C.W. mode). The energy levels of Si, being a semiconductor, have various degrees of band-bending, which depends on both doping type and doping levels. [7] The photoillumination affects these band-bending so that the Si2p peaks of freshly HF cleaned p- and n-type Si samples exhibit binding energy shifts as much as -0.19 eV and +0.11 eV, as shown in Figure 1b, c, respectively. As illustrated in Figure 1d, Si2p peaks of oxide layer (labeled as SiO2 on corresponding figure) and substrate (labeled as Si0 on corresponding figure) are separated from each other due to chemical as well as charging shifts. Upon photoillumination, the behavior of the Si2p peaks of SiO2/Si sample becomes more complicated due to additional effects, like as surface photovoltage, charging, IR drop or photoconductivity effect, contact potentials etc. At this point, we turn to our Dynamic XPS measurements to help distinguish among these complicated behaviors, using the frequency dependence as an additional tool. For a slightly different application of our technique, we have also investigated samples coated with thin PMMA layers to verify that the photoinduced shifts in the substrate Si transpires faithfully to the organic dielectric layer on top, where similar shifts are measured in the C1s and O1s peaks.

In summary, by subjecting samples to square wave pulses at ranges 10^{-3} - 10^{5} Hz, while recording XPS data, electrical information with chemical specificity is extracted. Moreover, the changes in the electronic structures in various Si samples upon photoillumination are probed by XPS in a dynamic (time-dependent) fashion.

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Screening theory of Laughlin quasi-particle interferometers defined at quantum-dots

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Abstract—The modeling of the quantum Hall based quasi-particle interferometers are studied at the quantum dots. The spatial distribution of edge states (ESs) are investigated at filling factor \( \nu = 1/3 \). The electron and potential distributions are obtained by a self-consistent calculation solving Poisson equation within Thomas-Fermi approximation. The ESs are considered as monochromatic beams that carry quasi-particles without scattering. The interference conditions at the Laughlin quasi-particle interferometers are investigated at the gate defined and etched defined samples.

The discovery of the integer [1] and fractional [2] quantum Hall effects make contribution to the understanding of two dimensional systems (2DES) and especially the transport phenomena in the 2DES. The (ESs) which are responsible for current transport are investigated at filling factor value \( \nu = 1/3 \). \( \nu = 1/3 \) state represents the fractional quantum Hall filling and described as Laughlin many electron wave functions for primary fillings \( f = 1/(2j+1) \), \( j \) is an integer [3, 4].

There are two fundamental particles in three dimensions; Fermions and Bosons, which obey Fermi-Dirac and Bose-Einstein statistics respectively. However, two dimensional space allows a new kind of particles, named anyons, which are described by fractional statistics. An anyon may be described flux-carrying boson (or a fermion) [5]. In the case of a two dimensional electron gas subject to strong perpendicular magnetic field, these anyonic particles are called Laughlin quasi-particles which obey fractional statistics and have a fractional electric charge.

The "quantum Hall" based interferometers, has revealed a novel technique to exploit the properties of the quasi-particles, which utilizes the so called ‘edge states’ (ES) in the extreme quantum limit. The ESs are considered as monochromatic beams that carry quasi-particles without scattering. Therefore, the overall interference pattern strongly depends on the spatial distribution of these states. A key element of these experiments is the quantum point contacts (QPCs) and the electrostatic potential (ESP) profile near these QPCs together with the quantum dot. Electrostatic plays an important role in the rearrangement of the ES. Moreover, the interaction of the electrons or quasi-particles was proposed to be a possible origin of the dephasing and a better understanding requires a self-consistent (SC) calculation of the ESP. Here we present an implementation of the SC-Thomas-Fermi-Poisson approach to an homogeneous two dimensional electron system, where interferometer is defined by a quantum dot, in order to obtain the ESP and electron distribution at the mentioned interferometers as in the paper [6].

In this work we first obtained the electron and potential densities by solving Poisson equation within Thomas-Fermi approximation in 3D self-consistently. Then the spatial distribution of the incompressible strips, i.e. the edge-states, are investigated at filling factor \( \nu = 1/3 \) in the presence of strong, perpendicular magnetic field. We present a microscopic picture of the fractional quantum Hall effect, based on a phenomenological model. The partially occupied lowest Landau level is assumed to form an energy gap due to strong correlations, hence becomes incompressible. We adopt the findings of Jain et al [7] in our calculation scheme by simply including this gap to our energy spectrum and obtain the incompressible strips of \( \nu = 1/3 \). The interference conditions are investigated as a function of the gate voltage and steepness of the confinement potential, together with the strength of the applied magnetic field.

Figure 1: The spatial distribution of electron density for a quantum dot sample. The electron density changes are shown in the color scale and density is considered for a very smoothly varying potential, i.e. a etched defined sample.

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Inhomogeneous Barrier Height of FeCrNiC/n-GaAs Structures Caused by Lateral Nanoscale Patches

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Abstract—The effective barrier heights (BHs) and ideality factors of identically fabricated FeCrNiC/n-GaAs alloy Schottky Barrier Diodes (SBDs) (23 dots) have been calculated from their experimental forward bias current-voltage (I-V) characteristics. A statistical study related to the experimental BHs and ideality factors of the diodes has been made. The mean value of BH and n of the FeCrNiC/n-GaAs SBDs were found to be 0.798±0.005 eV and 1.026±0.014, respectively by using Gaussian distribution function. Our results clearly demonstrated that electron transport at the metal-semiconductor (MS) interface is significantly affected by nanoscale spatial variations.

Understanding the mechanisms giving rise to the apparent Schottky barrier height (SBH) of metal-semiconductor (MS) contacts is still an unsolved problem despite decades of intensive investigations [1,2]. The electronic properties of such a contact are characterized by its barrier height (BH) and ideality factor (n). The BH is likely to be a function of the interface atomic structure, and the atomic inhomogeneities at MS interface which are caused by grain boundaries, multiple phases, facets, defects, a mixture of different phases etc. [3,4].

The interpretation of current-voltage (I-V) characteristics of real MS contacts has implicitly assumed uniformity of SBH at MS interface. Recent experimental investigations, however, reveal non-uniformities of the local SBH on a nanometer scale at MS interface. Recent experimental investigations, however, reveal non-uniformities of the local SBH on a nanometer scale [5,6]. In a recent model of potential pinch-off effect in MS contacts, Tung and co-workers has modeled the influence of mesoscopic SBH inhomogeneities on macroscopic properties like the integral SBH [7,8]. They have patterned imperfect Schottky contacts by assuming lateral nanoscale variations of the BH, i.e patchy of interfaces, and speculated that the BHs become smaller as the ideality factors increase. Moreover, it has been pointed out that the BH inhomogeneity model may also be explained by the linear relationship between effective BHs and ideality factors that is often observed on sets of the identically prepared diodes [7-11].

In this work, we aim to determine laterally homogeneous BH of the alloy FeCrNiC/n-GaAs SBDs by assistance of the linear relationship between the effective BHs and ideality factors which is experimentally and theoretically confirmed. The effective BHs and ideality factors evaluated from the experimental forward bias I-V characteristics of these diodes have been calculated using the thermionic emission (TE) theory. The lateral homogeneous BH value for the device was obtained from the linear relationship between effective BHs (φ_eff.) and ideality factors, n. The statistical distribution of the characteristics of the devices was made by means of the Gaussian function. Inhomogeneities of some Schottky contacts and their statistical description by a Gaussian distribution is already documented in the literature, but such information for FeCrNiC/n-GaAs alloy SBDs has not been, to our knowledge, reported in the literature.

The samples have been prepared using cleaned and polished n-GaAs (as received from the manufactured) with (100) orientation and 8x10^{15} cm^{-2} carrier concentration. Before making contacts, the n-GaAs substrate were dipped in 5H_{2}SO_{4}+H_{2}O_{2}+H_{2}O solution for 1.0 min to remove surface damage layer and undesirable impurities and then in H_{2}O+HCl solution and then followed by a rinse in de-ionized water of 18 MΩ. The substrate dried with high-purity nitrogen and inserted into the deposition chamber immediately after the etching process. Ohmic contact on the n-type GaAs substrate was fabricated by using an Au/AuGe system. Because the annealing procedure at high temperatures for the ohmic contact preparation may destroy the FeCrNiC/GaAs Schottky barrier, the Au/AuGe (88-12 %) contact is prepared first. AuGe and Au was successively evaporated on the back of the wafer in a vacuum-coating unit of 4x10^{-6} Torr. Then low resistance ohmic contacts were formed by thermal annealing at 450 °C for 3 min in flowing N_{2} in a quartz tube furnace. The alloy Schottky contacts were formed on the front face of the n-GaAs substrate as dots with diameter of about 1.0 mm by successively evaporation of FeCrNiC (71:18:8:0.2) and Au. The reason why the gold film evaporation on the FeCrNiC contacts preventing the alloy layer from probable oxidation during post-annealing process. I-V measurements were carried out by using Keithley 487 Picoammeter/Voltage source at the room temperature and in dark.

The BHs obtained from the I-V characteristics varied from 0.783 to 0.805 eV, the ideality factors varied from 1.000 to 1.056. The results showed that both parameters of SBDs differ from one diode to another even if they are identically prepared. The experimental BH and ideality factor distributions obtained from the I-V characteristics are fitted by a Gaussian function, and their mean values were found to be 0.798±0.005 eV and 1.026±0.014, respectively. The lateral homogeneous SBH (φ_{hom}) value of 0.830 eV for the FeCrNiC/n-GaAs alloy contacts has been obtained from the φ_eff. vs n plot by using n_{inf}=1.01 and Δφ_{inf}=29.1 meV. It has also been seen that the value of φ_{hom}=0.830 eV for the FeCrNiC/n-GaAs contacts is lower than those of the Fe/n-GaAs (0.942 eV) ferromagnetic contacts [12].

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The Effect of Annealing Temperature on Magnetic Properties of Cu$_2$MnAl Heusler Films

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Abstract - Cu$_2$MnAl Heusler films were prepared by using ion beam sputtering technique on MgO substrates. The films were post-annealed at varying temperatures in order to study the effect of annealing on magnetic properties and crystal structure. The structural and magnetic properties of Cu$_2$MnAl films have been investigated by using vibrating sample magnetometry (VSM) and ferromagnetic resonance (FMR) techniques. Experimental results indicate that the crystal structure and magnetic properties of the films strongly depend on annealing.

Since suggested in 1983 by de Groot [1], the half-metallic ferromagnets have become one of the most promising materials for applications in tunneling magnetoresistance (TMR), giant magnetoresistance (GMR) and magnetic random access memory (MRAM) devices. To obtain high magnetoresistance, spin polarization of ferromagnet should be 100%. In the half metallic ferromagnets, while one of the two spin channels is metallic, the other is insulating or semiconducting. Therefore, they exhibit 100% spin polarization at Fermi level. Among the Heusler alloy families, the copper series and mainly Cu$_2$MnAl are the mostly studied ones [2-4].

![Figure 1](image_url)

Figure 1. Out of plane angular variation of resonance field of Cu$_2$MnAl films for varying annealing temperatures.

In this work, 30 nm thick Cu$_2$MnAl thin films were prepared by using ion beam sputtering technique on MgO and Si substrates. The films were also post-annealed for 30 minutes at 200 °C, 300 °C, 400°C and 500 °C, respectively, in order to investigate the annealing effects on magnetic properties. The films were finally covered a 20 nm thick Al$_2$O$_3$ layer in order to prevent the Heusler films from oxidation. The structural properties of the samples were characterized by small and high angle x-ray diffraction (XRD). The effect of substrate and annealing temperature on magnetic properties is investigated by using vibrating sample magnetometry (VSM) and ferromagnetic resonance (FMR) techniques in a temperature range of 10–300 °K. FMR technique is powerful and useful in order to determine magnetic properties of the samples which are magnetic anisotropy and damping constants. FMR measurements were carried out in two different geometries: in plane geometry (both dc field and magnetic field of microwave lie in the film plane) and out of plane geometry (dc field was rotated from the sample plane toward the film normal). The experimental data have been simulated by a self-written computer. The samples show ferromagnetic behavior at room temperature and 10K. As a result of post-annealing, while the magnetization of the film with T$_a$=200 °C increased, the coercive field of this film decreased. Room temperature out of plane FMR measurements shows that resonance field of the film with T$_a$=200 °C is the highest in all samples while film normal is parallel to external dc field, that of this film is the lowest in all samples while the film normal is perpendicular to external dc field (Figure). This shows that effective magnetization of the film with T$_a$=200 °C is the highest in all samples. Combination of the structural and magnetic data exhibit that the crystal quality of the film with T$_a$=200 °C is the best.

In summary, we investigated the structural and magnetic properties of Cu$_2$MnAl heusler alloys for varying annealing temperatures. The results indicate that the annealing effect increases the structural quality and magnetism in the Heusler until certain temperature and then, both the crystal quality and magnetism goes down.

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Abstract-In this complex picture of spin dependent tunneling (SDT), role of defect states inside the barrier, the surface effects have not been understood yet. Our work focuses on room temperature measurements of 1/f resistance noise in magnetic tunnel junctions (MTJs) with MgO barrier. 1/f resistance noise has been measured on MTJs with TMRs ranging from 50%-230% at room temperature. The origin of electronic noise is attributed to charge traps inside the barrier. Temperature dependence of 1/f noise indicates that noise consists of a broad distribution of these thermally activated processes. Normalized 1/f noise power that is the Hooge-like parameter, $a$, is on the order of $10^{-7}$ to $10^{-5}$ mm$^{-2}$ and shows bias dependent anomalies at room temperature and low temperature. An investigation of the bias dependence indicates similarities with the bias dependence of the transport characteristics. A scaling between ln$\sigma$ and the differential resistance is discovered which may mean that the mechanisms that drive the differential resistance are also responsible for the noise bias dependence. Origin of such a scaling has not been fully understood. A decreased noise power, $a$, for increased biases may indicate transport of electrons via hopping-conduction channels.

The bias dependence of resistance is observed to cause a bias dependences in magnetic 1/f noise, as well.

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Investigation of Correlation Between Matrix-Texture, Intrinsic Residual Stress and Magnetoresistance Effect in Co-Sputter Deposited Co$_{25}$Ag$_{75}$ Nano Granular Films

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Abstract—Ag$_{75}$Co$_{25}$ granular films with different film thickness ranging between 8.8 and 188.5 nm were deposited by DC magnetron co-sputtering on Si(100) substrates with a 100nm SiO$_2$-buffer layer at room temperature. The evolution of residual stress as function of film thickness and investigation of correlation between matrix-texture and magnetoresistance (MR) effect in Ag$_{75}$Co$_{25}$ granular films were studied using grazing incidence X-ray diffraction (GIXD) technique in Bragg-Brentano Geometry (BBG). Besides, the resulting thickness dependence of phase separation was also discussed in relation to the residual stress state of the films. Furthermore, in the present study, a correlation between matrix-texture and MR effect has been found for the first time. The electrical resistivity of the films as a function of film thickness was investigated by four-point probe (FPP) technique. The results have revealed that in Ag$_{75}$Co$_{25}$ films the metastable phase appears below and at the film thickness of 31.3 nm. The residual stress measurements have shown that the film is under the compressive stress condition at the metastable phase state, while the film is under the tensile stress condition at the phase separation state. We have observed that the electrical resistivity decreases with increasing of film thickness and almost reaches toward the resistivity of pure silver at 188.5 nm film thickness. The Ag$_{75}$Co$_{25}$ texture effect occurs over the film thickness of 31.3 nm and increases with increasing film thickness. In addition to that the Ag matrix-texture effect leads to an enhancement of MR effect.

The residual stress strongly influences mechanical and other physical properties because of the deformation of the crystal structure [1]. According to our knowledge, there is no report on the dependence of film thickness on the stress properties and a correlation between matrix-texture and MR effect for the Ag$_{75}$Co$_{25}$ granular films produced by co-sputtering technique. Therefore, the investigation of residual stress state and correlation between matrix-texture and MR has great importance.

Figure 1 indicates the correlation between lattice spacing $d_{Ag(111)}$ and film thickness. For an average $\Delta r = 0.05$ mm error, the lattice spacing that smaller than bulk value of pure silver ($d_{Ag(111)}=0.2359$ nm) indicates that Co and Ag grains grow in different phases. The lattice spacing bigger than bulk value of pure silver shows that Co grains sit in the Ag matrix. These results indicate that the immiscible Ag and Co elements form a metastable state below and at the film thickness of 31.3 nm.

The residual stress evolution is shown in Fig. 2 as a function of film thickness for different $\Delta r$ values at constant incidence angle (1°). We found that the increasing of film thickness results in the change in the nature of stress. The film is under the compressive stress until the film thickness of 31.3 nm and is under the tensile stress condition above the film thickness of 31.3 nm for $\Delta r = 0.05$ mm error.

The resistivity measurements indicate that the electrical resistivity of films decreases with increasing film thickness and almost reaches at 188.5 nm film thickness toward the resistivity of pure silver as shown in Fig. 3.

The texture effect appears above the film thickness of 31.3 nm and increases with increasing film thickness as shown in Fig. 4. In the previous study, it has been reported that when the film thickness changes between 31.3 and 53.7 nm, the enhancement of MR is more rapidly than the other ranges [2]. This situation can be attributed Ag$_{75}(111)$ matrix-texture effect that starts above the film thickness of 31.3 nm.

The residual stress strongly influences mechanical and other physical properties because of the deformation of the crystal structure [1]. According to our knowledge, there is no report on the dependence of film thickness on the stress properties and a correlation between matrix-texture and MR effect for the Ag$_{75}$Co$_{25}$ granular films produced by co-sputtering technique. Therefore, the investigation of residual stress state and correlation between matrix-texture and MR has great importance.

Figure 3. The correlation between electrical resistivity and film thickness.

Figure 4. Ag$_{75}(111)$ matrix-texture effect as a function of thickness a) 17.5 nm, b) 31.3 nm, c) 53.9 nm, d) 116.9 nm, e) 188.5 nm.

In summary, the compressive stress and higher resistivity at small thickness of film can be attributed to forming of metastable phase state. That result indicates how the stress can change from compressive to tensile as a function of film thickness even though the deposition conditions have not been changed. In comparison to previous investigation, texture effect leads to an enhancement of MR effect.

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Characterization of Microstructure and Evolution of Intrinsic Residual Stress in Co-Sputter Deposited Ag$_{75}$Co$_{25}$ Granular Thin Films

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Abstract—Ag$_{75}$Co$_{25}$ granular film with film thickness of 188.5 nm was deposited by DC magnetron co-sputtering on Si substrates with a 100 nm SiO$_2$-buffer layer at room temperature. The characterization of microstructure and the evolution of residual stress as a function of penetration depth in Ag$_{75}$Co$_{25}$ granular film were studied using grazing incidence x-ray diffraction (GIXD) technique in Bragg-Brentano Geometry (BBG). We found that the increasing of penetration depth results in the change in the nature of residual stress. The residual compressive stress changes into residual tensile stress with increasing penetration depth. Furthermore, the penetration depth of X-ray beam found to be dependent on critical reflection angle. Besides, the refraction effects were studied as a function of incidence angle. The refraction effects reach its maximum at the critical reflection angle for the Ag$_{75}$Co$_{25}$ granular thin film.

In thin films and multilayers, the quantification of stress has been effectively pursued due to the fact that this parameter affects required properties of thin film structures [1]. The intrinsic residual stresses such as compressive and tensile types are generated during the deposition process of films on the substrate [2, 3]. Co and Ag are immiscible and according to our knowledge, there is no report on the dependence of penetration depth on the stress properties for the Ag$_{75}$Co$_{25}$ granular films produced by co-sputtering technique. Therefore, the investigation of residual stress and microstructural characterization appears to be of tremendous importance.

In Figure 1, the correlation between lattice spacing and penetration depth is shown for different $\Delta r$ deviation values in Ag$_{75}$Co$_{25}$ (d=188.5 nm). We observed that the lattice spacing decreases with increasing penetration depth. But this diminish is more rapidly between penetration depth of 32.4 and 42.4 nm (or between incidence angle of 0.8 and 1˚). This correlation is the same for all $\Delta r$ values.

![Figure 1. Evolution of lattice spacing as a function of penetration depth.](image1)

The evolution of penetration depth and refraction effects as a function of incidence angle are shown in Figure 2.

![Figure 2. Left—Evolution of penetration depth, right—refraction effects as a function of incidence angle.](image2)

The penetration depth of X-ray beam decreases sharply at angles that close to critical reflection angle. On the other hand, we observed that the refraction effects reach its maximum at the critical angle and decrease with increasing incidence angle above the critical reflection angle.

The residual stress evolution is shown in Fig. 3 as a function of penetration depth for different $\Delta r$ values. We have observed from the stress measurement that the film is under the compressive stress until the penetration depth of 32.4 nm and is under the tensile stress condition at and above the penetration depth of 42.4 nm for $\Delta r = 0.05$ mm error.

![Figure 3. Evolution of the residual stress as a function of penetration depth for different deviation values.](image3)

In summary, the evolution of residual stress as a function of penetration depth and microstructural characterization have been studied. The residual stress in the film at and below the penetration depth of 32.4 nm (or below and at the incidence angle of 0.8˚) is compressive, while the residual stress in the film at and over the penetration depth of 42.4 nm (or at and over the incidence angle of 1˚) is tensile. Thus, in opposite growth direction, the initial tensile state is transformed to compressive over the thickness of 156.1 nm. That result shows how the stress can changes from compressive to tensile as a function of film thickness even though the deposition conditions have not been changed.

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Comparison of Magnetic Behaviour of Cobalt, Cobalt-ferrite and Iron Oxide Nanoparticles With Different Surface Coatings

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Abstract- Different types of magnetic nanoparticles (MNPs) were prepared by wet chemistry. The particles were coated with silica and polymetacrylic acid (PMAA). The particles were characterized by Field Emission Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX) and vibrating sample magnetometry (VSM).

Magnetic nanoparticles are used in a variety of biochemical and biomedicine applications including cell identification and separation [1], Magnetic Resonance Imaging (MRI) contrast factor [2], enzyme and protein separation [3], drug delivery to the target cell [4], magnetic iron fluid hyperthermia [5], biomagnetically directed radiotherapy [6], retina separation treatment [7] and cancer cell imaging [8]. Most of these applications require that these magnetic nanoparticles are chemically stable, homogeneous in size, well disperse in liquid medium [9], biocompatible and nontoxic [10].

For application of magnetic nanoparticles, the nanoparticles have to be coated with amorphous silica or polymer for enhanced surface reactivity. Due to their nontoxic nature, optical transparency, chemical inertness, thermal stability, high biocompatibility, silica and polymer surfaces have been mostly preferred [11]. Coating effect on magnetization is also investigated that magnetic behavior has changed when the particles modified with polymer or silica [12].

Aim of this study is to compare magnetic behavior of three magnetic nanoparticles and observe the effect of coating on magnetization of the particles.

In this work, cobalt (Co), cobalt-ferrite (CoFe2O4) and iron oxide (Fe3O4) nanoparticles were prepared by wet chemistry techniques. Silica coating of Co, CoFe2O4, Fe3O4 were performed according to Stöber method, in which coating was done in water/ethanolic solution with tetraethyl orthosilicate (TEOS). Polymer coating for CoFe2O4 was done at the stage of coprecipitation. Amine modification of silica surface was performed by adding 3-aminopropyl-triethoxysilane (APTES) and ammonia. Characterization of the core-shell nanoparticles was done by FESEM, EDX and VSM.

Figure 1. FESEM images of synthesized magnetic particles; Co Nps; A, CoFe2O4; B, Fe3O4; C.

On going work is characterization of the three samples with VSM, Infrared spectrometry and compare their magnetic behavior.

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AFM and STM Studies, Magnetic and Structural Properties of NiFeCu/Cu Thin Films Produced by Electrodeposition Technique

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Abstract—NiFeCu/Cu films have been grown on mechanically polished Ti substrates under galvanostatic conditions at different non-magnetic layer thicknesses such as 0.7 and 1.1 nm. However, the thickness of the magnetic layer was designed as 2.7 nm. Structural properties were studied by using XRD (X-ray Diffraction). XRD measurements have indicated that preferred orientations and structures of the films are in the [111] direction and FCC, respectively. Magnetoresistance (MR) measurements were carried out by using four point probe in the Van der Pauw geometry at room temperature. Magnetoresistance curves exhibited non-saturating behaviour due to SPM (Superparamagnetic) contribution. Magnetization measurements of the films were carried out using vibrating sample magnetometer (VSM) at the room temperature. The hysteresis loops have shown soft magnetic feature with low coercivity ($H_{c} = 1.09$ Oe). Surface morphological structure of the film was investigated by AFM (Atomic Force Microscopy) and STM (Scanning Tunnelling Microscopy). We have observed granular growth from the AFM and STM images. AFM image has indicated that the film with non-magnetic layer thickness of 1.1 nm has main grains of various sizes on the surface. Secondary grains on the main grains were observed from the AFM image. The main grain sizes are around 3μm and secondary grain sizes vary between 40 and 250 nm.

NiFe/Cu system has attracted substantial attention both technologically and scientifically due to their low coercive field [1]. An exchange reaction occurs inevitably during the galvanostatic deposition of more nobel non-magnetic layer, the less nobel magnetic layer dissolution during the deposition of the more nobel non-magnetic layer leads to the formation of SPM (superparamagnetic) regions [2]. Especially magnetic properties of electrodeposited films are affected by the presence of SPM regions. Therefore, the investigation of structural and magnetic properties, and surface morphological structure of electrodeposited films has great importance.

We have observed granular growth for present NiFeCu/Cu film from the AFM and STM images as shown in Figure 1. We found that root-mean square (RMS) roughness of the surface larger than nominal thickness of layers. Consequently, we concluded that the film has alloy structure instead of layered multilayer structure.

![Figure 1. Left- AFM image, right- STM image of the film.](image)

The preferred crystallographic orientation of the films are in the [111] direction. The structures of the films are FCC as shown in Fig. 2. Satellite peaks have not been observed from the XRD pattern. Therefore, we have concluded that our films have granular alloy structure instead of layered multilayer structure. This result is in accordance with the result obtained by AFM.

![Figure 2. The XRD pattern of electrodeposited NiFeCu/Cu films.](image)

The coercivity of the film is rather low, showing that the film is soft ferromagnetic ($H_{c} = 1.12$ Oe) as shown in Figure 3. The presence of low hysteresis indicates the presence of larger ferromagnetic particles in our sample.

We have observed that the MR characteristics change from an AMR (anisotropic magnetoresistance) behaviour to a GMR behaviour with increasing thickness of non-magnetic Cu layer as shown in Figure 4. The present magnetoresistance curves of film exhibit a non-saturating behaviour. This result is shown that the existence of smaller SPM particles in our sample.

In summary, the secondary grains that have been observed from the AFM image are possibly SPM grains. The sizes of our superparamagnetic grains are in the range of 40-250 nm.

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Magnetic Properties of Fe$^{+3}$ Implanted Nanoparticles into Single Crystal Yttria-Stabilized Zirconia(100) (YSZ)

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Abstract—Fe nanoparticles were implanted into YSZ single crystalline substrate with implant energy of 45 keV, a fluence of 5.0 x 10$^{17}$ ions/cm$^2$. We investigated the magnetic properties of the sample by using both vibrating sample magnetometer (VSM) and ferromagnetic resonance (FMR) techniques.

The fabrication and analysis of Fe nanoparticles are attractive research topic in new magnetism area [1]. These kind of magnetic Fe nanoparticles have a wide range of application such as data storage [2], biosensors [3], drug, and gene delivery [3]. To obtain the nanoparticles the ion implantation technique is one of the powerful tools. During the last a few years, a wide variety of magnetic alloys and nanocomposites have been fabricated using this technique.

Fe ions have been implanted into the near-surface region of single crystal yttria-stabilized zirconia (YSZ) to form embedded Fe nanoparticles with implant energy of 45 keV, a fluence of 5.0 x 10$^{17}$ ions/cm$^2$. FMR technique were exploited to determine magnetic parameters of the films in the temperature range of 10–300 K. Magnetization measurements were carried out at ±1T external magnetic field region at various orientations of the applied field.

As seen as from figure, there is a major distinction between $H||n$ (hard direction) and $H\perp n$ (easy direction) where n is the normal of film surface. A unidirectional (ex-change) anisotropy field was investigated as evidence from a shift of the resonance field for the r-FC case relative to that of the n-FC case at lower temperature. Using a field-induced unidirectional exchange and bulk anisotropy, with the usual magneto-crystalline cubic anisotropy energy, we have simulated both the experimental spectra and angular dependence of resonance field to deduce anisotropy and other magnetic parameters as a function of temperature.

In conclusion, the results of FMR and magnetization measurements showed us the interaction between the particles related to magnetostatic interactions. Magnetostatic interactions among nanoparticles play a significant role during the determination of the static and dynamic properties of the Fe nanoparticles. This work was partially supported by DPT (State Planning Organization of Turkey) through the project No 2009K120730, DFG through SFB 491 and BAPKO project of Marmara University (FEN-KPS-100105-0073).

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Investigation of Magnetic Properties of Fe$^{3+}$ Implanted into SiO$_2$/Si(100)

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Abstract—Fe nanoparticles were implanted into SiO$_2$/Si (100) single crystalline substrate with implant energy of 45 keV, a fluence of $5.0 \times 10^{17}$ ions/cm$^2$. We have investigated the magnetic properties of the Fe$^{3+}$ implanted into SiO$_2$/Si(100) by using both vibrating sample magnetometer (VSM) and ferromagnetic resonance (FMR) techniques.

The production and investigation of Fe nanoparticles are an attractive research topic in a field of magnetism [1]. These kind of Fe magnetic nanoparticles have a wide range of application such as data storage [2], biosensors [3], drug and gene delivery [3]. To obtain the nanoparticles the Ion implantation technique is one of the powerful tools.

Fe ions have been implanted into the near-surface region of SiO$_2$ in single crystal Si(100) to form embedded Fe nanoparticles with an implant energy of 45 keV, a fluence of $5.0 \times 10^{17}$ ions/cm$^2$. As a result, Fe nanoparticles were synthesized inside SiO$_2$. FMR technique were exploited to determine magnetic parameters of the films in the temperature range of 10–300 K. Magnetization measurements were carried out at ±1T external magnetic field region at various orientations of the applied field.

![Figure 1](image.png)

Figure 1. Out of plane resonance field vs. angle of the Fe$^{3+}$ implanted into SiO$_2$/Si(100).

Strongly anisotropic ferromagnetic resonance (FMR) signals have been observed for the Fe$^{3+}$ implanted into SiO$_2$/Si(100). To exhibit the strong temperature dependence both resonance field and line shape in ESR spectra between 4 and 300K were obtained.

The ESR spectra of Fe-doped SiO$_2$ at low temperature were seen to consist of overlapping low-energy spin wave resonance (SWR) modes excited across opposite surfaces of the film.

The SWR data were analyzed by using a magnetic energy density including usual Zeeman and exchange terms contained both in bulk and surface anisotropy energies. The magnetic parameters for Fe-doped SiO$_2$, such as magnetization, exchange stiffness, relaxation and exchange anisotropy energy, have been deduced as a function of temperature by fitting the simulated spectra to the experimental ones. The theoretical analysis of FMR data has revealed the magnetic anisotropy energy. This work was partially supported by DPT (State Planning Organization of Turkey) through the project No 2009K120730, DFG through SFB 491 and BAPKO project of Marmara University (FEN-KPS-100105-0073).

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Chitosan Coated Magnetic Nanoparticles for Adsorption of Laccase

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Abstract- In the current study, magnetite nanoparticles were functionalized by chitosan using reversed-phase suspension method and the structural, magnetic properties were characterized by FT-IR, XRD, TEM, VSM and EPR. The immobilization of laccase enzyme on chitosan coated magnetic nanoparticles was studied and the properties of immobilized laccase were investigated in terms of optimum pH, temperature, kinetic parameters and enzyme activity against repeated use.

In the last decade, increased number of investigations have been carried out in the field of nanosized magnetic particles (maghemite, γ-Fe₂O₃ or magnetite, Fe₃O₄ single domains of about 5-20 nm in diameter) and their biotechnological applications such as; magnetic resonance imaging (MRI), hyperthermia generation, magnetically controlled transport of anticancer drugs, RNA and DNA purification, magnetic cell separation and purification, enzyme and protein immobilization [1,2]. Immobilization of enzymes on magnetic nanoparticles provides effective enzyme loading due to high surface area and allows easy recovery of the immobilized system with the applied magnetic field. In order to increase the leading amount of the enzyme on the magnetic particles and improve the stability of immobilized biomolecules, the surface functionalized magnetic nanoparticles with biocompatible and reactive groups are desired [3]. For these purposes, natural and synthetic polymers have been used to prepare functionalized magnetic nanoparticles and successfully applied to enzyme immobilization [4,5].

In this study, magnetite nanoparticles were coated with chitosan by using reversed-phase suspension method [6] and structural and magnetic properties were investigated. FT-IR spectrum of magnetic chitosan nanoparticles was showed that both chitosan and magnetite exist on the prepared nanoparticles. XRD patterns indicated that coating of chitosan did not make a phase change in Fe₃O₄ spinel structure. TEM images showed the thickness of chitosan on the magnetic chitosan nanoparticles (Fe₃O₄-CS) were ~1.0-4.8 nm (Fig. 1.).

The saturation magnetization of Fe₃O₄-CS nanoparticles determined from vibrating sample magnetometry (VSM) were found to be 25.2 emu/g and the results indicated that these nanoparticles were almost superparamagnetic. EPR analysis showed that Fe₃O₄-CS nanoparticles were in the state of low spin Fe³⁺ complex.

Laccase enzyme from *Trametes versicolor* was immobilized onto chitosan coated magnetite by adsorption. Laccase is a potentially attractive catalyst for bioremediation of environmental pollutants, especially organic substances such as chlorophenols or aromatic hydrocarbons of petrochemical industry, toxins of olive oil mill wastewater, delignification in paper industry, and dye decolorization in textile industry. The presence of enzyme in the on the magnetic chitosan nanoparticles were detected by SEM/EDX analysis. The optimum pH, temperature and Michaelis-Menten constant (Kₘ) of immobilized laccase against ABTS (2,2′-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid)) were determined. Immobilized laccase retained 71% of its initial activity at the end of 30th use against the same substrate.

The laccase immobilized magnetic chitosan nanoparticles were rapidly recovered from the reaction media by a magnet and provided repeated use of the enzyme with a high activity.

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Magnetic Properties of Co$_2$MnAl$_{1-x}$Sn$_x$ Heusler Alloy Thin Films

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Abstract—Co$_2$MnAl$_{1-x}$Sn$_x$ Heusler alloy thin films were grown on Si/SiO$_2$ substrates by magnetron sputtering technique. The samples were post-annealed at varying temperatures to study the effect of annealing on magnetic properties and crystal structure. The magnetic properties of the films were investigated by using vibrating sample magnetometer (VSM) and ferromagnetic resonance (FMR) techniques. Experimental results point out that the crystal structure and magnetic properties of the films strongly depend on annealing.

The discovery of the giant magneto-resistance (GMR) and the large tunnel magneto-resistance (TMR) effect at room temperature have attracted great attention to the spintronics studies. Heusler alloys such as Co$_2$MnAl and Co$_2$MnSn alloys have large spin polarizations, and many scientists predict a large potential for applications of these alloys in spin-electronics devices. Therefore intensive experiments have been carried out to determine the magnetic properties of Heusler alloys in recent years [1]. Gilbert damping constant ($\mathcal{G} = \alpha \gamma M_s$, where $\alpha$ and $\gamma$ are, respectively, intrinsic damping parameter and gyro-magnetic ratio and $M_s$ is saturation magnetization) of ferromagnetic materials is extremely important for achieving high-speed magnetization switching for MRAM and reduction of critical current density for spin-transfer-driven magnetic reversal [2].

In this study, we investigated magnetic properties of Co$_2$MnAl$_{1-x}$Sn$_x$ Heusler alloy films with varying thicknesses, prepared using magnetron sputtering on Si/SiO$_2$ substrates. The films were also post-annealed for one hour at 200°C, 300°C, 400°C, 500°C and 600°C, respectively, in order to investigate the annealing effects on magnetic properties. The effect of annealing temperature on magnetic properties was studied by using vibrating sample magnetometry (VSM) and ferromagnetic resonance (FMR) techniques. FMR technique was used to determine the magnetic properties such as $g$-value, effective magnetization and magneto-crystalline anisotropy constants and intrinsic Gilbert damping constants of the prepared films. Out-of-plane angular dependences of the resonance field ($H_R$) and the linewidth ($H_{pp}$) of the FMR spectra were measured and analyzed using the Landau-Lifshitz-Gilbert (LLG) equation, considering the effect of magnetic inhomogeneities in the films. The experimental data have been simulated by a self-written computer program. The samples show ferromagnetic behavior. Due to post-annealing the magnetization of most of the films increase till 400°C while the magnetization of some films increase till 500°C.

![Magnetic hysteresis curve of 50 nm Co$_2$MnAl$_{1-x}$Sn$_x$ Heusler alloy thin films with $T_A$ (Annealing temperature) = 500 °C.](image1)

In summary, we investigated the structural and magnetic properties of Co$_2$MnAl$_{1-x}$Sn$_x$ heusler alloys for varying annealing temperatures. The results indicate that the annealing effect increases the structural quality and magnetism in the Heusler until a certain temperature and then, both the crystal quality and magnetism declines. This work was supported by The Scientific and Technological Council of Turkey (TUBITAK) under contract number TBAG-107T648. Also we acknowledge partial support from The State Planning Organization of Turkey (DPT-Project No: 2009K120730).

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Carrier Transport Mechanisms in In$_x$Ga$_{1-x}$N Bulk Structures
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Abstract—As the carriers travel through a semiconductor, they undergo a variety of interactions with the host material. The electron mobility is the most important transport parameter used to characterize the microscopic quality of epitaxial layers. Mobility is considered to be the figure of merit for materials used for electronic devices. In this study, it has been calculated the temperature dependence of the the mobilities of some major scatterings in In$_x$Ga$_{1-x}$N bulk structures for $x=0.36$.

InGaN alloy is already an integral part of important device design and appreciable for the fabrication of electrical and optical devices, such as LEDs and lasers, which can emit in the violet or blue wavelength range [1]. It can be a promising strained quantum well material for these devices. Owing to significant progress in the growth and characterization of this material during the last several years. It’s known conduction, and thus the resistance of a semiconductor material and device, is not only determined by the number of available free carriers but also the ease with which the carriers can traverse through the structure. Carrier mobility is a universal figure of merit used not only for testing the material quality but also as an indicator of the series resistances in any device. In some cases, the carrier motion can be within an impurity band or within a band caused by a high concentration of defects which is typically characterized by relatively low mobilities. Because the mechanisms affecting the mobility depends on the temperature, the carrier mobility is a strong function of temperature [1, 2]. It has been used some parameters given below and mobility expressions [1] for all calculations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Unit</th>
<th>Formula for In$<em>x$Ga$</em>{1-x}$N</th>
</tr>
</thead>
<tbody>
<tr>
<td>High frequency dielectric constant</td>
<td>$\varepsilon_3$</td>
<td>Fm$^{-1}$</td>
<td>5.47 + 2.93x</td>
</tr>
<tr>
<td>Low frequency dielectric constant</td>
<td>$\varepsilon_0$</td>
<td>Fm$^{-1}$</td>
<td>10.4 + 4.9x</td>
</tr>
<tr>
<td>Polar phonon Debye temperature</td>
<td>$\theta_{LO}$</td>
<td>K</td>
<td>1044 - 11x</td>
</tr>
<tr>
<td>Mass density</td>
<td>$\rho$</td>
<td>kgm$^{-3}$</td>
<td>(6.1 + 0.71x)10$^7$</td>
</tr>
<tr>
<td>Sound velocity</td>
<td>$u_1$</td>
<td>ms$^{-1}$</td>
<td>(6.59 - 0.35x)10$^7$</td>
</tr>
<tr>
<td>Piezoelectric constant</td>
<td>$\varepsilon_{14}$</td>
<td>Cm$^{-2}$</td>
<td>0.375 - 0.5</td>
</tr>
<tr>
<td>Acoustic deformation potential</td>
<td>$D_{ac}$</td>
<td>eV</td>
<td>9.2 - 2.1x</td>
</tr>
<tr>
<td>Effective mass</td>
<td>$m^*$</td>
<td>kg</td>
<td>0.22 - 0.105x</td>
</tr>
</tbody>
</table>
| Elastic constant | $C_1$ | Fm$^{-2}$ | $C_{11}=11.88 \pm 0.84x$
| | | | $C_{12}=5.38 \pm 0.32x$
| | | | $C_{44}=5.94 \pm 0.55x$
| | | | $C_1=(3C_{11}+2C_{12}+4C_{44})/5$ |
| Alloy disorder scattering potential | $E_{AB}$ | eV | 3.42x + 0.77x(1-x) - 1.43x(1-x) |
| Electron density | $n$ | cm$^{-3}$ | 5.10$^{18}$ |

Fig. (a) The parameters used in mobility calculations [1, 2].

In semiconductors, in order to determinate to electron transport mobility, the momentum relaxation times of all scattering mechanisms should be determined, and then total mobility should be calculated. According to Matthiessen rule, total mobility is given by

$$\frac{1}{\mu_T} = \sum \frac{1}{\mu_j}$$

where $j$ is an index for different scattering mechanism [3, 4]. According to Matthiessen rule, each scattering process is independent from energy and the other scattering processes. In degenerated semiconductors, in the other words low temperature regions, this rule gives good results. However, applicable of this rule can be discussed for high temperature regions.

In this work, we have used some parameters given by Fig(a) for In$_x$Ga$_{1-x}$N alloy to calculate the mobilities of scattering mechanisms and thus total carrier mobility of this alloy. In the calculations, we have used approximate analytical expressions available. The results suggest that the effects of ionized impurity scattering, neutral impurity scattering, piezoelectric scattering, polar optical phonon scattering, alloy disorder scattering and space charge scattering on the transport mobility of 2 dimension electrons are orders of magnitude smaller than those of acoustic phonon scattering and hence the electron mobility is limited primarily by acoustic phonon scattering at low temperatures (T<100K). At high temperatures (T>100K), the ionized impurity scattering is dominant. The mobility is controlled by polar optical phonon scattering at higher temperatures.

Acknowledgements: This study was supported by The Scientific and Technological Research Council of Turkey which project number 108T721.

Intrinsic Josephson Junctions of High Temperature Superconducting Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) for Powerful Terahertz Emission

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Abstract: THz sources have potential application areas in materials characterization, biology, communication, medicine and security. There is still lack of coherent, continuous, tunable and compact solid-state sources of electromagnetic radiation at THz frequency range. Recently, the observation of THz radiation from intrinsic Josephson junction (IJJ) made Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) single crystals better candidate to generate THz emission. In order to obtain powerful emission, it is necessary to find optimum materials conditions. We annealed high temperature superconducting Bi2212 single crystals at 425$^\circ$C in vacuum or under purified Ar flow at 600$^\circ$C to obtain various doping levels. We characterized the $T_c$ and critical current density of heat treated crystals for THz studies.

Terahertz radiation is part of the electromagnetic spectrum lying between microwaves and the far-IR. This region has frequencies ranging from 0.1 – 10 THz and wavelengths from 3 mm to 0.03 mm.

High temperature superconducting Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) single crystals have natural junctions along the c-axis called intrinsic Josephson Junctions (IJJs). Since Bi2212 is a stack of Josephson junctions, with atomically thin superconducting layers (0.3 nm) separated by thicker dielectric layers (1.2 nm), it is extremely anisotropic. Josephson junction is a simplest converter from DC-voltage to high frequency radiation. A powerful and coherent electromagnetic radiation source at THz frequencies has been recently observed in relatively large mesa structures patterned on a Bi2212 crystal [1]. It is also shown that, all of the THz emitting rectangular mesa structures are below a certain underdoped level of Bi2212 single crystal [2]. It is necessary to find heat treatment recipes for single crystals.

In order to obtain various doping levels, we annealed the high temperature superconducting Bi2212 single crystals at 425$^\circ$C in vacuum (Figure 1) or gettering furnace purified argon gas flow at 425$^\circ$C. The heat treatment duration is varied to change the $T_c$ and critical current of crystals. To obtain natural IJJ stacks with various size and height, mesas on Bi2212 crystals have been fabricated using photolithography and argon ion beam etching techniques. The details of mesa fabrication can be found in ref. [2].

After the mesa fabrication, the exact dimensions of the mesas were obtained using surface profilometer. The number of Josephson junctions were determined which gives emission voltage. The electrical characterization of the mesas was obtained room temperature through low temperatures. In order to characterize the Bi2212 mesas, c-axis resistance versus temperature ($R$–$T$), and current–voltage behavior ($I$–$V$) were measured in a He flow cryostat. During $I$–$V$ characterization, we used a Si composite bolometer to detect the THz emission. Figure 2 shows temperature dependence of normalized c-axis resistance of two mesas with different O$_2$ concentration obtained by annealing. It can be seen from figure that mesa A has lower O$_2$ concentration than mesa B.

I-V characteristics of mesas at low temperatures also give Josephson critical current density ($J_c$). We are currently investigating annealing conditions on $T_c$ and $J_c$ of mesas. We will present details of heat treatment on electrical properties of THz wave emitting mesas.

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Exchange-Bias Effect in Co/CoO Bilayers Studied by Ferromagnetic Resonance

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Abstract—CoO/Co bilayer thin films were prepared by using ion beam sputtering technique on MgO substrates. We have studied the magnetic properties of Co/CoO bilayer thin films as a function Co film thickness by using vibrating sample magnetometer (VSM) and ferromagnetic resonance (FMR) techniques. By using a self-written computer program we have simulated the experimental data and determined magnetic parameters such as anisotropy constant and damping term.

In a ferromagnetic (F)/antiferromagnetic (AF) bilayer system, the presence of the AF layer strongly influences the magnetic properties of the F via the exchange coupling at their common interface. Thus, exchange bias refers to a shift of the F hysteresis loop to positive or negative values when a F system is in contact with an AF system and cooled in an applied magnetic field through the Néel temperature of the AF system. The exchange bias phenomenon is associated with the interfacial exchange coupling between ferromagnetic and antiferromagnetic spin structures, resulting in an unidirectional magnetic anisotropy [1-3]. The exchange bias effect is essential for the development of magneto-electronic switching devices (spin valves) and for random access magnetic storage units. For these applications a predictable, robust, and tunable exchange bias effect is required [4]. Recently, Co/CoO bilayer has been grown on different substrates and exchange bias effect in this system is studied in many aspects [5]. However, the magnetic anisotropies and their dependence on Co layer thickness have not been studied. In this work, we focus on the magnetic anisotropies of CoO/Co bilayer epitaxially grown on MgO (100) substrate.

The samples were grown on MgO (100) substrates by using ion beam sputtering technique. Before sputtering, a base pressure of ~10^-9 mbar was provided and the substrate was etched for 20 seconds with Ar. Then the Co layer was grown on the top of the substrate with a pressure of 4.4×10^-7 mbar. Finally, the AF CoO layer was deposited with a pressure of ~10^-1 mbar. The thickness of Co layer was varied between 1nm and 30 nm and the thickness of CoO was chosen as 20nm. The thickness of both layers has been checked by x-ray reflectivity measurements.

Magnetic properties of the samples were studied by using vibrating sample magnetometer (VSM) and ferromagnetic resonance (FMR) techniques at room temperature and below the Néel temperature of CoO. FMR measurements were carried out at two different conventional geometries: in-plane geometry (IPG: effective field lies in film plane) and out of plane geometry (OPG: effective field is rotated from the sample plane toward the film normal). The temperature-dependent magnetic anisotropies of the Co layer and the easy axis of the systems have been determined by using advantages of ferromagnetic resonance technique. The extraordinary two well-resolved and highly anisotropic FMR resonance lines have been observed as the external dc field orientation comes close to the film normal (Figure). As seen in figure, resonance fields are very sensitive to the relative orientation of the external dc field. We have also observed that the magnetic anisotropies strongly depend on ferromagnetic Co thickness. The experimental data for different Co thicknesses have successfully been simulated by using developed theoretical model.

Figure 1. Out of plane angular variation of resonance field of CoO/Co bilayer with a Co thickness of 30nm.

We would like to acknowledge P. Stauche for technical support. This work was partially supported by DPT (State Planning Organization of Turkey) through the project No 2009K120730, DFG through SFB 491 and BAPKO project of Marmara University (FEN-KPS-100105-0073). S. Kazan acknowledges TUBITAK for financial support during his postdoctoral studies at Ruhr-Universitaet Bochum.

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Magnetron Sputtering Growth and Characterizations of Large Area ITO Thin Films

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Abstract— We have grown indium tin oxide (ITO) thin films on large area (60 x 90 cm²) glass substrates by DC magnetron sputtering with 70 nm thicknesses and annealed them at various annealing temperatures in vacuum. Structural, electrical and optical properties of these samples were studied before and after the heat treatment. It is found that heat treatment improves both surface resistance and optical transmission of films.

Among transparent conductive oxides (TCO), indium tin oxide (ITO) is widely preferred because of its unique properties such as high transparency in the visible region and low resistivity. ITO thin films are used in many applications such as OLEDs, LCDs, Solar Cells, plasma display panels electrochromic and transparent heat reflecting windows [1-2].

There are various techniques to deposit ITO thin films on various substrates, such as DC and RF magnetron sputtering, electron beam evaporation, pulsed laser ablation, ion beam sputtering. Among these methods, magnetron sputtering is widely preferred over others due to its advantages to grow on different substrates and large areas.

The main goal of this study is to grow ITO thin films with good electrical and optical properties on large areas. The growth of ITO with excellent electrical and optical characteristics by DC and RF magnetron sputtering on small area such as microscope glass (2x2 cm²) is very well controlled [3-4]. However, growth of ITO on large areas, required by industrial needs, is quite complicated.

In this work, we explored the effects of vacuum annealing on structural, electrical and optical properties of large area coated ITO thin films. The growth was carried out on 4 mm thick and 60 x 90 cm² regular window glass using Planar DC magnetron sputtering. We grew thin films with thickness of 70 nm and applied annealing process to them. Annealing was done in a chamber pumped with turbo molecular pump down to 2.0x10⁻⁶ torr. The samples were heated to set temperature and kept at that for one hour. Table 1 shows deposition parameters and surface resistance of the prepared films.

XRD diffraction patterns showed that as grown ITO films, which were not annealed, were amorphous (Fig. 1). After the annealing ITO thin films exhibit polycrystalline structure. Surface resistances also show substantial improvement with heat treatment as seen in Table 1. The values are compatible with commercially available ITO films for various applications.

The transmission of the samples was measured by a spectroscopic ellipsometer in the range of 280 to 850 nm illustrated in Fig. 2. The observed transmission was about 75% in the visible region including 4 mm thick glass. The high transmission is associated with the large band gap of the ITO which was about 3.67 eV and it was found from transmission spectra. The heat treatment also improves transmission of the films. We are under development of in-situ heating during ITO growth. The preliminary result will be discussed.

This research partially supported by Ministry of Industry under SANTEZ project number 00058.STZ.2007-1 and Teknoma Technological Materials Ltd.

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Table 1: Growth conditions, annealing temperatures and surface resistance values of LAITO thin films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Power (W)</th>
<th>Argon flow (sccm)</th>
<th>Annealed Temperature (°C)</th>
<th>Rs (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAITO-A</td>
<td>125</td>
<td>40</td>
<td>As Grown</td>
<td>6.4 x 10⁻³</td>
</tr>
<tr>
<td>LAITO-A</td>
<td>125</td>
<td>40</td>
<td>400</td>
<td>1.6 x 10⁻³</td>
</tr>
<tr>
<td>LAITO-B</td>
<td>75</td>
<td>40</td>
<td>As Grown</td>
<td>7.4 x 10⁻⁴</td>
</tr>
<tr>
<td>LAITO-B</td>
<td>75</td>
<td>40</td>
<td>400</td>
<td>4.3 x 10⁻⁴</td>
</tr>
</tbody>
</table>

Figure 1: The XRD pattern of a large area coated ITO thin film before and after heat treatment.

Figure 2: Optical transmission of LAITO thin films

The transmission of the samples was measured by a spectroscopic ellipsometer in the range of 280 to 850 nm illustrated in Fig. 2. The observed transmission was about 75% in the visible region including 4 mm thick glass. The high transmission is associated with the large band gap of the ITO which was about 3.67 eV and it was found from transmission spectra. The heat treatment also improves transmission of the films. We are under development of in-situ heating during ITO growth. The preliminary result will be discussed.

This research partially supported by Ministry of Industry under SANTEZ project number 00058.STZ.2007-1 and Teknoma Technological Materials Ltd.

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Bio-separation Using Magnetic Nanoparticles: A Review
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Abstract-It should be noted that the current technology of magnetic separation using a nanomagnet is entirely dependent upon a two-step process that involves (i) tagging or labelling of the desired biological/chemical entity on colloid magnetic nanoparticles for recognition of complementary species in solution, and (ii) separation of the resulting solid entities via a fluid-based magnetic separation followed by regeneration of the species from the particles.

Magnetic nanoparticles have infiltrated a variety of fields of physics, chemistry and bio-medicine, particularly imaging (e.g. as imaging contrast enhancer) and transdermal drug delivery. However, their application to the field of biomolecule separation has been very limited to date, as the fabrication of nanoparticles of many materials has been difficult until recently, and the options to regenerate the retained biomolecules after separation also remain limited. In contrast, commercial suspension of magnetic beads of submicrometre or micrometre size in solution for magnetic isolation and separation of biomolecules (e.g. DNA, proteins) has been applied for a number of years. An area of notable success has been in the field of fine chemical manufacture, where free forms of paramagnetic nanomaterials coupled to chemical catalysts have been shown to be stable in harsh chemical conditions and have been successfully captured for reuse following dispersal by magnetic retrieval. Promising results were obtained using such magnetised nanomaterials as bio-catalysts, where they were shown to successfully carry β-lactamase via chemical linkage to the silica overlayer. Enzyme activities were as good as the free enzyme, and recovery and reusability upon application of magnetic separation was achieved. It should be noted that the current technology of magnetic separation using a nanomagnet is entirely dependent upon a two-step process that involves (i) tagging or labelling of the desired biological/chemical entity on colloid magnetic nanoparticles for recognition of complementary species in solution, and (ii) separation of the resulting solid entities via a fluid-based magnetic separation followed by regeneration of the species from the particles. Although this technique is now widely adopted in protein purification, immunoassays, pre-processing in polymerase chain reactions and pre-concentration of biological entities, the combination of highly specific tagging and recognition chemistry and generally weak magnetic response of the nanoparticle–biomolecule conjugates towards external magnetic field in solution does not allow efficient separation of closely related specie.

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Entanglement in Two Qubit Magnetic Models with DM Antisymmetric Anisotropic Exchange Interaction

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Abstract: We studied an influence of the anisotropic antisymmetric exchange interaction, the Dzialoshinskii-Moriya (DM) interaction, on entanglement of two qubits in various magnetic spin models, including the pure DM model and the most general XYZ model. We find that the time evolution generated by DM interaction can implement the SWAP gate and discuss realistic quasi-one-dimensional magnets where it can be realized. It is shown that inclusion of the DM interaction to any Heisenberg model creates, when it does not exist, or strengthens, when it exists, the entanglement. We give physical explanation of these results by studying the ground state of the systems at T=0. Nonanalytic dependence of the concurrence on the DM interaction and its relation with quantum phase transition is indicated. Our results show that spin models with the DM coupling have some potential applications in quantum computations and the DM interaction could be an efficient control parameter of entanglement.

The entanglement property has been discussed at the early years of quantum mechanics as a specific quantum mechanical nonlocal correlation [1, 3] and recently it becomes a key point of the quantum information theory, quantum computations, information processing, quantum cryptography, teleportation and etc. [4]. Due to the intrinsic pairwise character of the entanglement, entangled qubit pairs play a crucial role in such computations. Since single qubit gates are unable to generate entanglement in an N qubit system, one needs an inter qubit interaction, which is a two qubit gate to prepare an entangled state. The simplest two qubit interaction is described by the Ising one between spin 1/2 particles in the form of $J \sigma_1^x \sigma_2^x$. More general interaction between two qubits is given by the Heisenberg magnetic spin interaction models. Now these models become promising to realize quantum computation and information processing, by generating entangled qubits and constructing quantum gates [5,6] in a more general context than the magnetic chains. A significant point in the study of such models is how to increase entanglement in situation when it already exists or to create entanglement in situation when it does not exist. Certainly this can be expected from a generalization of bilinear spin-spin interaction of the Heisenberg form. Dzialoshinskii [7] from phenomenological arguments, and Moriya [8] from microscopic grounds, have introduced anisotropic antisymmetric exchange interaction, the Dzialoshinskii-Moriya (DM) interaction, expressed by $D \cdot (\vec{S}_1 \times \vec{S}_2)$. This interaction is important not only for the weak ferromagnetism but also for the spin arrangement in antiferromagnets of low symmetry.

In this work we study the influence of the Dzialoshinskii-Moriya interaction on entanglement of two qubits in all particular magnetic spin models. We formulate the general XYZ model with DM coupling and find the density matrix and eigenvalues for the concurrence [9]. Then we consider the time evolution and its relation with the SWAP gate. Starting from the Ising model with DM interaction in particular we study realization of the model for description of two nuclear spins with DM coupling and implications for the quantum phase transitions in the presence of magnetic field. Then we consider the XY model and its particular reduction to the XX case. We also analyze the XXX and XXZ models and study the influence of DM coupling and magnetic field on the concurrence and the quantum phase transitions. Finally we study XYZ model in both antiferromagnetic and ferromagnetic cases, with inclusion of the DM coupling and find the nonanalytic behavior at T=0.

We find that in all cases, inclusion of the DM interaction creates, when it does not exist, or strengthens, when it exists, entanglement. We give detailed physical explanations of these results by studying ground state of the system at T=0. In this state we find nonanalytic dependence of concurrence on the DM interaction and establish its relation with the quantum phase transition. These results indicate that spin models with DM coupling have some potential applications in quantum computations, and DM interaction could be an efficient control parameter of entanglement. For more details on these results we refer the reader to our recent paper [10].

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Thickness Dependence of Magnetic Properties of Polycrystalline \( \text{Co}_2\text{MnAl}_{x}\text{Sn}_{1-x} \) Heusler Alloy Thin Films

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Abstract—\( \text{Co}_2\text{MnAl}_{x}\text{Sn}_{1-x} \) Heusler alloy thin films with different thicknesses were grown on Si/SiO\(_2\) substrates by using magnetron sputtering technique. We investigated thickness dependence of the magnetic properties of \( \text{Co}_2\text{MnAl}_{x}\text{Sn}_{1-x} \) Heusler alloy thin films by using both vibrating sample magnetometer (VSM) and ferromagnetic resonance (FMR) techniques. The experimental SWR (spin wave resonance) spectra have been observed and analyzed by using SWR theory by a self-written computer program to extract magnetic parameters.

The Heusler alloy thin films have attracted considerable attention from researchers since applications in tunneling magnetoresistance (TMR) and spin electron applications especially magnetic random access memory (MRAM) devices. Since the existence of one spin direction at Fermi level, some Heusler alloys exhibit 100\% spin polarization [1]. To increase magnetoresistance ratio and also develop performance of a spintronic device, the spin polarization of the ferromagnet (electrode) should be 100\%. Therefore, the suitable thickness of these alloys is the important parameter to increase magnetization, magnetoresistance ratio.

In this work, \( \text{Co}_2\text{MnAl}_{x}\text{Sn}_{1-x} \) Heusler alloy thin films with different thicknesses were grown on Si/SiO\(_2\) substrates by using magnetron sputtering technique. The thickness dependence of magnetic properties of \( \text{Co}_2\text{MnAl}_{x}\text{Sn}_{1-x} \) (x: 0, 0.25, 0.5, 0.75) Heusler alloy thin films were investigated by ferromagnetic resonance (FMR) and vibrating magnetometer (VSM) techniques at room temperature (RT). FMR technique is powerful and useful in order to determine magnetic properties of the samples which are effective magnetization (2\(K_{\text{eff}}/M_0\)), exchange stiffness (D) and damping constant. FMR experiments were carried out using microwave frequency of 9.5 GHz. as a function of the angle between the dc field and film normal. Some of the films exhibit multi-peak SWR spectra when the dc field is both parallel and perpendicular to film normal (Figure 1). To extract the magnetic parameters of the films, the experimental SWR spectra were analyzed by classical SWR theory [2]. For this sample surface anisotropy coefficients are obtained as same parameter (9.6) for both sides. Magnetization measurements were carried out at in plane geometry (IPG: magnetic field is parallel to film plane) at RT. Figure 2 shows magnetic hysteresis curve of 50nm \( \text{Co}_2\text{MnAl}_{0.25}\text{Sn}_{0.75} \) thin film. Saturation magnetization of this film is determined as 278 emu/cm\(^3\).

In summary, we investigated the magnetic properties of \( \text{Co}_2\text{MnAl}_{x}\text{Sn}_{1-x} \) Heusler alloy thin films with different thicknesses. The experimental data for the films with different thicknesses have successfully been simulated by using SWR theory by a self-written computer program. This work was partly supported State Planning Organization of Turkey (DPT-Project No: 2009K120730).

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Magnetic Anisotropy in Half Metallic CrO₃ Thin Films
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Ordinary electronics uses only charge degree of freedom of electrons. However, further progress in electronics requires utilizing new physical phenomena, which incorporate manipulation not only with charge but also spin and optical degrees of freedom of the electron as well magneto-electronic devices which exploit spin-polarized currents and spin-dependent conduction. Performance of the magneto-electronic devices depends critically on the spin polarization of the conduction band of the ferromagnetic components. In this respect, half-metallic ferromagnets are considered to be a key material due to high spin polarization of their conduction band. One of such half-metallic materials is chromium dioxide (CrO₂), which has the conduction band polarization as high as 100% [1–5]. Magnetic anisotropies of single-crystalline CrO₂ films as well as possibilities to tailor them in a desirable way have crucial importance for applications in magneto-electronic devices.

Epitaxial thin films of CrO₂ have been fabricated by chemical vapour deposition (CVD) onto TiO₂ (100) and (110) single-crystal substrates using the CrO₃ solid precursor, as described in [6] and presented in Fig. 1. A set of films with thicknesses between 58 nm and 300 nm are prepared by deposition onto the HF pre-etched (110) TiO₂ substrates. The Ferromagnetic Resonance (FMR) spectra were taken on Bruker EMX electron spin resonance spectrometer at X-band frequency (9.8 GHz). The angular dependence of the FMR spectra has been studied by rotating the direction of the external magnetic field with respect to the crystalline axes in the two standard experimental geometries: in the sample plane (in-plane geometry) and out of the sample plane towards the film normal (out-of-plane geometry).

It is well known that both the CrO₂ epitaxial film and the TiO₂ single-crystalline (100) substrate have the rutile structure (tetragonal symmetry), and the lattice parameters of CrO₂ unit cell in the bulk are: a = b = 4.421 Å, and c = 2.916 Å. The lattice mismatch between CrO₂ with (100) TiO₂ substrate is about –3.79 %. The X-Ray results (Fig. 2) shows that, the (110) surface of TiO₂ is strain-free surface and (100) surface is strain surface for CrO₂.

Figure 1. Chemical Vapour Deposition (CVD) of CrO₂

Figure 2. X-Ray results of epitaxial CrO₂ thin films grown on (110) TiO₂ and (100) TiO₂

The unstrained crystal structure of the film is the tetragonal magnetocrystalline anisotropy with an easy axis parallel to the (c) crystal axis, while the additional perturbation due to the lattice mismatch produces magnetoelastic anisotropy energy. Thus, the anisotropy energy may be written as follows:

\[ E_{ani} = K_{1} \sin^{2}\theta + K_{2} \sin^{4}\theta + K_{cc} \sin^{2}\theta \cos^{2}\theta \]

where \( \theta \) is the angle between the magnetization M and the (c) axis of the CrO₂ crystal, \( K_{1} \) are the anisotropy constants of CrO₂ crystalline anisotropy, \( K_{cc} \) and \( K_{cr} \) are the magnetoelastic anisotropy constants associated with (b) and (c) axes directions, respectively. For the FMR result of CrO₂/TiO₂ (110) films multiple FMR modes were observed at in plane and out of plane geometries. The angular variation of the main mode can be seen in Figure 3.

Figure 3. The Angular variation of resonance fields at in plane (solid rectangle), at out of planes (solid triangle is in hard plane and solid circle is in easy plane)

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The Mathematical Modeling for the Oscillatory Behavior During Synthesis of Conducting Polymer Coating in Nanoscale Systems, Formed by Electropolymerization of Heterocyclic Compounds
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Abstract-By using the linear stability theory and bifurcation analysis we predict that the oscillatory behaviour during the electropolymerization of heterocyclic compounds can be caused by attractive adsorbate-adsorbate interaction and anodic oxidation of strong reducents, formed while the polymerization process.

Since 1977, increasing interest has been focused on a new class of material – doped polyheterocyclic polymers, that combine the light weight, toughness, resiliency and corrosion resistance of plastics and the conductivity of metals[1]. These conductive polymers can be used to prepare nanoscale biosensors[2-4], one-electronic transistors, electrochemical devices, electrochromic coatings and high-capacity condensers [4].

Although it’s known much of the oscillatory behavior in electrochemical systems, such a behavior during the electropolymerization is not studied deeply. Nowadays the researchers reported the presence of instabilities during the electropolymerization of 5-member heterocyclic compounds, such as thiophene [2] and pyrrole [5,6]. But the explanation of such a phenomena was mainly phenomenological and the mathematical model, that could adequately explain such a scenario, isn’t built yet.

We have to build mathematical model for this process to explain electrochemical instabilities that may occur during the synthesis of conducting polymer nanocoating.

The electropolymerization mechanism includes:
1) monomer oxidation to form cation-radical

2) dimer formation by electrophilic substitution or cation-radical recombination

3) chain propagation analogically to (1-2)

We build the mathematical model of the electropolymerization process, including such stages as:
1) Monomer diffusion to the boundary layer
2) Specific adsorption to the electrode surface
3) Electrochemical polymerization of the heterocyclic compound (coating formation)

To describe this process mathematically we use such variables:
- $c_{b}$ – monomer concentration near the electrode surface
- $\theta_{h}$ – the heterocyclic monomer coverage
- $\theta_{p}$ – the resulting polymer coverage
- $q$ – the charge density of the electrode

The process in such a system in the constant voltage mode can be described by the equation set (1).

\[
\begin{align*}
F_1 &= \frac{dc_{b}}{dt} = \frac{2}{\delta} \left( -r_1 + r_4 + \frac{D}{\delta} (c_{b} - c_{b}) \right) \\
F_2 &= \frac{d\theta_{h}}{dt} = \Gamma_{max} (r_1 - r_4 - r_2) \\
F_3 &= \frac{d\theta_{p}}{dt} = r_2 \\
F_4 &= \frac{dq}{dt} = \frac{U}{AR} - i_p
\end{align*}
\]

In which: $r_1,r_2$ – adsorption and desorption rates, $r_2$ – polymerization rate, $D$ –diffusion factor, $c_{b}$ – monomer bulk concentration, $i_p$ – polymerization current density, $\Gamma_{max}$ – maximal surface monomer concentration, $U$ – potential difference

The linear stability analysis for this system shows, that the oscillatory behavior succeeds during the autocatalytic polymer coating formation and can be caused by attractive adsorptive-adsorptive interaction, supported by Coulomb forces, and by anodic oxidation of strong reducents forming while the polymerization process. Also such a behavior can succeed in cause of passivity of the electrode by resulting polymer

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Aza-BODIPYs: Photoinduced processes in a Photodynamic Therapy Agent

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Abstract- Despite their properties in terms of NIR-emitting fluorophores and singlet oxygen sensitizers, time-resolved studies on aza-BODIPY molecules have been largely overlooked. Herein we report on the time-resolved fluorescence and transient absorption studies of two analogues, one of them containing bromine and potentially useful as photodynamic therapy agent.

Aza-BODIPYs (where X = N, see figure), like structurally related BODIPY dyes (X = C), show interesting properties as NIR-emitting fluorophores and singlet oxygen sensitizers, but have received much less attention [1, 2].

Notably dynamic fluorescence and transient absorption spectra of two recently synthesized analogues, one of which bears heavy bromine atoms are presented [2, 3].

Although in 2 no phosphorescence was observed even in low temperature glasses in the presence of heavy atoms, this compound exhibits efficient triplet state population ($\Phi_{ISC} = 0.72$), denoted by a characteristic transient absorption signature.

The transient absorption gives an unprecedented insight into the excited-state dynamics and properties of aza-BODIPY molecules, including fluorescence, intersystem crossing, triplet energy and lifetime. The latter parameters describe applicability as Photodynamic Therapy agents, complementing ongoing pre-clinical studies [4].

Figure: Spectro-temporal evolution of transient absorption signal of 2.

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**Ultrafast processes in fluorescent Ca$^{2+}$ receptors**

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**Abstract-** In this report, it will be presented ultrafast studies on some new Ca$^{2+}$ receptors based on BAPTA which contain anthracenes, coumarins and BODIPYs as chromophores.

Most of the cellular systems are using Ca$^{2+}$ for regulating their intercellular functions. To understand cellular Ca$^{2+}$, one must be able to measure it[1]. Therefore the research on synthetic Ca$^{2+}$ receptors is important. BAPTA[2] (1,2-bis(2-aminophenoxy)ethane-N,N,N',N'-tetraacetic acid) (developed by Tsien, Nobel Prize 2008) is quite useful since in the presence of Ca$^{2+}$, chromophore (see figure) emission may be altered spectacularly.

This motif has been exploited in the development of various fluorescent supramolecular systems by different groups including our own[3,4].

In this report we will present ultrafast studies on some new Ca$^{2+}$ receptors containing anthracenes, coumarins and BODIPYs as chromophores. We have observed two different operation regimes in our Ca$^{2+}$ sensors. BODIPYs appear useful for Ca$^{2+}$ detection in strong light scattering media such as living cells and micelles due to its red shifted absorption band and excitation wavelengths which are not harmful for living organisms.

On the other hand, anthracenes can exhibit excimer formation when irradiated by UV light and in such way one can switch ON and OFF Ca$^{2+}$ sensing functionality up to the point when Ca$^{2+}$ sensor becomes Ca$^{2+}$ releaser. This situation appears when two intramolecular antracenes form excimer in the excited state with photodimerization followed. A new restricted geometry of compound is not optimal for Ca$^{2+}$ coordination and the cation is released definitively.

**Figure:** Transient absorption kinetics for BODIPY chromophores at 570 nm.

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Synthesis and Characterization of the PANi Based Materials as in its Thin Films

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Abstract - It is predicted that styrene sulfonate of PANi and series of (MMA-co-MAA)-g-PAni, (BuA-co-MAA)-g-PAni and (BuA-co-MMA-co-MAA)-g-PAni copolymers could be synthesized by free radical polymerization through emulsion polymerization pathway to obtain novel class of conducting materials. The resulting materials were applied on to glass-ITO slides by air-brushing technique to characterize chemical, physical and electrical properties. Results showed that the copolymers of conducting PANi consisted of spherical particles with particle size ~ 30 nm and spray method allowed the application of conductive materials in the form of thin films in the range of 280 and 600 nm.

In recent years, intrinsic electrically conductive (ICP) polymers have been studied because of their applications have demonstrated to be changed over the full range from an insulator to a metallic conductor. The current commercial applications of conducting polymers are in: thin film transistors, batteries, antistatic coatings, gas sensors, actuators, electromagnetic shielding, artificial muscles, light emitting diodes, gas and bio sensors, fuel and solar cells, fillers, corrosion protective coatings, etc. [1]. Polyaniline (PANi) is one of the most intensively investigated ICPs due to its environmental stability, low cost of raw materials and ease of synthesis [2]. However, as in other ICPs PANi is insoluble, infusible and almost non-processable, which makes difficult its potential application. Its properties such as processability [3], solubility [4], spectroscopic and electrochromic properties [5] and optical activity, can be modified and improved by suggested methods [6,7,8].

In the presented work was aimed to obtain copolymers of Polyaniline with the maintainance of the electrical conductivity in its thin films. Firstly, styrene sulfonate of PANi (PAni-SSA) synthesis, via oxidative polymerization pathway, and secondly, the synthesis of the graft copolymers of PANi-acrylic copolymer, were studied. The morphology of PANi-SSA and the three copolymers was characterized by Scanning Electron Microscopy for studies.

Synthesization of PANi-SSA and graft copolymers of PANi-SSA by free radical pathway through emulsion polymerization technique, permitted to achieve the particle size ~ 30 nm as seen in Fig. 1. The images of the copolymers consist BuA (image c and d), changed evidently from spherical shape to flake-like shape due to its low glass transition. In this case, the thickness was measured by inclining the films 45 °. As seen in Fig. 2 the materials were deposited on the glass slides in nanometric thickness.

The depositions were studied by Electrochemical Impedance Spectroscopy (EIS) and Cyclic Voltammetry (CV) to characterize the electrochemical behaviour of the thin films, which were deposited on ITO slides. As shown in the Fig. 3, electrochemical activities of the materials were in the following order: PAni-SSA>(BuA-co-MAA)-g-PAni>(BuA-co-MMA-co-MAA)-g-PAni>(MMA-co-MAA)-g-PAni.

As a conclusion; the objective of the study which based on maintenance the electrical conductivity of the PANi in its copolymer thin films realized successfully.

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Abstract—Anthracene-based electroluminescent compounds with an anthracene core and carbazole or fluorene side groups were synthesized. The hole-transporting groups were attached to the anthracene core through different positions to optimize charge transport characteristics and solubility of the materials. Furthermore, conjugation lengths of the materials were changed in order to determine the effect of conjugation on the emission properties of the compounds. The compounds exhibited intense emission in the green and yellow region of the visible spectrum. Photoluminescence studies both in solution and solid state indicate that these materials have potential use in organic light-emitting diodes as emissive materials.

Organic light-emitting diode (OLED) technology has been advancing rapidly as a major next-generation technology that can compete with liquid crystal displays (LCDs), today’s dominant flat panel display technology. Compared to LCDs, OLEDs feature wider viewing angle, lower power consumption and operating voltages, lighter weight, faster data display, and brighter, more saturated colors [1,2]. Furthermore, OLEDs do not require backlight to function, another significant advantage of OLEDs over LCDs [3]. Even though OLED technology is still an emerging technology, devices containing OLEDs are already on the market. It has been proposed that the OLED market will exceed $10 billion in the next 5 years.

OLED operation mechanism depends on electroluminescence, in which light emission is obtained by the recombination of opposite charges injected from two unsymmetrical electrodes [1,4]. Although organic electroluminescent materials have been known since the 1950s [5], intense research on organic compounds as key components in light-emitting diodes (LED) did not begin until 1987 when Tang and VanSlyke discovered tris-8-hydroxyquinoline aluminum (Alq3) as an efficient emissive layer in LED devices [5]. Since then, small molecule organic compounds, organometallic complexes, conjugated polymers, and polymers containing photoactive groups have been the focus of extensive research in academia and industry due to their promise as low cost materials and the ease of modification of the emission wavelength of these materials using simple synthetic procedures.

In this work, we describe the synthesis and characterization of anthracene-based emitters for OLED applications. Anthracene derivatives are widely employed in OLEDs as emissive materials. In this study, we functionalize anthracene with hole-transport compounds such as carbazole, fluorene and triphenyl amine (Figure 1). All compounds are characterized by 1H-NMR, 13C-NMR, DSC, LC-TOF, UV-Vis spectrophotometer, spectrofluorophotometer, and cyclic voltammetry (Figure 2).

In summary, we have synthesized green and yellow emitters with anthracene units functionalized with hole-transport groups. Cyclic voltammetry and photoluminescence studies both in solution and solid state indicate that these materials have potential use in organic light-emitting diodes as emissive materials. This work was supported by State Planning Organization (DPT).

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 Kelvin Probe Force Microscopy Study of MPP-BA SAM Modified ITO Surface

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**Abstract**— Self-assembly monolayer (SAM) was formed on indium–tin oxide (ITO) to measure its surface potential by using Kelvin Probe Force Microscopy (KPFM). 4-(3-methylphenyl) (phenyl) amino benzoic acid (MPP-BA) self-assembly monolayer (SAM) molecules with 1 mM concentration were prepared at room temperature in ethanol solution. ITO substrate was kept in ethanol-SAM solution for 48 hours to be covered with MPP-BA monolayer. Our KPFM results show that the surface potential of SAM modified ITO is increased around +100 mV with respect to bare ITO surface as a result of SAM formation.

One of the most important issues in OLED devices is to be able to control electrode/organic interface and the differences between the work function of the anode (ITO) and HOMO level of the organic semiconducting hole transport layer (HTL) material. This difference can cause high turn on voltage, low efficiency and restricts hole-injection [1-5]. Increasing work function of ITO electrodes by modifying with self assembly monolayer (SAM) technique has been used to improve the carrier injection in OLED devices [6].

In this work, 4-(3-methylphenyl) (phenyl) amino benzoic acid (MPP-BA) has been used as self-assembly monolayer (SAM) to modify ITO surface. MPP-BA SAM molecule with 1 mM was prepared at room temperature in ethanol solution. ITO substrate was kept in ethanol-SAM solution for 48 hours to be covered with MPP-BA monolayer. Kelvin Probe Force Microscopy (KPFM) is mostly utilized to measure the surface potential between the tip and the sample surface, thus giving information on the work function of conductive thin films [7].

For KPFM measurements, AFM tip and sample surface should be conducting. During operation a constant voltage \( U_0 \) and a variable voltage \( U = U_0 + U_1 \sin(\omega t) \) are applied to the substrate as given in Fig. 1(a). When \( \varphi(x,y) \) is the potential distribution on the sample, the voltage between AFM tip and the surface will be

\[ U = U_0 + U_1 \sin(\omega t) - \Delta \varphi(x,y) \]  \hspace{1cm} (1)

The electrostatic force between tip and sample becomes,

\[ F = -\frac{1}{2} \left[U_0 - \varphi(x,y) + U_1 \sin \omega t \right] \frac{\partial \varphi}{\partial z} \]  \hspace{1cm} (2)

The constant component at \( F_0(\omega) \) at first harmonic frequency is given as

\[ F_0(\omega) = -\left[U_0 - \varphi(x,y) \right] \frac{\partial \varphi}{\partial z} \]  \hspace{1cm} (3)

which is the base of Kelvin Probe Force Microscopy (KPFM).

The voltage \( U_0 \) applied to the tip is equals to the surface potential \( U_{0\varphi}=\Delta \varphi \) to be measured, when \( F_0 \) becomes zero \( (F_0=0) \) as shown in Fig 1(b). Fig 1(b) shows KPFM measurement to obtain surface potential on the bare ITO and modified ITO with MPPBA SAM. Fig.2 shows the Surface Potential map measured with KPFM technique of bare ITO (a) and of modified ITO with MPPBA SAM (b).

Our KPFM results show that the surface potential of SAM modified ITO is increased around 0.1V with respect to bare ITO surface. The surface RMS roughness and the surface potential differences reveal the modification of ITO surface with MPPBA SAM molecular film.

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Polymer Gel Insulator for OFET Application

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Abstract- In this study polymer gel has been produced and used in the fabrication of organic field effect transistor, as a result of the characterization of the transistor produced, high mobility and low operation voltage is reached.

Nowadays, a new dimension and acceleration to the polymer electronics is gained by the improvement in the performance of organic field effect transistors (1). OFET’s have many advantages over silicon based transistors such as low cost, easy production and usability on flexible surfaces (2). While Most of the studies done till now are based on SiO\textsubscript{2}, the usage various gate materials on glass is reported (4) but the operation voltage of these works is very high. Low operation voltage demands low threshold voltage and low sub threshold curve. To realize OFET’s as circuit elements they have to be operated under low voltages and have high field-effect mobility and wide on/off ration. To provide these parameters the material used as insulator is as important as the active semiconductor (5). Lately many studies upon OFET’s, prepared by gel electrolyte with high capacity, published and low operation voltages are obtained.

![Figure 1](image)

Figure 1. Outline of process P3HT-OFETs sandwich model

In this study, we produced and characterized a high performance OFET thanks to polymer gel with high capacity by using an easy low cost production technique. rr-P3HT is used as semi-conductor polymer as shown in the Fig.1 Ag coated by thermal evaporator on one glass substrate as gate, on another as source-drain. Polymer gel is prepared by using polymethylmethacrylate Poly(methyl methacrylate) and Propylene Carbonate. On source-drain coated glass rr-P3HT is coated and gel applied onto gate coated glass, later it is closed to each other. The device which is pressed and waited for a day is characterized by the 4200 semiconductor characterization system. Low gate voltage (\(< 1 \text{ V})\) and low threshold voltage (0.26 V) and high mobility value ($\mu = 0.38$) obtained (Figure 2).

![Figure 2](image)

Figure 2. Output characteristic of P3HT-OFETs with PMMA/PC gel as gate dielectric layer.

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A Novel Gel-Dielectric Material as Gate Insulator for Organic Field Effect Transistors

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Abstract - In this study we compared the performance of the OFETs based P3HT with PMMA and poly (MMA-co-MTM). Our results are quite remarkable and open a new approach to obtain high mobility an low operating voltage. A new fabrication process, sandwich model, for the OFETs with a novel gel-dielectric materials has been developed using an appropriate gel copolymer and this process are discussed.

Organic field-effect transistor (OFET) is a three terminal device whose characteristics can be modulated by the electrical field. It is composed of organic conjugated molecules as active channels, inorganic or polymer insulators as dielectric layer and metals as electrodes. OFETs have drawn more and more attention because of their low cost, flexibility as well as the capability for large area preparation. In the past decade, many novel organic semiconductors were synthesized and device performances were significantly improved. OFETs are becoming a significant and much discussed topic in organic electronics [1].

With the advanced of OFETs, the interface between semiconductor and dielectrics has received much attention due to its dramatic effects on the morphology and charge-transport of organic semiconductors in OFETs. It is common knowledge that the field-effect conduction occurs in a narrow region of the active material at the interface with the dielectric layer [2]. Therefore, a careful control of the physical and chemical characteristics of this interface is crucial to improve the performance of OFET devices.

The use of organic polymers such as PMMA has generally resulted in higher mobilities and better device reliability compared to the highly process dependent SiO2 [3]. PMMA is considered to be one of the cheapest and its widespread usage because of its abundance, easy synthesis. And also, poly(MMA-co-MTM) was synthesized as reported in reference [4] is appropriate when used in OFETs based on poly (3-hexylthiophene) (P3HT). Our gel is not proton conductive and it contains Propylene carbonate (PC), whose dielectric constant is really high (64.92 at 25 °C) [5]. This material is penetrating the PMMA molecules and brings about the adhesive gel property.

The aim of this work is to realize sandwich-processed OFETs operating at low supply voltages and so, enhance the field effect mobility with use appropriate gel copolymer gate dielectric for future organic circuit applications. In this work, we especially compared with PMMA and poly(MMA-co-MTM) dielectrics in P3HT-OFET applications.

Firstly, the capacitor of polymer gel was constructed to investigate the impedance peculiarity of the gel material, which was made by commercial components such as acetonitrile (ACN), Propylene carbonate (PC) and PMMA or poly(MMA-co-MTM). During the preparations, PMMA and poly(MMA-co-MTM) were dissolved in ACN and PC are added these solution. 250 ºC aided mixing yields the temper of the mixtures. Because PC has a high dielectric constant, it has dominating effect regarding to determine the specific capacitance in the gel. Thereby, the specific capacitance of both gel-PMMA and gel-poly(MMA-co-MTM) is found about 1 μF/cm² at 100 Hz that provides low operation voltage.

Secondly, to study the comparison of the OFETs characteristic these gels were used. These gels are sandwiched between the glass substrates, which were prepared with Ag electrodes (figure). Usage of these gel were inspired from one of our previous works devoted to electro chromic devices [6]. The devices were fabricated with channel length (L) and width (W) values: L= 65 μm and W= 4 mm. The device which was prepared with poly(MMA-co-MTM) has a field-effect mobility of 0.57 cm²/Vs, a threshold voltage of -0.20 V, on/off current ratio of 10³ and the device prepared with PMMA has a field-effect mobility of 0.38 cm²/Vs, a threshold voltage of -0.26 V and on/off current ratio of 10³.

In summary, we showed that the device which was prepared with copolymer showed higher field-effect mobility and lower threshold voltage. This result may be attributed the chemical similarity of semiconductor and dielectric layers. Because both layers have thiophene group and this provides better interfacial properties, which may result in a combination of a number of effects, such as changes in surface energy, surface roughness, molecular orientation, and the neutralization of surface defects. We can second point out the very low operating voltage of both of device. This work supported by TUBITAK under Grant No. TBAG-108T725.

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Synthesis and Luminescence Properties of Tetraphenylethene-Based Emitter with Carbazole Side Groups

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Abstract—Tetraphenylethene-based electroluminescent compound with a tetraphenylethene core and tert-butyl carbazole side groups was synthesized. Tetraphenylethene core was synthesized by McMurry Reaction of 4,4'-Difluorobenzophenone. To enhance the solubility of the product tert-butyl groups were attached to carbazole groups. The luminescence properties of the product show that this compound has potential use in organic light-emitting diodes as emissive material.

Organic light-emitting diodes (OLED) have been one of the most important and extensively explored research areas in chemistry and applied physics due to their wide applications in full-color displays with color filters, backlighting for liquid crystal displays, and general lighting sources. The advantages of organic materials over inorganic materials are their high fluorescence efficiency and excellent color tuneability. Color tuneability is dependent on the energy difference between the excited states and the molecular ground state which can be easily modified by simple structural changes in the molecule.

Organic light-emitting diode technology has been advancing rapidly as the next-generation technology that can compete with liquid crystal displays (LCDs), today’s dominant flat panel display technology. Compared to LCDs, OLEDs feature wider viewing angle, lower power consumption and operating voltages, lighter weight, faster data display, and brighter, more saturated colors. Furthermore, OLEDs do not require backlight to function, another significant advantage of OLEDs over LCDs. Up to now, OLED technology has already been used for small displays in several commercial products such as mobile phones, MP3 players, digital cameras, etc.

Investigations on electroluminescence from organic molecules with a conjugated π electron system can be traced back for more than fifty years. The first demonstration of an efficient organic light-emitting diode (OLED) was made by Tang and Van Slyke in 1987. Since this breakthrough, studies on organic light-emitting diodes (OLEDs) have been intensified and many highly efficient OLEDs have been demonstrated.

In this study, we have done the synthesis and characterization of tetraphenylethene-based emitter for OLED applications. In this study, we functionalize tetraphenylethene with carbazole. In order to overcome the solubility problem tert-butyl side groups were attached to carbazole groups. The compound is characterized by 1H-NMR, 13C-NMR, DSC, CV, LC-TOF, UV-Vis.

In summary, we have synthesized an emitter with tetraphenylethene core and carbazole side groups. Cyclic voltammetry and photoluminescence studies both in solution and solid state indicate that these materials have potential use in organic light-emitting diodes as emissive materials. This work is supported by the Turkish State Planning Organization (DPT).

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An Impedance Study On The Effect Of A Perylene Diimide Usage In A Blue Organic Light Emitting Diode

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Abstract—An organic light emitting diode with a structure of ITO/PEDOT:PSS (33nm)/PFH(60nm)/Ca(40nm)/Al (80nm) was fabricated and a perylene diimide derivative namely, N,N'-bis-2-(1-hydroxyhexyl)-3,4,9,10-perylenebis (dicarboximide) (HHPER) was used as i) a dopant in emissive layer or ii) an electron transport layer (ETL) in this device. The optical and electrical properties of OLEDs were characterized. Although the use of HHPER as a dopant caused a small shift in C.I.E coordinates, it enhanced the device characteristics. The use of HHPER as an ETL resulted in a significant color shift, increase in capacitance and decrease in charge mobility. The addition of Alq₃ as an ETL layer into the doped device was also investigated and this device gave a whitish emission.

Organic light emitting diodes (OLEDs) have attracted much attention because of their low-cost production, variety of materials and numerous possible applications [1]. As for the light emitting materials, many electroluminescent conjugated polymers, such as polyfluorene and its copolymers can emit light covering the visible spectrum. After the first publication focusing on (Poly(9,9-d,n-hexyl fluorenyl-2,7 diyl)) PFH (Figure 1a) as polymer material in emitting blue luminescence [2], a number of PF-based OLED investigations are still examining.

Doping to the emitter layer is a way to enhance the performance of the devices. The reason for using dopant in OLED, is to have lower impedance, higher charge carrier mobility and conductance and also to have better current density, lower turn-on voltage, higher luminance [3,4].

For electronic and optoelectronic devices such as OLEDs, solar cells (SC), thin film transistors (TFT) etc, impedance spectroscopy (IS) has great attention for explaining the electrical performance of devices [6,7,8].

In this study, optical characteristics of thin films of PFH and HHPER on the glass substrates absorption and photo luminescence characteristics were analyzed by UV-VIS and Fluorescence Spectrophotometer. Thickness and surface morphologies of thin films were obtained with XRD and AFM, respectively. To study the electrical properties and physics, different concentrations of HHPER was used in the device structures of:

1) ITO/PEDOT:PSS(33nm)/PFH(60nm)/Ca(40nm)/Al(80nm);
2) ITO/ PEDOT:PSS(33nm)/PFH:HHPER (5,10 and 15wt%) /Ca(40nm)/Al(80nm);
3) ITO/PEDOT:PSS(33nm)/PFH(60nm)/HHPER(7,15 and 30nm)/Ca(40nm)/Al(80nm).

OLEDs were characterized by current density-voltage (I-V), luminance-voltage (L-V) and impedance spectroscopy (charge carrier resistance, capacitance, mobility of charge carriers etc). The energy levels of the materials used are given in Figure 2.

Figure 1. Chemical structure of a) PFH, b) HHPER.

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OLEDs were characterized by current density-voltage (I-V), luminance-voltage (L-V) and impedance spectroscopy (charge carrier resistance, capacitance, mobility of charge carriers etc). The energy levels of the materials used are given in Figure 2.

Figure 2. Energy levels of the used materials.

N,N’-bis-2-(1-hydroxyhexyl)-3,4,9,10-perylenebis (dicarboximide) (HHPER) (Figure 2b) was synthesized as reported before [5].

The use of HHPER as a dopant caused a small shift in C.I.E coordinates and enhanced the device characteristics. The use of HHPER as an ETL resulted in a significant color shift, increase in capacitance and decrease in charge mobility.

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Mn-doped TiO₂ Thin Film for Hybrid Polymer Solar Cell
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Abstract-Mn doping effects on TiO₂/P3HT:PCBM were researched for increasing the solar cell efficiency. We were able to obtain %1.83 power efficiency at %1.5 molar doping ratio.

Conjugated polymers are often utilized to fabricate large area, physically flexible and low cost solar cells. Photovoltaic devices merely composed of conjugated polymers as the only active material have extremely low electron mobility, and thus, limited performance.[1] Hybrid solar cells were improved for solving these problems. One of the advantages of hybrid solar cells based on conjugated polymers and metal oxides is the high electron mobility of the organic acceptor materials, particularly n-type polymers. Titanium dioxide (TiO₂) nanocrystal is a promising electron accepting material in organic: inorganic hybrid photovoltaic applications.[2] Dye sensitized solar cells based on nanocrystalline TiO₂ have attracted considerable interest because of the excellent power conversion performance and the efficient low cost as an silicon solar cell.[3]

The ITO substrates were cleaned with detergent, de-ionized water, acetone and isopropyl alcohol. Isopropyl alcohol, titanium n-butoxide, ethanol and acidic acid mixed at 20:1:20:0.5 molar ratios. Manganese (II) chloride was added in solvent for doping TiO₂. The solvent was stirred vigorously one hour at room temperature.TiO₂ and Mn doped TiO₂ thin films were coated by spin coating method. Thin films were annealed at 400 °C. Polymer blend of P3HT:PCBM was prepared in 1:0.8 wt/wt ratio in the chlorobenzene solution and spin coating method is applied in the coating process.

Current density–voltage (J–V) curves were measured with a Keithley4200 semiconductor characterization system, under the illumination of 100mW/cm² from a 150W Oriel Solar Simulator with AM1.5 filter. Solar Simulator was calibrated by a reference solar cell during the measurements.

Table1. Efficiency parameters of TiO₂, Mn- doped TiO₂ solar cells

<table>
<thead>
<tr>
<th>Mn</th>
<th>V_{oc} (V)</th>
<th>I_{sc} (mA/cm²)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.47</td>
<td>7.56</td>
<td>0.34</td>
<td>1.21</td>
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<td>1.5</td>
<td>0.49</td>
<td>10.13</td>
<td>0.37</td>
<td>1.83</td>
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<td>3.5</td>
<td>0.47</td>
<td>6.06</td>
<td>0.34</td>
<td>0.97</td>
</tr>
</tbody>
</table>

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Figure 1. I–V curve of TiO₂, Mn-doped TiO₂ solar cells

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Encapsulation of Organic Solar Cells to Protect from Oxygen and Humidity

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Abstract—We have applied lab-made ultraviolet (UV) curable organic/inorganic hybrid nanocomposite with excellent barrier capability for the encapsulation of organic solar cells. Nanocomposite blocked the penetration of moisture and oxygen in the air into the devices and promotes the lifetime of organic solar cells. The lifetime of organic solar cells with their package is much longer than that without package in the air.

Same as other organic devices, the organic photovoltaic cells (OPVs) without encapsulation have very short lifetime, ranging from a few minutes to a few days. The organic materials and metal used as the electrodes react with oxygen and water which are diffused from both electrodes or lateral of the device are believed the major reason causing short lifetime of OPVs [1]. Oxygen and water diffuse into the device and react with the active materials in the OPV resulting in degradation of the photovoltaic performance [2]. Organic/inorganic hybrid nanocomposites, which are composed of polymer matrices, fillers, and initiators, have attracted lots of attention for several decades because they can resist the penetration of oxygen as well as moisture in the atmosphere [3]. UV curable organic/inorganic hybrid nanocomposites (acrylics resins/epoxy resins/silica/TiO2) with excellent gas barrier performance, good electrical conductivity, moderate adhesion strength, low shrinkage, good thermal resistance, and fast curing speed have been successfully synthesized and applied for the encapsulation of organic solar cells.

At the first stage; ITO / PEDOT:PSS / PCBM:P3HT / AL structured solar cells were produced. PEDOT:PSS was deposited onto the ITO glass by spin-coating and than annealed at 105°C for 15 min. Afterwards, the P3HT powder was ground together with PCBM to form P3HT/PCBM mixture. Then the P3HT/PCBM mixture was dissolved in chlorobenzene and deposited onto the PEDOT layer by spin-coating. Finally, we deposited Al electrode onto the P3HT/PCBM layer by thermal evaporation.

At the second stage; ultraviolet (UV) curable organic/inorganic hybrid nanocomposite was synthesized by thermal curable acrylics resin (1,6-Hexanediol diacrylate) and UV curable epoxy resin (3,4-epoxycyclohexane carboxylode) as polymeric materials, photo initiators (Triaryl sulfonium hexafluoroantimonate, Irgacure 1173, Irgacure 184), thermal initiator (Benzoyl peroxide), fillers (silica and TiO2), solvent (PGMEA: Propylene glycol monomethyl ether acetate). Acrylics resin and thermal initiator mixture (weight ratio = 100/1) was dissolved in PGMEA at 70°C for 3 h. After blended with epoxy resin, Irg 1173, Irg 184, Triaryl sulfonium hexafluoroantimonate mixture (weight ratio = 100/1), the acrylics/epoxy resins (polymer matrices) were obtained. Later, we added silica (50 wt%) and TiO2 (1,5 wt%) into the polymer matrices and lab-made organic/inorganic hybrid nanocomposite was finally prepared. The encapsulation of lab-made organic solar cell was executed with spin-coating of nanocomposite on the Al electrode. After coated on the Al electrode with spin-coating technique and irradiated by UV with 315 nm for 1 min, lab-made organic/inorganic hybrid nanocomposite was cured and bonded with the glass.

As a consequence, I-t values of organic solar cell with its package and without package were measured every day and compared with each other. The experimental results reveal that solar cell with encapsulation demonstrated working life for 10 days but working life of solar cell without encapsulation was 5 days.

Figure 1. I–t curve of organic solar cell without encapsulation and with encapsulation

Figure 2. SEM of organik solar cell with encapsulation

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[3] Chen-Ming Chen a, Ming-Hua Chung a, Tsung-Eong Hsieh a,*, Mark O. Liu b, Jen-Lien Lin b, Wei-Ping Chu c, Rong-Ming Tang c, Yu-Sheng Tsai c, Fuh-Shyang Juang e Composites Science and Technology 68 (2008) 3041–3046
Electrical Characterizations of Schottky Diodes Modified by Self-assembled Monolayer Organic Thin Films

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²Solar Energy Institute, Ege University, TR-35040 Izmir, Turkey

Abstract—The electrical characterization of the Al/4-(3-metilfenil)(fenil)amino)benzoik asit (MPBA)/n-pSi and Al/ 4'-Iodobifenil-4-il)trihidroksisilan (THIBSi)/n-pSi structures have been investigated. Schottky barrier diodes demonstrated rectifying behavior.

Owing to their potential applications in electronic and optoelectronic devices, metal-semiconductor (MS) contact plays an important role. An important example of a simplest MS contact devices is Schottky Barrier Diode in modern semiconductor device technology. Modifying the surface by inserting organic thin film between metal and semiconductor interfaces makes device to show unusual electrical, properties that can be used for the fabrication of molecular electronic devices. [1]

One side polished n type and p type Silicon wafers with, 2.0 Ωcm resistivity and 530μm thickness were purchased from Si-Mat Silicon Wafers Company. The crystal silicon wafers were cleaned in ultrasonic cleaner for 10 min. with acetone and ethanol respectively and dipped into 20% HF solution to remove the SiO₂ layer. The wafers were rinsed thoroughly in de-ionized water.

Organic thin films were prepared with self-assembly monolayer (SAM) technique. MPBA SAM solutions were prepared with chloroform as a solvent. THIBSi SAM solutions were prepared with ethanol and THIBSi SAM solutions were thoroughly in de-ionized water.

Figure 1. Chemical structure of MPBA and THIBSi molecules.

To form the top contact Au metal with high purity (99.9%) was thermally evaporated on the MPBA and THIBSi monolayer films. Again to remove the oxide layer from the back side of the films, 5μl of 20% HF solution was dropped, rinsed with de-ionized water and Au contacts were formed.

The I-V characteristics of MPBA and THIBSi monolayer films on n-type and p-type silicon crystals are shown in fig.2.

Current-Voltage characteristics of an organic film inserted between the metal-semiconductor interface can be analysed by the following relation [2],

\[ I = I_0 \exp \left( \frac{q(V-I_R s)}{n k T} \right) \left( 1 - \exp \left( - \frac{q(V-I_R s)}{k T} \right) \right) \]

where \( R_s \) is the series resistance, \( V \) is the applied voltage, \( n \) is the ideality factor, \( k \) is the Boltzman constant, \( T \) is the temperature and \( I_0 \) is the reverse saturation current. The ideality factor (\( n \)) and the series resistance (\( R_s \)) can be determined by the analysis of Cheung [3],

\[ \frac{dV}{d\ln(I)} = n \frac{kT}{q} + IR_s \]  \hspace{1cm} (2)

\[ H(I) = n \frac{kT}{q} \ln \left( \frac{I_0}{A^*A^*T^2} \right) = IR_s + n\Phi_B \]  \hspace{1cm} (3)

where \( \Phi_B \) is the barrier height and \( q \) is the electronic charge. The \( R_s, n \) and \( \Phi_B \) values were calculated from the slope and the intercept of \( dV/d\ln(I) \) vs. \( I \) and \( H(I) \) vs. \( I \) plots.

<table>
<thead>
<tr>
<th>Diode</th>
<th>( R_s (\Omega) )</th>
<th>( n )</th>
<th>( \Phi_B ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nSi/MPBA/Au</td>
<td>0.13</td>
<td>3.95</td>
<td>0.089</td>
</tr>
<tr>
<td>nSi/THIBSi/Au</td>
<td>0.09</td>
<td>11.8</td>
<td>0.102</td>
</tr>
<tr>
<td>pSi/MPBA/Au</td>
<td>17.15</td>
<td>2.51</td>
<td>0.099</td>
</tr>
<tr>
<td>pSi/THIBSi/Au</td>
<td>0.20</td>
<td>5.24</td>
<td>0.297</td>
</tr>
</tbody>
</table>

The electrical characterization parameters show that SAM organic molecules modify the electronic parameters of metal-semiconductor (MS) devices.

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Manufacturing of Inorganic-Organic Hybrid Solar Cells Screen Printing Method
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Abstract- In this study, hybrid bulk heterojunction (BHJ) organic solar cells which have poly(3-hexylthiophene-2,5-diyl)(P3HT)-(6,6)-phenyl C 61-butyric acid methyl ester (PC61BM) active layer, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)(PEDOT:PSS) buffer layer and electrochemically deposited Zinc oxide (ZnO) n-type inorganic layer have been produced. PET/ITO/ZnO/PEDOT: PSS/P3HT: PC61BM/Al device has been manufactured and tested under solar illumination (AM1.5G, 100mW/cm²).

Much attention has been focused on organic solar cells based on bulk heterojunction due to the potential for low-cost and large area manufacturing to conventional photovoltaic [1]. Organic solar cells manufacture in large area on flexible substrates [2, 3], from solution by printing and coating techniques [4, 5], at low temperature, with no need vacuum coating steps [6]. A promising efficiency η = 4.8% was obtained in one of these basic organic solar cell structure, ITO/PEDOT:PSS (poly(3,4-ethylenedioxythiophene–polystyrenesulfonic acid)/P3HT:PCBM/Al [8]. Although this efficiency is not enough for commercial applications yet.

The production of polymer based photovoltaics using industrial screen printing have demonstrated the possibility of producing on the order of 1000–100,000 m² on a process line per day. The production of the same solar cell area based on silicon in a state-of-the-art production plant typically takes 1 year [3].

In this study, hybrid bulk heterojunction (BHJ) organic solar cells which have P3HT:PC61BM active layer, PEDOT:PSS buffer layer and Zinc oxide (ZnO) n-type inorganic layer have been produced. Inorganic ZnO layer deposited by electrochemical deposition (ECD) method. ZnO is one of the most promising semiconductor materials for manufacturing optoelectronic device. As ZnO is a non-toxic, cheap wide band gap semiconductor. In addition ZnO is a natural n-type semiconductor [7]. In this device ZnO layer deposited to prevent from short paths which reduce device efficiency, between top electrode Al and ITO electrode [9] and acts as a n-type semiconductor layer to enhance open circuit voltage. Organic layer produced by screen printing method on PET/ITO substrate.

Polymer and PCBM were bought from Aldrich Inc. Polymer blend of P3HT:PCBM was prepared in 1:1 wt/wt ratio in the chlorobenzene solution. Then the solution evaporated for 10 minutes for feasible viscosity. After evaporation printing process has been achieved with a 200-μm mask on substrate which ZnO deposited on ITO:PET and PEDOT:PSS coated by spin coating method. Figure 1 reveals schematic representation of the device architecture.

![Figure 1. Schematic representation of the hybrid solar cell](image_url)

Effects of printing parameters which are viscosity of solution and screen resolution on power conversion efficiency of devices has been investigated to obtain optimum conditions for highly efficient inorganic-organic hybrid solar cell producing by screen printing method.

In the conclusion the hybrid device PET/ITO/ZnO/PEDOT: PSS/P3HT: PC61BM/Al device has been manufactured and tested under solar illumination (AM1.5G, 100mW/cm²). For better fabrication method, I-V parameters and XRD plots of devices obtained and discussed.

This study has been supported by The Scientific and Technological Research Council of Turkey (TÜBİTAK-Project number 107M270).

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Modification of an ITO Anode Surface by SAM Technique to Enhance OLED Device Characteristics

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Abstract—An (4'-iodobifenil-4-il) trihydroxyl silan (THIBSi) functionalized hole-transporting was synthesized and was self-assembled to form a monolayer on an indium tin oxide (ITO) anode. The modified surface was characterized by and atomic force microscopy (AFM). The increase in surface work function is expected to facilitate hole injection from the ITO anode. To investigate the effect of a self-assembled monolayer (SAM) on the characteristics an organic light-emitting diode (OLED), a typical OLED device [SAM-modified ITO/PEDOT: PSS/TPD/polymer or small molecule/Al] was fabricated. The SAM-modified device could endure a higher current than the bare ITO device. The variation of the terminal group of the SAM and possible further optimization of SAM-modified OLEDs are under investigation.

Organic light-emitting devices (OLEDs) have grown progressively during the last decade owing to their potential applications as commercial devices in organic electronic. The interfacial phenomena are important for performance and stability of an OLED device. A variety of interfacial treatments have been taken to both cathode/organic and anode/organic junctions to modify the charge injection, and hence device performance[1]. The modification of indium tin oxide (ITO) anode/hole-transport layer (HTL) interface play a significant role about hole injection. SAM uses for surface modification and have been used to improve the interfacial compatibility between the hydrophilic oxide anode and hydrophobic HTL. Moreover, the other functions of SAMs reported in the literature for OLED application include: as a current blocking layer, change the work function of ITO and enhance the adhesion and stability of HTL layer [2,3].

In this work, we report on the application of a SAM to an ITO anode and report the characteristics of an OLED that makes use of this modified anode. We have introduced a trihidroksisilan in figure 1 as hole-transporting and as constituents of a SAM for application to the hydroxy surfaces.

Figure 1. Synthesis and structure of SAM molecule

Figure 2 shows AFM images of bare ITO and SAM-modified ITO. Introduction of a hole-transporting moiety at the end of the SAM is expected to change the surface work function as well as to enhance the adhesion between the inorganic ITO and the hole-transporting organic layers.

Figure 2. AFM images of bare ITO (a) and SAM-modified ITO (b)

The OLED devices were fabricated in a thermal evaporation coater. The conducting polymer PEDOT:PSS was spin coated at 1500rpm on top of the ITO or SAM-modified ITO. The active polymer (PFO) film was spin coated onto the PEDOT:PSS layer from a toluene. The small molecular film layers were made by thermal evaporation. The organic layers were deposited at a rate of 1 Å/s under a base pressure of 5×10^-6 mbar. For the metal layers, the deposition rate was 3 Å/s for aluminum. Two polymer OLED structures were fabricated for comparison: ITO/PEDOT:PSS/PFO/Al and, ITO/SAM/PEDOT:PSS/PFO/Al. Two small molecules OLED structures were also fabricated: ITO/PEDOT:PSS / TPD / Alq3 / Al and ITO/SAM/PEDOT:PSS/TPD/Alq3/Al.

The I–V characteristics of the both polymer and small molecule devices with and without SAM layer were shown in Fig.3 (a) and (b) respectively. The turn-on voltages for both polymer and small molecule devices are strongly improved compared with the base one. The turn-on voltage for the SAM-modified OLED devices increases for both devices in the order: ITO/SAM<bare ITO, which implies that the hole injection is enhanced by SAM layer. There are two kinds of effect of SAM-modification on the device characteristics. One is the lowering the threshold of charge injection, and the other is the improvement of interfacial contact between the electrode and organics. The possible further optimization of SAM-modified OLEDs and theoretical understanding are under investigation. This work was supported by TUBITAK under Grant No. TBAG-108T718.

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A Novel Fluorene-Carbazole-2,5-bis(2-thienyl)-1H-(pyrrole) Hybrid Dendron for Electrochromic Device and Organic Light Emitting Diode Applications

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Abstract—We report here the synthesis of a new hybrid dendron 9,9'-((9,9-dihexyl-9H-fluorene-2,7-diyl)bis[3,6-bis(2,5-di-2-thienyl-1H-pyrrolo-1-yl)-9H-carbazole] (FCSNS) in four steps and then coated on to ITO/glass surface by using crosslinked electropolymerization process to give a very stable electrochromic film. Further, a multilayer organic light-emitting diode (OLED) having the structure of ITO/PEDOT:PSS/FCSNS/Alq3/LiF:Al showed a turn-on voltage of approximately 6 V and exhibited a bright green emission with a luminance of 3700 cd/m².

Charge transporting dendrimers, as a very special type of macromolecules with hyperbranched and perfectly defined structure, have attracted much interest for the opto-electronic device technologies [1-3]. In this study, a novel hybrid dendron containing fluorene-carbazole-2,5-bis(2-thienyl)-1H-(pyrrole) (FCSNS) was synthesized in four steps (Scheme 1). The chemical structure of FCSNS was elucidated from its FT-IR, 1H-NMR, and MALDI-ToF data.

Figure 1 Synthetic route to hybrid dendron (FCSNS).(a)Carbazole, Cu, K2CO3, nitrobenzene, 24h, reflux (b)acetic acid-acetic anhydride (1:2; v:v),Cu(NO3)2.R x 2.5 H2O, 24h, 80 °C (c) Pd/C, N2H4.H2O, EtOH, 24 h, reflux, (d) PTSA, toluene, reflux, 72 h

The FCSNS was coated on to ITO/glass surface by repeated cyclic scan between -0.4 and 0.8 V to give a very stable electrochromic film. Upon increasing the potential from 0 V to 1 V, the band at about 880 nm intensified and also yellowish green color of the film turned into dark blue. Besides, the optical contrast (%ΔT) was measured as 21% at 880 nm, and oxidation-reduction response time was calculated as 1.9 and 1.1 s, respectively (Figure 1).

The electrochromic device (ECD) was assembled in sandwich configuration: ITO coated glass/anodically coloring polymer (FCSNS)/gel electrolyte/catodically coloring polymer (PEDOT)/ITO coated glass. The optical activity of the device is retained by 97.2% after 5000 cycles evidencing high redox stability. The neutral and oxidized state photos of the ECDs are presented in Fig. 2.

Figure 2. Neutral and oxidized state photos of electrochromic device

A multilayer organic light-emitting diode (OLED) having the structure of ITO/PEDOT:PSS/FCSNS/Alq3/LiF:Al showed a turn-on voltage of approximately 6 V and exhibited a bright green emission with a maximum luminance of 3700 cd/m². The maximum luminance efficiency was found as 2 cd/A at 14V and 11.75 mA/cm². The coordinate value of CIE was measured as (x, y) = (0.3279, 0.5398), which suggested that the device can emit a green light (Figure 3).

Figure 3. a) EL spectrum and b) Current density- appliedvoltage-luminescence characteristics of the OLED device.
Electrosynthesis and Characterization of Semiconductor Polyaniline Thin Films

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Abstract—Polyaniline thin films were synthesized via electrochemical method from aqueous solution containing perchloric acid on ITO coated glass electrode. The structure and properties of these films were characterized by cyclic voltammetry, optical method, SEM, EDS and AFM. Redox parameters, electroactive behaviour and stability of these films were determined by electrochemical tests. Also, conductivity measurements of polyaniline films were done using four point probe technique.

Thin films are widely using in optoelectronic application, semiconductors applications, gas sensors, fuel cell etc. In this work, we present the electrosynthesis and characterizations of semiconductor polyaniline thin films. Polyaniline thin films exhibit p-type semiconductivity all temperatures [1]. Polyaniline thin films were synthesized using cyclic voltammetric method from aqueous solution containing perchloric acid at applied different upper potential limits (-0.2 to 1.0 and 1.3 V) on ITO coated glass electrode. Cyclic voltammograms of films can be seen below figures 1.

Figure 1. Cyclic voltammograms of PANi1 and PANi2 films

Homogenous and adherent polymer films were obtained on electrode surface. The color of polyaniline films were green and blue for applied upper potential 1.0 V (PANi1) and 1.3 V (PANi2), respectively. Electrochemically synthesized film shows thin film behavior according to electrochemical test. Optical method, SEM, EDS and AFM were used for characterize of these films.

These methods were shown the optical parameters like transmittances, absorbance, reflection, reflection index, extinction coefficient, bang bap, reel dielectric; imaginary dielectric constants were determined by using Uv-Vis spectrophotometers (200-1100nm). According to optical results, polymer films are semiconductor thin films and have band gap energies of 3.9-4 eV. Transmittances of these films were changed according to applied upper potentials limit. Additionally, thicknesses of the films also were strongly depending on experimental procedures. Extinction coefficients of films were determined and these values are very low.

Morphology of PANi1 and PANi2 thin films were analyzed by SEM microscopy in 5kx magnification. PANi1 was growth locally on ITO coated glass surface. The growth rate of PANi2 film was bigger than the PANi1. As can be seen figure 2, Polymeric chain is clearly seen from SEM images.

Figure 2. SEM images of PANi and PANi2

EDS analyses were summarized following table 1.

Table 1. EDS analyses results

<table>
<thead>
<tr>
<th></th>
<th>PANi1</th>
<th>PANi2</th>
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<tbody>
<tr>
<td>Conc. (%)</td>
<td>Cl 0.856</td>
<td>7.378</td>
</tr>
<tr>
<td></td>
<td>C 15.186</td>
<td>36.563</td>
</tr>
<tr>
<td></td>
<td>O 83.958</td>
<td>56.059</td>
</tr>
</tbody>
</table>

AFM images of electrosynthesis PANi thin films:

Figure 3. AFM images of PANi1 and PANi2 films

Roughness Rₐ values of the produced thin films were 50.7 nm and 188 nm, also Rₛ values were 249 nm and 691 nm respectively.

Also, conductivity measurements of polyaniline films were done using four point probe technique. Result of conductivity measurements were 6.68 10⁻⁵ S cm⁻¹ and 1.45 10⁻⁵ S cm⁻¹ for PANi1 and PANi2, respectively.

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Low Voltage Operation of Organic Field Effect Transistors Based on Poly(1-vinyl-1,2,4-triazole)

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Abstract-In this work, we investigated poly (1-vinyl-1,2,4-triazole) (PVT) as dielectric layer for n-channel C60 OFET exploiting its excellent film formation property. OFET with anodized AlOx and PVT bilayer dielectric was applied where the thickness of PVT is as low as 45 nm. The device operated below 1 V. Our results showed that PVT can be applied for OFETs with low voltage operation with a simple process of spin coating from aqueous solution.

Devices with organic materials possess huge application potential in electronics due to their easy processibility and low cost. Moreover, realizing future plastic electronics relies on the development of the efficient organic electronic components. Organic field effect transistors (OFETs) are being extensively studied as basic components of such devices [1]. One of the major problems in OFETs is their high voltage operation because organic semiconductors as active layers generally have relatively low charge carrier mobilities. However, dielectric layer can be optimized to achieve low voltage operation. One of the approaches is using high dielectric constant oxides [2]. Passivation of the oxide surface is necessary in order to decrease intrinsic traps at the dielectric/semiconductor interface. To obtain similar capacitance as of the oxide layer, passivation layer has to be very thin. Therefore, good film formation property of the organic layer is prerequisite for such bilayer dielectric structure.

In this work, we investigated poly (1-vinyl-1,2,4-triazole) (PVT) as dielectric layer for n-channel C60 OFET exploring its excellent film formation property. OFET with anodized AlOx and PVT bilayer dielectric was applied where the thickness of PVT is as low as 45 nm. Total capacitance of 50 nF/cm² was obtained. The device operated below 1 V with threshold voltage of 0.12 V and I on/Ioff of 10³. Device showed no hysteresis indicating superb performance of PVT as passivation layer. More surprisingly, device with PVT as single dielectric thin layer also showed rather good performance although with somehow higher leakage current (see Figure 1).

Our results showed that PVT is an excellent organic dielectric towards realizing low voltage operation of OFETs.

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High Tg Carbazole-Based Hole-Transporting Materials for White Organic Light-Emitting Diodes

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Abstract—We describe the synthesis, characterization and OLED applications of two amorphous hole-transporting carbazole dendrimers. They were conveniently prepared using the standard Ullmann coupling conditions and characterized by 1H NMR, 13C NMR, MALDI-ToF and FT-IR spectroscopic means. Their photophysical properties were also determined by UV–Vis, PL spectroscopy, CV, TGA and DSC. OLED devices having a luminance of 1360 cd/m² and 1180 cd/m² have been fabricated.

White organic light-emitting diodes (WOLEDs) have attracted much attention because of their potential use in display backlights, full color display applications, and solid-state lighting purposes [1].

There have been many ways to develop the white-light emission at OLEDs, such as a single layer polymer blends with white emission material [2], multilayer device with RGB (red/green/blue) emission layers [3], a doped device with a host material [4], Fluorescent or/and phosphorescent [5] dyes.

Carbazole-based compounds demonstrate high thermal, morphological and photochemical stability [6]. These compounds have been extensively studied in many applications such as electrochromic devices, organic light-emitting diodes, organic field-effect transistors and photovoltaic cells, exploiting their intrinsic photophysical and redox properties [7].

In this work, two novel amorphous hole-transporting carbazole dendrimers [9',9''-(9,9'-dioctyl-9H-fluorene-2,7-diyl)-bis-9'H-9,3':6',9''-tercarbazole (OU17) and 9',9''-(9,9'-spirobi[fluorene]-2,7-diyl)bis-9'H-9,3':6',9''-tercarbazole (OU25)] were synthesized by a divergent approach involving bromination and Ullmann coupling reactions. The chemical structures of OU17 and OU25 were elucidated from their FT-IR, 1H-NMR, 13C-NMR and MALDI-ToF data.

OLED devices having the materials of OU17 or OU25 as the active layer showed turn-on voltage of 5 V and exhibited white light emission. The luminance values obtained from OU17 and OU25 were 1360 and 1180 cd/m², respectively. The color coordinate values according to CIE 1931 were measured as (x,y) = (0.2708, 0.3054) for OU17 and (0.2826, 0.3084) for OU25 which suggested that the devices can emit white light.

Figure 1. The molecular structures of OU17 and OU25

![Molecular structures](image)

Figure 2. EL spectrum of ITO/PEDOT:PSS/OU17/PSP/LiF:Al and ITO/PEDOT:PSS/OU25/PSP/ LiF:Al devices.

![EL spectrum graph](image)

Figure 3. Luminescence-applied voltage characteristics of the ITO/PEDOT:PSS/OU17/PSP/LiF:Al and ITO/PEDOT:PSS/OU25/PSP/ LiF:Al devices.

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A novel Tetranuclear Ni(II) complex: Synthesis, Structure and Low Temperature Magnetic Behavior
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Abstract—Novel tetranuclear cubane-like complexes (C₄H₉₀N₄Ni₄O₁₇) have been characterized by X-ray crystal structure analyses, magnetic measurements and spectroscopic properties. The structure analyses reveal that this complex consists of a Ni₄O₄ cubane core and the different coordinate environments of the nickel (II) ions result in a cubane structure with differing Ni–Ni distances and Ni–O–Ni angles. The intermolecular Ni–Ni distances are in the range from 3.206, 3.376 Å for the longest to 3.027, 3.031 Å for the shortest. The Ni (II) ion displays a distorted square pyramidal coordination. The magnetic measurement showed this complex to exhibit ferromagnetic behavior.

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Title: Optical Response of J-aggregate Shells Coating Metal Nanorods

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Abstract: The goal of this study is to evaluate the optical response of J-aggregate (JA) shells which uniformly coat Au and Ag nanorods. The “nanorod” systems considered are: spheroidal and spherical nanoparticles. For spheroidal nanoparticles the JA layer coats the metallic core directly. For the spherical nanoparticles two different coating geometries are considered: metal nanoparticles covered with a double-shell consisting of a spacer layer and a JA layer, and silica core covered with a double-shell consisting of a metal layer and a JA layer. The model systems are freestanding in a homogeneous non-absorbing embedding medium hosting the core which is also non-absorbing. On the other hand, JA shell is an absorbing medium. The J-aggregates have a single-transition optical resonance in solution. We would like to address the changes in the JA response upon coating in the geometries mentioned above in the presence of different dielectric media. The absorption cross-section of the JA layer will be calculated using the Mie algorithm¹ within classical electrodynamics.

In the absorption cross section calculations only the dipolar response to incident light and quasi-static approximation are considered since the core-shell nanoparticles are nanoscale objects. The dielectric function of the JA shell is described using a homogeneously broadened one-oscillator Lorentzian model.

Rational Design of Two Photon Absorbing BODIPY Derivatives

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Abstract—A novel class of distyryl-substituted boradiazaindacene (BODIPY) dyes were designed and synthesized which absorb two one photon in the green or two photons in the near IR regions of the (electromagnetic) spectrum and have D-A-D structure.

Two photon absorption is a nonlinear process which is of particular interest in various applications such as optical data storage [1], fluorescence imaging [2], O₂ sensing [3] and photodynamic therapy [4]. These applications have created a strong demand for new dyes which have high two photon absorption cross section. In the two-photon absorption process there is an interaction of the two photons which are simultaneously absorbed by materials. In the two photon absorption phenomena the strength of the absorption of the chromophore depends on the light intensity. On the other hand, one photon absorption is a linear optical process since it is based linearly on the light intensity. It is the main difference between one and two-photon absorption [5]. Generally speaking, the half of the energy (or twice the wavelength) of the corresponding one photon supplies the access to a given excited state.

In recent years, the design of two photon absorbing chromophores has gained much attention and there has been a growing interest in developing such two photon absorbing materials. Among these materials boradiazaindacenes commonly known as BODIPY dyes have particularly attracted considerable attention due to their high photostability and significant two photon absorption cross section [7]. Furthermore, BODIPY dyes have been investigated recently because of the fact that they show relatively sharp fluorescence peaks and have high quantum yields [8]. The rarity of the good chromophores in the long wavelength region of the spectrum is one of the big problems for various applications such as photodynamic therapy, optical power limiting, two photon cellular imaging and etc. [9]. This can be coped with by tuning the absorption wavelength of the chromophores. It is a well known fact that the linear absorption wavelength of the BODIPY is tunable to the near-IR range by introducing of the styryl groups [10].

In this study, we have synthesized and characterized such novel BODIPY dyes which display the two photon absorption property. They have linear absorption peaks between ~500 and 900 nm.

Figure 1. Jablonski diagram showing one and two-photon absorption [6].

In summary, we have successfully synthesized a novel class of BODIPY derivatives which are expected to have large TPA cross section. Initial data confirm our expectations.

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Novel Panchromatic Sensitizers for Dye Sensitized Solar Cells
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Abstract-A novel distyryl-substituted boradiazaindacene (BODIPY) dye displays interesting properties as a sensitizer at longer wavelengths in both DSSC systems with electrolyte or solid state, opening the way to further exploration of structure-efficiency correlation within this class of dyes.

In recent years, concerns about the effective usage of energy route scientists to design new systems that offer environmental friendly and economical treatment for this problem. Among renewable sources of energy, solar cells have always been high on the list of likely candidates. Unfortunately, large-scale commercialization is hampered by the production costs. Dye-sensitized solar cells [1] (DSSCs) appear to be highly promising alternatives to more expensive solar cell technologies. These metal-free dyes can be used in two different systems, either bulk heterojunction [2] or TiO2 based devices. Considering the current maximal level of overall conversion efficiency (η) under simulated sunlight for DSSCs (11%) which was achieved by Ruthenium complexes [3], improvements in efficiency and durability would certainly facilitate widespread utilization of this technology.

It is clear that there are a number of factors determining the efficiency of solar cells, but the structural and physical properties of the sensitizer are clearly important ones. Ruthenium dyes have some disadvantages so research groups are trying to design organic dyes as sensitizers [4]. For the most efficient of these sensitizers, the overall conversion efficiency is limited to 1-9% in traditional solar cells. Solvent-free solar cells (bulk heterojunction) are attractive systems due their ease of use. In bulk heterojunction devices charge carriers are polymers so there is no need to redox couple. Maximum reported conversion efficiencies are around 5% for carriers are polymers so there is no need to redox couple.

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BODIPY dyes have certain unique features that could make them highly advantageous compared to most other organic dyes, and thus, they are highly promising in this regard. (i) BODIPY dyes have high extinction coefficients (70 000-100 000 M⁻¹ cm⁻¹) and can easily be modified with any desired functionalities. (ii) Absorption peak can be moved to longer wavelengths through simple modifications, keeping strong absorption cross sections. (iii) BODIPY dyes have inherent asymmetry in charge redistribution when they undergo S0→S1 transition upon excitation, increasing the charge density on the meso-carbon (C-8), while decreasing it in most other positions in the boradiazaindacene system. This inherent directionality of charge redistribution pinpoints C-8 as the optimal position of charge injection. (iv) The directionality observed in excitation can be further enhanced with strategically placed electron withdrawing and electron-donating groups.

Now we propose novel BODIPY dyes which are designed cleverly to work at longer wavelengths efficiently. In Figure 2 it is shown the schematic representation of BODIPY sensitizer with its suitable positions for modification.

The performance of the sensitizers in the near IR region is particularly impressive. BDP-Xme has the highest conversion efficiency that is achieved by BODIPY dyes.

Figure 2. Sensitizers with further modifications and solar cell performance of these sensitizers.

The performance of the sensitizers in the near IR region is particularly impressive. BDP-Xme has the highest conversion efficiency that is achieved by BODIPY dyes.

Figure 3. Current vs. Voltage graphs of BODIPY dyes.

TiO2 sensitized device (with liquid electrolyte) construction and all efficiency calculations were performed by collaborative study with Michael Gratzel laboratory in Ecole Polytechnique Fédérale de Lausanne in Switzerland. Bulk heterojunction studies were done in University of Bayreuth in Mukkundan Thelakkat research group. Recent progress will be discussed in relation to more established ruthenium complexes.

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Divergent synthesis and light harvesting properties of tetra-styryl functionalized BODIPY Core

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Abstract—Novel light harvesting dendrimer which has eight BODIPY units at the periphery and a perylenediimide (PDI) dye at the core was synthesized by our group using “click-chemistry”1. This dye demonstrated that visible light was effectively collected as a result of large absorption cross section of the dendrimer and efficiently channeled to the core PDI unit, resulting in a significant antenna effect. In our work, we extrapolate the same idea using the first example of tetra-styryl functionalized BODIPY core for energy transfer.

In recent years, a number of skillfully designed examples of dendritic light harvesting systems (LHS) have appeared in the literature.2 In such systems, organizing a large number of chromophores around an energy acceptor is most effectively realized by a dendritic structure. We are particularly interested in the synthesis of such structures by making use of the “click-chemistry” version2 of the well-known Huisgen reaction.

In one of the published studies of our group1, as the donor-acceptor chromophore pair boradiazaindacene (BODIPY) and perylenediimide dyes were preffered, as it is already demonstrated that very efficient energy transfer is possible within this pair.3 Boradiazaindacenes are well known,4 bright green emitting fluorescent dyes with many diverse applications, such as fluorescent labeling of biomolecules,5 efficient sensitizers for photodynamic therapy,6 ion sensing and signaling,7 energy transfer cassettes,8 light harvesting systems,2 and supramolecular polymers.9 The parent dye absorbs near 480 nm and emits around 490 nm, but it is amenable to modifications,10 through which the absorption and the emission peaks can be shifted to the red end of the visible spectrum.

Fig. 1 Structure of dendrimer 1 and absorbance spectra of compounds 1, 2 and 3 at equal absorbances at 588 nm in CHCl3.

Through space energy transfer efficiency is primarily controlled by two parameters, (1) the distance between the energy donor and the acceptor chromophores, and (2) the spectral overlap between the emission spectrum of the energy donor and the absorption spectrum of the energy acceptor. In published study, two different dendritic BODIPY substituted PDI dyes (1 and 2) were synthesized (Fig. 1).

Excitation of a solution of the reference boradiazaindacene 3 at 526 nm (boradiazaindacene absorption peak) yields a very strong emission at around 538 nm (Fig. 1). When a solution of the dendrimer 1 having the same absorption at 526 nm was excited, very weak emission (almost at the baseline level) from boradiazaindacene chromophores were observed (Fig. 1). This is in accordance with the proposed energy transfer scheme. The residual emissions of the energy donor BODIPY units in compounds 1 and 2 have emission lifetimes of 0.05 ns and 0.11 ns, respectively, indicating a fast energy transfer.

Following same dendritic light harvesting system approach, we have designed and synthesized another light harvesting tetra-styryl BODIPY dendrimer 3 which has four BODIPY units as donor groups at tetra-styryl sides (Fig. 3). Synthesizing this dendrimer, we will show the first example of energy transfer in tetra styryl11 functionalized BODIPY core. And we expect longer wavelength energy transfer than previously reported. Also, we will obtain higher quantum yield and greater solubility because BODIPY dyes have higher quantum yield and greater solubility than perylenediimide dyes.

Fig. 3 Functionalized BODIPY core dendrimer 3

In our synthesis, we utilize click chemistry which is very useful for functionalization between terminal alkyne and azide units.

In summary, we have synthesized the first generation of tetra-styryl BODIPY core dendrimer 3 and plan to proceed with synthesis of higher generations. Our concept will certainly find use in a wide spectrum of applications, e.g. artificial photosynthesis, solar cells and OLED.

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Ratiometric Analysis of Hg(II) with Near-IR Fluorescent Molecular Sensor via an Energy-Transfer System
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Abstract-In this study, we have targeted to synthesize BODIPY based near-IR dyes as a selective fluorophore for Hg (II) cations. We have also demonstrated that the versatile BODIPY fluorophore can be functionalized for long wavelength emission on the 3 and 5 position of the BODIPY core with multiple and distinct functional groups in a stepwise manner. Thus we are able to link two BODIPY cores with a different absorption wavelengths to each other first time with click chemistry strategy to generate a chemosensor for Hg (II) cation.

Near-IR dyes [1,2] that absorb and emit in the red visible or near-IR region have attracted great interest in the fields of medicinal chemistry and biochemistry for the last few decades. Therefore the development of cation selective and sensitive sensors have been a hot subject for many researchers. Consequently, fluorescence based sensors are the most efficient and favorable ones among its counterparts in the field of sensor research.

In this work we present the synthesis, characterization and spectral studies of a novel Hg2+ selective chemosensor. A diverse strategy is used to afford this chemosensor. One, on the trunk, is enhanced with extended conjugation at methyl groups which are next to BF3:bridge unit on the BODIPY core with stepwise reactions with distinctive aldehyde to yield a near-IR dye. One arm on this main core comprise dithia-dioxo-mono aza crown-ether moiety (represented as red color in Fig. 1) which has specific recognition ability to the Hg2+ ion. ICT process was presented with this extended conjugation. Moreover, second arm is extended with a different aldehyde to yield near-IR dye and to yield more reactions on the core. The combination of these two fluorophore is presented to achieve energy transfer process from shorter wavelength absorption, corresponds to the second dye (assigned as a purple color in Fig. 1), to longer wavelength absorption dye, corresponds to first dye (represented as orange color in Fig. 1). The connection of these two fluorescent probes are achieved with a long carbon chain thus a Förster type energy transfer is presented. This energy transfer and ICT process results in a ratiometric fluorescent chemosensor with large Stokes shift result in three different wavelength observation.

As seen in Figure 2 (left), fluorescent measurements of dye with various metal ions displayed excellent selectivity for Hg2+ and energy transfer process from donor to acceptor is enhanced with addition of Hg2+. It is observed as a decrease in intensity of the second dye at 510 nm with increase in intensity of the first dye with a new fluorescence emission maxima at 660 nm, following the intensity of the fluorescent peak at 730 nm decreases. Other metal ions do not induce any changes in the fluorescence spectrum of this well-designed dye. To illustrate the energy transfer process a fluorescence study was done as seen in Fig. 2 (right). It is obviously seen that coordination of second dye to first dye via click chemistry relatively affects the emission intensity of the second dye as a result in energy transfer process through the first dye. A large change in two different absorption wavelengths and three different emission wavelengths were clearly presented.

In conclusion, we have present a new type-FRET based fluorescent chemosensor, for Hg2+ that show a remarkable selectivity over the other metal cations with a new strategy using versatile BODIPY core.

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Novel Near-IR Absorbing Chromophores; Synthesis, Characterization and Applications

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Abstract—We designed and synthesized BODIPY based novel near IR absorbing chromophores. These new dyes are expected to be important in DNA sequencing and photodynamic therapy applications.

There are many reported fluorescent dyes in literature in recent years. A class of these fluorescent dyes is known as 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) dyes. Several different BODIPY dyes have been synthesized and used for many different applications since the first BODIPY dyes have been reported in 1968 [1]. BODIPY dyes have been used as chemosensors [2], laser dyes [3], biological labeling reagents [4], energy transfer reagents [5], light harvesters [6], photodynamic therapy reagents [7].

Several excellent characteristics of BODIPY dyes such as high fluorescent quantum yield, narrower emission band widths, the thermal and photostability, great solubility and ease of functionalization from various positions allow using BODIPY dyes in different application areas. The ease and variety of functionalization is the most important characteristic of BODIPY core. The BODIPY core gives several different reactions from different positions (Figure 1).

Figure 1. Points of functionalization on the BODIPY core

In the functionalization of BODIPY core, the 3- and 5-positioned methyl groups are moderately acidic and give Knoevenagel reactions. The synthesis of different styryl substituted BODIPY derivatives are possible, by these condensation reactions between methyl groups of BODIPY cores and different aromatic aldehydes.

However, functionalization of 1 and 7 methyl groups has not been demonstrated until very recently. It is also possible to synthesize different chromophores with different absorption and emission wavelength by decorating the BODIPY core with different styryl groups. For example, 4-metoxyphenyl substituted BODIPY dyes show different absorption and emission spectra. Absorption maxima for parent BODIPY (0), monostyryl BODIPY (1), distyryl BODIPY (2), tristyryl BODIPY (3) and tetrastyryl BODIPY (4) are at 502, 560, 640, 662 and 683 nm, respectively (Figure 2).

Previously in our lab [8], we have reported several new tetra-styryl substituted BODIPY dyes. Those styryl substitutions yield BODIPY cores which have long absorption and emission wavelength in the near-IR region. Although near-IR dyes do not have sufficient stability towards light, heat, etc. our near-IR BODIPY dyes show adequate photo- and chemical stability for most applications.

In this study, two different tetra-styryl functionalized near-IR emitting BODIPY derivatives (Figure-3) were synthesized for photodynamic therapy applications. The improved water solubility and strong absorption peaks at near-IR region make these probes superior over the other photodynamic therapy agents.

Figure 2. Absorption spectra of styryl-substituted BODIPY Chromophores

Figure 3. General structure of the tetrastyryl-BODIPY dyes.

In addition, the PEG (polyethylene glycol) group installed on the BODIPY core not only provides better water solubility, but provides targeting towards tumor tissues.

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Polymer Matrix Embedded Molecular Sensors for Fluoride Ions

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Abstract—Two Bodipy derivatives with silyl-protected phenolic functionalities, signal fluoride concentrations both in solution and polymer methacrylate (PMMA) matrix.

Anion sensing is a challenging task [1,2]. This is due to large variations in size, shape, charge distribution and strong solvation in polar and/or H-bond donor solvents. While continuous monitoring and real time imaging of anionic species require reversible molecular sensors, for some anions, a reaction based sensor [3,4]a “chemical dosimeter” would be equally useful. For practical applications, one can easily envision a “dipstick” for selected anions such as cyanide or fluoride considering how and where it could be relevant to measure the concentrations of these ions.

In this sense, we designed compounds 1 and 2 as potential fluoride responsive molecules. Previous work in our group [5]and in others, has demonstrated that a phenoxy substituent at the meso (8) position of the Bodipy core is a very strong PET (Photoinduced Electron Transfer) donor. The spectral signature of PET is quenching of fluorescence without any significant changes in the emission wavelength. So, using probe compound 1, fluoride anions should be signaled by a decrease in the emission intensity as a consequence of the removal of the TIPS (trisopropylsilyl) protective group.

In the second design, we made use of a Knoevenagel type of a reaction of Bodipy methyl groups (methyl groups at 3 and 5 were previously shown to be reactive in condensation with aldehydes; TIPS-protected phenol moiety. Here, the expectation is that the deprotection reaction facilitated by fluoride ions will generate strong ICT (Intramolecular Charge Transfer) donor phenoxy ion in full conjugation to Bodipy dye, which would raise the HOMO level, reduce the energy gap for Sβ-Sγ transition, and thus result in a large red shift in the major peak in absorbance. In most instances, such large red shifts result in a decrease in the emission intensity (Figure 2).

In order to emphasize practical potential of these probe compounds, we prepared PMMA films impregnated with the probe compounds 1 and 2. The probes in the polymer matrix responded to tetrabutylammonium fluoride solution as expected. Figure 3 shows the appearance of the fluoride exposed polymer films in the ambient light conditions and under UV illumination at 360 nm.

Figure 1. Absorbance and emission spectra of compound 1+ F- in acetonitrile in the presence of increasing F- concentrations.

Figure 2. Absorbance and emission spectra of compound 2+F- in the presence of increasing F- concentrations after 5 min.

Quenching of the emission is clear on the fluoride exposed regions in both cases, and for the polymer film containing fluoride probe 2, color is visibly changed. The polymer films are stable under ambient light and temperature over weeks, with no discernable change in color or in response. The dyes do not wash off from the films as well. This simple demonstration shows the viability of polymer-strip design for fluoride monitoring in environmental samples.

Figure 3. Digital photographs PMMA polymer sheets doped with chemosensor 1 (top) and 2 (bottom) under UV irradiation.

In conclusion, in this work, we were able to demonstrate that the designs based on selective chemical reactions, especially when parameters which influence triggering of certain photophysical processes are incorporated, can be quite successful. In the probes, or dosimetric reagents reported above, this has been achieved for PET and ICT. Thus, it is clear that depending on the exact requirements for a particular application, either an emission change or visible color change can reproducibly be produced. We believe other rationally designed reaction based probes, with built-in triggers for photophysical and even photochemical processes will appear in due course. Work to that end is in progress in our laboratory.

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Selective Manipulation of ICT and PET Processes in Styryl-Bodipy Derivatives: Applications in Molecular Logic and Fluorescence Sensing of Multiple Metal Ions.

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Abstract-In this study, we have demonstrated that metal ions acting as modulators (or inputs, in digital design parlance), can generate absorbance changes in accordance with the operation of a half-adder. In addition, an AND logic gate in the emission mode was delivered using a different binucleating arrangement of ligands. The results suggest that different metal ions can be used as non-annihilating inputs, selectively targeting various ligands incorporated within a single fluorophore.

Molecular logic research today is built on an initial recognition by de Silva \cite{1} that fluorescence signals obtained in response to cations, could be considered to be analogous to the digital responses in electronic logic gates. Molecules can undergo changes in the ground or excited states, in response to modulators which can be other molecules, ions, or light of a certain wavelength. In most cases, these changes could then be signaled by changes in the emission intensity or wavelength and can be related to the operation of logic gates, via the familiar Boolean logic. \cite{2}

It has become apparent that logic gate design using molecules may not necessarily be subject to the same limitations as the silicon-based analogs. One can design a single molecule which can simultaneously behave as two (or more) distinct logic gates, depending on the exact choice or definition of outputs. \cite{3} On the other hand, while functional integration is possible within single molecule, integration of logic gates to implement more complex functions is far from being straightforward. Nevertheless, molecular logic gates represent a true bottom-up approach for information processing at the molecular level. Strongest aspect of molecular logic gates is the fresh new look, which provides a novel mental platform to build new ideas.

The fluoroionophores of choice in this work is Bodipy-derived. Bodipy dyes have become a rising star of fluorophores in the fluorescent chemosensor community \cite{4} due to their remarkable properties such as high quantum yield and large extinction coefficients. But more importantly, these dyes are open to derivatization in a multitude of ways through recently expanding “Bodipy chemistry”.

![Figure 1. Structure of a Bodipy core (L-ligand)](Image)

Versatile chemistry of Bodipy dyes allowed us to design new Bodipy-based fluorescent molecules with different ligands attached at locations where the modulation of ICT and PET processes can be achieved independently. This is not an easy synthetic task for most other fluorophores. But, with Bodipy dyes, it is just couple of well coordinated sequence of transformations.

Rational installation of three ligands (receptors) on the different parts of the Bodipy core yielded smart molecules mimicking logic functions such as two and three input AND gates and a Half Adder. Metal ions Zn(II), Hg(II), and Ca(II) were chosen as the (non annihilating) inputs. When considering the two input AND gate (Figure 2) the fluorescence at 570 nm was monitored as the output signal. Intensity was significant (high, 1), only when both inputs were present.

![Figure 2. Emission spectra of 2 (1.67 μM) in Acetoni trile in the presence of Hg(II) and Zn(II) (6.68 μM and 1.67 μM, respectively). Inset shows truth table for AND gate. (λex=555 nm)](Image)

On the other hand when those ligands were attached to the Bodipy core as ICT donors (Figure 3), and appropriate absorbance signals were recorded as an output, this molecule will work in accordance with the operation of a half adder.

![Figure 3. Absorption spectra of compound 4 (3.2 μM) in Acetonitrile in the presence of Hg(II) and Zn(II) (28.8 μM and 32.0 μM, respectively). Inset shows truth table for half-adder](Image)

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The investigation of geometrical properties of 2,5 pyridinedicarboxylic acid, synthesis and vibrational properties of some metal halogen compounds

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Abstract—In this work, the theoretical and experimental vibrational spectra of 2,5 pyridinedicarboxylic acid were studied. FT-IR spectra of the molecule in the liquid phase were recorded in the region 4000-400 cm\(^{-1}\). The structural and spectroscopic data were calculated by using density functional method (B3LYP, HF, BLYP) with the 6-31G(d) basis set in the ground state. The vibrational frequencies were calculated and scaled values were compared with experimental FT-IR spectra. The observed and calculated frequencies are found to be in good agreement. In addition to these five new complexes of 2,5 pyridinedicarboxylic acid molecule Ni(2,5 PDA)Cl\(_2\), Hg(2,5 PDA)Cl\(_2\), Cu(2,5 PDA)Cl\(_2\), Fe(2,5 PDA)Cl\(_2\), Mn(2,5 PDA)Cl\(_2\) [where; 2,5 PDA: 2,5 pyridinedicarboxylic acid] were synthesized for the first time. The FT-IR spectra of the new complexes were recorded, and their C,H,N analysis results were reported. The possible structures for complexes were proposed according to elemental analysis and FT-IR spectra.

As a result in the present work, we have performed the experimental and theoretical vibrational analysis of 2,5PDA for the first time. The molecular geometry, vibrational frequencies, have been calculated by using DFT, B3LYP method with 6-31G(d) basis set in the ground state. They are in good agreement with experimental results. Also the analysis of the experimental values indicates that there are some structure-spectra corelations. It was found that the frequency shift values depend on the metal in order Hg<Cu.

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Recent studies concerning to use of 2,5PDA as a ligand towards transition metal salts[2-6] and lanthanite-transition metal salts[2,3] have shown that a great variety of polymeric structures can be obtained as a result of the different conformation and coordination modes of the 2,5PDA. More recently, the X-ray crystal structures and photophysical properties of four lanthanite complexes[7].

In this work The molecular structure of 2,5 pyridinedicarboxylic acid in the ground state is computed by performing DFT/B3LYP methods 6-31G(d) basis set. The wavenumbers in the ranges from400-1700cm\(^{-1}\) and lower than 1700cm\(^{-1}\) are scaled with 0.958 and 0.983, respectively[8]. All calculations are performed by using GaussView molecular visualization program[9] and GAUSSIAN 03 program package on the personal computer[10]. In addition to these we prepared and reported the FT-IR spectra of some metal(II) halide complexes 2,5PDA for detecting any possible relation ship between the ligand vibrational values and the metal, and presented their IR data.

2,5 pyridinedicarboxylic acid (2,5PDA) with divergent function groups, which could give more possibility to form bridging hydrogen bonds, in interesting and has potential for self assembly [1].

Figure. 2.5 pyridine dicarboxylic acid[10]

Recent studies concerning to use of 2,5PDA as a ligand towards transition metal salts[2-6] and lanthanite-transition metal salts[2,3] have shown that a great variety of polymeric structures can be obtained as a result of the different conformation and coordination modes of the 2,5PDA. More recently, the X-ray crystal structures and photophysical properties of four lanthanite complexes [7].

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As a result in the present work, we have performed the experimental and theoretical vibrational analysis of 2,5PDA for the first time. The molecular geometry, vibrational frequencies, have been calculated by using DFT, B3LYP method with 6-31G(d) basis set in the ground state. They are in good agreement with experimental results. Also the analysis of the experimental values indicates that there are some structure-spectra corelations. It was found that the frequency shift values depend on the metal in order Hg<Cu.

This work was supported Celal Bayar University Research Fund under Grand No:FBE 2008-054

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References

Experimental and theoretical FT-IR spectroscopic analysis of 3,5 pyridinedicarboxylic acid, synthesis and vibrational properties of its some metal halogen compounds

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Abstract: In this study, the theoretical and experimental vibrational spectra of 3,5 pyridinedicarboxylic acid were studied. FT-IR spectra of the molecule in the liquid phase were recorded in the region 4000-400 cm⁻¹. The structural and spectroscopic data were calculated by using density functional method (B3LYP, HF, BLYP) with the 6-31G(d) basis set in the ground state. The vibrational frequencies were calculated and scaled values were compared with experimental FT-IR spectra. The observed and calculated frequencies are found to be in good agreement. In addition to these seven new complexes of 3,5 pyridinedicarboxylic acid molecule Mn(3,5 PDA)Cl₂, Ni(3,5 PDA)I₂, Cd(3,5 PDA)Cl₂, Fe(3,5 PDA)Cl₂, Ni(3,5 PDA)Cl₂, Mn(3,5 PDA)I₂, Co(3,5 PDA)Cl₂ [where; 3,5PDA: 3,5 pyridinedicarboxylic acid(Fig1)] were synthesized for the first time. The FT-IR spectra of the new complexes were recorded, and their C, H, N analysis results were reported. The possible structures for complexes were proposed according to elemental analysis and FT-IR spectra.

Pyridinecarboxylic acids are beneficial compounds for human organism and they are involved in several essential biochemical processes. 3-pyridine carboxylic acid is converted to nicotinamide adenine nucleotide (NAD) which serves as intermediate in two-electron transfer in organism [1].

As a result in the present work, we have performed the experimental and theoretical vibrational analysis of 3,5PDA for the first time. The molecular geometry, vibrational frequencies, have been calculated by using DFT, B3LYP method with 6-31G(d) basis set in the ground state. They are in good agreement with experimental results. Also the analysis of the experimental values indicates that there are some structure-spectra correlations. It was found that the frequency shift values depend on the metal in order Cd < Cu and decreases in the order Cl > I.

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**pH Regulation of Singlet Oxygen Generation Efficiency**

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**Abstract**

Photodynamic therapy relies on the activation of photosensitizer by using light of certain wavelength and generation of cytotoxic singlet oxygen species in response. Design, synthesis, characterization of a novel water soluble, near IR absorbing BODIPY photosensitizer is accomplished. As opposed to other photosensitizers in literature, this photosensitizer is rationally designed to have singlet oxygen generation capability only in acidic environment like in the case of tumor tissue.

Photodynamic therapy is a new treatment modality used for certain diseases such as neck, lung, brain, head, pancreas, breast, skin cancers, cardiovascular diseases and some other diseases such as age-related macular degeneration [1].

New therapeutic techniques having toxic effects against tumors while giving no harm to normal tissues are aimed in many researches. With this in mind, scientists try to find ways to distinguish malignant tissue from the normal ones. One important difference that is observed between tumors and normal tissues is the nutritional and metabolic environment. Vasculatures of tumors are not sufficient to supply nutritional need of the growing population of tumors. Thus, oxygen deficiency is observed in tumor cells. [2] Also production of lactic acid and the hydrolysis of ATP in energy-deficient area are the reasons for acidic environment in many tumors. Many experiments were done to measure pH in animal and human tissues by Wike-Hooley, et al. Their results show that there is a wide range of pH values in malignant tissue, from about pH 5.8 to pH 7.6 in both human and rodent tumors. To generalize these results we can conclude that tumor microenvironment is more acidic than normal tissues, with the pH values much lower in tumors compared to normal tissues.[2]

**Figure 1. Structure of Target photosensitizer**

These pH differences between normal tissue and tumor give us a chance to apply effective therapeutic techniques towards tumors without damaging normal tissues. In a previous work done in our group, the acidity of the environment and sodium concentration were considered as two inputs to activate the sensitizer [3]. However, this molecule is not water soluble. Here, a water soluble photosensitizer that is to be activated only when the pH of the tissue is comparably acidic is used to differentiate malignant tissues from the normal ones (Figure 1). Through this approach, in principle, more selective and noninvasive therapy can be developed.

Conjugated BODIPY (borondipyromethene) core is required for near IR absorbance. Iodine atoms are added to enhance intersystem crossing which in turn increase photodynamic ability of the sensitizer. Pyridine moieties are used for pH sensitivity, this group is expected to be protonated at acidic cancer tissues which results in a red shift in absorbance spectrum of the photosensitizer. This shift enables selective activation of protonated molecule rather thus provides further selectivity. Photosensitizer is functionalized with polyethylene glycol (PEG) unit for improving of water solubility. With the likes of the photosensitizer presented here, photodynamic therapy can be more selectively applied to the malignant tissue without minimal damage to the surrounding normal tissue.

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Design and Synthesis of Calixarene-Bodipy Tandem as Near IR Absorbing Amphiphilic Photodynamic Therapy Reagent

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Abstract- Calix[4]arene-Bodipy tandem was used as an efficient photodynamic therapy reagent. Calix[4]arene have been used as a scaffold which carries two highly efficient Bodipy photosensitzers. Also, bodipy and calixarene linked directly for the first time for photodynamic activity. Furthermore, the agent have water solubility conferring polyethylene glycol and hydrophobic (deciyl groups) parts needed for an amphilic character.

Photodynamic therapy (PDT) is a method for treating various cancer types. The concept of PDT first emerged in 1913¹, but until 1960s the development did not begin. Since then, a large number of different lines of research became active within this field.² However, the current photosensitzers (PSs) clinically used are far from being ideal photosensitzers. Therefore, improved PDT is a challenge for many research groups. PDT concept is based on the three main components: light, photosensitizer and singlet oxygen. By combination of these three, malignant cancer tissues are killed. Beside these, there are some other important features that should be employed, in order to prove the efficacy of the treatment. First, the PDT agent should be water soluble to be studied in the body. However, this is not the most crucial thing, since hydrophobic photosensitzers can work in body by being carried in micellar compositions with surfactants.³ Second, the photosensitizer should have an absorption maximum at the therapeutic window 650-900 nm. This wavelength range has many advantages; biomolecules almost do not absorb and fluoresce, light scattering is low, NIR light penetrates through the body deeply and NIR sources cost low.⁴ Although these advantages are valid above 900 nm, too, singlet oxygen generating ability is low due to the low energy inadequacy of light to excite the PS. Third, the photosensitizer should have a targeting group, leading it to the malignant cancer tissues. Fourth, the PS should have a high efficiency of producing singlet oxygen. It is observed experimentally that some properties such as heavy atom effect increases the triplet state quantum yield.⁵ Fifth, the PS should be harmless in dark. The photosensitzers which absorb at long wavelengths possess this feature; since sunlight phototoxicity is observed at the photosensitzers having absorption maxima around 500 nm. The target compound we designed has unique properties. Calix[4]arene and bodipy units have been used together in past⁶ for other purposes, such as ion sensing. However, in present work, for the first time they have been used for photodynamic activity and connected in conjugative manner. N,N-dimethylaminobenzaldehyde groups are also attached to the bodipy core in order to shift the absorbance to the near IR region. With these modifications absorbance maximum in isopropanol have been measured to be at 709 nm. Other unique aspect of the molecule is its proposed cell permeability. This has been ensured by the decyl groups on the calix[4]arene. These groups also enable good solubility in common organic solvents. The other aspect of the tandem is its water solubility. This have been supplied by polyethylene glycol (MW=2000 g/mol) molecule which have been attached by a click reaction.

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Light Harvesting Dendrimers for Use in Organic Solar Concentrators
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Abstract—Light harvesting dendrimer with three different BODIPY chromophores is synthesized and used in an organic solar concentrator. Förster type energy transfer within the molecule from the outer chromophores to the core decreases self quenching, enhances the core emission and allows large Stokes shift required in organic solar concentrators. This novel concentrator is promising since it requires only single layer with single type of photovoltaic cell.

Organic solar cells are becoming attractive within the last 20 years due to their cheap and easy fabrication yet their efficiencies are far from the values achieved by traditional semiconductor solar cells [1]. Besides, absorption of dyes used for this purpose usually do not span large parts of the solar spectrum [1]. One approach to overcome these problems is to build organic solar concentrators (OSC) which rely on the internal reflection from the surface of the system that funnel the energy to photovoltaic cells (PVC) attached at the edges [2,3]. As oppose to their optical counterparts they do not result in heating thus do not decrease the longevity of the solar cells [2]. Further, there is no requirement for large surface decorated with PVC or optical positioning apparatus which are the most expensive parts of the solar cells.

Up to present, different OSC approaches are investigated such as the ones that use highly concentrated spectrally different dye mixtures to enable Förster type energy transfer or dyes/quantum dots that are placed in different layers of plate [4-7]. However, for multi-layer systems PVC placement at the edges of each layer increases the cost considerably, for the case in dye mixtures, high concentrations are required to bring the donor-acceptor in Förster proximity. This indeed increases the self absorption thus decrease the efficiency.

In the research presented here, a dendritic light harvesting molecule is synthesized and used in solar concentrators. Three different dyes of different absorption characteristics, namely BODIPY, monostyryl-BODIPY and distyryl-BODIPYs are attached covalently to one another using click chemistry. Energy transfer efficiencies are determined to be greater than 90% by using time resolved fluorescence measurements. The molecule is embedded into epoxy resin and solar concentrator efficiencies are investigated.

It has been observed that light harvesting dendrimer allows absorption in a large part of the solar spectrum (450-700 nm) and provides large Stokes shift (150 nm). Highly efficient unidirectional energy transfer from the outer shell to the inner acceptor enhance the core emission both by decreasing the self-absorption of core chromophore and by decreasing the environment dependent deactivation pathways, so called “shell effect” [8]. Since chromophores are placed in the dendritic structure in accordance with their spectral overlap within appropriate Förster distance, high concentrations are not necessary. Yet, since the emission is exclusively from the core chromophore, single layer with single type of PVC is enough.

This promising novel approach in which chromophores with different but conjugate spectral properties are covalently attached to one another provides channeling of emitted light in concentrator with high efficiencies thus solves most of the problems faced by organic solar concentrators.

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Abstract-A cyano-bridged Mn(III)–Fe(III) complex, [Mn(L)RFe(CN)R]3(MeOH)12 (1) (L=N,N’-bis(5-bromo-salicylidene)-2,2-dimethyl-1,3-diaminopropane) was prepared and characterized. The compound 1 crystallizes in Trigonal space group P32 with a=28.5554, b=28.5554, c=19.2155 Å, γ=120.00°. Single crystal X-ray analysis reveals that the complex assumes a cyano-bridged Mn3Fe3 unit. The four CN\(^-\) in the equatorial plane of the [Fe(CN)\(_3\)]\(^{3-}\) moiety bridge four Mn ions, each in the cis position, which results in a 3D neutral layered structure giving a [-Mn-N=C-Fe-CN-Mn-] linkage. The Mn ions assume an elongated octahedral geometry, in which the equatorial sites are occupied by N\(_2\)O\(_2\) donor atoms of the Schiff base ligand, and the two axial positions are filled by two cyanide ion of [Fe(CN)\(_3\)]\(^{-}\). The magnetic measurement showed this complex to exhibit anti-ferromagnetic behavior.

Since the beginning of the 1990s, the design and synthetic strategies of molecule-based magnets are current interests for their potential application in molecular memory device, thermal and optical switching of molecular spin states [1]. The search for new polynuclear molecules displaying high spin ground state and anisotropy attracted synthetic chemists’ attention [2]. These anisotropic high spin molecules show magnetic properties such as single molecule magnet (SMM) [3], single-chain magnet (SCM) behaviour and magnetic quantum tunnelling effect [4]. Our research program has focused to the synthesis of such complexes in order to get SMMs. To obtain anisotropic high spin molecules, we developed a step by step synthetic strategy based on the coupling reaction of polycyaanometalate precursors and mononuclear complexes of transition metal ions with a polydentate ligand, leaving a unique accessible position only [5].

The decrease in the low temperature can be described by the spin-only value of 9.95 \(\mu_B\) for the magnetically dilute five-spin system \((\text{SMn x 4, SFe}) = (2 \times 4, 1/2)\). On lowering the temperature, the \(\mu_{\text{eff}}\) value decreases gradually and then sharply to reach a minimum of 5.69 \(\mu_B\) at 1.9 K. This behavior indicates that an antiferromagnetic interaction is operating for complex 1. The decrease in the low temperature can be described by the intermolecular magnetic interactions between the Mn(III)-Fe(III)-Mn(III) ions.

\[ \mu_{\text{eff}} \text{ value at room temperature, } 10.17 \mu_B, \text{ is slightly larger than the spin-only value of 9.95 } \mu_B \text{ for the magnetically dilute five-spin system (SMn x 4, SFe) = (2 x 4, 1/2). On lowering the temperature, the } \mu_{\text{eff}} \text{ value decreases gradually and then sharply to reach a minimum of 5.69 } \mu_B \text{ at 1.9 K. This behavior indicates that an antiferromagnetic interaction is operating for complex 1. The decrease in the low temperature can be described by the intermolecular magnetic interactions between the Mn(III)-Fe(III)-Mn(III) ions.} \]

\[ \text{Figure 2. Magnetic susceptibility } \chi \text{ and effective magnetic moment } \mu_{\text{eff}} \text{ per Mn}_3\text{Fe versus } T \text{ for 1.} \]

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Fabrication and Characterization of Solid State Dye Sensitized Solar Cells using Organic Dyes

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Abstract—We report the solid state cell performances of novel dyes using nanoporous TiO2 electrodes. Solid-state dye-sensitized solar cells were fabricated using the organic hole-transporting medium (HTM) 2,2’7,7’-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9’-pirofluorene (spiro-OMeTAD). The solar cell with 2,2’7,7’-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9’-pirofluorene (spiro-OMeTAD) as a hole conductor and sensitzers on mesoporous TiO2 shows a short-circuit current of 2.27 mA/cm², an open circuit voltage of 795 mV and filling factor 37.43%.

The first dye-sensitized solar cell based on a nanoporous TiO2 layer with an iodine-iodide electrolyte was realized by O’Regan and Graetzel [1]. New investigations use an iodine-free solid organic hole transporting material (HTM) [2-4] instead of the liquid electrolyte. The ionic transport is replaced by electronic transport in the amorphous HTM. Solid-state dye-sensitized solar cells (SDSC) are promising due to their large potential to convert solar energy to electrical energy at low cost and their capability to solve the leakage or sealing problems that exist in liquid electrolyte dye-sensitized solar cells [5].

Solid state dye sensitized solar cell consists of transparent conductive oxide layer, compact TiO2 layer; a dye adsorbed on mesoporous nanocrystalline-titanium dioxide acting as n-type semiconductor layer; hole transport material and a gold counter electrode. Figure 1 shows the schematic representation of a solid state dye sensitized solar cell. We present novel organic dyes in SDSc application.

Figure 2 also shows the I-V curve of solid state dye sensitized solar cells.

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Divergent synthesis and light harvesting properties of tetra-styryl functionalized BODIPY Core

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Abstract—Novel light harvesting dendrimer which has eight BODIPY units at the periphery and a perylenediimide (PDI) dye at the core was synthesized by our group using "click-chemistry"\textsuperscript{11}. This dye demonstrated that visible light was effectively collected as a result of large absorption cross section of the dendrimer and efficiently channeled to the core PDI unit, resulting in a significant antenna effect. In our work, we extrapolate the same idea using the first example of tetra-styryl functionalized BODIPY core for energy transfer.

In recent years, a number of skillfully designed examples of dendritic light harvesting systems (LHS) have appeared in the literature\textsuperscript{2}. In such systems, organizing a large number of chromophores around an energy acceptor is most effectively realized by a dendritic structure. We are particularly interested in the synthesis of such structures by making use of the “click-chemistry” version\textsuperscript{2} of the well-known Huisgen reaction.

In one of the published studies of our group\textsuperscript{1}, as the donor-acceptor chromophore pair boradiazaindacene (BODIPY) and perylenediimide dyes were preffered, as it is already demonstrated that very efficient energy transfer is possible within this pair\textsuperscript{3}. Boradiazaindacenes are well known\textsuperscript{4}, bright green emitting fluorescent dyes with many diverse applications, such as fluorescent labeling of biomolecules\textsuperscript{5}, efficient sensitizers for photodynamic therapy\textsuperscript{6}, ion sensing and signaling\textsuperscript{7}, energy transfer cassettes\textsuperscript{8}, light harvesting systems\textsuperscript{2}. and supramolecular polymers\textsuperscript{9}. The parent dye absorbs near 480 nm and emits around 490 nm, but it is amenable to modifications\textsuperscript{10}, through which the absorption and the emission peaks can be shifted to the red end of the visible spectrum.

Through space energy transfer efficiency is primarily controlled by two parameters, (1) the distance between the energy donor and the acceptor chromophores, and (2) the spectral overlap between the emission spectrum of the energy donor and the absorption spectrum of the energy acceptor. In published study, two different dendritic BODIPY substituted PDI dyes (1 and 2) were synthesized (Figure 1).

Excitation of a solution of the reference boradiazaindacene 3 at 526 nm (boradiazaindacene absorption peak) yields a very strong emission at around 538 nm (Figure 1). When a solution of the dendrimer 1 having the same absorption at 526 nm was excited, very weak emission (almost at the baseline level) from boradiazaindacene chromophores were observed (Figure 1). This is in accordance with the proposed energy transfer scheme. The residual emissions of the energy donor BODIPY units in compounds 1 and 2 have emission lifetimes of 0.05 ns and 0.11 ns, respectively, indicating a fast energy transfer.

Following same dendritic light harvesting system approach, we have designed and synthesized another light harvesting tetra-styryl BODIPY dendrimer 3 which has four BODIPY units as donor groups at tetra-styryl sides (Figure 2). Synthesizing this dendrimer, we will show the first example of energy transfer in tetra styryl\textsuperscript{11} functionalized BODIPY core and we expect longer wavelength energy transfer than previously reported. Also, we will obtain higher quantum yield and greater solubility because BODIPY dyes have higher quantum yield and greater solubility than perylenediimide dyes.

In our synthesis, we utilize click chemistry which is very useful for functionalization between terminal alkyne and azide units.

In summary, we have synthesized the first generation of tetra-styryl BODIPY core dendrimer 3 and plan to proceed with synthesis of higher generations. Our concept will certainly find use in a wide spectrum of applications, e.g. artificial photosynthesis, solar cells and OLED.

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Structural Analysis and Magnetic Properties of a Novel Cubane-Type Cobalt (II) Complex with ONO Tridentate Ligands

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Abstract- A novel tetranuclear Co(II) tridentate Schiff base complex \([\text{C}_{45}\text{H}_{56}\text{Cl}_2\text{Co}_4\text{N}_4\text{O}_{13}]\) (1) has been synthesized and its crystal structure has been determined by single crystal X-ray diffraction analysis. This cubane-type Co(II) complex consists of a \(\text{O}_3\)-alkoxo bridged tetranuclear core, giving an approximately cubic array of alternating cobalt and oxygen atoms. Structural analysis of (1) shows that coordination geometry about each Co(II) ion is a pseudo octahedron with one nitrogen and four oxygen atoms from tridentate ligands and methanol molecule. Magnetic susceptibilities for (1) in the solid state have been measured over the temperature range 2-350 °K as a function of temperature and the magnetic parameters have been determined with fitting procedure.

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Performance of organic thin film transistors based on arylene bisimides

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Abstract—We analyzed the effect of polymeric dielectric with hydroxyl and hydroxyl-free group on current-voltage characteristics of organic thin film transistor by the use of novel arylene bisimide derivatives. For this purpose, we used polyvinyl alcohol (PVA) with polar group and benzocyclobutene (BCB) with non-polar group as a solution processed dielectric. We find that the surface morphology is influenced by chemical structure of polymeric dielectric concerning surface energy. The electron field effect mobility of both arylene bisimides is enhanced by decreased surface energy of dielectric related to polar functional groups and was obtained highest value by employing naphthalene bis-benzimidazole as an active layer on both dielectrics compared with perylene bis-benzimidazole semiconductor.

Organic thin film transistors (OTFT) based on highly conjugated p-channel or n-channel active layers are most interested organic electronic devices that have been used on active and passive matrix displays, radio frequency identification tags, chemical sensors, biological sensors, etc. [1,2]. Remarkable studies have been reported by using various perylene and naphthalene bisimides substituted benzimidazole groups on hydroxyl and hydroxyl-free polymeric insulators. Hydroxyl-free divinyltetramethyl-disiloxane-bis (benzocyclobutene) (BCB, called “cyclotene”) and hydroxyl polyvinyl alcohol (PVA) were chosen to evaluate performances of fabricated transistors depend on different dielectric surface properties.

The OTFT device geometry and chemical structure of used NBBI and PBBI semiconductors with together polymeric insulator were shown in Fig. 1 (a-c). NBBI and PBBI semiconductors with thicknesses 100 nm were thermally evaporated under vacuum (10^-5 mbar) at a rate of 0.05 nm/sec on BCB and PVA coated ITO substrates under same conditions, respectively. To make a ohmic contact, source/drain electrodes, LiF/Al, were deposited on active layers of NBBI and PBBI with vacuum evaporator under 1×10^-6 mbar. All OTFTs were fabricated under same conditions to compare with each other clearly. All devices show typical n-channel transistor output characteristics as a function of Vgs. The output characteristics of all devices fabricated on top of the polymeric gate-insulator were shown in Fig. 2 (a-d). The drain current \( I_D \) increases linearly with \( V_{DS} \) at low voltages, implies that good establishment of ohmic contact for electron injection between semiconductors and LiF/Al contacts.

Figure 1. (a) Cross-sectional illustration of fabricated top contact OTFT, (b) chemical structures of naphthalene bis-benzimidazole (NBBI), (c) perylene bis-benzimidazole (PBBI), (d) divinyltetramethyl-disiloxane-bis (benzocyclobutene) (BCB) and (e) polyvinyl alcohol (PVA).

The electric characteristics of NBBI with BCB gate insulator were obtained with highest mobility of \( 1 \times 10^{-3} \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) and threshold voltage of 15 V, while the mobility and threshold voltage of PBBI on same dielectric was \( 1.6 \times 10^{-4} \text{cm}^2\text{V}^{-1}\text{s}^{-1}, 18 \text{V} \), respectively. The calculated mobility of NBBI and PBBI active layer on PVA gate insulated layer was lower than BCB gate insulated OTFTs.

Figure 2. Output characteristics (\( I_D-V_{DS} \)) of NBBI and PBBI transistors on different dielectrics for various \( V_{GS} \): NBBI on BCB (a), PBBI on BCB (b), NBBI on PVA (c) and PBBI on BCB (d).

In order to examine the surface effects on the charge carrier mobility depends on dielectric and semiconductors, an atomic force microscopy (AFM) was used. The grain heights of NBBI deposited on PVA insulating-film were decreased with the exception of some island formations locally which are sufficiently separated from each other, while PBBI semiconductor shows as amorphous-like films whole the surface. The semiconductor surfaces for each other on BCB dielectric have island shapes and observable grains. The morphology images show an evidence of lower mobility due to grain shape properties on surface. The grain size difference of same semiconductors on different insulating-films can be attributed to the RMS differences and hydrophilic-hydrophobic property of insulator films.

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Synthesis and Structure Analysis of Cu(II) Dimeric Compound

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Abstract—Novel dimeric complex \((\text{C}_{20}\text{Cu}_{2}\text{N}_{2}\text{O}_{4}\text{Br}_{2})\) (1) has been synthesized and characterized by X-ray crystal structure analyses. Compound 1 consists of a structurally dinuclear system in which two Cu ions are bridged by the oxygen atoms of \(\mu\)-phenoxy ligands. The title compound crystallizes in monoclinic space group \(\text{P2}1/\text{n}\) with \(a=9.0043\ \text{Å}, \ b=10.2212\ \text{Å}, \ c=22.7814\ \text{Å}, \ \alpha=90°, \ \beta=92.085°, \ \gamma=90°\). The intramolecular Cu----O distances are almost same.

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**Electrical and Optical properties of Poled DAN/ P3HT Thin Films**

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**Abstract** - In this study a comparative work on electrical and optical properties of DAN/P3HT guest–host polymer thin film is done. Surface resistivities of samples are carried out by four point probe measurement technique. Surface resistivity of poled DAN/P3HT thin film is lower than both unpoled DAN/P3HT and P3HT samples. Polar induced alignment of DAN guest molecules in the P3HT host matrix caused an increase in conductivity. UV-Visible absorption spectrums of all three samples are taken. The peak value of absorption of poled DAN/P3HT sample is the lowest in all.

These days so much work is done on conductive polymers to improve electrical and optical properties. Also so many research groups concentrated on to improve device performance of OFET or OLED. Here in this work well known DAN Non-Linear Optical (NLO) molecules doped into P3HT conductive polymers to improve electrical and optical properties.

8 mg P3HT is dissolved in 800 μl chlorobenzene. The solution is kept an hour in ultrasonic bath. DAN molecules dissolved in 200 μl dichloromethane. Both of the solutions mixed together and kept in ultrasonic bath further. P3HT and DAN doped P3HT thin films were prepared by spin coating on ITO substrates are shown in Figure 1. To remove solvents, films kept for half an hour in an oven at 110 °C. DAN/P3HT samples poled by corona discharge method [1,2]. First the film heated up to 80 °C and than 6 kV applied to the needle. After 10 minutes while the field is on the temperature reduced to room temperature.

![Figure 1. DAN/P3HT thin films.](image1)

The surface resistivity of thin film samples were measured by four point probe technique [3]. The result of measurement is shown in Figure 2.

![Figure 2. Surface resistivity of thin films.](image2)

Doping of DAN is increased the resistivity of P3HT. Poling of DAN/P3HT caused a decrease in resistivity even beyond the P3HT.

UV-visible absorption spectrums of these three samples were also taken (Figure 3). Doping of DAN increased the absorption of P3HT. The decrease in the absorption peak of poled DAN/P3HT with compare to the unpoled one is the certain proof of poling. Alignment of DAN molecules caused this decrease in the peak value of the absorption.

![Figure 3. UV-visible spectrum of thin films.](image3)

This decrease in resistivity is due to the alignment of DAN guest molecules in P3HT host. DAN molecules act as sites for the charges. According the hopping process increase in sites certainly will increase the conductivity [4].

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Investigation of Electron Transport Properties in Dye Sensitized Solar Cells Based on Carbazole Dyes by Electrochemical Impedance Spectroscopy (EIS)

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Abstract—Electron transport properties of carbazole-based organic dye sensitized solar cells were investigated by Electrochemical Impedance Spectroscopy. Impedance spectroscopy has proven to be a useful technique for the characterization of electronic and ionic transport processes in dye sensitized solar cells. Carbazole derivative dyes are well known in the literature with their thermal and photochemical stabilities and improved electron donor properties.[1]

Electrical impedance spectroscopy (EIS) has become a major tool to investigate the properties and quality of dye-sensitized solar cell devices. EIS is a useful technique to investigate the kinetic processes of DSSC. [2] By using impedance spectroscopy on DSSCs, different cell parameters such as chemical capacitance, transport resistance, diffusion coefficient and charge-transfer resistance (recombination resistance) can be determined. These parameters can be realized with the shape of impedance response as a function of frequency. Excitations, charge recombination and charge separations can be represented by suitable circuit element for fitting. We operate at reverse voltage and evaluate the energy levels of majority carrier traps as well as trap densities of states.

Transmission Line (TL) Model is a suitable model for fitting DSSC’s. We can determine the recombination resistances (Rct) at TiO2/dye/electrolyte interface by fitting this model and changes of Fermi level can be calculated from these data. Rct is an important parameter to improve cell performance.

Figure 1. Transmission Line Model for DSSC at transmission line region.

A typical EIS spectrum of DSSC exhibits three characteristic semicircles in a Nyquist plot as shown in Fig. 3. The lower frequency peak corresponds to the diffusion within the electrolyte; the middle frequency peak corresponds to the electron recombination at the TiO2/electrolyte interface and together with electron transport in TiO2 network and charge transfer at counter electrode. For fitting DSSC we have used three different models at low potential, at TL line region and at high potential as shown in Figure 3. According to Nyquist results, it is evident that BG-1 has small recombination resistance than BG-2.

Table 1. Impedance data of BG-1, BG-2 and Z907.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Rs (Ohm)</th>
<th>Rct1 (Ohm)</th>
<th>Rct2 (Ohm)</th>
<th>T_life (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z907</td>
<td>14.52</td>
<td>2.592</td>
<td>12.19</td>
<td>1/1460.9 m/s (1.560 s)</td>
</tr>
<tr>
<td>BG301</td>
<td>14.16</td>
<td>2.113</td>
<td>6.816</td>
<td>1/714.8 m/s (1.398 s)</td>
</tr>
<tr>
<td>BG302</td>
<td>13.49</td>
<td>2.645</td>
<td>9.562</td>
<td>1/1756.7 m/s (1.321 s)</td>
</tr>
</tbody>
</table>

Figure 2. a) Low potential fitting model b) Transmission Line Region fitting model and c) High potential fitting model for DSSCs.

The BG-1-sensitized solar cell exhibited conversion efficiency (η) of 3.95% under standard global AM 1.5 simulated solar irradiation. At the same time, the DSSC, sensitized with BG-2 showed efficiency (η) of 2.73%.

Figure 3. Nyquist and Bode Phase plots of BG-1 and BG-2 sensitized cells measured in the dark under forward bias of -0.66 V.

From Figure 4 one can see three phase from bode plots and the main peaks shows that BG-1 has long electron lifetime than BG-2. (Table 1)

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Electroluminescence Enhancement of Alloyed Cd$_{x}$Se$_{1-x}$ Doped Polymer-Hybrid Light Emitting Diodes (PLEDs)

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Abstract—We report on influence of alloyed Cd$_{x}$Se$_{1-x}$ doping to hybrid organic/inorganic light emitting diodes (PLEDs). Optimum performance is observed by 5% Cd$_{x}$Se$_{1-x}$ doping in polyfluorene (PFO). Our results highlight that alloyed Cd$_{x}$Se$_{1-x}$ quantum dots make a remarkable effect on electroluminescence intensity and show promising for future research in efficient PLEDs.

Polymer light-emitting diodes (PLEDs) have been developed for more than 20 years and there have been much progress in the device performances. The efficiency of the PLEDs was significantly enhanced and the lifetime was also extended by developing device architectures, polymer emitting materials and polymer charge transport materials. [1,2]

However, material development was required to improve the quantum efficiency of the PLEDs. A quantum dot (QD) is a material with quantitized energy levels and it could be effectively used as an electron trapping material. Electron transport was retarded by the QD due to the electron trapping effect [3]. On the other hand, the quantum dots are themselves photoluminescent materials and can also enhance the total luminescence by incorporating into polymer matrices.

The combination of both polymers and QDs is expected to lead to devices of good optical and electronic properties. The adjustable and sharp emission characteristics of these materials make them interesting to be used in light emitting diodes by just varying the particle size because of quantum confinement effects [4–7].

In this work, we investigated the effect of QD doping on the hybrid organic/inorganic light emitting diodes for the tuning of performance. We fabricated organic light-emitting diodes using a single active layer consisting of Cd$_{x}$Se$_{1-x}$ alloyed type quantum dots passivated with hexadecylamine (HDA) caps dispersed in poly (9,9-dioctylfluorene) (PFO). An improvement of the electroluminescent intensity was demonstrated from the blue PLEDs by incorporation of quantum dots into the active polymer film.

A standard device structure of indium tin oxide (ITO) / poly ethylene -3,4 dioxy thiophene : poly styrene sulfonate (PEDOT:PSS)/PFO-QD/Ca/Al was used for the device fabrication. Cd$_{x}$Se$_{1-x}$ (HDA) was embedded into polymer layer with different percentage (1%, 2.5% and 5%). Electroluminescence intensity was enhanced by a factor of 6 with 5% QD doping ratio (Figure 1).

As a summary, our results show that embedded Cd$_{x}$Se$_{1-x}$ alloyed type quantum dots into polymer active layer makes a remarkable increase in electroluminescent intensity and can be a good candidate for future research and applications in hybrid organic/inorganic light emitting diodes.

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Figure 1. Electroluminescent spectra of devices (measured at room temperature, applied current = 80mA.).

Anthracene Containing PPE-PPV: Correlation Between \( \pi-\pi \)-Stacking Ability and Electroluminescence Properties

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Abstract: We studied anthracene containing poly(\(p\)-phenylene-ethynylene)-\textit{alt}-poly(\(p\)-phenylene-vinylene) (PPE-PPVs) for applications in organic light emitting diodes. The motivation of this study is to characterize the electroluminescence properties with respect to the degree of stacking.

Poly(1,4-phenylenevinylene) (PPV) and its derivatives are the mostly investigated polymers for OLEDs because of their physical, chemical and optical properties. Structural properties, ease of device fabrication, low operating voltage in combination with high efficiency make this class of the polymer the important candidate for large area OLED applications [1,2].

A major hindrance for the use in OLED technology arising from the interchain interactions. The formation of emissive aggregates such as excimers and exciplexes, in general, may reduce the efficiency and leads to unstable color coordinates depending on aging and also often on driving current.

Many methods have been developed to overcome these defects: Conjugated segments have been separated from each other by using non-conjugated units in the main chain to reduce the aggregation and to increase the EL efficiencies [3]. Also solubility is an important parameter to control the thin film morphology and the aggregation behavior. Blending of inorganic nanoparticles in semiconducting polymers or an inert polymer polystyrene have been attributed to the dilution effect and reduce inter-chain interaction. [4,5]

The emissive polymers of interest are anthracene-containing poly(phenylene-ethynylene)-\textit{alt}-poly(phenylene-vinylene) PPE-PPVs, denoted AnE-PV with different length of the side chain. Different branched and/or linear alkoxy side chains have been attached to the backbone, in order to tune the interchain interaction (\( \pi-\pi \)-stacking). AnE-PV\textit{bb} incorporates solely of bulky branched 2-ethylhexyloxy side chains which separates, the emissive units and thus inhibits the aggregation in the non-excited state. The grafting of short methoxy side chain in AnE-PV\textit{cc}, on the other hand, allows \( \pi-\pi \) stacking and aggregation in non-excited state (Figure 1,Table 1) [6]

![Figure 1. Structure of anthracene-containing poly(phenylene-ethynylene)-alt-poly(phenylene-vinylene) denoted AnE-PV](image)

Table 1.

<table>
<thead>
<tr>
<th>Code</th>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>( R_3 )</th>
<th>( R_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>bb</td>
<td>2-ethylhexyl</td>
<td>2-ethylhexyl</td>
<td>2-ethylhexyl</td>
<td>2-ethylhexyl</td>
</tr>
<tr>
<td>cc</td>
<td>methyl</td>
<td>2-ethylhexyl</td>
<td>methyl</td>
<td>2-ethylhexyl</td>
</tr>
</tbody>
</table>

If we compare the electroluminescence spectra; \textit{bb} has EL maximum at 608 nm and \textit{cc} has EL maximum at 656 nm. At the same time, \textit{cc} has second emission peak about 700 nm. This peak may be attributed to the excimer or aggregate emission of the polymer. (Figure 2)

![Figure 2. Electroluminescence of pure polymers](image)

Figure 2. Electroluminescence of pure polymers

Increase of the efficiencies in PS blends (Figure 3a) have been observed for \textit{cc}, where as the efficiency for \textit{bb} is nearly constant under same preparation conditions due to the dilution and hindering of the excimer emission.

Using a n-type polymer, a poly fluorene derivative (Figure 3b), PFO on the other hand, we reduced the interchain interaction and improved the charge balance between hole and electron simultaneously. Therefore the electroluminescence efficiency is increased for both materials, but more significantly for \textit{cc}. Luminance between 1500 Cd/m\(^2\) to 6000 Cd/m\(^2\) were achieved using the same emissive unit by blending with PFO.

![Figure 3. a) Blend with Polystyrene, b) Blend with PFO](image)

If we compare the electroluminescence spectra; \textit{bb} has EL maximum at 608 nm and \textit{cc} has EL maximum at 656 nm. At the same time, \textit{cc} has second emission peak about 700 nm. This peak may be attributed to the excimer or aggregate emission of the polymer. (Figure 2)

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Organic Light Emitting Field Effect Transistors Based on Conjugated Polyelectrolytes

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Abstract—Solution processed organic light emitting field effect transistors (OLEFETs) using conjugated polyelectrolytes as active layer are reported. The OLEFETs were fabricated in the bottom gate architecture with bottom contact interdigitated gold source and drain electrodes. Conjugated polyelectrolytes may play an important role for the development of OLEFETs.

We first measured output characteristics and transfer characteristics of the device. It exhibits the characteristics of a p-type field effect transistor with good saturation behavior. We calculated the mobility from linear regime using the standard transistor equation to be $7.6 \times 10^{-2} \, \text{cm}^2/\text{V s}$. Orange-yellow light emission was observed from operating OLEFET.

Although electrolytes have been demonstrated as gate insulators in silicon-based transistors and in OFETs or as ion-transferring layer in polymer based electrochemical transistors; this work is first attempt to demonstrate that electrolytes can be mixed with organic luminescent polymers and they can be used as active layer to produce an OLEFET.

C.Y. gratefully acknowledges the financial support of European Science Foundation (ESF) for providing a grant that enabled her to carry out this research at Linz Institute for Organic Solar Cells (LIOS).

Organic light emitting field effect transistors (OLEFETs) are attracting interest due to a number of applications such as simplified pixels in flat panel displays, optoelectronic devices in communications, and potentially electrically driven lasers. Combining optical and electrical functionality in a single device, i.e., an OLEFET, would not only increase the number of potential applications in integrated circuitry for signal processing that involves both optical and electrical signals, but also present an ideal structure for lifetime studies of organic light emitting materials under different driving conditions and charge-carrier balances.

On the other hand, most of organic semiconductors employed as OLEFET active layers were already known in organic electronics. Whereas mixed ionic/electronic conduction in conjugated organic materials—conjugated polyelectrolytes (CPEs)—introduces exciting functionality, the understanding of the fundamental processes that take place is still in its infancy. These materials combine the optical and electronic qualities of conjugated polymers with the fact that the properties of polyelectrolytes can be modified by electrostatic interactions.

One of the first known effects of the inclusion of an ionic species in a conjugated polymer is the increase in electrical conductivity associated with the electrochemical doping of the material. The conductivity increase in these materials arises from the introduction of polaronic and/or bipolaronic species on the polymer backbone, which is charge-compensated by a counterion.

Additional functionality can be introduced by the incorporation of ionic carriers through changes to device energetic. Band bending and dipole effects at the electrode interface due to ion accumulation lead to a reduction of charge injection barriers in optoelectronic devices. These effects are most relevant for the operation of the polymer light emitting electrochemical cell (LEC), but are emerging as useful benefits in applications such as the organic field effect transistor (OFET).

In this work, we fabricated OLEFET devices using organic luminescent semiconductor MDMO-PPV (Poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene]) and solid electrolyte mixture poly (ethylene oxide)+lithium trifluoromethanesulfonate as active layer. The polymer blend was then spin-cast onto the Si/SiO$_2$ substrate, followed by drying. A bottom gate and bottom contact structure with interdigitated Au source and drain contacts was used for these investigations. Heavily doped n-type Si wafers were used as the gate electrode, with a 230 ± 10 nm thick layer of thermally oxidized SiO$_2$ for the gate insulator.

We calculated the mobility from linear regime using the standard transistor equation to be $7.6 \times 10^{-2} \, \text{cm}^2/\text{V s}$. Orange-yellow light emission was observed from operating OLEFET.
Synthesis and Raman Spectroscopic Investigation of new self assembly Monolayer (SAM) material 4-(N-phenyl-N-(3-methylphenyl)-amino)benzoic acid for organic light-emitting devices (OLEDs)

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Abstract

We have synthesized 4-(N-phenyl-N-(3-methylphenyl)-amino)benzoic acid (abbreviated as 4-[3-MPBA]) and investigated their molecular vibrations by infrared and Raman spectroscopies as well as by calculation based on the density functional theory (DFT) approach. Finally, the calculation results were applied to simulated and Raman and IR spectra of the title compound, which show agreement with the observed spectra.

Triphenylamine and several of its derivatives have received application in Organic Light Emitting Diodes (OLED) particularly in the blue region as photoconductors and semiconductors [1]. The IR, FT-Raman and Dispersive Raman spectroscopy combined with quantum chemical computations has been recently used as an effective tool in the vibrational analysis of drug molecules, biological compounds and natural products, since fluorescence-free Raman spectra and the computed results can help unambiguous identification of vibrational modes as well as the bonding and structural features of complex organic molecular systems [2].

The optimized structure parameters of 4-[3-MPBA] calculated by DFT(B3LYP) level with 6-31G(d) and 6-311++G(d,p) basis sets are listed as a table accordance with atom numbering scheme given in Fig.1. From the theoretical values we can find that most of the optimized bond lengths are slightly larger and shorter than the experimental values at the DFT level, due to that the theoretical calculations belong to isolated molecule in gaseous phase and the experimental results belong to molecule in solid state[3].

The molecular structure of 4-[3-MPBA] in the ground state was optimized by B3LYP method with 6-311++G(d,p) and 6-31G(d) basis sets. The vibrational frequencies were calculated with this method using 6-31G(d) basis set and then scaled by 0.96. The molecule consist of 40 atoms. It has 114 normal vibrational modes. The 114 normal vibrations are distributed as 77A'+ 37A'' considering C\textsubscript{s} symmetry. All the vibrations are active both in infrared and Raman. The Total Energy Distribution (TED) of vibrational modes was calculated by using the Scaled Quantum Mechanical (SQM) program [4,5].

We present the calculated vibrational frequencies, IR intensities and Raman scattering activities along with measured experimental vibrational frequencies. In spite of the good agreement between the experimental and calculated spectra, as usual the theoretical frequencies are slightly overestimated, mainly due to neglect of anharmonicity.

The Dispersive Raman, FT-Raman(see fig.2), theoretical Raman and FT-IR spectrum of 4-(N-phenyl-N-(3-methylphenyl)-amino)benzoic acid molecule is reported for the first time. Theoretical simulations predict the equilibrium geometry of the molecule belong to C\textsubscript{s} symmetry. A good agreement between the experimental and theoretically calculated spectra allowed a positive assignment of all the observed FT-IR and FT-and Dispersive Raman bands and indicates that the theoretically optimized geometry of 4-[3-Methyl(phenyl)amino]benzoic acid closely matches with related crystal data of triphenylamine molecule.

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References

Preparation of Calix[4]arene-Based Magnetite Nanoparticles Exhibit Remarkable High Selectivity Towards Uranyl Cation

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Abstract- We have synthesized two new calixarene-based magnetic nanoparticles (CB-MNs). The prepared magnetite nanoparticles (CB-MNs) have been characterized by a combination of elemental analyses, FTIR transmission electron microscopy (TEM) and thermogravimetric analyses (TGA). These materials have been used to remove of uranyl ion (UO$_2^{2+}$) from aqueous solution.

Superparamagnetic nanoparticles of iron oxide have been used as great potential applications in many biological fields, including bioseparation, tumor hyperthermia, magnetic resonance imaging (MRI), diagnostic contrast agents, magnetically guided site-specific drug delivery agents, biomolecules immobilization and also recently used to remove of toxic oxoanions like arsenic and dichromate [1-3]. In this case, the nanotechnology science is a attract attention science day by day.

Uranium is an important element as well as being radioactive and toxic [4]. The removal and recovery of this radioactive element utilized in the production of nuclear fuels represent important problems of special interest, especially as to the environment protection [5]. Unlike other radioactive elements, half life of uranium element is commensurate with the age of the earth and as a result of this its remnants are found almost everywhere in the rocks, soil and water [6,7]. For instance the WHO Health Canada and Australian drinking water guidelines showed the maximum uranium concentration in drinking water to be less than 9 and 20 μg L$^{-1}$ [8]. In this case, there has been recently increased special interest for Uranium (VI), uranyl ions analysis in nuclear industry, especially to use in fuel separation and processing which compose from a few steps including leaching from ores, purification by ion exchange and solvent extraction, precipitation, reduction and etc. [9,10].

Herein, we report the preparation of magnetic calix[4]arene derivatives bearing pridinium units and application of these materials as selective carriers to remove of UO$_2^{2+}$. By using magnetic Fe$_3$O$_4$ nanoparticles, a simple method and an efficient way for the determination of uranyl ion in aqueous solution was developed to improve the separation capability of the calixarene composite silica carriers [3] bearing pyridinium units that can easily be separated from both reaction mixture and aqueous phase. In view of the above facts, magnetic Fe$_3$O$_4$ nanoparticles and EPPTMS were prepared according to the literature [3]. To obtain final materials, followed by the grafting of substituted p-tert-butylcalix[4]arene derivatives onto the surface of the modified nanoparticles. Thus, two new CB-MNs were prepared to compare their affinity toward uranyl ion and investigated effects of magnetism by means of sorption process.

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Figure 1. Proposed interactions of CB-MNs with uranyl cation.

Calixarenes have been attracting the interest of chemists for more than three decades [3,11]. Chemical modification from the upper or lower rim has made this class of synthetic ionophores as effective extractants for transferring anionic and cationic ions or neutral molecules from aqueous solution into an organic layer [12]. Especially, up till now, calixarene based materials have been increased asuranophiles which has either a pseudoplanar pentaco-ordinate or hexaco-ordinate structure [13,14]. It is well known that the high selectivity is attributed to the rigid skeleton of calix[5]arene and calix[6]arene [13]. It is well known that the high selectivity is attributed to the rigid skeleton of calix[5]arene and calix[6]arene derivatives towards uranyl ion. Because these derivatives can provide the pre-organised hexa- or penta- ordination geometry for the binding of UO$_2^{2+}$ [13].

References:


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Abstract—In this study, 5,17-bis-(N-methylglucamine)methyl)-25,26,27,28-tetrahydroxy-calix[4]arene has been synthesized by the treatment of calix[4]arene with a secondary amine N-methylglucamine and formaldehyde. Using the macrocyclic building block, the compound has been immobilized by [3-(2,3-epoxypropoxy)propyl]trimethoxysilane-modified Fe₃O₄ magnetite nanoparticles (EPPTMS-MN). The prepared calix[4]arene immobilized material has been characterized by a combination of Fourier Transform Infrared Spectroscopy (FTIR), Transmission Electron Microscopy (TEM) and Thermogravimetric Analyses (TGA). The immobilized magnetite nanoparticles have been used the removal of arsenate and dichromate ions from the aqueous solutions.

The development of supramolecular chemistry has been dominated largely by the design and synthesis of macrocyclic compounds. Calix[n]arenes widely represent macrocyclic compounds used in third generation of supramolecular chemistry for the construction of variously receptors for the complexation of anion, cation and neutral molecules [1]. The complexation properties of calixarene derivatives appear to be highly dependent on the nature, number of donor atoms and the conformation of the calix[4]arene moiety [2,3]. Therefore, variety of sophisticated anion complexing ligands containing calix[4]arene backbones have been designed and synthesized to serve as selective anion extractants [1,4]. These molecules are generally calix[4]arene derivatives bearing amine or amide functions which are capable of interacting with anions by hydrogen bonds [5]. Recently, we have reported calix[4]arene-based receptors those effectively bind anions and used for laboratory, clinical, environmental, and industrial process analyses [6-10].

Figure: Proposed interactions of magnetic calix[4]arene derivative (Calix-MN) with anions

Superparamagnetic nanoparticles of iron oxides have shown great potential applications in many biological fields, including bioseparation [11], tumor hyperthermia [12], magnetic resonance imaging (MRI) diagnostic contrast agents [13], magnetically guided site specific drug delivery agents [14], and biomolecules immobilization [15]. The application for biomolecules immobilization is mainly based on the solid-phase magnetic feature which is able to achieve a rapidly easy separation and recovery from the reaction medium in an external magnetic field.

In this paper, magnetic Fe₃O₄ nanoparticles were prepared by chemical co-precipitation of Fe³⁺ and Fe²⁺ ions. Flowingly the nanoparticles were directly modified by [3-(2,3-epoxypropoxy)propyl]trimethoxysilane (EPPTMS) to introduce reactive groups onto the particles surface. The substituted calix[4]arene was immobilized onto the surface of modified nanoparticles. This strategy provides an efficient way to improve the separation capability of the calixarene composite silica carriers as well as those can easily be separated from reaction mixture due to its magnetism. Finally, extraction capability of functionalized magnetic particles for dichromate and arsanete anions in aqueous solution were investigated.

In summary, we have prepared new magnetic nanoparticles containing calix[4]arene derivatives and one of them is believed to be an efficient way to improve the separation capability of the calixarene composite silica carriers as well as those may be helped for separation process due to magnetic properties. Then, prepared hosts have been used to remove toxic oxoanions like arsenate and dichromate in aqueous solution. The magnetic calix[4]arene derivative (Calix-MN) has notable increased the anion extraction ability at low pH by means of interactions include electrostatic interaction and hydrogen bonding between protonable amine and the oxygens of arsenate anions.

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Computing Topological Indices of Nanostar Dendrimers
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Abstract—A map taking graphs as arguments is called a graph invariant or topological index if it assigns equal values to isomorphic graphs. A dendrimer is an artificially manufactured or synthesized molecule built up from branched units called monomers. In this talk, we report our latest results on the subject of topological indices of nanostar dendrimers.

Nanobiotechnology is a rapidly advancing area of scientific and technological opportunity that applies the tools and processes of nanofabrication to build devices for studying biosystems. Dendrimers are one of the main objects of this new area of science. Here a dendrimer is a synthetic 3-dimensional macromolecule that is prepared in a step-wise fashion from simple branched monomer units, the nature and functionality of which can be easily controlled and varied. The nanostar dendrimer is part of a new group of macromolecules that the structure and the energy transfer mechanism must be understood.

We recall some algebraic definitions that will be used in the paper. Let G be a simple molecular graph. A topological index for G is a numerical value for correlation of chemical structure with various physical properties, chemical reactivity or biological activity.1 The Wiener index3 is the first topological index introduced by chemist Harold Wiener.3 This index is defined as the sum of all topological distances between the pair of vertices.

Khadikar et al4 defined a new topological, named PI index. It is defined as \( PI(G) = \sum_{u \leq v \in G} [m_u(e) + m_v(e)] \), where \( m_u(e) \) is the number of edges of G lying closer to u than to v and \( m_v(e) \) is the number of edges of G lying closer to v than to u. Edges equidistant from both ends of the edge uv are not counted. The Szeged index, is another topological index which is introduced by Ivan Gutman.5 To define the Szeged index of a graph G, we assume that e = uv is an edge connecting the vertices u and v. Suppose \( n_u(e) \) is the number of vertices of G lying closer to u and \( n_v(e) \) is the number of vertices of G lying closer to v. Then the Szeged index of the graph G is defined as \( Sz(G) = \sum_{e \in E(G)} n_u(e)n_v(e) \). Notice that vertices equidistant from u and v are not taken into account.

Figure 1. The Nanostar Dendrimer NS2[2].

We now consider the nanostar dendrimer NS[n], Figures 1. Using a simple calculation, one can show that \( |V(NS[n])| = 18.2^{n+1} - 12 \) and \( |E(NS[n])| = 21.2^{n+1} - 15 \). We prove that:

**Theorem 1.** The Szeged and PI indices of the nanostar dendrimer NS[n] are computed as follows:
\[
Sz(NS[n]) = -3024 \cdot 4^n + 5724.2^n + 6480.2^n - 432.
\]
\[
PI(NS[n]) = 504.4^n - 408.2^n + 82.
\]

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First principle study of the size effect on trans-polyacetylene nanoparticles energy gap

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Abstract— In this work we have calculated the electronic states of the trans-polyacetylene (t-PA) molecule within the framework of Density Functional Theory (DFT). For this purpose we have used SIESTA code based on the DFT within the Local Density Approximation (LDA). Fully self-consistent Kohn-Sham functional was performed. We used the Ceperley-Alder (CA) form of the exchange-correlation Potential in LDA. Following the above procedures we have calculated Density of State (DOS) of t-PA nano-molecules of few carbon atoms. Our results show that the energy gap has a considerable decrease with increasing the length of the nanoparticles.

Recently conductive polymers have received a great interest due to their potential applications for Nano-electronic devices [1]. Their applications in new technology, especially nanotechnology, have attracted much attention from both physicists and chemist’s society. One of the most interesting polymer materials with huge interest in theoretical and experimental scientific society is t-PA. Polyacetylene is a 1D chain of CH groups with alternating single and double bonds, therefore, from the theoretical point of view; it can be used for theoretical studying of one dimensional sample, like 1D version of grapheme [2–4]. From the experimental point of view, Polyacetylene has been used in new semiconductor devices [5].

In spite of the great effort in the last decade dedicated to making nano devices and new developments in nanotechnology, still the cost of nano devices is a big challenge and is expensive. One way for decreasing the costs, is predicting the physical properties of material by doing simulations and theoretical calculations. Ab initio calculations, with the development of new and fast computers, are one of the most reliable ways for studying the properties of nanoparticles.

We have used a linear scaling, fully self-consistent density functional method for performing first-principles calculations, as implemented in SIESTA code [6-8]. In our calculations we have used Density Functional Theory (DFT) based on the work by Hohenberg and Kohn [9] and by Kohn and Sham [10].We have also used the Local Density Approximation (LDA) for the exchange-correlation potential. We used the Ceperley-Alder (CA) form of the exchange-correlation potential in LDA. Troullier-Martins pseudopotentials were used to represent the nuclei plus core electrons[11-12].

In this study, we have calculated DOS and band gap energy of a long t-PA chain as well as a few t-PA nano-molecules of Carbon and Hydrogen atoms with different lengths which has been discussed in the following section.

We constructed a unit cell consisting of 8 Carbon and 8 Hydrogen atoms which has been shown in Fig. 1. The distances between C=C, C-C and C-H atoms was selected from experimental data to be 1.429, 1.368 and 1.091 Angstrom, respectively [13].We used supercell approximation to construct 9 nano-molecules of t-PA with lengths around 0.3 to 5.2 nanometers. We have calculated the DOS of these molecules, where some of them have been shown in Fig. 2. We see that the difference between HOMO and LUMO or energy gap decreases with increasing the dimension of the nano-molecules.

The change of the energy gap with respect to the size of nano-molecules has been drawn in Fig. 3. The trend of the variation looks like an exponential change. It seems that $E_g$ converge to its infinite chain value with increasing the length of t-PA nanomolecules. The decrease of $E_g$ is obvious, regarding the fundamental of well-known tight binding method.

Figure 1: a diagram of 1D t-PA chain. The bigger atoms are C and smaller ones are H atoms. The alternating single and double bonds has not been shown.

Figure 2: Density of State for nano-molecules of t-PA.

Figure 3 The change of energy gap versus length of nano-molecules:
Abstract—Undoped and boron doped nanocrystalline structure ZnO films (nominal volume B/Zn ratio=1% and 3%) deposited onto quartz substrates by the sol gel method using spin coating technique. The structural and morphological properties of the films were performed by XRD, FESEM and AFM measurements.

ZnO nanostructures have attracted much interest due to their unique piezoelectric, semiconducting and catalytic properties and wide range of applications in sensors, optoelectronics, transducers and in medical sciences. Various nanostructures of ZnO have been reported like nanotubes [1], nanowires [2], nanofibers [3, 4], nanorod [5] and nanosheets [6]. ZnO nanostructures have been synthesized by various methods such as thermal evaporation [7], spray pyrolysis [8], pulsed laser deposition [9], chemical vapor deposition [10], sol gel [11], hydrothermal synthesis [12], etc. The sol gel spin coating method still has distinct advantages such as cost effectiveness, thin, transparent, multicomponent oxide layers of many compositions on various substrates, simplicity, excellent compositional control, homogeneity and lower crystallization temperature.

In present work, we report the structural, morphological and optical properties of the undoped and boron doped nanocrystalline structure ZnO films deposited by sol-gel spin coating method.

These films have been deposited by a sol-gel spin coating method onto quartz substrates. Zinc acetate dihydrate (ZnAc), 2-methoxyethanol and monoethanolamine (MEA) were used as a starting material, solvent and stabilizer, respectively. Trimethyl borate (TMB) was used as a dopant source. The molar ratios of ZnAc and TMB to MEA were maintained at 1:1. B/Zn ratio was 1% and 3. Ammonia was added drop by drop until the pH values reach 7.00±0.05. The spinner speed was maintained 3000 rpm for 30 s. After each coating, the coated film was dried at 300°C for 10 min. This spinning-drying procedure was repeated ten times. The film was finally annealed at 500°C for 1 h.

All of the films crystallized with the hexagonal wurtzite structure and a preferred orientation of (002). Boron incorporation leads to substantial changes in the structural characteristics of nanostructure ZnO films. The crystallinity of the films was changed with increasing boron content. The grain size and lattice constants of the films are calculated.

Figure 1 shows FESEM image of the undoped and boron doped nanostructure ZnO films. Boron incorporation leads to changes in the morphological characteristics of nanostructure ZnO films. The FESEM micrographs reveal that the average grain size decreases with boron doping.

AFM images showed that the surface morphology of the films was affected from the boron incorporation. From also AFM images, the surface root mean square (RMS) roughness and average grain size fort the films were determined. So, the SEM and AFM images confirm to each other.

Figure 1: FESEM image for the films.