

Nanoscience and nanotechnology research in Turkish universities: institutes, research groups and networks

Berna Beyhan^{1*}

¹Science and Technology Policy Research Institute (TEKPOL), Middle East Technical University, Ankara 06531, Turkey

Abstract-This study provides a detailed analysis of nanoscience and nanotechnology research literature generated in Turkish universities through articles published in SCI (Science Citation Index) journals. For this study, bibliometric data related to 4408 articles (published between the years 2000-2009) written at least one author affiliated to Turkish institutes are investigated. It is found that the number of articles produced by the contribution of Turkish universities increased from 115 in the year 2000 to 928 in 2009 with an almost 8 fold increase. The number of local institutes or organizations contributing to the literature has increased from 29 to 105 in this ten year period.

Global nanoscience and nanotechnology (NST) literature has grown exponentially for the last two decades. The number of records regarding to NST publications in the SCI / SSCI was 11265 in 1991 however it reached to 64737 records in 2005 [1]. Again in this period, nanotechnology-related patenting activity has dramatically grown. In the 1980s, an average of 1213 nanotechnology-related patents per year was issued; however this number increased to 3209 per year in the 1990s and to 7536 per year in the first half of the new millennium [2].

Bibliometric methods are widely used in the identification of global and national knowledge structures in this novel technology field; and academic literature is identified as a powerful indicator of the potentials of individual countries. With the accumulation of NST research literature and patents the number of scientometric / bibliometric / text mining studies aiming to investigate the emergence and development of this new technology has been dramatically increased.

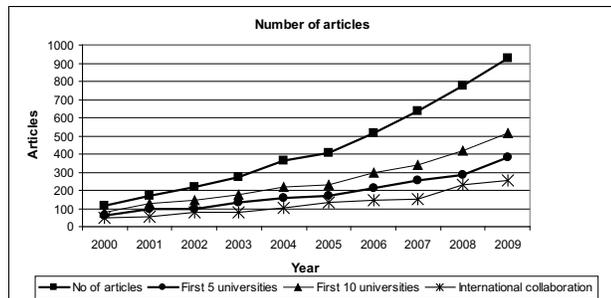


Figure 1. (a) shows increase in the number of NST articles, shares of the most productive universities in the total literature and the trend in the international collaboration.

In this study, more than 300 keywords provided by Kostoff et al [3] were used for the determination of articles produced by the scholars affiliated to Turkish institutes. The query for the detection of articles was entered into “ISI Web of Knowledge” database; and articles including any of these words either in their titles or abstracts, and having at least one author affiliated to Turkish institutions were selected.

As indicated by Figure 1 (a) the number of NST related research articles generated by Turkish institutes has increased from 115 in the year 2000 to 928 in 2009. While the number of local institutes and organizations contributing to NST literature was only 29 in 2000, it increased to 105 in 2009. On the other hand, with the increase in the number of Turkish institutes contributing to the literature the share of international collaboration has decreased; in 2000 44% of articles were generated in collaboration with a foreign research partner however this ratio decreased to 28% in 2009.

The most important actor of the NST research is universities. Industry contributes only 1.1% of articles and governmental bodies and research institutes contribute 3.3% of articles; however universities contribute 99.2%. Nano-institutes (research centers, labs etc) as authors’ affiliations first appeared in 2004 and their share in publications increased to nearly 11% in 2009.

Results also indicate that 68% of articles are written by at least one contributor from either physics or chemistry departments. While researchers in biological sciences (including medical sciences and pharmacy) contribute 13.6% of articles, the share of articles written by those affiliated to engineering sciences (physics engineering, chemical engineering, mechanical engineering and electronic engineering) reaches 19%.

Analysis of national and international research networks of Turkish universities indicates three types of universities: (1) the first niche group includes universities which are well connected to international research networks; (2) these universities have moderate national and international links and they are like gatekeepers or knowledge bridges between international knowledge networks and local peripheral universities (3) these are peripheral universities with lower number of articles and moreover they do not have very high number of national and international links. Therefore they are generally located in the periphery of research networks, or sometimes out of these networks.

This study, after a detailed analysis of NST research networks and characteristics, provides some ideas about the implications of those characteristics in terms of science and technology policies, national innovation system and technological and economic development.

*Corresponding author: 1Tberna.beyhan@gmail.com

[1] Kostoff, R. N., Koytcheff, R. G. and Lau, C. G. Y.(2007). Global nanotechnology research literature overview. *Technological Forecasting & Social Change* 74: 1733–1747

[2] Shea, C., M. (2005). Future management research directions in nanotechnology: a case study. *Journal of Engineering and Technology Management*, 22: 185-200

[3] Kostoff, R. N., Koytcheff, R. G. and Lau, C. G. Y.(2007). Structure of the global nanoscience and nanotechnology research literature. DTIC Technical Report Number (<http://www.dtic.mil/>).

Entry Barriers to the Nanotechnology Sector in Turkey

Neslihan Aydoğan-Duda^{1*} and İrge Şener²

¹Department of Business Administration, İzmir University of Economics, İzmir 35330, Turkey

²Department of International Trade, Çankaya University, Ankara 06530, Turkey

Abstract-Since nanotechnology is related to many different fields, it has received considerable attention among researchers from all over the world, and also from Turkey. However, this interest did not lead to the commercialization of the researched materials. In this research, we conducted interviews with researchers in four of Turkish nanotechnology centers. Our findings demonstrate the major issues behind the lack of commercialization and diffusion of the nanotechnology sector in Turkey.

Nanotechnology has the potential to create many new materials and devices with wide-ranging applications, such as in medicine, electronics and energy production. Although nanotechnology is at its nascent stages, it has become apparent that it will cause in stark changes in every area of our lives. Nano-technology has its basis in many different sciences, and this makes the basic difference when compared with the impact of other sciences. The many different underlying progenitor technologies, of which have bases in molecular biology, electronics, materials science, physics (optics and quantum) and others, contribute to the composition of nanotechnology and hence this makes nanotechnology as inherently complex and diverse with diverse applications [1]. The broad spectrum of nanotechnology has lead to the development of various materials. For example, widespread commercial adoption of nanotechnology is growing rapidly; where early commercial applications are focused on the improvement of cosmetics, coatings, textiles and displays [2]. Until now, there had been a disconnection between the nanotechnological advancement undertaken in the research centers or laboratories, and the commercialization of these products. Successful commercialization of developed products is still problematic in many countries. Since nanotechnology is still at its infancy, there exist few research on the commercialization problems. Given the recent origins of nanotechnology research, there is heretofore no systematic research on barriers inhibiting the diffusion of nanotechnology from the laboratory to commercial application [2].

Although many countries have been developing strategies for the development of the nanotechnology sector since the beginning of the 1990's, Turkey has been lagging behind such efforts. Only with the year 2000 some steps have been taken in this direction. Particularly nanotechnology has been identified as one of the critical sectors for the development of the Turkish economy. In particular a very well-equipped nanotechnology center at Bilkent, one of the most prominent universities in Turkey has been funded by the Prime Ministry State Planning Organization. Following this a number of centers have been established. In particular it appears that there are ten nanotechnology research centers in ten different universities in Turkey. However, the commercialization process of the nanotechnology sector in Turkey has been stalled majorly. Currently there are only thirteen nanotechnology companies in Turkey.

It is obvious that entry barriers to the nanotechnology sector should be discussed in detail if it is the case that such entry is barred for a variety of reasons and that the public can not benefit from the nanotechnology products. Turkey is a significant example to such occurrence. The current nanotechnology centers are furnished with strong infrastructure both physically and research wise. Most of the

researchers have their doctorate degrees from the prominent universities in the U.S. and they are working on cutting edge issues on nanotechnology. However, it appears that there are only thirteen companies in the entire country which can be classified as operating in the nanotechnology sector. Such observation is as alarming as it might be perceived as natural. For example, one could easily claim that in a developing country such as Turkey a sector which requires a long-term R&D investment might not develop as the fruits of such investment would take years to materialize. However such argument can easily be refuted as there are 41 nanotechnology firms in China and 17 in India and 195 for example in Germany. The country size and development levels do not seem to be the main determinants here. So what determines the lack of nanotechnology to be commercialized? [3]

In particular, in this research we survey ten academicians from four different nanotechnology Centers in Turkey [4] to gather their thoughts on this pressing issue of the lack of commercialization in the nanotechnology sector in Turkey. The finding of this research suggests that there are various major important issues behind the lack of commercialization and diffusion of the nanotechnology sector in Turkey. These findings are listed as strong theoretical focus in university research, the significance of theoretical research for the promotion of university professors, lack of interface between the university and industry, lack of a supportive culture for academician-entrepreneurs, lack of skilled labor, prejudice on university researchers from the practitioners, lack of venture capital, lack of funding agencies for projects that require large funds, lack of incubation centers, weak patent and copyright laws, lack of trust in Turkish produced goods, competition from cheap imports, lack of fully-operational industry clusters, and disconnection between the industrial and the underdeveloped part of the country.

In sum, the research on the commercialization of the nanotechnology sector appears to be rather scant. However, given its significance a thorough theoretical and empirical work is urgently needed. In particular, issues that are laid out in this research need to be systematically analyzed within an empirical framework.

*Corresponding author: neslihan.aydogan@ieu.edu.tr

[1] J. Niosi and S.E. Reid, *World Development* **35**, No. 3 (2007).

[2] B. Bozeman, J. Hardin and A.N. Link, *Economics of Innovation and New Technology* **17**, No:7-8 (2008).

[3] See N. Aydoğan and Y.P. Chen (2008) and N. Aydoğan (2009), Springer Publications, *for a detailed account of the significance of high-tech industry development*.

[4] Interviews were conducted at Marmara University, İstanbul Technical University, Koç University and Sabancı University.

Recent Survey of Nanotechnology in Higher Education in OIC Countries

M. Yahaya, I, Ho-Abdullah, M.M. Salleh & C.C. Yap
Universiti Kebangsaan Malaysia
Email: myahya@ukm.my

1.Introduction

Nanotechnology has been identified as having strong linkages with the top ten S&T fields of interest within each country of the OIC region. The technology will most likely to benefit developing countries in the areas of water, agriculture, nutrition, health, energy, and environment¹. In addition, nanotechnology is acknowledged as potentially one of the most beneficial for the development of developing countries. In line with this, the IDB under the Quick Win Project commissioned a roadmap² for achieving excellence in nanotechnology in higher education. The paper reports on the survey conducted in drawing up that roadmap. In the next section, a brief overview of the development and imperatives in the field of Nanotechnology will be discussed. This is followed by a discussion of the salient points of the Nanotechnology in Higher Education Survey 2009-NHES2009 which is designed to elicit three dimensions in nanotechnology in higher education, namely the perception of the importance of nanotechnology, the current status of institutional contribution to capacity building in nanotechnology and the curriculum aspects of nanotechnology programmes in higher education.

2.Methodology

Nanotechnology in Higher Education Survey 2009 (NHES 2009) aims to identify three main issues: a. the state of nanotechnology awareness; b. the contribution of various institutions to nanotechnology capacity building; and c. key features of a nanotechnology programmes. The survey was conducted between April – June 2009 and administered online (<http://ewarga2.ukm.my/perseus/se.ashx?s=4CCBF9477BEED8A3>). In total 150 academicians and scientist from seventy over institutions in ten countries with interest in nanotechnology were invited to participate. The survey team received 94 responses (response rate of 62.6%). The lists of institutions and countries who participated are shown in Appendix A.

¹ Islamic Development Bank. 2008. Strategic science and technology fields in IDB member countries. http://www.educationdev.net/educationdev/Docs/Strategic_S&T_fields.PDF; COMSTECH *Status of Scientific Research in OIC Member States* (2005)

² Muhammad Yahaya, Imran Ho, M.M.Salleh and C.C.Yap, Achieving excellence in nanotechnology in higher education, IDB Preliminary report,2009

Description Knowledge, Attitude and Behavior of Teacher Candidates Towards GDO's Products Which are to be Product of Biotechnology

Sevil Özcan

Education Faculty Department of primary education , Celal Bayar University, Demirci / Manisa- 45900, Turkey

Abstract: The aim of this study is two folded: to determine of teacher candidates how much they are aware from technological developments in the world and products which are produced as a result of this emerging. Also the attitude and behaviors of them was identified against this products. It appears that participants, especially primary school teacher candidates who will impart to new generations their knowledge and attitudes, haven't sufficient information about GMOs and technological developments, and it was determined that they have extreme prejudice against such products, because of the information was obtained from media.

Genetically Modified Organisms (GMO) are obtained by which their genetic material (DNA) has been altered by biotechnology. But there are arguments about could damage to human health and disrupt the natural environment of this production form [6]. Consumers and the environmental organizations are to attitude towards this products and researchs [8, 9]. So determination of the consumers' point of view against this technology is essential for the similar new techniques can be developed [7]. Moving from this point, in this study we have aimed to identify the opinion relating to this issue of teacher candidates, which will be shape future generations' knowledge, attitude and behavior.

Two surveys [1, 3] that they are occur from fourteen close- ended and an open- ended questions was applied to all of the 4th grade students (n=176), of which them % 23 (n=41) of Science Education students and % 77 (n=135) of the Elementary Education students in Education Faculty of Celal Bayar University. The surveys questionnaire included question on knowledge , the risk perception and attitude about GMOs, and GMO has been defined by us in one of surveys, but in the other GMO description was asked from students. The data was analyzed using SPSS.11 programme.

We found that, while % 28,4 of teacher candidates specified that they don't want any GM products; % 3,4 of them defined a GMO product that want to be produced. In addition to % 15,3 of them could want, if they don't have any adverse effect on humans, % 1,7 of them could accept, if produced GMOs will use in undeveloped or developing country such as African countries, or in forest areas. % 52 of participants didn't representation. % 62 of the participants indicated that they learned GMOs for the first time from TV (figure 1). Furthermore % 78,2 of the candidates think that GMOs causes to health problems. They admitted that stress is the most harmful factor on the human health, on the other hand GM products take 3th (figure 2).

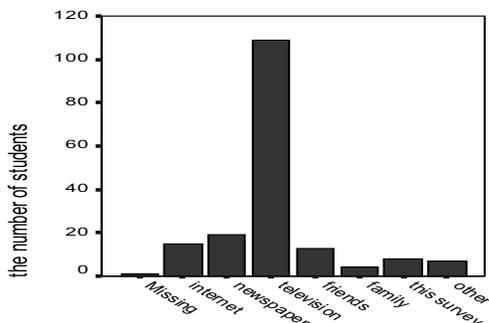


Figure 1. The answers to question “Where did you learn GMO term the first time?”

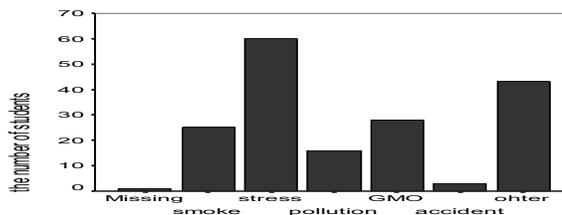


Figure 2. In your opinion, which is more threaten to human health than others?

It is important that the decision about the risks is shaped based on reliable information. In a research, consumers remarked to put trust in knowledge about food risks obtained from medicine and scientist, but they specified not trust to the given knowledge from media, industrialists, cultivators and farmers [5]. We showed that the teacher candidates have not enough knowledge about what GMO is and in which areas are used. Also they are against GMO technologies and all of products which are produced by this technology. How risks are perceived by society and whether they are accepted. These are shaped depend on the confidence to who gave to knowledge about this danger [2, 4]. Shouldn't be forgotten, cultural and social facts could change this decisions.

*corresponding author: sevil.ozcan@bayar.edu.tr

- [1] Demir, A., Pala, A., 2007. Perceptions of Society Towards Genetically Modified Organisms , Animal production 48(1): 33-43.
- [2] Eiser, J-R., Miles, S., Lynnn, J., Frewer, J-L., 2002. Trust, Perceived Risk, and Attitudes Toward Food Technologies. Journal of Applied Social Psychology, 32(11): 2423-2433.
- [3] Ergin, I., Gürsoy, Ş-T., Öcek, Z-A., Çiçeklioğlu, M., 2008. Knowledge Attitude and Behavior of Medical Technology Vocational Training School Students About Genetically Modified Organisms, TAF Prev Med Bull, 7(6):503-508.
- [4] Frewer, L-J., Howard, C., Hedderley, D., Shepherd, R., 1999. Reactions to information about genetic engineering: Impact of source characteristics, perceived personal relevance, and persuasiveness. Public Understanding of Science, 8(1): 35-50.
- [5] http://www.zmo.org.tr/genel/bizden_detay.php?kod=153&ipi=5&sube=0
- [6] Ho, M-W., Ching, L-L., 2003. The Case For A GM-Free Sustainable World, Independent Science Panel, Institute of Science in Society & Third World Network. Malaysia. Jutaprint.
- [7] Saba, A., Moles, A., Frewer, L-J., 1998. Public concerns about general and specific applications of genetic engineering: a comparative study between the UK and Italy. Nutrition & Food Science 98(1): 19-29.
- [8] Saher, M., Lindeman, M., Hursti, U-K., 2006. Attitudes towards genetically modified and organic foods. Appetite, 46(3): 324-31.
- [9] Varzakas, T-H., Arvantoyannis, I-S., Baltas, H., 2007. The Politics and Science behind GMO Acceptance. Critical Reviews in Food Science and Nutrition, 47: 335-361.

Do we need Nanofoods? Who is Earning, Companies or the Consumers?

Abstract – Nutritious and safe foods are the main concern of the consumers. However, technology used in food cultivation, production, processing, preservation and packaging at nanolevels to improve quality measures of the foods may cause harm to the consumers health. In this article beneficial and harmful aspects of nanotechnology usage in foods are discussed.

Food nanotechnology is started to be used in food cultivation, production, processing, preservation and packaging in many developed countries mostly by widely recognized firms. Once considered science-fiction kind of a thing is now becoming a reality and many food products are now being displayed on the market with different color, texture and more appealing properties. There is a great competition between the food production companies for it is possible to make any kind of change in the food products and packaging by nanotechnology. What food nanotechnology is promising can be enumerated as: 1)giving desired flavor, 2) acquiring desired color, 3)increasing density in the nutritive value, 4)enhancing solubility, 5)protecting the nutrient stability, 6)improvement of bioavailability, 7) encapsulating the elements to mix with others, 8) adding dissolving property into substance not soluble in nature, 9)giving adhesive property to the substance to bind and clear the gut from harmful elements, 10) improving shelf life by using specific coating nano particles in packaging, 11)putting sensory particles to detect the spoilage, 12)reducing waste by qualified packaging, 13)increasing the production amount, 14) cost effectiveness.

These benefits look very appealing and improving the nutritive value of food specifically with the nutrients that are lacking in a given society, such as iron, zinc, vitamin A and folic acid, can alleviate these nutrients deficiency are the most popular claims of the firms involved. However, as nano particles are very reactive elements, toxicity is an issue to take into consideration in using nanofoods in regard to public health concern. Researchers are warning that their accumulation in the body can increase oxidative stress that may trigger DNA mutation and cancer. Therefore the consumer must be aware of these potential danger and wait till the studies and responsible bodies assure its consumption. As there is no regulation and sanction for not showing if nanotechnology is used for the given food products on its label the consumer is very worried and confused. Nanoparticles effect to the body is not easy to show and there are no informative action for consumers leaving them head to-head with their confusion. There are some surveys conducted among the consumers showing that the consumers are happy for nanotechnology usage in packaging but they have a fear of using the product[1,2,3].

At this point one has to ask if using nanotechnology in food production is a must or not? It is very well known that all foods contain nanostructures in nature. If certain properties of food are desired to be improved it is necessary to consider the reactions at nano level. Nanotechnology gave way to food

industry to modify their product at supramolecular level. Certainly food industry was very keen to use this opportunities to contribute the solutions for their problems encountered in the production processes. Plus, as nanotechnology gives way to produce new protein products such as meat products economically from plant sources similar to meat, companies in a competitive environment wants to use this technology although it is highly polluting process. When these applications are causing pollution in one hand, they can also cause toxicity to human being in another hand.

The industry claims that their major aim of creating nanofood is to improving the safety and quality of foods. For the growing world population this is in a way understandable as food damages can occur during the storage and transportation. But is it really necessary to apply nanotechnology to store and transport the foods, or can this be achieved by other means?. Today there are more than 200 companies involved in this new technology, America is acting as a leader and comes Japan and China.

In general, people want their foods fresh and natural. However in modern societies people started to be addictive to ready-made food staffs as they are extremely convenient to use not needing preparation, cooking and easy to store. If we look at this phenomena in a larger scale like polluting the earth, risking the human beings health etc. it is vital to discuss the beneficial and harmful aspects of nanotechnology with related disciplines experts. Human being has many problems to deal with to continue his existence on earth. Family planning, education, health monitoring are only a few. Plus most of the efforts and money must be spent to grow the food organically not by other means. Nanotechnology may be used to understand the human physiology, specifically the brain functioning and DNA formation and mutation to be able to treat the patients struggling with alzheimer, parkinson, epilepsy etc. The most important questions to be answered are these: Do we need nanofoods ? Who is earning, the industry or the consumers?

[1].Bouwmeester, H, Dekkers, S.,Noordam, MY. et al.:Review of health safety aspects of nanotechnologies in food production, Regul Toxicol Pharmacol, 53(1):52-62, 2009.

[2]. Dingman, J.:Nanotechnology: Its impact on food safety, J Environ Health, 70(6):47-50, 2008

[3]. 2Henson, S., Annou, M., Cranfield, J. Ryks, J: Understanding consumer attitudes toward food technologies in Canada, Risk Analysis, 28(6):1601-17 2008.

Advances in Small Scale Processing Equipment for Polymers and Additives

Bernd Jakob

Thermo Fisher Scientific, Karlsruhe, (Germany)

Abstract

The use of a conical twin screw extruder with backflow channel combines aspects of mixing and extrusion in a batch process. With a small force feeder and a conveyor belt the micro compounder operates continuously producing a strand or a small sheet. With a total filling volume of 7 ml and a built in slit capillary die the applications focus ison compounding and reactions of small amounts of polymers in molten stage. Two great areas of application: mixing and rheological recording of melt characteristics are combined in the micro compounder. For further tests the polymer melt can be transferred into a micro injection moulding machine to shape different kind of test specimens for further analyses.

Mechanical Properties of thin DLC coatings

Michael G. Berg

Hysitron, Inc., Valley View Road 10025, Minneapolis 55344, USA, www.hysitron.com

Abstract— Thin DLC coatings are widely used to improve the tribological behavior of technical surfaces. The thicknesses of these coatings can range between 3nm and 500nm depending of the application. We use nanoIndentation and other related advanced techniques for characterizing critical mechanical properties.

Diamond-like carbon coatings are being utilized in a wide field of technical applications such as hard-disk drives, razor blades, MEMS or NEMS, watches and bearings. Usually they are used in tribological applications. A low friction coefficient and inert behavior allows increasing the live-time of technical products. Typically the film is very dense and also seals the underlying substrate against corrosion.

DLC is a general term for a thin layer that can have soft and rubber type properties until very hard thin layers that reach Young's moduli as high as 300GPa and hardnesses around 30GPa. The properties can be tuned during the deposition of the film and it is hence of largest importance to characterize the mechanical behavior of these films. The dominating bond types are defined by the deposition process and have a considerable influence on the material properties of amorphous carbon films. If the sp² type is predominant the film will be softer, if the sp³ type is predominant the film will be harder.

The hardness and Young's modulus, internal stresses, interfacial adhesion to the substrate, friction and wear properties are critical for all these applications. NanoIndentation is the only technique that allows studying these properties with high spatial resolution. The most common measures taken from a nano-indentation are hardness and modulus which characterize the yield strength and elastic behavior of the material (for further reading; [1]). Moreover it is possible to utilize the force and displacement curve to gain more insight into the materials behavior; thus it is possible to observe creep and relaxation, fracture or other mechanisms of deformation in the load displacement curve.

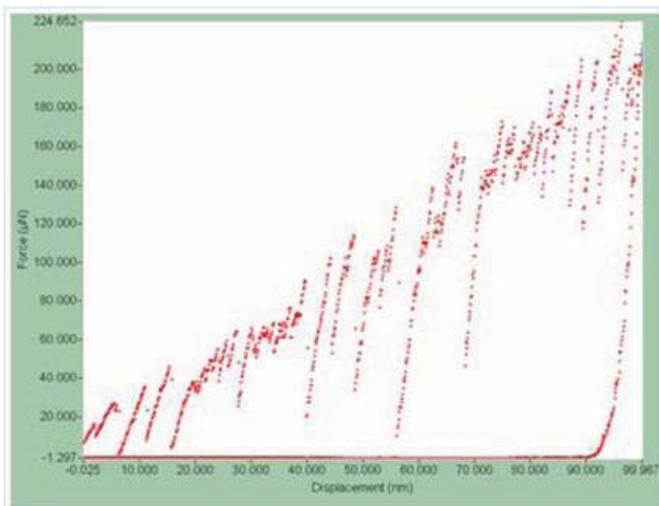


Fig.1: Discrete yielding events observed on an Al-sample as an example for deformation mechanisms that can be studied in displacement controlled nanoIndentation experiments. [2]

The presentation will discuss the effect of the underlying substrate for measurements of properties of very thin films and will present nano-tribological studies of very thin DLC coatings. These studies will cover the wear behavior observed under a small sub-critical load. A critical load on the thin films will be studied by nanoScratch testing. The delamination of the thin films caused by the stress of large indentation tests is studied by combining the indentation experiment with a modulus mapping of the tested area with the same indenter stylus (Fig.2).

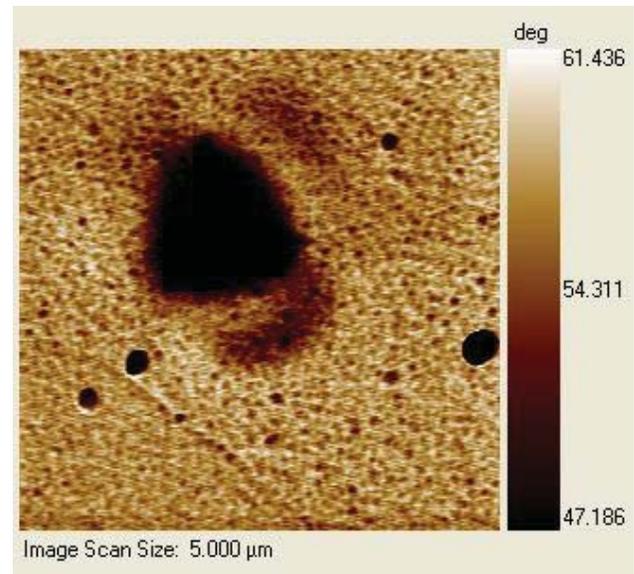


Fig.2: Delamination of a thin DLC coating around an indent. This figure visualizes the delaminated zone by stiffness mapping. The dark spot is the indentation cup while the brown spot that surround the indent are delaminated areas.

*Corresponding author: uhangen@hysitron.com

[1] ISO 14577 - Metallic Materials – Instrumented Indentation Test For Hardness and Materials Parameters

[2] Warren, Downs, Wyrobek, Z. Metallkd. 95, 287 (2004)

Organic Nanostructures for Solar Energy Conversion

Niyazi Serdar Sariciftci

Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, Altenbergerstrasse 69, A-4040 Linz, Austria

Abstract— Organic photovoltaic diodes (OPVs) and organic solar cells are reviewed. The different energy and electron transfer mechanisms of solar energy harvesting as well as conversion are discussed. Pure organic nanostructures and organic/inorganic hybrid nanostructures are comparatively studied for photovoltaic devices. This talk gives an overview of materials' aspect, charge-carrier-transport, and device physics of such diodes. Furthermore, the use of solar photoenergy to reduce CO₂ into hydrocarbon based synthetic fuels is introduced. Such artificial photosynthesis type fuel production can simultaneously solve the energy storage and energy transport problems of photovoltaic electricity.

In organic, polymer-based photovoltaic devices the primary step upon exposure to solar light is a photoinduced electron transfer between donor and acceptor type semiconducting polymers or molecules yielding a charge-separated state. This process is schematically illustrated in Figure 1A. The photoinduced electron transfer at the junction of donor-acceptor molecular materials boosts the photogeneration of free charge carriers compared to the pure materials, in which the formation of bound electron-hole pairs, or excitons is generally favored. Interestingly, the photoinduced charge transfer employed in polymer solar cells mimics the process of natural photosynthesis.

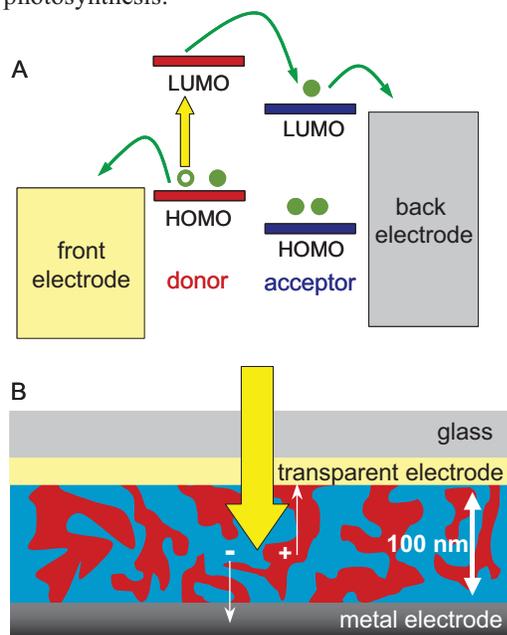


Figure 1. A: Photoinduced excitation of the donor followed by electron transfer to the acceptor and subsequent charge collection of holes at the front electrode and electrons at the metal back electrode. HOMO = highest occupied molecular orbital and LUMO = lowest unoccupied molecular orbital. B: Schematic representation of a bulk-heterojunction solar cell, showing the phase separation between donor (red) and acceptor (blue) materials.

In combining electron donating (*p*-type) and electron accepting (*n*-type) materials in the active layer of a solar cell, care must be taken that excitons created in either material can diffuse to the interface, to enable charge separation. Due to their short lifetime and low mobility, the diffusion length of

excitons in organic semiconductors is limited to about ~10 nm only. This imposes an important condition to efficient charge generation. Anywhere in the active layer, the distance to the interface should be on the order of the exciton diffusion length. Photogenerated charges then must be able to migrate to the collecting electrodes through this intimately mixed blend. Because holes are transported by the *p*-type semiconductor and electrons by the *n*-type material, these materials should be preferably mixed into a bicontinuous, interpenetrating network. (Figure 1B)

In the highly efficient (up to 7-8 %) organic solar cells, the photoactive composite layer is sandwiched between two electrodes with different work functions: a transparent front electrode consisting of indium tin oxide covered with a conducting polymer polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS) for hole collection and a metal back electrode consisting of a very thin (~ 1 nm) layer of LiF and covered with Al for electron collection. The layout of this device and a cross-sectional transmission electron microscopy (TEM) image of an actual device slab are shown in Figure 2. Except for LiF, all layers are about 100 nm thick.

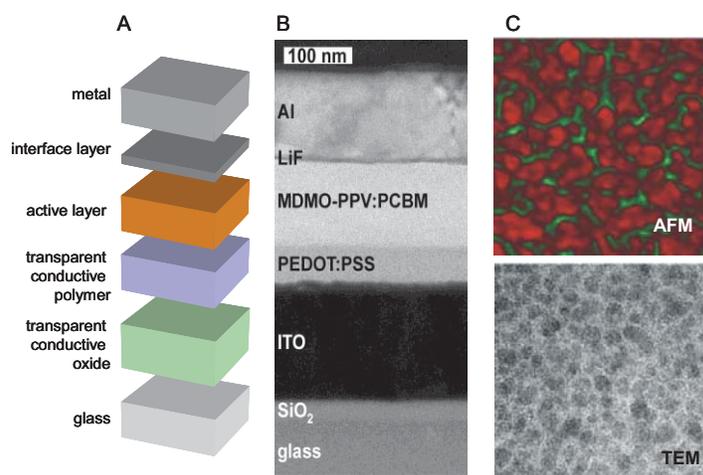


Figure 2. A: Schematic layout of the device architecture of a polymer-fullerene bulk-heterojunction solar cell. B: TEM image of a thin slab of an actual device, C: AFM phase and TEM images (1 × 1 μm²) of a MDMO-PPV/PCBM (1:4 by wt.) composite

Netherlands Nano Initiative: Strategic Research Agenda towards Applications

Dave H.A. Blank

Scientific Director MESA+ Institute for Nanotechnology
Chair of the Netherlands Nano Initiative, Board member NanoNed
University of Twente, The Netherlands

Abstract- In 2010 a new initiative on nanotechnology will start in the Netherlands. This initiative merges the science and technology at the university level with industry, large companies as well as small medium enterprises. This initiative will be the continuation of NanoNed, a successful research programme in the Netherlands.

In 2003 an initiative on nanotechnology started in the Netherlands that had it full size in 2005. The programme called NanoNed is a national nanotechnology R&D initiative that combines the Dutch strengths in nanoscience and technology in a national network with scientifically, economically and socially relevant research and infrastructure projects. The total budget amounts to 235 M€ and the program runs until 2010.

NanoNed is executed by a consortium of 9 partners. All partners are devoted to developing strong cooperations on the subject of nanotechnology in its different application areas. Therefore, the program is organised in 11 large interdependent programs called Flagships, based on national R&D strengths and industrial relevance.

Several partners are working in each program under the leadership of an independent scientist. The partnership covers about 200 research projects, which over the next 5 years will represent more than 1200 man-years of research. Generic, technology-oriented Flagships run together with more application-oriented programs, to create a cohesive nationwide multidisciplinary program.

Part of the budget is reserved for NanoLab NL, an investment program of high-level, state-of-the-art nanotechnology infrastructure that is accessible to NanoNed and the Dutch research community as a whole. This NanoLab NL is part of the large scale infrastructures of the Netherlands.

Additionally, a Technology Assessment program is an integrated part of NanoNed. The assessment will result in a mapping of the societal impact of nanotechnology in close collaboration with the scientists involved.

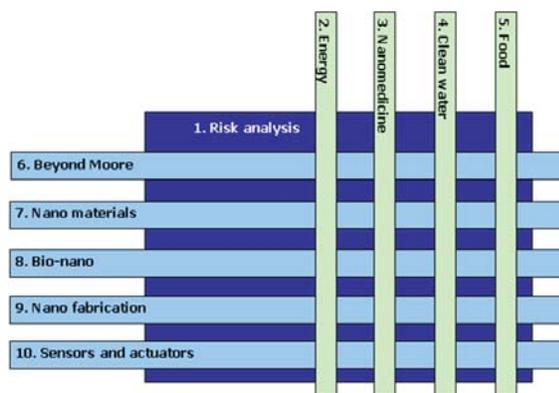


Figure 1. New initiative on nanotechnology in the Netherlands. The programme is divided into generic themes (horizontal) and application areas (vertical). Important is the risk analysis and technology assessment of nanotechnology, which is a serious issue for decision makers.

End 2009, a continuation of NanoNed for the next period 2010 till 2015 is granted by the Dutch Government. This strategic agenda focuses on generic themes, like bio-nano, beyond Moore, nano-materials, nano-fabrication, sensors and actuators, as well as applications areas like nanomedicine, energy, water, and food, see figure 1. Special attention is paid towards risk analysis and technology assessment of nanotechnology.

In this presentation I like to reveal the results and future of NanoNed and NNI. Furthermore, I like to mention briefly the role of the MESA+ Institute for Nanotechnology in the Netherlands. This institute, located at the University of Twente, hosts 500 scientists on nanotechnology and has a comprehensive infrastructure. Since 2000 more than 40 spin-offs have been launched from this institute.

One of the enterprises is the so-called High Tech Factory, a shared production facility. The High Tech Factory initiative aims to establish a pilot production infrastructure and organization for products based on microsystems and nanotechnology. Many of the companies involved market these products in the medical and pharmaceutical sectors and in the food industry.

High Tech Factory is designed to ensure that the (microsystems and nanotechnology) companies involved can concentrate on business operations and focus their energies on growth rather than on realizing the basic infrastructure required to achieve that growth.

Individual SMEs find it impossible to establish their own state-of-the-art production facilities. A shared production facility is essential in order to guarantee continued growth and to retain these companies.

During my presentation I will discuss several of these successful SMEs, including their potentials in nanotechnology.

Multiphase polymer nanocomposites by incorporation of inorganic nanoparticles – properties and achievements

K. Schulte*, S. Buschhorn, L. Böger, J. Sumfleth, M.H.G. Wichmann, L.A.S.A Prado

Technische Universität Hamburg-Harburg, Institute for Polymers and Composites, Denickestr. 15, 21073 Hamburg, Germany

Abstract- In this work, the piezoresistive response of electrically conductive epoxy nanocomposites is studied by means of combined electrical/mechanical tests, showing the possibility to monitor the stress/strain behaviour of such nanocomposites by conductivity methods. Furthermore, nanoparticle modified epoxy matrix systems in glass fibre reinforced composites can be used to evaluate the state of load and damage in quasistatic and dynamic tests.

Electrically conductive polymer-based nanocomposites can be produced by dispersing carbon nanoparticles such as Carbon Nanotubes (CNTs) and Carbon Black (CB) in the polymer matrix. In the case of epoxy matrix systems, the percolation threshold can be very low (~ 0.1 vol.%), because of dynamic percolation processes occurring during curing prior to gelation. Recent investigations have shown that the conducting networks of carbon nanoparticles in epoxy matrices are sensitive to applied mechanical load and can be used for stress/strain sensing and damage detection in composite structures [1,2]. In this presentation, the electromechanical behaviour of nanocomposites will be discussed in detail. The “piezoresistive” response of different carbon nanoparticle/epoxy based nanocomposites was measured and evaluated for different loading cases, in order to gain a fundamental understanding of the observed sensing characteristics. Mechanical and electrical resistivity tests were performed simultaneously. The experiments revealed a pronounced dependency of the electrical resistivity on the mechanical load.

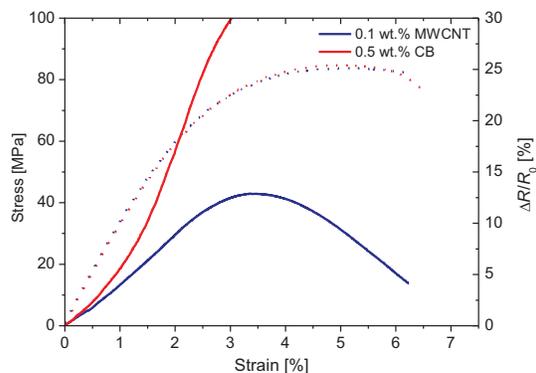


Figure 1. Piezoresistive response of conductive nanocomposite under uniaxial tensile strain [1]

In the elastic regime, the resistance/strain characteristics are of an exponential nature (see Figure 1) [1]. These results are in good agreement with the hypothesis that the charge carrier transport between the conducting particles in carbon nanoparticle composites can be explained by the tunnelling theory. The volume content as well as the geometry of the carbon nanoparticles was found to have a distinct influence on the “piezoresistive” response of the nanocomposites. At low strains (below 2.5 %), the CNT based composites exhibit a very weak exponential dependence of resistance vs. strain, allowing a very good linear approximation [1]. This makes them superior candidates for potential strain sensing applications.

In the regime of plastic deformation, pronounced differences in the electromechanical behaviour were found between the nanocomposites containing different types of nanoparticles (CNTs and CB). While nanocomposites containing CNTs exhibit a maximum at $\sim 4\%$ of strain, the resistance of CB nanocomposites increases monotonically until final failure of the specimen. The different behaviour of the nanocomposites containing CB, especially at higher strain values in the regime of plastic deformation, can be attributed to the different aspect ratio of the conducting particles, being around one for the CB particles and up to several thousands for CNTs [1,3].

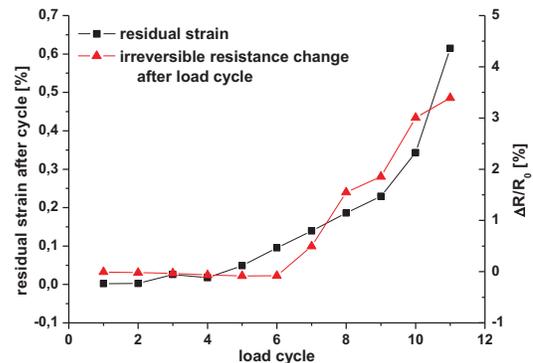


Figure 2. Residual strain and resistance change of glass fibre reinforced composites under cyclic loading [4]

In fibre reinforced composites with a conductive matrix, similar effects can be found and correlated to damage, such as transverse cracks in 90° layers, especially in fatigue loaded coupons (see Figure 2) [4,5]. Here the electromechanical variation can be used for in situ life monitoring.

*schulte@tuhh.de

[1] Wichmann, M.H.G., Buschhorn, S.T., Gehrman, J., Schulte, K. Piezoresistive response of carbon nanoparticle/epoxy composites under tensile load, 2009. *Physical Review B*, 80.

[2] Thostenson, E.T., Chou, T.W. Carbon nanotube networks: Sensing of distributed strain and damage for life prediction and self healing, 2006, *Advanced Materials*, 18.

[3] Kovacs, J.Z., Velagala, B.S., Schulte, K., Bauhofer, W. Two percolation thresholds in carbon nanotube epoxy composites, 2007, *Composites Science and Technology*, 67.

[4] Böger, L., Wichmann, M.H.G., Meyer, L.O., Schulte, K. Load and health monitoring in glass fibre reinforced composites with an electrically conductive nanocomposite epoxy matrix, 2008, *Composites Science and Technology*, 68.

[5] Böger, L., Sumfleth J., Hedemann, H., Schulte, K. Improvement of Fatigue Life by Incorporation of Nanoparticles in Glass Fibre Reinforced Epoxy, 2010, *Composites A*, submitted.

In recent years numerous studies have focused on a generating a deeper understanding of these Polymer/PCBM bulk heterojunctions. Investigations into the nano morphology, electronic structure, and charge transport have provided detailed understanding of the degree and dimensions of the phase separation in the active layer. Photophysical studies have provided insights in charge generation, separation, and recombination, in these layers and more recently in working devices.

Future directions for improving efficiencies

New materials combinations that are being developed in various laboratories focus on improving the three parameters that determine the energy conversion efficiency of a solar cell, *i.e.* the open-circuit voltage (V_{oc}), the short-circuit current (J_{sc}), and the fill factor (FF) that represents the curvature of the current-voltage characteristic.

- For ohmic contacts the open-circuit voltage of bulk-heterojunction polymer photovoltaic cells is governed by the HOMO and LUMO energy levels of donor and acceptor, respectively. In most polymer/fullerene solar cells, the positioning of these band levels of donor and acceptor is such that up to ~ 0.4 - 0.8 eV is lost in the electron-transfer reaction.
- One of the crucial parameters for increasing the photocurrent is the absorption of more photons. This may be achieved by increasing the layer thickness and by shifting the absorption spectrum of the active layer to longer wavelengths.
- A high fill factor (strongly curved J - V characteristic) is advantageous and indicates that fairly strong photocurrents can be extracted close to the open-circuit voltage. Consequently a high fill factor can be obtained when the charge mobility of both charges is high. Presently the fill factor is limited to about 60% in the best devices, but values up to 70% have been achieved recently.
- Apart from developing improved materials, a further gain in device performance can be expected from the combined optimization of the optical field distribution present in the device. Optical effects, such as interference of light in multilayer cavities, have received only limited attention so far but will likely contribute to a better light-management in these devices.

Conclusion

In the last 5 years there has been an enormous increase in the understanding and performance of polymer-fullerene bulk-heterojunction solar cells. Comprehensive insights have been obtained in crucial materials parameters in terms of morphology, energy levels, charge transport, and electrode materials. To date, power conversion efficiencies close to 5% are routinely obtained and some laboratories have reported power conversion efficiencies of ~ 7 - 8 %. Even more important for the future is that a vibrant community of industrial and university scientists and engineers has assembled in this area to actively pursue the quest for new materials and device architectures, aiming at increasing the efficiency to 10-15%. By combining synthesis, processing, and materials science with device physics and fabrication there is little doubt that these appealing levels of performance will be achieved in the near future.

Acknowledgement

The work described has been the result of the enthusiastic efforts of numerous talented co-workers at our institute and the fruitful collaboration with many leading scientists in this field. We gratefully acknowledge their important contributions.



Nanoporous Framework Materials for Hydrogen Storage and Carbon Capture Applications

Taner Yildirim*

*NIST Center for Neutron Research, Gaithersburg MD 20899-6102, USA and
Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia PA 19104, USA,*

Abstract- We present a brief review of our recent studies of various nanoporous materials for hydrogen storage and carbon capture applications. We will propose a new nanoporous material, a so called graphene oxide framework (GOF) formed of layers of graphene oxide connected by benzene-1,4-diboronic acid (B14DBA) “pillars” as a potential storage medium for H₂ and other gases.

In this talk we will discuss two different but closely related grand energy challenges, namely hydrogen storage and carbon-capture. The reduction of fossil fuel use in vehicles is key to reducing greenhouse emissions. Vehicles and other systems powered by hydrogen have the advantage of emitting only water as a waste product. An important challenge, however, is storing enough hydrogen on board to give it a range comparable to a vehicle powered by fossil fuels. Unfortunately, current materials still lack the ability to store significant amounts of hydrogen under technologically useful conditions. Hence there is urgent need for new ideas and materials to solve the hydrogen storage problem. Nanoporous framework materials are a novel family of physisorptive materials that have exhibited great promise for both hydrogen storage and CO₂ capture and separation.

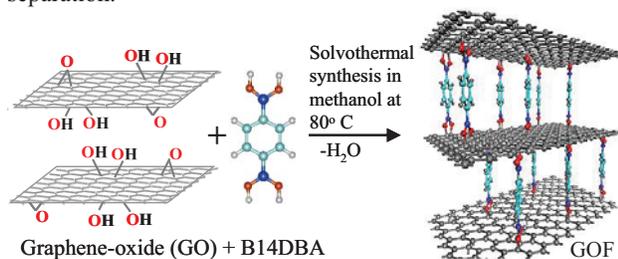


Figure 1. A schematic view of graphene-oxide framework (GOF) formation. GOFs are formed of layers of graphene oxide connected by benzene-diboronic acid “pillars”.

In the first part of this talk, we present our recent study in which we show that one-and-a-half-century-old graphene oxide (GO) can be easily turned into a potentially useful hydrogen storage and carbon capture material. GO is a sheet of carbon atoms with many hydroxyl, epoxide and carboxyl surface groups. In principle, hydrogen can be stored between layers of this lightweight material. However, the challenge is to separate the layers without filling the space between them. Here we show that by using the well-known chemistry between boronic acids and hydroxyl groups, GO layers can be linked together to form a new layered structure (Fig.1). Such GOF structures have tunable pore widths, volumes, and binding sites depending on the linkers chosen, and could exhibit interesting gas sorption properties.

Based on our Grand Canonical Monte Carlo adsorption simulations, the ideal GOF structure can adsorb hydrogen up to 6 wt% at 77 K and 1 bar, a value higher than any other porous material known. We show that our initial synthesized GOF materials exhibit 9 kJ/mol and 32 kJ/mol isosteric heat of adsorption for H₂ and CO₂, significantly larger than those found in similar nanoporous materials. The nitrogen BET surface area reaches a maximum at 470 m²/g. Despite this low surface area, GOF exhibits 1 wt% H₂ uptake at 1 bar. This is less than one fifth of what the 'ideal' GOF structure

can hold, suggesting that our initial synthesized GOF materials could be significantly optimized in the near future.

In the second part of the talk we will discuss carbon capture application of various metal-organic framework materials. With the current prevalence of hydrocarbon-based energy sources, carbon capture and sequestration are essential technologies for minimizing the emission of carbon dioxide and the resulting increased atmospheric concentration of CO₂. Current technologies based on absorption require high temperature regeneration of the solvent, ultimately leading to significantly decreased efficiency and increased cost. Development of an adsorption-based technology, based on physical adsorption in optimized porous media, would greatly reduce the regeneration costs.

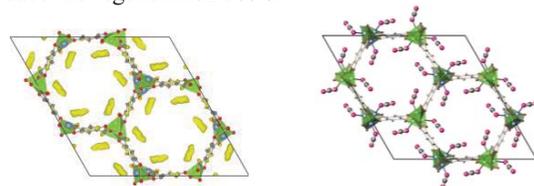


Figure 2. Experimental (left) and DFT calculated (right) carbon capture sites in 1D hexagonal channels of MOF-74.

So far, understanding of the CO₂ adsorption sites and binding mechanism in MOFs is still limited. Here we first report a detailed study of CO₂ adsorption in two important prototypical MOF compounds containing coordinatively unsaturated metal centers (Mg-MOF-74 and HKUST-1). The major CO₂ adsorption sites in both MOFs were clearly identified through neutron diffraction measurements (Fig.2), and the open metal ions were found to be the primary binding sites. The relatively strong metal-CO₂ interaction was attributed to the enhanced electrostatic interaction due to charge overlap between the open metal and one of the oxygen atoms of the CO₂ molecule. Interestingly, the overall metal-CO₂ binding strength is right in the range which can facilitate both adsorption (CO₂ capture) and desorption (MOF regeneration) under typical flue gas conditions.

We then discuss carbon capture performance of a range of MOFs, including both high surface area materials as well as those with sites that have been engineered to have enhanced binding. We demonstrate that MOFs can capture significant amounts of CO₂ and that the CO₂ can be readily removed from the MOF using standard pressure/vacuum swing techniques, yielding cyclic capture capacities in excess of 5 mmol/g. Further, we discuss the role of nano-pore geometry and surface chemistry in the capacity of CO₂ that can be removed in order to best optimize these materials.

This work was supported by DOE BES Grant No. DE-FG02-08ER46522.

*taner@seas.upenn.edu

[1] For more info. see: <http://www.ncnr.nist.gov/staff/taner>

Fullerenes for Organic Electronics

Nazario Martín

Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, E-28040 Madrid, Spain IMDEA-Nanociencia, Cantoblanco.E-28049 Madrid, Spain.

(Tel., +34 91 3944227; e-mail: nazmar@quim.ucm.es), <http://www.ucm.es/info/fullerene>

Abstract- Fullerene derivatives have been synthesized and used in different fields of the “so called” molecular electronics. In particular, a wide variety of molecules with interest for the study of molecular wires as well as organic photovoltaics will be presented. In both topics, the organization of materials at the nanometric scale represents an important challenge for future applications.

Fullerenes are electron accepting carbon allotropes which have been successfully used as materials of interest in the so called *organic electronics*. In our research group we have studied the molecular wire behaviour of a series of conjugated oligomers.[1] The synthesis of dyads formed by an electron donor moiety and fullerene as the acceptor unit, covalently connected through the conjugated oligomer, has allowed to determine the attenuation factor of different conjugated oligomers. The measurements of the conductance through the conjugated system in dumbbell-type fullerene derivatives by using STM techniques will complement this study (Figure 1).

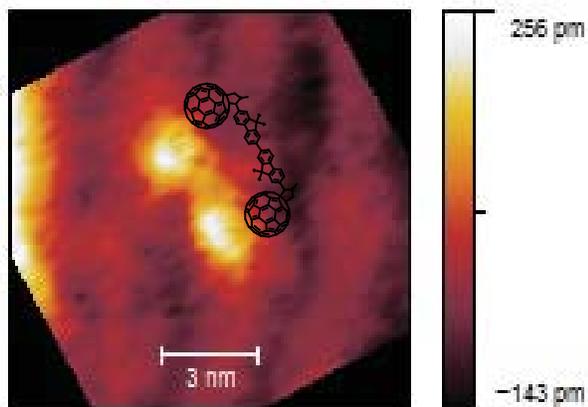


Figure 1. STM image of a dumbbell-type fullerene derivative for conductance measurements.

On the other hand, we have also used fullerenes in organic photovoltaics (PV), by blending with a variety of semiconducting polymeric materials (Figure 2). The former PV devices were based on the concept of mixing an electron donor polymer (p-type component) and the fullerene derivative as the acceptor (n-type component) in two layer (p/n) photovoltaic cells, in which the electronic interaction was limited to the interface between both materials. A further improvement resulted from the concept of “bulk heterojunction” solar cells, which drastically enhanced the interaction between the two components and, therefore, the efficiency of electron transfer and the photovoltaic device. In this lecture, the state of the art in fullerene-based fully organic PV devices will be presented,[2] followed by those results from our group directed to the preparation of alternative fullerenes in the search for better materials and efficiencies.[3] The ordering of fullerenes on solid surfaces will be also presented.[4] Finally, the last approaches to new fullerene-based materials as alternatives to the “classic” systems will be also discussed.[5]



Figure 2. Fullerenes are the base for the preparation of new materials with application in organic photovoltaic devices.

Financial support by the MICINN of Spain (CTQ2008-0795/BQU.), the ESF (SOHYD MAT2006-28170-E), the CAM MADRISOLAR-2 S2009/PPQ-1533)

- [1] Molina-Ontoria, A., Fernández, A., Wielopolski, M., Atienza, C., Sánchez, L., Gouloumis, A., Clark, T., Martín, N., Guldi, D.M., Self-Association and Electron Transfer in Donor-Acceptor Dyads Connected by *meta*-Substituted Oligomers, 2009. *J. Am. Chem. Soc.*, *131*, 12218.
- [2] Delgado, J.L., Filippone, S., Herranz, M. A., Bouit, P. A., Martín, N., Organic photovoltaics: a chemical approach, 2010. *Chem. Commun.* in press.
- [3] Delgado, J. L., Espíldora, E., Liedtke, M., Sperlich, A., Rauh, D., Baumann, A., Deibel, C., Dyakonov, V., Martín, N., Fullerene Dimers (C60/C70) for Energy Harvesting, 2009. *Chem. Eur. J.*, *15*, 13474.
- [4] a) Otero, R., Écija, D., Fernández, G., Gallego, J. M., Sánchez, L., Martín, N., Miranda, R., An Organic Donor/Acceptor Lateral Superlattice at the Nanoscale, 2007. *Nano Lett.*, *7*, 2602; b) Écija, D., Otero, R., Sánchez, L., Gallego, J. M., Wang, Y., Alcamí, M., Martín, F., Martín, N., Miranda, R., An Organic Donor/Acceptor Lateral Superlattice at the Nanoscale, 2007. *Angew. Chem., Int. Ed.* *46*, 7844. c)
- [5] Pinzón, J. R., Plonska-Brzezinska, M. E., Cardona, C. M., Athans, A. J., Shankara, S., Guldi, D. M. Herranz, M. A., Martín, N. Torres, T. Echegoyen, L., Sc3N@C80-Ferrocene Electron-Donor/Acceptor Conjugates as Promising Materials for Photovoltaic Applications, 2008. *Angew. Chem. Int. Ed.* *47*, 4173.

Photovoltaic and Photoelectrochemical Energy Conversion with Nanostructured Oxide Solar Cells

Kevin Sivula* and Michael Grätzel

Institut des sciences et ingénierie chimiques, Ecole Polytechnique Fédérale de Lausanne, Switzerland

Abstract- Mesoscopic and nanostructured oxide electrode are advancing a new paradigm of solar energy conversion using inexpensive and widely available materials in combination with low cost processing methods. Here we describe advances in the dye-sensitized solar cell and electrodes for photoelectrochemical hydrogen production via solar water splitting.

The development of tools to control materials on the nanometer length scale has catalyzed the development of a new class of solar energy conversion devices.[1] The prototype of this new family of devices is the dye-sensitized solar cell (DSC). These devices operate in an entirely different fashion than conventional silicon p-n junction devices as they achieve the separation of light harvesting and charge carrier transport. A nanostructured and mesoporous layer of Titanium dioxide is the key to the efficient operation of this device and the continued research has resulted in devices with power conversion efficiencies over 11 percent and excellent stability. Here we will describe the operation mechanism of the DSC, and illustrate the benefits of the nanostructure used. In addition, we will describe the latest advances with the dye technology and the nanostructure of the TiO₂ electrode.[2] Finally we will highlight some of the recent advances and challenges to be overcome with this technology.

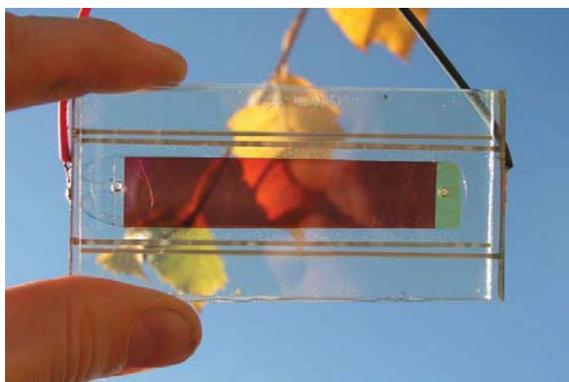


Figure 1. A semitransparent dye-sensitized solar cell based on mesoporous TiO₂.

Nanostructured systems also show great promise for the generation of hydrogen from sunlight. With a favorable band-gap of 2.0 – 2.2 eV, chemical stability in aqueous environments, and ample abundance, using hematite (alpha-Fe₂O₃) as a photocatalyst to produce hydrogen at a scale corresponding to the world energy demand is realistic. Silicon doped alpha-Fe₂O₃ films are shown capable of an overall solar to chemical conversion efficiency of 4.5 percent in a tandem device using a DSC as a bottom electrode. However, its performance as a photoanode has been limited by a very short excited state lifetime and poor minority charge carrier mobility as compared to the light penetration depth. These limitations can be overcome with nanostructuring approaches. Here we report progress on three approaches to control the morphology and performance of hematite for solar water splitting. First, a cauliflower-type structure with feature sizes down to 5 nm can be prepared by atmospheric pressure chemical vapor deposition (APCVD). We first reported this method in 2006.[3] We also present our latest advances to increase the photocurrent past 3.0 mA/cm²

under standard conditions and to understand of the limitations of this system. The next approach is to use an extremely thin layer of this visible light absorber on a nano-structured scaffold.[4] We have demonstrated this concept's effectiveness using a scaffold of tungsten trioxide, and further advanced the performance of extremely thin layers of hematite by introducing an amorphous buffer layer between it and the substrate.[5] Finally, the performance of mesoporous photoanodes prepared by a solution-based colloidal method is reported to be strongly dependant on the sintering temperature, which is necessary for the introduction of dopants. With further advances hematite can be viable contender for large-scale future solar energy conversion systems.

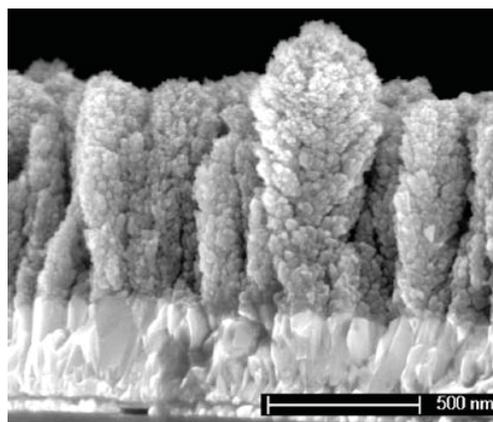


Figure 2. Cross sectional SEM image of a nanostructured Fe₂O₃ film on FTO used hydrogen production by solar water splitting.

These new technologies are both viable contenders for large-scale future solar energy conversion systems on the bases of cost, efficiency, stability, availability and environmental compatibility.

*kevin.sivula@epfl.ch

- [1] M. Grätzel, *Nature* **2001**, 414, 338.
- [2] M. Grätzel, *Acc. Chem. Res.* **2009**, 42, 1788.
- [3] A. Kay, I. Cesar, M. Grätzel, *J. Am. Chem. Soc.* **2006**, 128, 15714.
- [4] K. Sivula, F. Le Formal, M. Grätzel, *Chem. Mater.* **2009**, 21, 2862.
- [5] F. Le Formal, M. Grätzel, K. Sivula, *Adv. Funct. Mater.* **2010**, 20, 1099.

Nanomagnets – Created and Tailored by Ions

J. Fassbender*, T. Strache, M. O. Liedke, D. Markó, S. Wintz, K. Lenz, A. Keller, S. Facsko, J. McCord
 Institute of Ion Beam Physics and Materials Research, Forschungszentrum Dresden-Rossendorf, 01328 Dresden, Germany

Abstract- The potential of ion irradiation and ion implantation for the formation of new nanoscale magnetic materials will be reviewed.

Magnetism is a collective phenomenon. Hence, a local variation on the nanoscale of material properties, which act on the magnetic properties, affect the overall magnetism in an intriguing way [1-5]. In particular important are the length scales on which a material property changes. These might be related to the exchange length, the domain wall width, a typical roughness correlation length, or a length scale introduced by patterning of the material. Here we report on the influence of two artificially created length scales:

i) Ion erosion templates which serve as a source of a predefined surface morphology (ripple structure) and hence allow for the investigation of roughness phenomena. It is demonstrated that the ripple wave length can be easily tuned over a wide range (25 – 175 nm) by varying the primary ion energy (see Fig. 1). The effect of this ripple morphology on the induced uniaxial magnetic anisotropy in soft magnetic Permalloy films is studied. Only below a ripple wave length threshold (≈ 60 nm) a significant induced magnetic anisotropy is found. Above this threshold the corrugated Permalloy film acts as a flat film. This cross-over is discussed in the frame of dipolar interactions giving rise to the induced anisotropies.

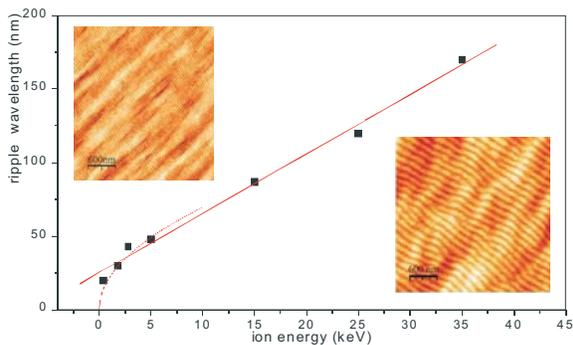


Figure 1. Ripple wavelength as a function of primary ion energy. The insets show two AFM images for ion erosion with a primary energy of 5 keV and 25 keV. Both image scan sizes are identical for a better comparison.

ii) Ion implantation through a lithographically defined mask, which is used for a magnetic property patterning on various length scales. The resulting magnetic properties are neither present in non-implanted nor in homogeneously implanted films. Here new insight is gained by the comparison of different stripe patterning width ranging from 1 - 10 μm . In addition to the appearance of more complicated magnetic domain structures (see Figure 2), i. e. spin-flop domain configurations and head-on domain walls, during hard axis magnetization reversal is demonstrated. In both cases the magnetic properties, the magnetization reversal process as well as the magnetic domain configurations depend sensitively on the artificially introduced length scale.

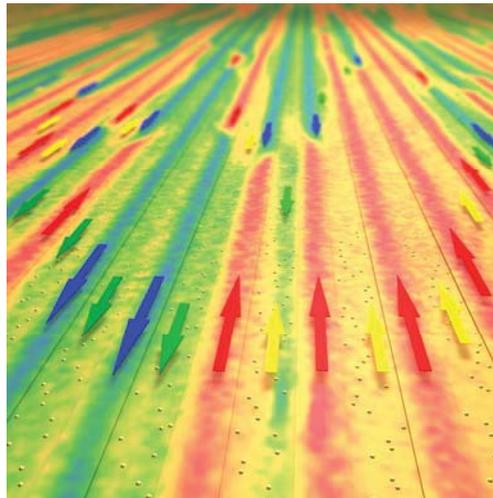


Figure 2. False-color image of magnetization configuration of the stripe structure during the process of magnetization reversal. In principal, the magnetization can take on four different values, marked by corresponding arrows (non-irradiated area: red, blue, irradiated area: yellow, green).

In addition the potential of nanomagnet fabrication by local ion irradiation of a binary alloy will be demonstrated.

This study was supported by Deutsche Forschungsgemeinschaft.

*J.Fassbender@fzd.de

- [1] E. Menendez, J. Sort, M. O. Liedke, J. Fassbender, T. Gemming, A. Weber, L. J. Heydermann, S. Surinach, K. V. Rao, S. C. Deevi, M. D. Baro, J. Nogues, *Creation of sub-100 nm ferromagnetic dots by selective irradiation of a paramagnetic intermetallic alloy*, *Small* 5, 229 (2009).
- [2] J. McCord, L. Schultz, J. Fassbender, *Hybrid soft-magnetic films with novel functionality created by magnetic property patterning*, *Advanced Materials* 20, 2090 (2008).
- [3] J. Fassbender, J. McCord, *Magnetic patterning by means of ion irradiation and implantation*, *J. Magn. Magn. Mater.* 320, 579 (2008).
- [4] M. O. Liedke, B. Liedke, A. Keller, B. Hillebrands, A. Mücklich, S. Facsko, J. Fassbender, *Induced anisotropies in exchange coupled systems on rippled substrates*, *Phys. Rev. B* 75, 220407(R) (2007).
- [5] J. Fassbender, T. Strache, M. O. Liedke, D. Markó, S. Wintz, K. Lenz, A. Keller, S. Facsko, I. Mönch, J. McCord, *Introducing artificial length scales to tailor magnetic properties*, *New J. Phys.* 11, 125002 (2009).

Hydrogen Sorption Thermodynamics in Covalently Linked Nanotube Scaffolds

T. CAGIN^{1,2} AND M. MANI-BISWAS²

Department of Chemical Engineering, Texas A&M University, Texas, TX 77843-3122, USA

Materials Science and Engineering, Texas A&M University, Texas, TX 77843, USA

Abstract- Hydrogen has the potential to replace petroleum as energy source. However efficient storage of hydrogen is a challenge. Carbon nanotube is a promising adsorption based storage material, due to its high surface area and curvature effect leading to high sorbate interaction energy. Furthermore spacer molecules can be used to hold the tubes at distance from each other in a scaffolded structure. Here, using molecular simulations, we show that such structures can achieve high sorption capacity, which increases with tube diameter and spacer distance.

Keywords: Hydrogen storage, Carbon Nanotube Scaffolds, sorption simulation, sorption thermodynamics.

Hydrogen has the potential to replace rapidly depleting hydrocarbons as an energy source.^{1,2} But, it has very low volumetric energy density (8 MJ/L) compared to liquid hydrocarbons (32 MJ/L) at normal temperature and pressure.³ The main challenge is how to store large amount of hydrogen with similar energy density as petroleum fuel. Carbon nanostructures like carbon nanotubes, fullerene, graphene, etc. have gained lot of interests after Dillon⁴ have demonstrated some promising results regarding hydrogen storage potential of SWNT. CNTs are particularly interesting because, in addition to the porosity and large surface area, curved surface and capillary effect can give additional impetus to the H₂ storage capacity. However adsorption on plain carbon nanotubes do not achieve the necessary storage capacity as required by US DOE.³ Fortunately there are several avenues which may be investigated to improve the adsorption capacity of CNT structures. A key approach to increase the adsorption capacity of CNTs is by increasing their effective adsorption surface area. Because of bundled arrangement of the tubes, most of the tube surface remains inaccessible for H₂ molecules, which results in lower H₂ adsorption capacity. If the outer surface areas of the tubes can be exposed to H₂ molecules, then that alone would have improved the adsorption capacity of CNTs. One way to expose the outer surface areas of CNTs is to insert spacers between the individual tubes, so that the tubes, instead of forming cohesive bundles, forms scaffolding structures as suggested in Figure 1. These scaffolding structures expose the outer tube surface for H₂ adsorption. Tour et al.⁵ found that the H₂ sorption capacity of a crosslinked CNT scaffold is almost twice of that of other carbon materials like activated carbon. The sorption capacity may depend on the diameter, crosslinker density and covalent functionalization of CNT surface. The adsorption capacity can be also improved by incorporating

certain metals like Li, K, and Ti in the tube wall. Thus a similar approach may be adopted for scaffolded CNT structures. Using molecular simulations, we show that such structures can achieve high sorption capacity, which increases with tube diameter and spacer distance. The (18,18) tube scaffold with inter-spacer distance of 29.5 Å, achieved a total sorption capacity of 14.4% wt% at 77 K 100 bar; 3.86 wt% at 298 K, 100 bar and when decorated with Li⁺, showed 6.2 wt% capacity at 243 K to achieve the DOE target of 6 wt%.

*Corresponding author: cagin@che.tamu.edu

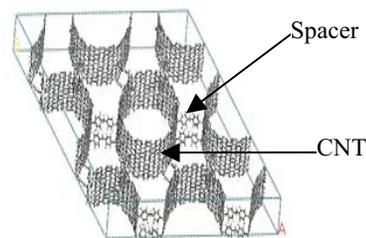


Figure 1. CNT scaffold.

REFERENCES

- [1] Schlapbach, L.; Züttel A. *Nature* **2001**, 414, 353-358.
- [2] Züttel, A. *Naturwissenschaften* **2004**, 91(4), 157-172.
- [3] Satyapal, S.; Petrovic, J.; Read, C.; Thomas, G.; Ordaz, G. *Catalysis Today* **2007**, 120(3-4), 246-256.
- [4] Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethune, D. S.; Heben, M. J. , *Nature* **1997**, 386, 377 – 379.
- [5] Leonard, A.D.; Hudson, J.L.; Fan, H.; Booker, R.; Simpson, L. J.; O'Neill, K. J.; Parilla, P. A.; Heben, M. J.; Pasquali, M.; Kittrell, C.; Tour, J. *M. J. Am. Chem. Soc.* **2009**, 131(2), 723-728.

Electroactive Materials in the nanoscale. Modulation of surfaces potential and applications in biological systems

N. Casan-Pastor.

Institut of Materials Science of Barcelona, CSIC
Campus UAB, 08193 Bellaterra, Barcelona, Spain

Abstract- Electroactive materials such as mixed-valence oxides or conducting polymers and their hybrids are ideal for electrodes in systems that go from energy, to catalysis or biomedicine. The existence of mixed valence or charge carriers allow modulation of surface potentials during preparation or in situ while acting in devices such as batteries, sensors, electrostimulators, or electrocatalytic reactions. The nanostructure that may be imposed modifies substantially the response in terms of speed and power in energy devices, and also the response of biological systems in case of use of electrodes for functional nervous stimulation. Other applications in neural directional growth, adhesion and cell survival will be shown.

Mixed conducting systems such as some mixed valence oxides, conducting polymers etc, allow modulation of surface potential through electrochemical methods. Such processes come usually together with intercalation and deintercalation of ions that allow charge neutrality upon application of the electrochemical field during the electrochemistry. This type of intercalation chemistry is the center of energy storage in *lithium batteries* [1] and also in the oxygen doping that allows to transform *semiconducting La_2CuO_4 into superconducting La_2CuO_{4+d}* , [2] or *huge magnetic changes in its Mn analogues*. [3] *Electrochromism* and other properties are also some of the cases. Other fields of application are the solid state transformation that may occur from $Ag_2Cu_2O_3$ to $Ag_2Cu_2O_4$, or from Cu and Ag metals to $Ag_2Cu_2O_4$, the first known silver copper mixed oxides known. [4]

Electrochemistry is a surface phenomenon where diffusion and interfacial properties are prime factors, and therefore the nanoscale of the material surface is an essential factor. Thus, lithium batteries have been shown to yield a power orders of magnitude larger when nanostructuring is induced in the active surface. The above mentioned chemical transformations also change from micro to nanoscale, in terms of processes occurring from months to days, hours or minutes.

A significant and new application for this type of materials has been developed in our lab, as well as the previous ones described. It involves the use of electroactive materials as electrodes in the nervous system, either for functional stimulation or neural growth [5]. The use of electroactive materials instead of noble metals in this applications prevents the formation of radicals that may damage the biological tissue. Instead, a parallel reaction occurs at the electrode itself, without modification of the medium and without change in its capacity to act as electrode. IrOx, Iridium oxide is among the best materials known for electrostimulation, and other electroactive materials are being tested in the same sense. Additionally, they can function as support for cell growth in controlled potential conditions, a fact that is being investigated. Conducting polymers of the polypyrrole and PEDOT type and hybrids of them are also being tested. Figure 1 shows macroscopic pictures of samples developed, while Figure 2 shows an example of the neural cell adhesion, growth and differentiation in this type of systems. Preparations are also achieved by electrochemical methods on transparent platinum coated glass slides, but can be made on three dimensional structures and scaffolds that later will be used in situ.

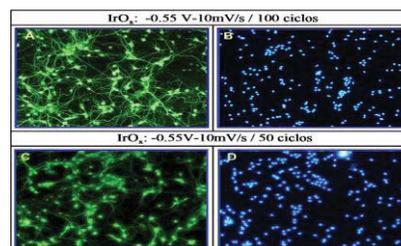


Figure 1. Conducting polymer transparent coatings (on Pt coated glass) used as electrodes



Figure 2. Neural growth on nanostructured transparent IrOx(OH) electrodes.

This study was supported by the Spanish Ministry of Science and Innovation (Plan Nacional 2005 and 2008 calls), by CSIC (PIF) and by the European Community Through FPVI STREP grant.

nieves@icmab.es

[1] R. Palacin, Chem. Soc. Rev., 2009, 38, 2565

[2] N. Casañ-Pastor, P. Gomez-Romero, A. Fuertes, J.M. Navarro, J. Sanchis, S. Ondoño-Castillo Physica C, (1993), 216 478. N. Casañ-Pastor, C.R. Michel, C. Zinck, E.M. Tejada-Rosales. Chem. Mater.. (2001) 13, 2118-2126

[3] C.R. Michel, R. Amigó and N. Casañ-Pastor, Chem. Materials (1999), 11, 195-197

[4] D. Muñoz-Rojas, J. Oró, J. Fraxedas, P. Gómez-Romero, J. Fraxedas, N. Casañ-Pastor, Electrochem. Comm. 4, (2002), 684.

[5] Casan-Pastor et al. Langmuir, submitted; Thin solid films 2009, 518, 160