TNA Posters (11)

Thickness and order enhancement in arrays of TiO2 nanotubes through a simple electropolishing pre-treatment

A. Apolinário[1], C.T Sousa[1], J.D. Costa[1], J. Azevedo[1], J. Ventura[1], H.A. Ribeiro[2], A.M. Mendes[2] and J. P Araújo[1]

[1]IN-IFIMUP and Física, Rua do Campo Alegre 687, 4169-007 Porto, Portugal
[2]LEPAE- Dep. Engenharia Química-Faculdade de Engenharia, R. Dr. Roberto Frias, 4200-465 Porto, Portugal

arletteapolinario@gmail.com

The highly-ordered TiO2 nanotubes (NTs) have gained much importance for application in hydrogen production by water splitting and dye-sensitized solar cells (DSCs).The DSCs have a great potential to be an alternative device for conventional photovoltaics due to their low cost and easy fabrication [1,2].

The TiO2 NTs arrays must have a high-aspect-ratio configuration to obtain higher conversion efficiency.The photoelectrochemical behaviour of TiO2 (anatase) with different nanoarchitectures (such as nanoparticles, nanowire, nanofiber, nanotubes [3]) and the same active surface area (or thickness) has been studied and applied to DSCs to overcome the limitation of TiO2 nanoparticle structure. Recently a new architecture as been in focus, among these structures: the TiO2 nanotube arrays have received a great attention due to their one dimensional structure to provide a direct path for electrons. However, the efficiency of TiO_2-nanotube-based DSCs is 6.89%, which is still lower than that of TiO_2-nanoparticle-based DSCs (~10%). The geometry of the nanotubes depends on different anodizing parameters (electrolyte type and concentration, pH, time, applied potencial) that determine the tube features (length, pore diameter, wall thickness, etc.).

We synthesized TiO2 NTs arrays by electrochemical anodization of a Ti foil (two-electrode cell) in fluoride ion containing baths in combination with non-aqueous organic polar electrolytes including ethyleneglycol or glycerol. These Ti foils were biased with an anodization potencial of 60 V for 17 h at room temperature. We then obtain highly self-ordered arrays of TiO2 NTs**,** with a length of 100 micron, an outer diameter of ~200 nm. The NT arrays morphology was characterized by scanning electron microscopy (SEM). The study of current density transients [$j(t)$] monitored during the anodization process allowed us to probe the different stages of the nanotubes formation. We also concentrate our study on the NT growth quality, i.e. the influence on the nanotubes length of: the type of electrolyte organic solvent, the Ti pre-treatment prior to the anodizition, and the electrolyte concentration. In the first case, by simply changing the organic solvent of the electrolyte we can pass from a 6 μm NT length (glycerol) to an 70 μm length (ethilenoglycol). In the second case, by using the same electrolyte tree times the 17 h we can see a decreasing in the NT length corroborated with the current density transients decrease. Finally, prior to the anodization we perform an electropolishing pre-treatment in the Ti foil (in a H2SO4/HF solution, with an applied potential of 15V during 4 min). We found that such process allows the growth of NTs of enhanced length (larger than 100 μm, i.e. an increase larger than 50% when compared with the as-rolled sample). The topography of the electropolished Ti surface was investigated by Atomic Force Microscopy. After the electropolishing, the Ti surface revealed a dimple-pattern structure (and a surface roughness decrease) that enhances the NTs growth and thus allows to obtain a higher NT length. The subsequent anodization of the dimpled Ti surface led to an increase in the array structural order.The structural analyses of the TiO2 NTs, was performed using X-Ray Diffraction. The corresponding diffraction patterns showed the as-prepared nanotubes are amorphous. We carried out a systematic study of different annealing temperatures to obtain the Anatase phase isolated. The NTs crystallize in Anatase phase after a proper annealing at 400 ºC (with O2).

References

[1] B.O'Regan,M.Gratzel, Nature, 353 (1991) 737–740.
[2] M.Gratzel, Photoelectrochemicalcells, Nature, 414 (2001) 338–344.
[3] G.K.Mor, K.Shankar, M.Paulose, O.K.Varghese, C.A.Grimes, NanoLett., 6 (2006) 215–218.

Ionic liquid based cathodic electrodeposition of metal oxides for energy field applications.

E. Azaceta[a], , M. Ungureanu[b], J. Echeberria[c], G. Cabañero[a], H.J. Grande[a], R. Tena-Zaera[a*]

[a]New Materials Department, CIDETEC-IK4, Centre for Electrochemical Technologies, Parque Tecnológico de San Sebastián, Paseo Miramón 196, Donostia-San Sebastián 20009, Spain

[b2]CIC BIOMAGUNE, Parque Tecnológico de San Sebastián, Paseo Miramón 182 C, Donostia-San Sebastián 20009, Spain
[c]CEIT- IK4, Pº de Manuel Lardizabal 15, 20018 Donostia-San Sebastian, Spain.

rtena@cidetec.es

Metal oxide nanostructured thin films are promising materials in different areas of the energy field such as photovoltaic cells [1], energy storage [2] and saving (e.g. light emitting diodes [3]). Among different deposition methods, electrochemical deposition is an attractive cost-effective method to obtain thin films materials. Various metal oxides can be deposited from the electroreduction of oxygen in aqueous electrolytes (*equation 1)* [4,5]. However, the production of hydroxides as intermediate species in this process limits the technique. Traces of OH- may remain in the metal oxide. In other cases, the metal oxide cannot be obtained due to the deposition of the metal hydroxide as stable phases [6,7].

$$O_2 + H_2O + 4e^- = 4(OH)^- \qquad (1)$$

$$M^{2+} + 2(OH)^- = M(OH)_2 = MO + H_2O \qquad (2)$$
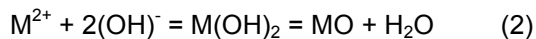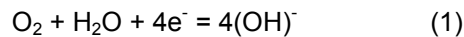
In this work, we present an electrochemical route for the deposition of metal oxides from aprotic N-buyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ionic liquid (PYR14TFSI) based electrolytes [8]. The new approach is based on the electrochemical reduction of O_2 in a solution containing metal bis(trifluoromethanesulfonyl) imide salt. The metal oxide is formed from the reaction of the metal cation (M^{2+}) and superoxide species (O_2^-) generated from the O_2 reduction (*equation 3)*. Since no OH- are involved in the process, the formation of metal hydroxide phase is avoided.

$$O_2 + e^- = O_2^- \qquad (3)$$

$$M^{2+} + 2O_4^- = MO_4 = MO + 3/2O_2 \qquad (4)$$
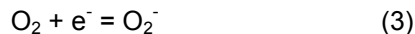
The presentation will be focused on the electrodeposition of two different metal oxides:ZnO and NiO. The mechanisms involved in both deposition processes were analyzed by cyclic voltammetry. The physico-chemical properties of the obtained thin films were analyzed by X-ray photoelectron spectroscopy (XPS), X-ray diffraction spectroscopy (XRD), optical spectroscopy and Scanning Electron Microscopy (SEM). NiO thin films were successfully electrodeposited [10] proving the potential of the present approach to deposit metal oxides, which are not possible to obtain in aqueous electrolytes [7]. On the other hand, ZnO nanocrystalline films with innovative microstructural properties in comparison to those generally obtained in aqueous media [9]. It is worth to highlight the wide range of morphologies obtained by just varying the electrodeposition parameters such temperature or zinc salt concentration, (Figure 1). In this context, the influence of the interaction between ionic liquid moieties and metal oxide surfaces on the crystal growth will be discussed.

Finally, ZnO-NiO heterostructures have been obtained by a sequential electrodeposition of zinc and nickel oxide films. Current-voltage characteristics show good rectifying behavior, suggesting the n-p heterojunction formation.

All in all, an innovative electrochemical route based on aprotic ionic liquids electrolytes to obtain nanocrystalline films of different metal oxides, avoiding metal hydroxide formation, will be presented. The peculiar properties of the obtained metal oxide films open wide possibilities for the integration of metal oxides in a new generation of optoelectronic devices and their application in the energy field.

References

- [1] B. O'Regan, M. Graetzel. Nature, 353 (24) 737-740, 1991.
- [2] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J-M. Tarascon, Nature 407, 2000, 496.
- [3] R.Könekamp, R.C.Word, M.Godinez, Nano Lett. 5, 2005, 2005.
- [4] A. Seshadri, N. R de Tacconi, C.R. Chenthamarakshan, K. Rajeshwar. Electrochem and Solid-sate lett. 9 (1) C1-C4, 2006.
- [5] S. Peulon, D. Lincot. J. Electrochem. Soc., Vol. 145 (3), 1998
- [6] Jeffrey R. S. Brownson, Claude Lévy-Clément. PSS. Vol 245 (9) 1785-1791. 2008
- [7] K.W. Nam, K.B. Kim J. Electrochem. Soc., Vol. 149 (3) A346-A354. 2002
- [8] E. Azaceta, R. Tena-Zaera, R. Marcilla, H.J. Grande, D. Mecerreyes *Electrochem. Comm. 11, 2184,* 2009
- [9] J. Elias, R. Tena-Zaera, C. Lévy-Clément. *J. Phys. Chem. C,* 2008, *112* (15), 5736, 2008
- [10] E. Azaceta, R. Tena-Zaera, M. Ungureanu, J. Echeberria, G. Cabañero, H.J. Grande.

Figures
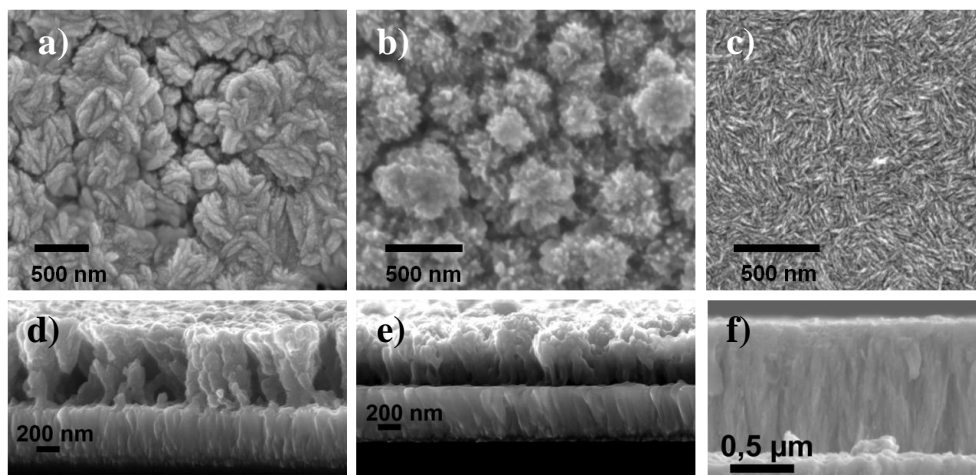
Figure 1: SEM micrographs of the top view (a, b and c) and cross sections (d, e and f) of ZnO films obtained under different electrodeposition conditions.
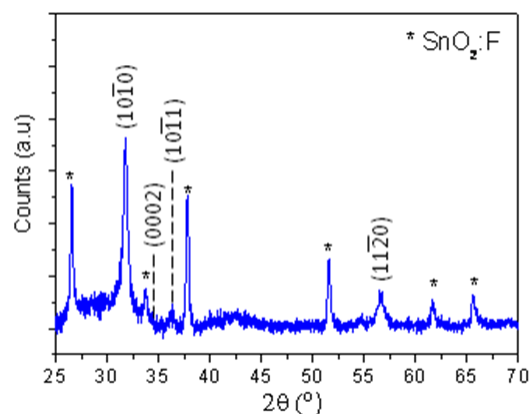
Figure 2: XRD pattern of ZnO films obtained from Pyr14TFSI based electrolytes.

Optimization of photonic crystals to reduce the reflectance of silicon surfaces for solar cell applications.

S. Domínguez [a], J. Bravo [a], I. Cornago [a], M. Ezquer [b], M. J. Rodríguez [b], A. R. Lagunas [b] and J.Pérez-Conde [c]

[a]FideNa, C/Tajonar s/n, 31006 Pamplona, Spain
[b]CENER, Ciudad de la Innovación, n°7, Sarriguren, 31621, Spain
[c]Departamento de Física, Universidad Pública de Navarra, E-31006, Pamplona, Spain
sagrario.dominguez@fidena.es

One factor that prevents silicon solar cells from reaching the 100% of their theoretical efficiency is the light reflection that occurs at their front surface. Many efforts have been done in the last few decades to reduce the reflectance by applying single or multi layers as antireflection coating [1-3] or by texturizing the front surface of the cell [4-7].

In this work, different kind of photonic crystals (PCs) have been employed to reduce the reflectance of a silicon surface. Since shape, periodicity, linewidth and height of the PC have an important influence on the spectral distribution of the reflectance, these parameters have been optimized by computer simulation to find the best periodic pattern. Some of the structures have been also fabricated by Laser Interference Lithography (LIL) and Reactive Ion Etching (RIE) and their reflectance has been optically characterized in the wavelength range from 400 to 1000 nm.

The study has been started with three types of 1D PC, shown in Fig. 1. The optimum dimensions of each type of PC have been found obtaining an average reflectance of 17.28%, 15.97% and 10.82% for the circular, rectangular and triangular PC respectively. Therefore, the best 1D PC found is the pattern of lines with triangular profile (Fig. 1 (b)) with a pitch of 460nm and a height of 323 nm. This structure has been fabricated and characterized by scanning electron microscope (SEM). Its reflectance has been measured with a spectrophotometer and compared with the simulation values, showing very good agreement (Fig. 2). As it can be seen in the graph, silicon reflectance has been reduced from values over 30% to an almost constant value of 10% for the simulated data and of 12% for the measurements in the range of wavelength from 600 to 900 nm.

Since triangular lines where the best 1D PC, inverted pyramids (2D PC) were also studied since they can be fabricated similarly to the triangular lines (Fig.3). This type of PC has been also optimized by computer simulation varying its parameters (pitch and height). The optimum structure found has a pitch of 760nm and a height of 537nm. Its reflectance is shown in Fig. 4 and can be compared with the reflectance of the best 1D PC. Except for a little peak at 640nm, the reflectance of the 2D PC is better than the one of the 1D PC in all the range of wavelengths simulated. The average reflectance for the inverted pyramids is of 9.5% in this range, having a minimum of 5% at 760nm.

References

[1] J. Zhao, M.A Green, IEE Transactions on Electron Devices, **38** (1991) 1925.
[2] S.Chattopadhyay, Y.F Huang, Y.J. Jen, A.Ganguly, K.H. Chen, L.C. Chen, Materials Science and Engineering R, **69** (2010) 1-35
[3] M.A Green, Semiconductor Science and Technology, **8** (1993) 1-12
[4] H.Li, W.Liu, A.Liu, F.Qiao, Z.Hu, Y.Liu, Solar Energy Materials & Solar Cells, **94** (2010) 942-945.
[5] S.Wang, X.Z.Yu, H.T.Fan, Applied Physics Letters, **91** (2007) 61105
[6] C. Aydin, A. Zaslavsky, G.J. Sonek, J. Goldstein, Applied Physics letters **80,** (2002) 13
[7] S. Domínguez, J. Bravo, O. García, M. Ezquer, M.J. Rodríguez and A.R. Lagunas, Conferencia Española de Nanofotónica, Segovia (2010)
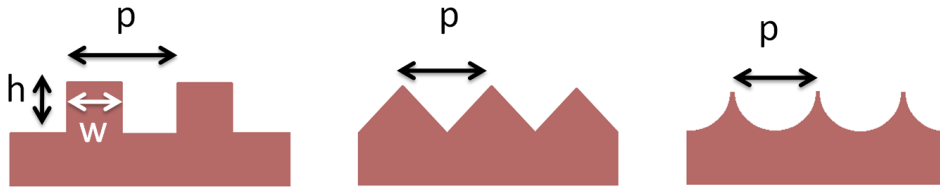
Figures

Fig 1. Designed 1D PCs with different profiles: (a) Rectangular; (b) triangular; (c) Circular.
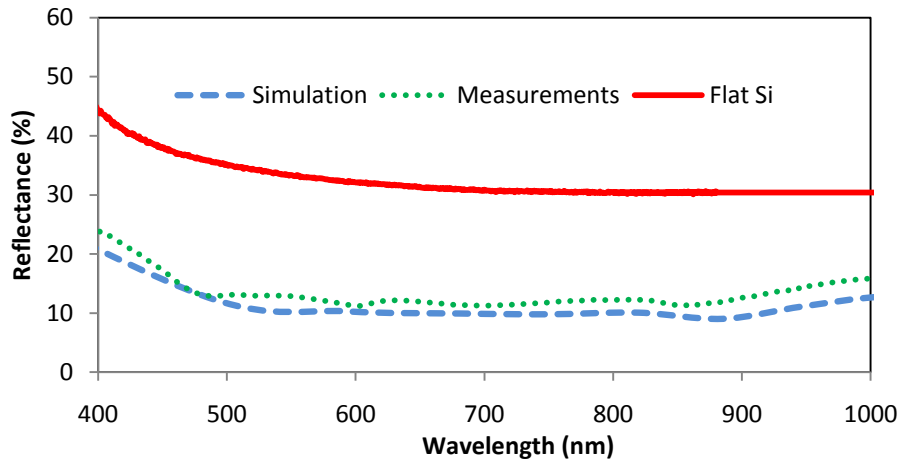

Fig. 2 Comparison between simulation and experimental measurements for the best 1D PC
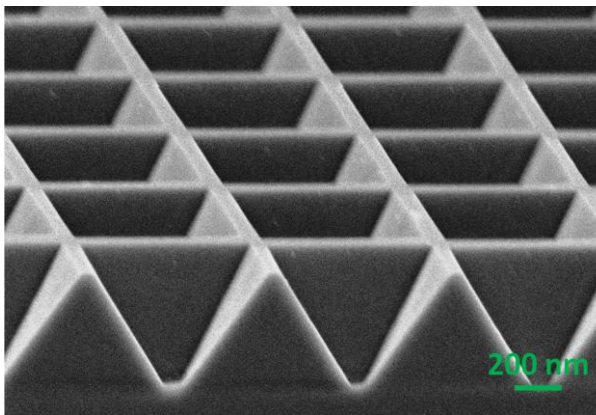

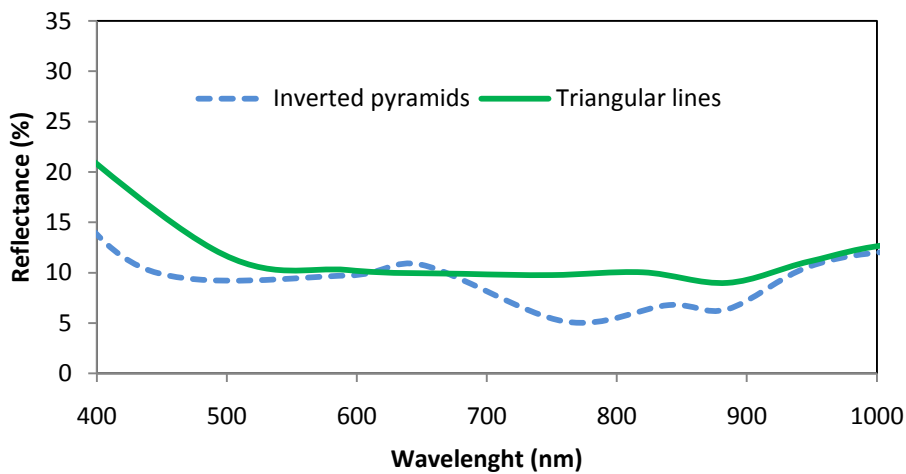Fig 3. A SEM Image of a fabricated Inverted Pyramids pattern.

Fig. 4. Comparison of simulated reflectance for the best 1D PC and the best 2D PC.

6

Graphene derivatives as positive electrode materials in a vanadium redox flow battery

Zoraida González, Cristina Botas, Silvia Roldán, Patricia Álvarez, Clara Blanco, Ricardo Santamaría, Marcos Granda and Rosa Menéndez

Instituto Nacional del Carbón, CSIC, Francisco Pintado Fe, 26, 33011 Oviedo, Spain

zoraidag@incar.csic.es

Graphene derivatives have been extensively studied for energy storage devices such as supercapacitors [1], lithium-ion batteries [2], and more recently for a vanadium redox flow battery (VRFB) [3]. This is because these carbon materials exhibit peculiar properties such as a high specific surface area, an excellent electrical conductivity and remarkable mechanical strength [4], which make them promising electrochemical active materials.

The objective of this work is to evaluate the use of different graphene derivatives as electrode materials in the positive half-cell of a VRFB, taking into account their textural and physico-chemical properties and comparing them with commercial multi-walled carbon nanontubes (MWCNT).

Graphene oxide (GO5) was prepared by a modified Hummers method and characterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM) analysis. Subsequently, it was thermally reduced at different temperatures (700, 800 and 1000º C) generating three different graphene samples (GO5TR700, GO5TR800 and GO5TR1000). The surface chemistry of all the samples were studied by temperature programmed desorption (TPD).

The electrochemical characterization was performed on a Swagelok-type three electrodes cell, consisting of: carbon material (graphene derivative or MWCNT) in a coin-type design as working electrode, a Pt wire as the counter electrode and a saturated calomel electrode as the reference one. The electrolyte used was a 1M H_2SO_4 + 0.5 M $VOSO_4$ solution. Cyclic voltammetry (CV) was carried out using a Biologic VMP Multichannel Potentiostat.

Accordingly to the TEM and AFM images shown in Figure 1, monolayers of graphene oxide with size of ~1 μm are obtained. In addition to the samples structure, the decisive influence of surface chemistry on the electrochemical properties of graphene materials, mainly on the electrical conductivity, made it essential to carry out an analysis of the carbon surface groups [4]. As can be seen in Table 1, the amount of oxygen-containing functional groups on the surface of the graphene oxide sheets is significantly high for the graphene oxide and decreases as a result of thermal treatment, which is in agreement with the TPD results.

Figure 2 presents the CV curves of V(IV)/V(V) redox couple on the graphene derivatives and MWCNT based electrodes tested. Both the oxidation and reduction peak currents are significantly larger on GO5TR1000, which is in agreement with the higher electrical conductiviy of this material. On the other hand, MWCNT and GO5TR800 present the smallest peak potential separation (ΔEp) and peak currents ratio respectively, indicating that these samples exhibit the best reversibility. In the case of GO5TR700, its higher oxygen content explain its electrochemical performance.

The selection of graphene materials suitable as electrodes in the positive half-cell of the VRFB has to be made taking into account their textural and physico-chemical properties. The ideal active material would present mainly high electrical conductivity. In this way, GO5TR1000 is a promising material for this application.

References

[1] S.R.C. Vivekchand, C. Sekhar Rout, K.S. Subrahmanyam, A. Gouindaraj and C.N.R. Rao, J.Chem. Sci., **120** (2008) 9..

[2] P. Guo, H. Song, X. Chen, Electrochem. Commun., **11** (2009) 1320.

[3] P. Han, H. Wang, Z. Liu, X. Chen, W. Ma, J. Yao, Y. Zhu, G. Cui, Carbon, **49** (2011) 693.

[4] C. Liu, Z. Yu, D. Neff, A. Zhamu, B.Z. Jang, Nanoletters, **10** (2010) 4863.

[5] D. Pantea, H. Darmstadt, S. Kaliaguine, C. Roy, Appl. Sur. Sci., **217** (2003) 181.
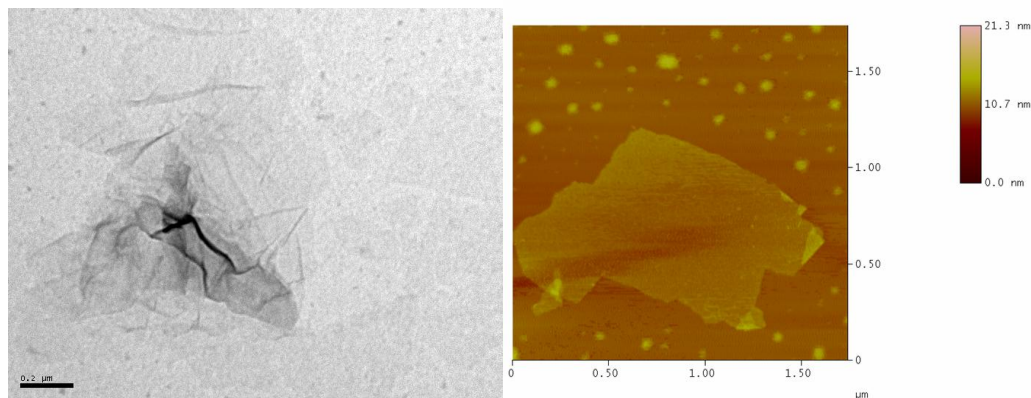
Figure 1: a) TEM image and b) AFM image of GO5

SAMPLE	TPD	
	CO (mmol/g)	CO₂ (mmol/g)
GO5	3,35	2,04
GO5TR700	2,06	0,22
GO5TR800	1,70	0,18
GO5TR1000	0,27	0,14
MWCNT	0,3	0,01

Table 1: TPD analysis of graphene materials and MWCNT

SAMPLE	$I_{p,a}$ / $I_{p,c}$	$E_{p,a}$ (V)	$E_{p,c}$ (V)	ΔE_p (V)
GO5	0,78	0,892	0,159	0,733
GO5TR1000	1,01	0,410	0,336	0,074
GO5TR800	0,95	0,395	0,352	0,043
GO5TR700	0,92	0,477	0,269	0,208
MWCNT	1,1	0,389	0,361	0,028

Table 2: Electrochemical parameters of graphene derivatives and MWCNT based electrodes.

Figure 2: CVs of V(IV) / V(V) redox couple on graphene derivatives and MWCNT based electrodes.

Vertically-aligned Semiconductor Oxides for Dye sensitized solar cells

Irene Gonzalez-Valls[a], Lola Gonzalez-Garcia[b], Belén Ballesteros[a], Frank Güell[c], Angel Barranco[b], Youhai Yu, Agustín R. Gonzalez-Elipe[b] and Mónica Lira-Cantu[a*]

a, Centre d'Investigació en Nanociència i Nanotecnologia, Campus UAB, Edifici ETSE, Bellaterra (SPAIN), 08193.
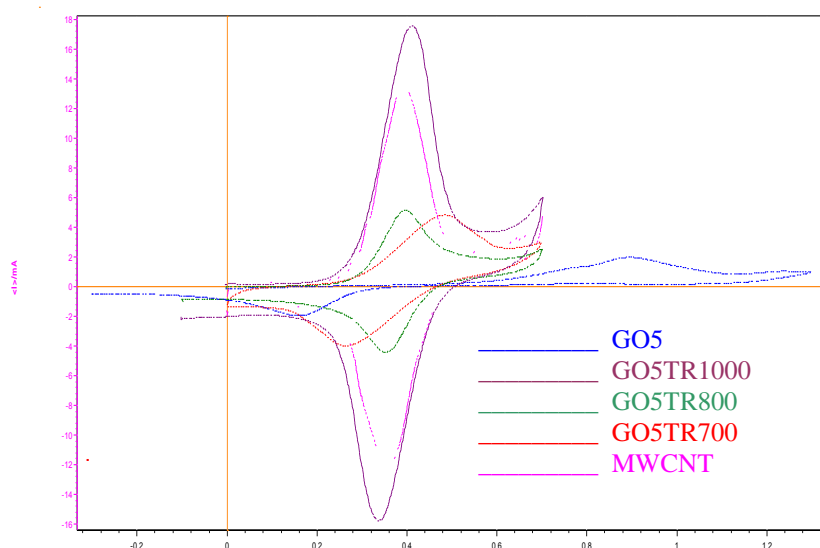b, Instituto de Ciencia de Materiales de Sevilla (CSIC-Univ. Sevilla), Avda. Americo Vespucio 49, 41092 Sevilla, Spain.
c, M-2E, IN2UB, Departament d'Electrònica, Universitat de Barcelona, C/Martí I Franquès 1. Barcelona (SPAIN), 08028.
monica.lira@cin2.es

Vertycal-aligned oxide nanostructures are interesting semiconductors for their electronic properties, they are thought to improve contact between the donor and acceptor material in organic solar cells (OSCs), or improve electron injection in Dye sensitized solar cells (DSCs) [1-5]. In this work we present the application of different aligned semiconductor oxides, like TiO_2 and ZnO, in Dye sensitized solar cells (DSC). The efficiency of DSC applying vertically-aligned ZnO nanorods (NRs) is still lower than DSCs with hierarchical ZnO nanoplates, nanosheets, disk-like nanostructures or aggregates that can achieve more than 6% efficiency [6]. In an effort to understand the factors that limit power conversion efficiency, we report in this work a slight modification of the hydrothermal synthesis technique for the obtention of vertically-aligned ZnO NRs. Our initial results show that, for the same NR growth time, shorter NR length but higher power conversion efficiencies are obtained with the modified method (Figure 1). For example, the same solar cell efficiency can be obtained for a 5 µm ZnO NR thickness obtained by the hydrothermal method and for 1 µm thick ZnO NR electrode applying the new method. The latter is attributed to the higher dye loading capacity of the ZnO NRs obtained with the modified synthesis methodology. Our work also encompasses the synthesis of transparent thin film electrodes made of vertically aligned nanocolumns of TiO_2 with well-controlled oblique angles. These electrodes were grown by physical vapor deposition at glancing incidence (PVD-GLAD). For an electrode thickness of 500 nm, we report a 40% variation on solar cell efficiency (from 0.6% to 1.04%) when the deposition angle was modified between 60º and 85º. Transparent thicker films with higher surface area deposited at the optimal angle of 70º were grown with a zigzag morphology which confers high mechanical strength to the thin films. Using this topology, the application of an electrode thickness of 3 µm in a DSC resulted in a power conversion efficiency of 2.78% maintaining electrode transparency [7].

References

[1] I. Gonzalez-Valls and M. Lira-Cantu, *Energy Environ. Sci.*, 2009, **2**, 19.
[2] B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
[3] M. Lira-Cantu, F.C. Krebs, P. Gomez-Romero and S. Yanagida, *Mater. Res. Soc. Symp. Proc.,* 2007, 1007-S14-04.
[4] M. Law, L.E. Greene, J.C. Johnson, R. Saykally and P. Yang, *Nat. Mater.,* 2005, **4**, 455.
[5] I. Gonzalez-Valls and M. Lira-Cantu, *Energy Environ. Sci.*, 2010, **3**, 789.
[6] Q-F. Zhang, C. S. Dandeneau, S. Candelaria, D. Liu, B. B. Garcia, X-Y. Zhou, Y-H. Jeong and G-Z. Cao, *Chem. Mat.,* 2010, **22**, 2427.K. Keis, E. Magnusson, H. Lindström, S.-E. Lindquist and A. Hagfeldt, *Solar Energ. Mater. & Solar Cells*, 2001, **73**, 51.
[7] L. Gonzalez-Garcia, I. Gonzalez-Valls, M. Lira-Cantu, A. Barranco, A. R. Gonzalez-Elipe, *Energy Environ. Sci.*, 2010, *Accepted*. DOI: 10.1039/c0ee00489h

Figures 1
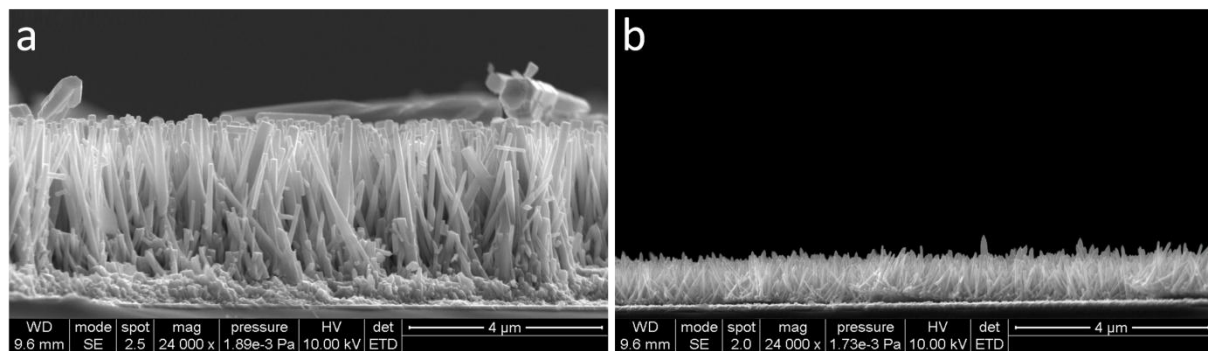
SEM pictures of the vertically-aligned ZnO nanorods grown for 12h by: a) standard hydrothermal synthesis and b) new synthesis.

Nanostructured front grid contacts for III-V solar cells.

Etor San Román, Iván Fernández-Martínez, José M. Ripalda and Fernando Briones.

Instituto de Microelectrónica de Madrid (IMM)

Consejo Superior de Investigaciones Científicas (CSIC)

C/Isaac Newton, 8 (PTM) 28760 Tres Cantos, Madrid, Spain

etor.sanroman@imm.cnm.csic.es

We report on the fabrication and electrical characterization of Ge/Pd/Au nanostructured grids used as front contact for III-V concentration solar cells. The nanogrids have been patterned by electron beam lithography (EBL) while the Ge/Pd/Au trilayer has been deposited by sputtering. After a lift-off process, linewidths ranging from 80 nm to 300 nm and periods of 250 nm to 20 µm over GaAs substrates have been achieved (Figure 1, 2). Different thickness combinations of the trilayer and Rapid Thermal Annealing (RTA) conditions have been studied in order to achieve a low contact resistance (R_c) to the solar cell emitter layer. Values in the range of $R_c \sim 10^{-6}$ Ωcm^2 have been obtained.

The use of metallic nanogrids for the management of photons and electrons inside the cell may lead to an improved performance of the solar cells [1]. But the design of the front contact grid (dimensions, shape and geometric arrangement) is not straightforward, due to the intrinsic complication related to the (series resistance)/(shadow factor) balance it implies. Moreover, it has been shown [2] that the front contact grid is a limiting factor for the maximum current density a concentration solar cell can sustain. On the other hand, the use of nanostructured metals in the surface of a semiconductor can give rise to effects such as diffraction, plasmon polariton resonances, extraordinary optical transmission, etc. [3] that can be used for light-trapping to increase the probability of carrier generation [1, 4]

References

[1] H.A. Atwater, A. Polman , Nature Materials, **9** (2010) 205-213

[2] I.García Vara. Tesis Doctoral, Dpto. de Electrónica Física, ETSI Telecomunicación UPM, 2010

[3] T.W. Ebbesen, H.J. Lezec, H.F. Ghaemi, T. Thio, P.A. Wolff, Nature, **391** (1998) 667-669

[4] F. J. Beck, S. Mokkapati, A. Polman, K.R. Catchpole, Applied Physics Letters, **96**(2010) 033113

Figures

Scanning Electron Micrographs of the fabricated nanogrids.

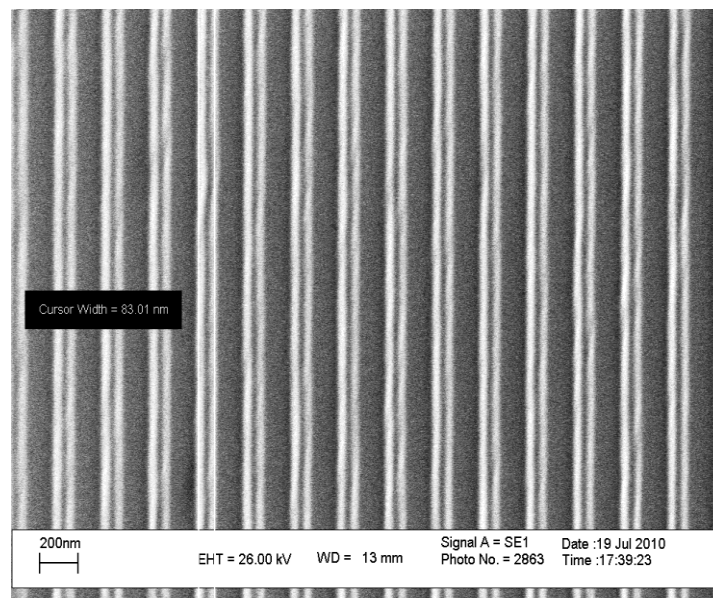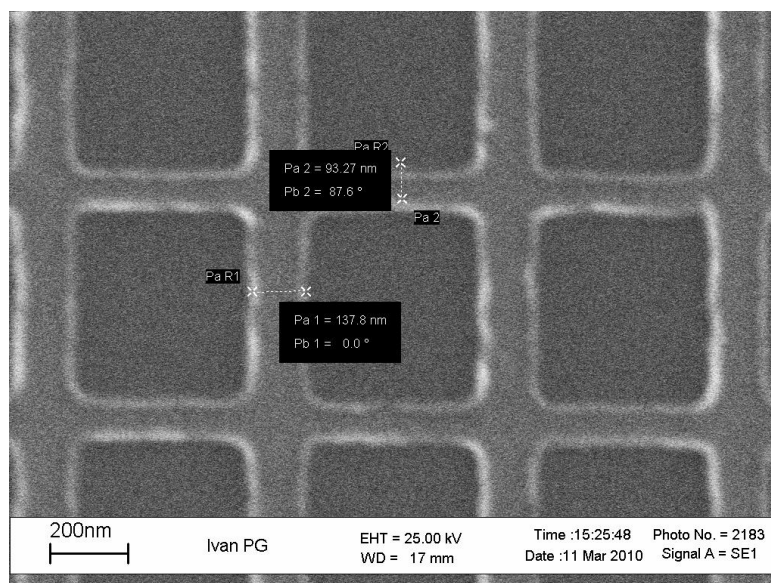Fig. 1: SEM micrograph of a grid with 83 nm linewidth

Fig. 2: SEM micrograph of a double-grid with 93 nm and 137 nm linewidth

Hydrothermal synthesis of NiO/carbon nanotubes nanocomposite for energy production and storage devices.

R. Pinedo[a], I. Ruiz de Larramendi[a], D. Jimenez de Aberasturi[a], M. Insausti[a],

J. I. Ruiz de Larramendi[a], and T. Rojo[a,b]*

[a]*Departamento de Química Inorgánica,Facultad de Ciencia y Tecnología (UPV/EHU), Apdo 644, 48080, Bilbao (Spain) and* [b]*CIC energiGUNE, Parque Tecnológico de Álava. Albert Einstein 46 - ED. E7, 01510 Miñano, Álava (Spain)*

teo.rojo@ehu.es

Because of their unique one-dimensional (1D) geometric and electronic structure,large surface area, good chemical and thermal stability, and excellent mechanical properties, carbon nanotubes (CNTs) provide a new model system for basic scientific study of materials science [1]. The modification of the CNTs with functional materials opens a wide range of applications which covers from microelectronics and energy devices to the biology and medicine [2,3]. There have been several researches concerning the attachment of various inorganic oxides onto single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). For example, oxide nanoparticles such as SiO_2 [4,5] SnO_2 [6], ZnO [7,8], TiO_2 [9-13] have been coated onto CNTs by impregnation, sol–gel, hydrothermal synthesis, thermal evaporation-deposition and so on. In order to facilitate the adsorption of the oxide particles onto the surface of the CNTs, several modification of the CNTs can been employed, such as their oxidation by strong acids, which introduces carboxyl groups and prevents the agglomeration of oxide nanoparticles, because of the strong interactions between the hydroxyl groups and the metallic oxide nanoparticles [14]. Other metal oxides have been coated on CNTs by redox reactions between CNTs and KMnO4 [15-18]. In addition, the surface of these nanostructured materials has been also modified by other reactants s polymers or surfactants [5, 12, 13, 19]

The aim of our research is focused on the search of nanostructured materials for application in energy devices, such as solid oxide fuel cells (SOFCs), lithium-air batteries or supercapacitors. In this work a composite system based on NiO particles coating the CNTs with possible application in the mentioned three fields is studied. The NiO is already used as anode for SOFC systems, however this composite system could enhance its properties providing a large increase of the surface area of the electrode which would promote the creation of reaction points, improving therefore its electrochemical performance [20 JACS argentinos]. However, in order to be used in SOFC devices it is necessary to reduce the operating temperature of these cells to 500 ºC were the nanotubes remain stable. Another interesting application is its use as cathode for lithium-air batteries, where some other similar materials such as the MnO_2/CNT have been found to be interesting [21, 22]. Moreover, this type of materials have shown excellent properties for energy storage devices, such as supercapacitors [23]

In order to obtain this composite system an easy, non-expensive, two step hydrothermal route has been followed, using MWCMT and $NiCl_2$ as starting reactants and sodium dodecyl sulfate (SDS) as surfactant agent. The obtained aqueous suspension was heated at 80 ºC for 4 hours. Once the sample was washed and dried, a thermal treatment at 400 ºC for 2 hours was necessary to reach to the NiO. In order to confirm this fact an X-ray diffraction analysis was carried out (see Figure 1).

The scanning electron microscopy (SEM) images reveal the nanostructured shape of the synthesized material with a large surface area with potential properties for its use in energy material devices (see Figure.2.).

The thermal stability of the nanocomposite system has been studied by thermogravimetric analysis, and the electrochemical measurements show an interesting performance for its use as supercapacitor, cathode in lithium-air batteries and anode in intermediate temperature SOFCs (IT-SOFCs).

References:

[1]. R. Saito, G. Dresselhause and M. S. Dresselhause, **Physical Properties of Carbon Nanotubes,** (1998), Imperial College Press, London.
[2]. J. A. Fagan , B. J. Bauer , E. K. Hobbie , M. L. Becker , A. R. Hight Walker ,J. R. Simpson , J. Chun , J.Obrzut , V. Bajpai , F. R. Phelan , D. Simien , J. Y. Huh and K. B. Migler, **Advanced Materials**, (2011), 23, 338–348.

[3]. Yue, G. Z.; Qiu, Q.; Gao, Bo; Cheng, Y.; Zhang, J.; Shimoda, H.; Chang, S.; Lu, J. P.; Zhou, O., **Applied Physics Letters**, (2002), 81(2), 355-357.

[4]. T. Seeger, T. Köhler, T. Frauenheim, N. Grobert, M. R€uhle, M. Terrones and G. Seifert, **Chem. Commun**., (2002), 34.

[5]. E. A. Whitsitt and A. R. Barron, **Nano Lett**., (2003), 3, 775.

[6]. W. Q. Han and A. Zettl, **Nano Lett**., (2003), 3, 681.

[7]. W. D. Zhang, **Nanotechnology**, (2006), 17, 1036.

[8]. S. Y. Bae, H. W. Seo, H. C. Choi, J. Park and J. Park, **J. Phys. Chem. B**, (2004), 108, 12318.

[9]. B. Liu and H. C. Zeng, **Chem. Mater.**, (2008), 20, 2711.

[10]. Q. Huang and L. Gao, J. **Mater. Chem.**, (2003), 13, 1517.

[11]. A. Jitianu, T. Cacciaguerra, R. Benoit, S. Delpeux, F. Beguin and S. Bonnamy, **Carbon**, (2004), 42, 1147.

[12]. S. W. Lee and W. M. Sigmund, **Chem.Commun**., (2003), 780.

[13]. T. Sainsbury and D. Fitzmaurice, **Chem.Mater.**, (2004), 16, 3780.

[14]. X. Li, J. Niu, J. Zhang, H. Li and Z. Liu,**J. Phys. Chem. B**, (2003), 107, 2453.

[15]. X. Jin, W. Zhou, S. Zhang and G. Z. Chen, **Small,** (2007), 3, 1513.

[16]. S. B. Ma, K. Y. Ahn, E. S. Lee, K. H. Oh and K. B. Kim, **Carbon**, (2007), 45, 375.

[17]. W. D. Zhang and J. Chen, **Pure Appl. Chem.**, (2009), 81, 2317.

[18]. J. Yan, Z. J. Fan, T. Wei, J. Cheng, B. Shao, K. Wang, L. P. Song and M. L. Zhang, **J. Power Sources**, (2009), 194, 1202.

[19]. A. Gonzalez-Campo, K. L. Orchard, N. Sato, M. S. P. Shaffer and C. K. Williams, **Chem. Commun**., (2009), 4034.

[20]. M. G. Bellino, J. G. Sacanell, D. G. Lamas, A. G. Leyva, N. E. Walsoe de Reca, **J. Am. Chem. Soc.**, (2007), 129, 3066-3067.

[21]. J. Xiao, W. Xu, D. Wang and J.-G. Zhang, **Journal of The Electrochemical Society**, (2010), 157, 3, A294-A297.

[22]. L. Jin, L. Xu, C. Morein, C. Chen, M. Lai,S. Dharmarathna, A. Dobley, and S. L. Sui, **Adv. Funct. Mater.** (2010), 22, 3373–3382.

[23]. W. Zhang, B. Xu and L. Jiang, **J. Mater. Chem**., (2010), 20, 6383–6391.

Figures

Figure caption1. Obtained diffractogram for the NiO-MWCNTs nanocomposites system

Figure caption2. SEM images of the nanocomposite system NiO/MWCNTs
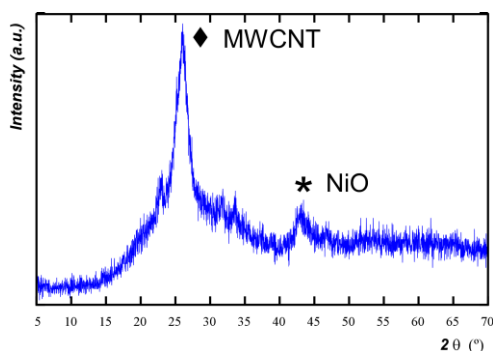

Figure 1. Obtained diffractogram for the NiO-MWCNTs nanocomposites system
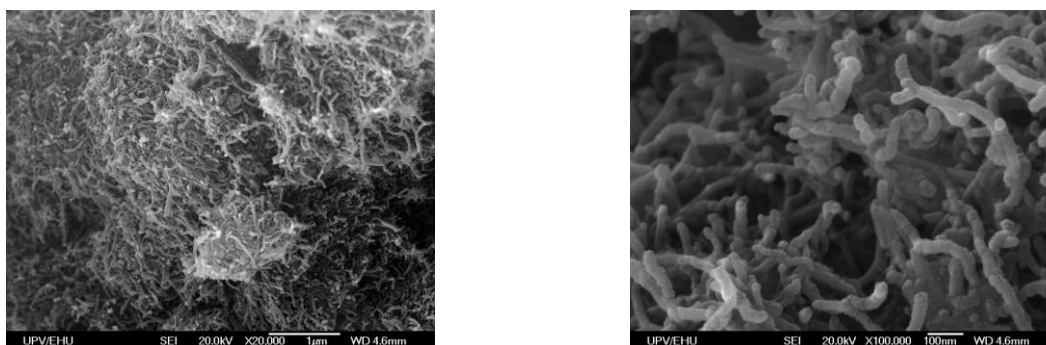

Figure 2. SEM images of the nanocomposite system NiO/MWCNTs

Redox-active electrolytes as a new route to obtain high-energy carbon-based supercapacitors

S.Roldán, Z. González, M. Granda, R. Menéndez, R. Santamaría, C. Blanco

Instituto Nacional del Carbón, CSIC, Francisco Pintado Fe, 26, 33011, Oviedo, Spain

silviarl@incar.csic.es

Supercapacitors (SCs) have attracted much interest as energy storage systems due to their high power density, long cycle life, short charging time, low maintenance, and good safety record (1). These factors make them highly attractive for use in electric devices and vehicles (2). However, for such applications it is first necessary to increase the amount of energy that can be stored by the SCs (3). Carbon materials are the most commonly used materials for electrodes in SCs because of their relatively low cost, good electrical conductivity and high surface area, being therefore ideal materials for the rapid storage and release of energy (4). There are two energy storage mechanisms for SCs: double-layer formation and pseudocapacitance. Although most of the capacitance of carbon materials arises from the formation of the double-layer, many of these materials reach an increase in their capacities thanks to pseudocapacitive effects, resulting from the quick faradaic reactions of surface functionalities, polymers or transition metal particles present in the electrodes (5). However, it is known that pseudocapacitance limits the lifetime of the SCs due to the instability of the fuctionalities with cycling and the degradation of the polymer and the composites.

Herein, we describe an alternative route to promote quick faradaic reactions in order to improve the specific capacitance (Ce) of carbon-based SCs through the use of redox-active electrolytes (6, 7). The combination of the capacitance of the SC with that provided by the redox reaction of the electrolyte will lead an increase in overall capacitance. This concept is demonstrated by showing the effects of adding electrochemically active compounds to carbon-based SCs.

Indigo carmine (IC), methylene blue (MB) and hydroquinone (HQ) were utilized as electrochemically active compounds, and their pseudocapacitance effects were studied in MWCNT-based SCs. Furthermore, four carbon materials were tested with the HQ solution: multiwalled carbon nanotubes (MWCNTs), a carbon aerogel (CA), and two chemically activated carbon materials from coke, prepared with KOH (AC-KOH) or NaOH (AC-NaOH). The working solutions were prepared using 1 M H_2SO_4 as supporting electrolyte in concentrations of 0.05 M, 0.07 M and 0.38 M for IC, MB and HQ, respectively. The electrochemical behaviour was studied in a Swagelok®-type cells by using a two-electrode configuration. Chrono-potenciometric studies of galvanostatic charge-discharge (0.88-88 mA cm^{-2}) and cyclic voltammetry experiments (1-50 mV s^{-1}) were carried out in an operating voltage window of 0-1 V using a VPM multichannel generator (Biologic, France).

All redox-active solutions studied in MWCNT-based SCs showed a great increase in the Ce values after the addition of the electrochemically active compound to the supporting electrolyte (Fig. 1a). A maximum value of 180 F g^{-1} was obtained in HQ solution at a constant current density of 0.88 mA cm^{-2}, and the use of IC and MB solutions led to Ce values 2.8 and 4.6 times higher, respectively, than those obtained in H_2SO_4. Obviously, theses increases are due to the additional capacitive contribution of the faradaic reactions of the electrochemically active compounds, as the voltammogram profiles show (Fig. 1b). The cyclic voltammograms obtained with redox-active electrolytes display well-defined redox peaks, while the voltammogram obtained for the MWCNTs in H_2SO_4 shows an ideal rectangular shape characteristic of an electrical double layer capacitor.

As can be seen before, the pseudocapacitive effects of the HQ-redox system were studied employing four carbon materials as electrodes (Fig. 2). The Ce values were at least two times higher after the addition of the redox compound. The greatest increase corresponded to the AC-KOH, for

which the Ce values trebled, reaching the value of 900 F g^{-1} at 2.7 mA cm^{-2}. It is worth mentioning that this value is much higher than the best value of Ce reported to date for SCs, which was obtained for the SC containing amorphous hydrated ruthenium oxide electrodes (8).

We can conclude therefore that these are innovative hybrid systems that combine two energy-storage processes: the double-layer formation characteristic of carbon-based SCs and faradaic reactions characteristic of batteries. This type of devices constitutes a breakthrough in the development of SCs, as it promises to be a highly efficient way to increase the storage of electrical energy.

**References**
[1] M. D. Stoller, S. Park, Y. Zhu, J. An, R. S. Ruoff, Nano Letters, **8** (2008) 3498.
[2] R. Kotz, M. Carlen, Electrochim. Acta, **45** (2000) 2483.
[3] P. Simon, Y. Gogotsi, Nat. Mater., **7** (2008) 845.
[4] J. Huang, B. G. Sumpter, V. Meunier, Angew. Chem., **120** (2008) 120.
[5] K. Jurewicz, K. Babel, A. Ziokowski, H. Wachowska, Electrochim. Acta, **48** (2003) 1491.
[6] S. Roldán, C. Blanco, M. Granda, R. Menéndez, R. Santamaría, Angew. Chem., **123** (2011), 1.
[7] S. Roldán, Z. González, C. Blanco, M. Granda, R. Menéndez, R. Santamaría, Electrochim. Acta, doi:10.1016/j.electacta.2010.10.017
[8] J. P. Zheng, P. J. Cygan, T. R. Jow, J. Electrochem. Soc. **142** (1995) 2699.

Figure captions
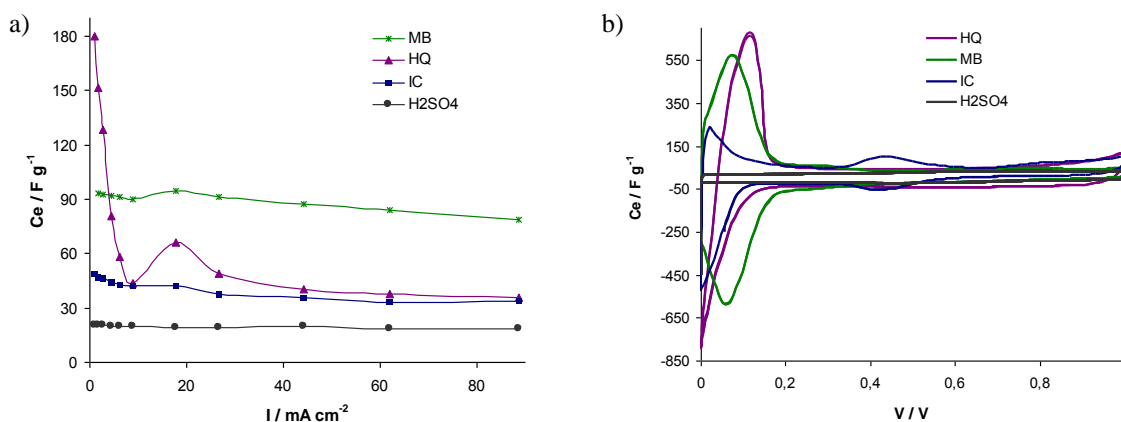
Variation of specific capacitance with current density and b) voltammetric profiles (1 mV s^{-1}) obtained in MB, HQ and IC solutions and in the supporting electrolyte.(Electrode active material: MWCNTs)
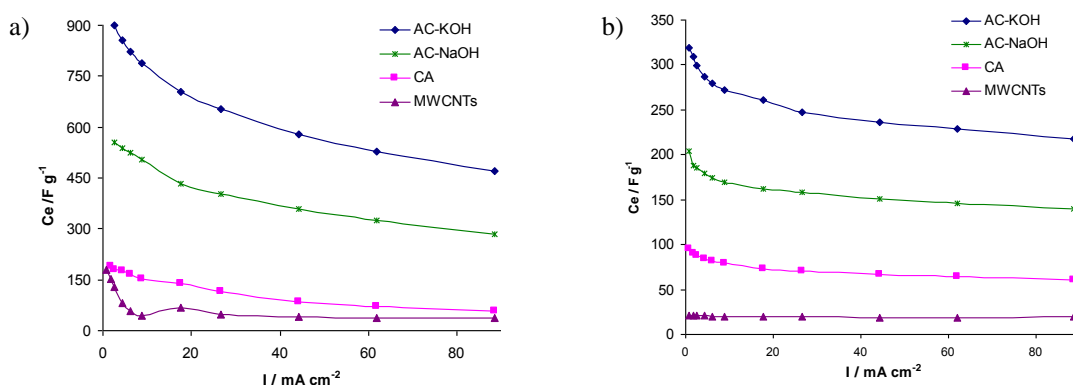
Variation of specific capacitance with current density in: a) HQ/H$_2$SO$_4$ and b) H$_2$SO$_4$ (1V).

First Principles study of Bi doped CdTe thin film solar cells: electronic and optical properties

Y. Seminóvski[a], P. Palacios[a,b], P. Wahnón[a]

[a] Instituto de Energía Solar & Dpt. TEAT, ETSI Telecomunicación, Universidad Politécnica de Madrid, Ciudad Universitaria s/n, Madrid, Spain.
[b] Dpt. Física y Química Aplicadas a la Técnica Aeronáutica, Escuela de Ingeniería Aeronáutica y del Espacio, Universidad Politécnica de Madrid, Pza de Cardenal Cisneros, 3, 28040, Madrid, Spain.
seminovski@etsit.upm.es

Nowadays, efficiency improvement of solar cells is one of the most important issues in photovoltaic systems and CdTe is one of the most promising thin film photovoltaic materials we can found. CdTe reported efficiencies in solar energy conversion have been as good as that found in polycrystalline Si thin film cell [1], besides CdTe can be easily produced at industrial scale.

Nevertheless, further higher efficiencies of CdTe can be obtained if some physical properties are enhanced and controlled. Resistivity in CdTe can be controlled by including high concentration of dopant atoms like Bi or Sb inside CdTe crystal. In previous works, experimental results of Bi in concentration over 1.10^{18} cm^{-1} in CdTe show desirables characteristics as, low resistivity and high photoconductivity [1-3].

In this work, first principles calculations are performed to study the improvement in electronic and optical properties that can be found when Bi is included inside CdTe crystal. Particularly, the electronic-band structures and densities of states of CdTe doped in high proportion with Bi in Cd or Te position, show the formation of states inside the host bandgap. The optical absorption coefficient related with the energy was also obtained and results give higher absorption values for the doped material.

References

[1] O. Vigil-Galán et al, Thin Solid Film, **516** (2008) 3818.
[2] E. Saucedo et al, J. Appl. Phys., **100** (2006) 104901.
[3] E. Saucedo et al, J. Appl. Phys., **103** (2008) 094901.

Figures
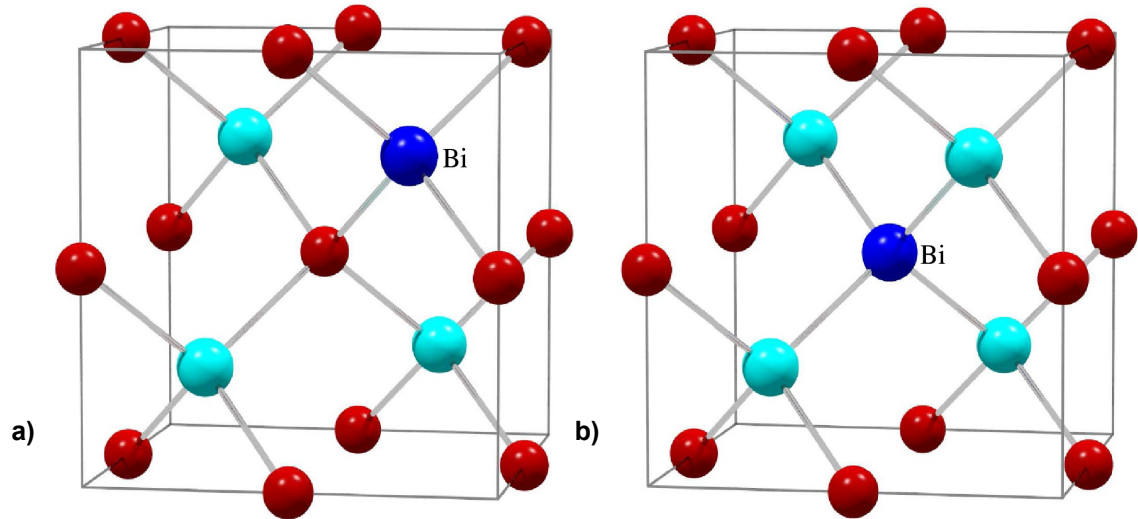
CdTe Structure doped with Bi (dark blue) in a) Cd position and b) Te position. Color of Cd (light blue), Te (red).

First evidence of the Photoconductivity of Single Wall Carbon Nanotubes films deposited on Silicon surface by Time Resolved Microwave Conductivity

Sébastien Sorgues[1], Claire Costa-Coquelard[2]

1- Laboratoire de Chimie Physique, Université Paris-Sud 11, bât 349 91405 Orsay Cedex, France
Sebastien.sorgues@u-psud.fr
2- Service de Physique de l'Etat Condensé CEA/DSM/IRAMIS/PEC, 91191 Gif/Yvette Cedex, France

Nowadays, semiconductors, such as silicon, are the most convenient materials employed for the photovoltaic cell production. To be efficient, these materials should (i) absorb the maximum of photons of the sun and (ii) exhibit the highest conductivity by preventing the charge carrier recombination. These performances should be reached at a minimum financial cost which is often associated with the simplicity of the employed methods. Besides, it is well known that Carbon Nanotubes, especially Single Wall Carbon Nanotubes (SWNT) are interesting candidates for the photovoltaics[1]: semiconductors SWNT exhibit low gap, extended absorption spectrum in the visible range, strong molar extinction coefficient and reduced carrier scattering.

The aim of this work is to graft SWNT on a surface of silicon in order to benefit of the SWNT properties, as well as the properties of silicon surfaces. We will present the preliminary results concerning the preparation of dense SWNT film on hydrophilic n-doped silicon surface by the bubble deposition method (BDM method, see for example ref[2]). The method consists in confining SWNT in two layers of surfactant via a bubble. This bubble is deposited on the treated silicon surface. The time of drainage enable us to control the quantity of SWNT which is deposited. The last step consists to remove the surfactant. An AFM image is presented in Figure 1. The BDM is an efficient and nevertheless simple and scalable method without being a time and solution consuming method.

In a second step, we studied for the first time the photoconductivity of these surfaces by a non-invasive method such as the Time Resolved Microwave Conductivity (TRMC) method[3]. This transient absorption technique is based on the microwave absorption of samples containing mobile charge carries. In this transient experiment, a nanosecond laser excitation of the semiconductor induces a charge separation via a transition from the valence band to the conduction band. The fate of the species created is probed by microwave absorption. It has been demonstrated that the signal measured is proportional to the conductance change and consequently to the number of charge carrier and to their mobility. We demonstrated by this method that at surface SWNT-modified surface, the lifetime of the charge carrier is 100 times longer compared to non-modified surface (Figure 2). These first results are very encouraging for the preparation of surfaces of solar cells and their characterization.
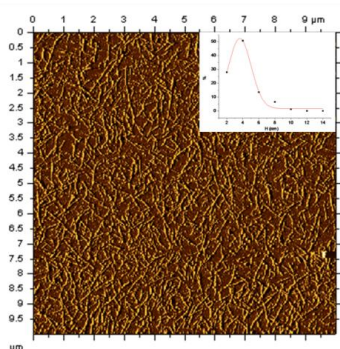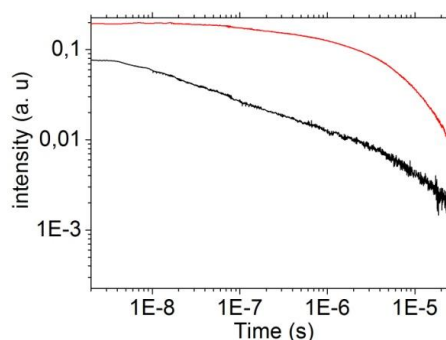

Figure 1

Figure 2

[1] J. U. Lee, Applied Physics Letters, 87 (2005), p. 073101
[1] G. Tang, X. Zhang, S. Yang, V. Derycke, and J.-J. Benattar, Small, 14(6) (2010), p. 1488
[3] C. Swiatkowski, A. Sanders, K.-D. Buhre and M. Kunst, Journal of Applied Physics, 78(3) (1995), p. 1763

Figure Caption

Figure 1: AFM image of SWNT film on Si substrate. Insert: Height distribution of the film

Figure 2: Amplitude of the TRMC signal in arbitrary unit of (–) Si Surface (–) Si-OH/ SWNT Surface

Nanostructured $Li_4Ti_5O_{12}$ spinel as an anode for three-dimensional Li-ion battery.

Marketa Zukalova, Jan Prochazka and Ladislav Kavan

J. Heyrovský Institute of Physical Chemistry, v.v.i. Academy of Sciences of the Czech Republic
Dolejskova 3, CZ-18223 Prague 8, Czech Republic
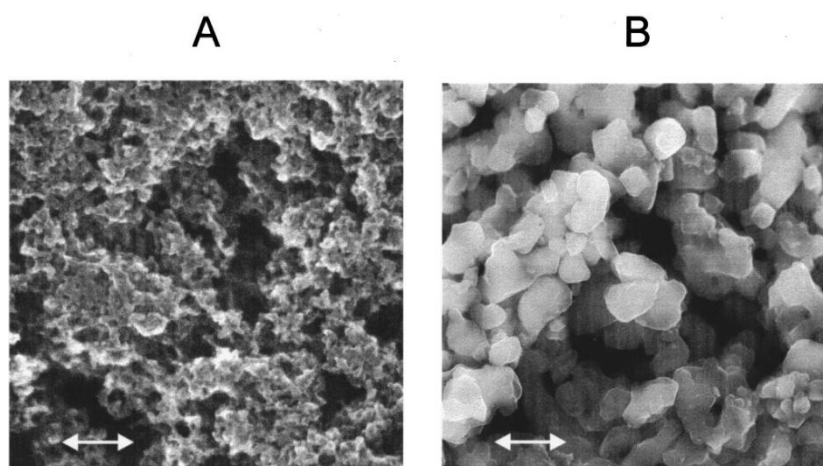marketa.zukalova@jh-inst.cas.cz

Nanocrystalline spinel prepared by sol-gel process exhibits excellent activity towards Li-insertion at high charging rates; smaller Li diffusion coefficients of nanoparticles are compensated by increase in active electrode area[1]. The optimum performance is achieved for nanocrystalline spinel with surface area between 20 and 100 m^2/g. These materials can be charged/discharged nearly to the nominal capacity of $Li_4Ti_5O_{12}$ (175 mAh/g) independently of the charging rate at the mentioned conditions.

Phase pure $Li_4Ti_5O_{12}$ nanofibres were prepared by electrospinning. They exhibited charge capacity of ~100 mAh/g at 2C, but this value decreased significantly at higher charging rates.

The electrochemical performance of nanosized $Li_4Ti_5O_{12}$ with optimized structure was studied both in the form of thick layer electrode incorporated in Al container and in complete experimental cell containing the above mentioned electrode, separator and Li sheet as a counter electrode. The electrochemical behavior of systems was examined by means of cyclic voltammetry of Li insertion, galvanostatic chronopotentiometry and chronoamperometry. The experimental cell exhibited very good stability even with the spinel electrode as thick as 7.5 mm. Introduced 3D concept represents promising fit for high capacity rechargeable microbatteries.

Figure 1:

Sample A: Classical solid state synthesis

Sample B: Nanocrystalline Li4Ti5O12 made by sol-gel process: hydrolysis of ethanolic solution of Li and Ti alkoxides

References

1) Kavan,L.; Prochazka,J.; Spitler,T.M.; Kalbac,M.; Zukalova,M.; Drezen,T.; Grätzel,M. *J.Electrochem.Soc.* **2003**, *150*, A1000-A1007