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Leaching of Nano-SiO₂ from Municipal Solid Waste

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Abstract: The commercial use of nanomaterials has significantly increased in recent years. However, there is still limited information about the potential impacts of nanomaterials on the environment within the integrated solid waste management systems (Boldrin *et al.*, 2014). Nano SiO₂ is used in numerous commercial applications ranging from paint, coating, fire resistant glassware, electronics, pharmaceuticals and UV protection (Marcoux *et al.*, 2013). The widespread synthesis and uses of SiO₂ mean that large volumes of this nanomaterial will ultimately end up in landfills (Keller *et al.*, 2013). The main objective of this experimental work is to evaluate the leaching potential and behavior of nano SiO₂ within the municipal solid waste-leachate matrix. Therefore, batch experiments were conducted using fresh solid waste samples obtained from a real municipal solid waste (MSW) landfill located close to Istanbul, Turkey. The waste samples were spiked with different concentrations of SiO₂ in batch reactors. During the experiments, two different pH values were considered, namely basic 8-9 and acidic 5-6. The effect of ionic strength on the leaching characteristics of SiO₂ was also evaluated. Leachate samples were regularly collected over a three-day period and analyzed for pH, conductivity, particle size distribution and total Si concentration. A kinetic model was also developed to evaluate the deposition and detachment of SiO₂ onto the solid surface.

Keywords: Landfill, leaching, municipal solid waste, nanomaterial, SiO₂

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The Role of Al₂O₃ and SiO₂ Nanoparticles on the Cycleability of Li-Air Batteries with TEGDME-PEO/LiPF₆ Electrolytes

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Abstract: Rechargeable lithium-air (Li-air) batteries have the potential to provide gravimetric energy three to five times greater than that of conventional Li-ion batteries. Identifying the appropriate electrolyte is one prerequisite for the application of Li-air batteries¹. In this work, an ether based electrolyte containing TEGDME/LiPF₆ was optimized, which possessed low viscosity and high ionic conductivity, under dry argon atmosphere in a glove box. In order to prevent air breathing cathode clogging by lithium oxide and provide stability of Li metal anode, an extensive work was carried out to provide most functional polymeric additives and Poly(ethylene oxide) (PEO) was found one of the most effective polymers as recently stated by different a work². Two different inorganic fillers were chosen to add into the electrolyte to prevent conductivity decrease and provide stability of the air cell. Nano Al₂O₃ and SiO₂ were incorporated into TEGDME-PEO/LiPF₆ composite homogeneously. Both PEO and nano ceramic powders were thought to promote the dissolution of lithium peroxide precipitates formed in course of discharge process and protect the anode against to the corrosion. Graphene/ α -MnO₂ nanocomposite air breathing structure was used as cathode. In the carbon cathode materials, Graphene nanosheets (GNS) have been reported as ideal cathode materials for Li-O₂ batteries because of their unique morphology and structure that provide both diffusion channels for O₂ and active sites for cathode reactions. On the other hand, α -MnO₂ catalysts is helpful to increase the reversibility of the lithium-oxygen interactions due to hollandite type crystal structure of MnO₂ consists 2x2 tunnels. A lithium disk was used as anode while glass fiber was used as the separator in ECC-Air test cell. The cells were cyclically tested using 0.1 mA/cm² current density over a voltage range of 2.15-4.25 V. Electrochemical impedance spectroscopy (EIS) measurements was applied to investigate the effect of the polymeric and inorganic additives on the resistivity of the electrolyte. Results revealed that nanocomposite electrolyte structures provided not only good discharge capacity

Keywords: Li-air battery, cycle life, stability, TEGDME, Al₂O₃ and SiO₂ additives, nanocomposite electrolyte, PEO,

but also excellent stability of the Li-air cells. As can be seen in Fig.1, excellent cycleability was obtained by using the nanocomposite electrolytes with both organic (PEO) and inorganic (Al₂O₃, SiO₂) additions. Up to After the electrochemical cycling test, the cycles no significant capacity fade was detected and the ongoing studies show the air cell will show excellent stability with increasing cycle number. Morphologies of the cathodes were analyzed using scanning electron microscopy, X-ray diffraction analysis, and Raman spectroscopy to determine the occurrence of reaction products.

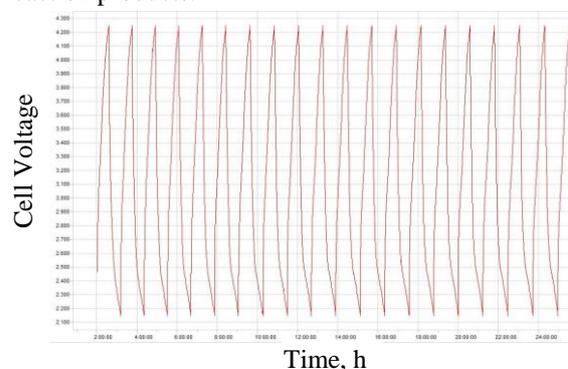


Fig. 1. Time-voltage behavior of TEGDME-PEO/LiPF₆/1 wt. % Al₂O₃ nanocomposite electrolyte.

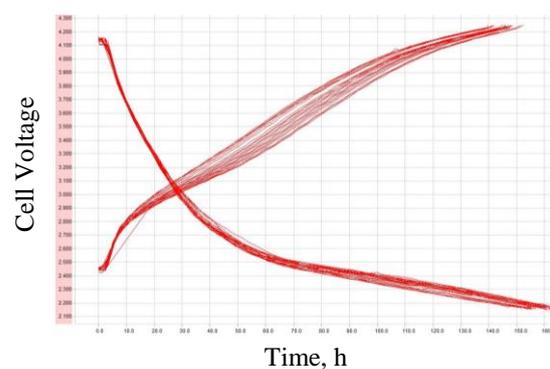


Fig. 1. Capacity-voltage behavior of TEGDME-PEO/LiPF₆/1 wt. % Al₂O₃ nanocomposite electrolyte

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Transparent Hydrophobic Nanolayers on ETFESiOx Substrates for Solar Cells Encapsulation

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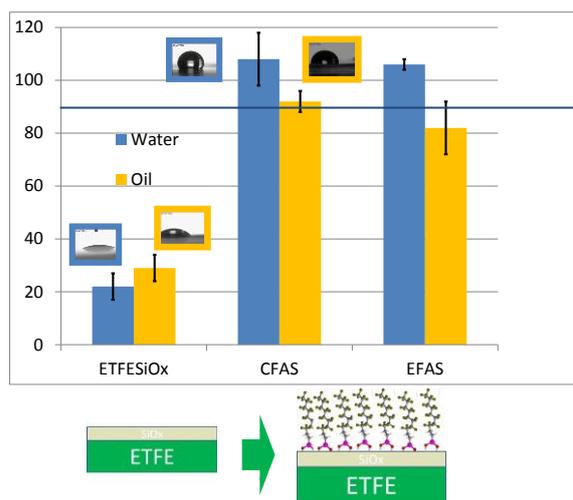
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Abstract: Polymer materials are recently emerging as an interesting alternative to glass as encapsulant and coating materials for preserving solar cells from the atmospheric degradation agents, due to their flexibility, affordable cost and transparency. However, they present the disadvantage of low barrier properties. Hydrophobic and more in general liquid barrier properties may significantly improve the protection guaranteed by the encapsulant materials, addressing issues like corrosion effects and loss of electrical performance and also adding self-cleaning properties to the surface thanks to the roll-off effect consequent to the hydrophobic behavior. Although several methods are reported in literature (Ling. Et al., 2009, Karunakaran et al., 2011) for obtaining hydrophobicity on substrates applicable to the solar cells sector, these methods are likely to be expensive and difficult to be implemented at industrial level because they are complex multi-step processes, including high temperature steps. In a previous work (Rossi et al., 2014) we developed a single step method to synthesise at room temperature a transparent hydrophobic self-assembled monolayer (SAM) chemisorbed on Polyethylene terephthalate (PET-SiOx) substrate, a standard coating for PV cells. In the present study, this method was applied on the bilayer Ethylene tetrafluoroethylene – Silicon Oxide (ETFE-SiOx), usually employed as frontsheet for solar cells, experimenting also a new precursor molecule. The SAM deposition was performed in anhydrous toluene using 1% concentration of two different precursor molecules: 1H,1H,2H,2H-per-fluorodecyltrichlorosilane (CFAS) and 1H,1H,2H,2H perfluorodecyltriethoxysilane (EFAS). FTIR (Fourier Transform Infrared Spectroscopy) measurements carried out on the uncoated and nanocoated samples confirmed the successful deposition of the SAM Nanolayer on ETFESiOx substrate. The hydrophobic properties characterization of the nanocoated samples indicated that the surface substrate was changed from hydrophilic to hydrophobic for all the nanocoated systems. The oleophobic properties were also significantly enhanced by the SAM deposition, particularly for the CFAS nanocoated system that was modified from oleophilic to oleophobic (oil CA: 92°). Furthermore, the optical properties assessment revealed that only a slight transparency decrease occurred for CFAS nanocoated sample, while no substantial reduction of transmittance was detected for the EFAS nanocoated system.

Concluding, the adopted SAM procedure can represent an effective route for obtaining nanocoated polymer materials with enhanced barrier properties at sustainable costs, suitable to extend the lifetime of encapsulated solar cells.

Keywords: Hydrophobic Coatings, Oleophobic Coatings, Self-Assembly of Monolayers, FluoroAlkylsilanes, Solar Cells, Ethylene tetrafluoroethylene – Silicon Oxide.

Figure 1: H₂O and oil Average static contact angle on the SiOx side for samples: ETFE-SiOx uncoated and nanocoated with SAM of CFAS and EFAS.



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Photovoltaic Response of Non-Toxic CuInS₂ Quantum Dot based Conducting Polymer Composite Films

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Abstract: I-III-VI ternary compound non-toxic quantum dots (QDs) have recently attracted the scientific community because of their attractive electrical and optical properties (Allen *et al.*; 2008). CuInS₂ (CIS) is the most extensively studied form among various I-III-VI ternary compositions. It is environment friendly, has a small direct band gap of 1.5 eV (which is nearly the optimum band gap for a single junction photovoltaic device), high absorption coefficient ($>10^5 \text{ cm}^{-1}$), high photoconductivity and possesses long term electronic stability (Lewerenz *et al.*; 2004). The Bohr exciton radius for CIS QDs is ~ 4 nm hence nanoparticles having size less than ~ 8 nm can show quantum confinement effects (Czekelius *et al.*; 1999). In the present work, we have studied the optical and electrical properties of poly(3-hexylthiophene) (P3HT) and CIS QDs based composite films. It is found that the absorption spectrum of the polymer film becomes broader by the incorporation of CIS QDs. The photoluminescence of the P3HT in the composite is also found to be quenched indicating an efficient charge transfer from polymer to the QDs. The electrical characterization of the P3HT:CIS composite film showed an improvement in the current density by more than an order of magnitude as compared with that of P3HT only device.

Keywords: conducting polymer, non toxic quantum dots, photovoltaic applications, thin films.

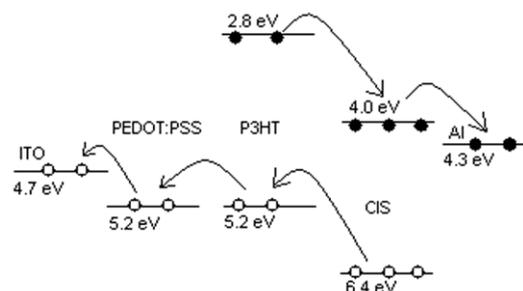


Figure 1: Energy band diagram of conducting polymer (P3HT): CIS QD composite structure

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Benefits of a compact TiO₂ layer for the elaboration of transparent TiO₂ nanotubes array on conducting glass

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Abstract: Titania nanotubes obtained by the anodization method have received much attention due to numerous possible fields of application including sensors, photocatalysis or photovoltaics. Anodization is classically performed on Ti foils but for photovoltaic applications, the TiO₂ nanotube array layer has to be elaborated on a transparent substrate such as transparent conducting oxide (TCO) coated glass. Therefore a metallic Ti layer is sputtered on TCO and then anodized to be converted to a transparent TiO₂ nanotube array (TNA) layer (figure 1). We describe the impact of introducing an additional compact TiO₂ layer under the metallic Ti layer during the sputtering deposition and compare morphological and optical properties of titania nanotubes films made with and without this intermediate compact layer. These results show considerable improvements in the TNA layer macroscopic homogeneity when a compact layer is used. They are attributed to the limitation of an undesirable reaction of oxygen evolution that takes place preferentially at the TCO-electrolyte interface during anodization, causing a deconstruction of the TNA layer. Thus, using a TiO₂ compact layer allows a better control of the anodization process and the transparency of the TNA layer in the visible range is also increased. Furthermore, for solar cell applications, the compact layer can act as a blocking layer which is a common way to reduce charge recombination.

Keywords: Titanium dioxide, thin films, nanotubes, 1-D nanostructures, anodization, solar cell applications.

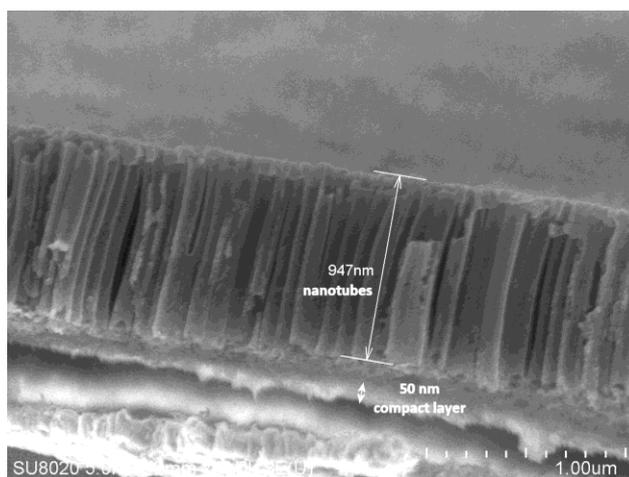


Figure 1: Scanning electron microscopy image of a 1 μm thick TiO₂ nanotube array film on TCO glass with an intermediate compact TiO₂ layer of approximately 50 nm.

Study of LiFePO₄ thin films as Li-ion battery cathode by in-situ electrochemical atomic force microscopy in aqueous electrolyte

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Abstract:

Lithium-ion (Li-ion) batteries have been widely used as power sources for portable and mobile applications (Armand *et al.*, 2008). In order to prolong battery life, it is important to study the mechanisms that make battery capacity reduce with aging. Published results have show that morphological changes occur in aged cathodes. In this study, in-situ electrochemical atomic force microscopy (EC-AFM) that is combined atomic force microscopy with electrochemical methods was used to investigate morphological changes of LiFePO₄ thin film electrodes during charge and discharge processes in real time under aqueous environment (Demirocak *et al.*, 2014; Ramdon *et al.*, 2014). LiFePO₄ thin films were prepared by depositing them on Au/Si substrate using radio frequency magnetron sputtering deposition method. The films were firstly characterized by X-ray diffraction, and results showed that them were composed of LiFePO₄ phase with olivine structure. The SEM and AFM results show that the average size of particle was ~100 nm. The electrochemical performance of the film electrodes in Li₂SO₄ aqueous electrolyte was investigated by cyclic voltammetry. The lithium ion diffusion coefficient of the film electrode was estimated to be $2.31 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which is larger than that of LiFePO₄ powder of 5.53×10^{-8} . The decrease and increase in the size of the LiFePO₄ particles during charge and discharge were directly observed by EC-AFM, and relevant mechanism is discussed.

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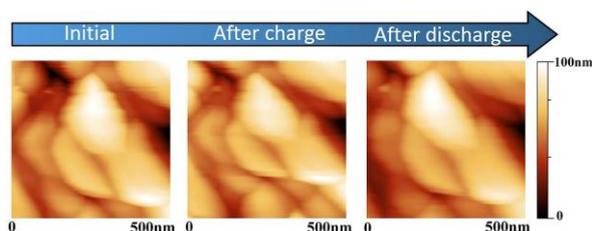


Figure 1: EC-AFM images show that the changes in the size of the LiFePO₄ film electrode during charge and discharge in the aqueous electrolyte.

Textured fabrication of CdS/CdTe thin film PV cell with back contacts

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Abstract: The basic function of a Solar cell is to absorb sunlight and convert light energy into electricity. The energy obtained is carbon free renewable source of energy without any moving part. The principle of solar cell came into lights when the great scientists Chapin, Pearson, and Fuller prepared a photovoltaic effect using poly-Si in 1954. Since silicon semiconductor technology was so widely studied, for more than 40 years solar cells were fabricated using silicon crystals. As a replacement for silicon, materials which can be used are amorphous silicon, CdTe, Cu (In, Ga) Se₂, InP, CdSe and GaAs. Thin film solar cells are considered to be large area diodes, to increase the absorption of light and reduce the cost of fabrication. Electron-hole pairs are generated by the absorbed photons, the electric energy is formed when the excited carrier is swept across the potential field. The voltage generated during the separation of opposite charge helps in driving the current through external electric circuit. In a CdS/CdTe based solar cell the potential field or the depletion layer is formed at the interface of the CdS and CdTe layers. In this paper CdS is the window layer which has a wide band gap of 2.45 eV which allows most of the light to the absorber layer CdTe with a band gap of 1.45 eV. Photons from the sunlight are absorbed only when the energy is higher than the band gap of the absorber layer. Thin film Solar cells have a record efficiency of 19.6%, and commercially available CdTe PV panels of 12% (Green, et al., 2013). The loss due to reflection has limited all types of solar cells to a great extent. Hence, one method of trapping the light for more absorption is through nano-texturing of junction area. In commercial thin-film CdTe solar panels 4% of its energy is already reflected in the glass-air interface of the modules (Kaminski, et al., 2014). Nanostructuring of silicon has produced extensive research in solar cell application because of its low reflectance and enhanced light trapping technique (Oelhafen, et al., 2005). Along with the texturing of junction area, the concept of backcontact is taken into account (Figure 1). As the front contact in a solar cell transmits only 50% of the solar radiation (Fan, et al., 2009), back contact research started after the publication of R.J Schwartz in 1975 as a substitute for cells which has front and rear contacts. The metal grids with narrow, closely packed metal lines can reduce series resistance (Dean, et al., 1975) but increases blockage of sunlight (by reflecting). As the front and rear contacts are placed at the rear surface,

increases the packaging density of the panel and also gives raise to performance gain (Kerschaver, et al., 2006). So the performance of back contact solar cell is to be tested along with the increased junction area by texturing the interface surface.

Keywords: textured solar cell, back contact, CdS/CdTe, nanowall design, thin film PV.

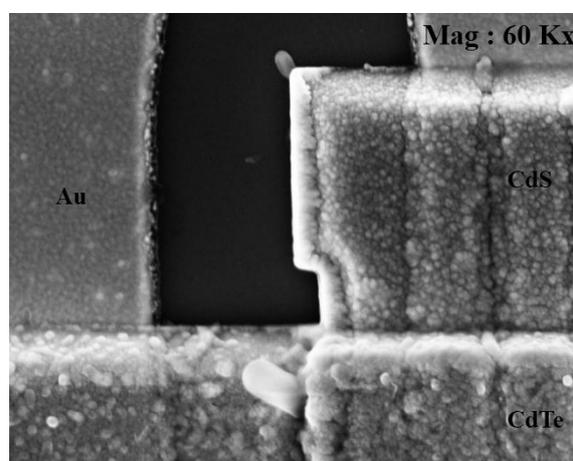


Figure 1: SEM image of Nano wall structure (Surface morphology)

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Nonradiative Electron and Hole Relaxation Dynamics in Organometallic Halide Perovskites

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Abstract: Hybrid organic-inorganic perovskites, such as methylammonium (MA) lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$ or MAPbI_3), are promising new absorber materials for solar energy applications that have attracted significant interest in the last few years. Solar conversion efficiencies of more than 19% have been reported for these materials [1]. This high efficiency is mainly due the long diffusion lengths of charge carriers, low sensitivity to defects and high mobility of charge carriers. However, many fundamental processes related to the photophysics of these materials remain not fully understood.

The excitation of electrons from the valence band to conduction band results in the formation of hot electrons and holes, both of which lose most of their energy by cooling down to the band edges. Extracting hot carriers before they thermalize towards the recombination would lead to higher efficiency. Consequently, simulating the relaxation dynamics of photoexcited charge carriers is of great importance for further optimization of photovoltaic devices.

In order to understand in more detail the process of charge carrier dynamics in perovskite materials, a theoretical description based on time-domain methods is required to enable shedding light on recent experimental finding on electron and hole relaxation dynamics [2] and also to guide future experimental investigations. A mixed quantum-classical approach based on trajectory surface hopping is used to describe the dynamics of hot charge carriers. In this approach, the electrons are described quantum mechanically by solving the Schrodinger equation and the nuclear degrees of freedom are propagated by independent classical trajectories, which are computed by solving the classical Newton's equations.

In this contribution, we address the non-radiative relaxation process of electrons and holes in organometallic perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ when electrons are promoted to the conduction band from the valence-band. We perform nonadiabatic molecular dynamics simulations using the combination of the PYthon eXtension for Ab Initio Dynamics [3] package for quantum dynamics simulations interfaced with the Quantum Espresso electronic structure code. Our aim is to get a fundamental understanding of the intraband relaxation process of hot electrons (holes) to the minimum (maximum) of the conduction (valence) band and how these processes are affected by perovskite composition and structure. Results on the per-

ovskite materials $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbBr}_3$, $\text{CH}_3\text{NH}_3\text{PbCl}_3$, $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$ and $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ will be presented.

The electron relaxation time values obtained from our simulation for $\text{CH}_3\text{NH}_3\text{PbI}_3$ are in good agreement with the experimental data reported in Ref. [2]. We also found that halogen-mixing $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ results in slowing down the electron and hole relaxation process, suggesting a longer life time in Cl-doped systems.

Keywords: Photovoltaic, perovskite, electron/hole transport, nonradiative carriers relaxation, nonadiabatic dynamics, surface hopping.

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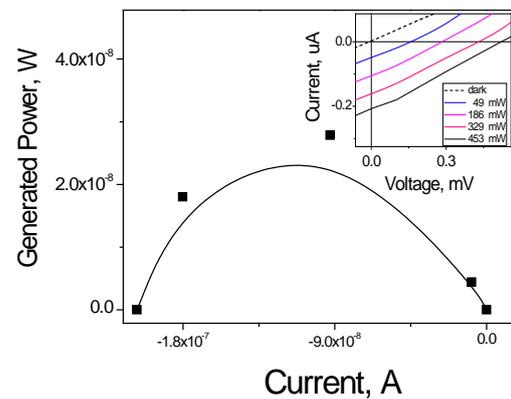
C-Nanotube Based Infrared Thermo-Voltaic Cells and Detectors

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Abstract: Sun radiation remains a key renewable energy source, with ~40% of its energy falling into the infrared part of the EM spectrum. This low grade energy, while available is thinly stretched over a relatively broad spectral window of ~ 0.7-3 μm . For a p-n junction based photovoltaic (PV) solar cell, a maximum voltage is limited by $V_{oc} \cong E_g/e$, where e stands for the unit charge. For ideal cells, the conversion efficiency is to scale linearly with E_g given by $\chi(\lambda) \sim \frac{1}{\lambda} \sim E_g$. [1] As the fabrication and deployment costs are to be on par with those of existing PV systems, IR-PV cells that inherit conventional design are to demonstrate at least order of magnitude lower efficiency-to-cost ratio. While several concepts were offered to harvest IR-sun radiation including antenna arrays and quantum dots, with their spectrally-broad absorption spectrum and the fabrication cost that has fallen precipitously, single-walled carbon nanotubes can pave a way to the development of indirect-type, cost-efficient photo-thermo-voltaic (PTV) cells.

Herein, we engineer and test two-terminal carbon nanotube photocells for the purpose of infrared photo-thermo-electric energy conversion and sensing. The photo-voltage and non-zero conversion efficiency were found to appear only for off-center illumination which can be explained within photo-generated heat flow model and not the contact effects. [2] Under incident optical powers of ca. 450 mW, the equivalent short-circuit current, I_{sc} , and open-circuit voltage, V_{oc} , stood at ca. 0.2 μA and ca. 0.5 mV, respectively. The cell prototypes yielded ~ 30 nW of electrical power that typically followed non-monotonic dependence on the incident light power given by $P_{out\ max} \sim P_{in}^\beta$, where $\beta = 1.08$. As the PTV cell can also utilized as IR-photosensor, its transient response was probed by carrying out off/on photocurrent tests at varied temperatures: 123, 253 & 300 $^\circ\text{K}$. The photo-current, I_{ph} decayed with



time as single exponential $I_{ph} \sim 1 - e^{-t/\tau}$ and the characteristic decay constant, τ was found to change linearly with I_{dark}^{-1} confirming that the transient response is controlled by device circuitry and not heating/cooling processes. The concept might enable engineering and implementation of the carbon nanotube based PTV devices for application in heat recycling and self-powered infrared detectors.

Keywords: infrared, carbon, nanotubes, photovoltaic, sensors, cell.

Figure 1: Showing power vs. current characteristic of the PTV cell obtained at RT and incident power of ~ 450 mW. The inset shows I-Vs for different

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Natural Biodefensive Nanoparticles for Pest Control in Soy Culture

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Abstract: Nanomed Inc. has been developing a new methods for natural compounds controlled delivery system. A polymeric nanoparticle obtained via solvent evaporation is a new approach to delivery a natural and reactive compound to improve the treatment in soy culture, the most important culture in Brazil. This is a bioactivity essential oil against insects and other pests, flavoring agent used in cosmetic and food products however it was previously reported to have a skin-sensitizing ability and to cause allergic reactions (ATSUMI; FUJISAWA; TONOSAKI, 2005; MURRAY B. ISMAN, 2006). In spite of huge bioactivity, its reactivity and volatility reduce the action time. So, a controlled delivery system was developed, changing the surface area which may influence its toxicity. The nanoparticles cytotoxicity was evaluated in L929 fibroblasts, against a negative control and literature.

The enhancement of the natural active by encapsulation was able to protect it from oxidative degradation, and improve their fungicidal activity (GARG; SINGH, 2011).

We observe that these nanoparticles showed a similar behavior even in different delivery system (polymer). However with the concentration increase, there is the decrease of toxicity, with the higher viability in fibroblasts. Based on the different concentrations studies, it is possible to conclude that the cytotoxicity is not dose dependent. However, one notice the increase in the cellular apoptosis as the nanoparticle size decreases. So, the nanotoxicity is directly linked to the size of nanoparticle, and not related to the essential oil concentration.

Keywords: biodefensive, polymeric nanoparticles, natural-based material, cytotoxicity, pest control, soy culture, agribusiness applications.

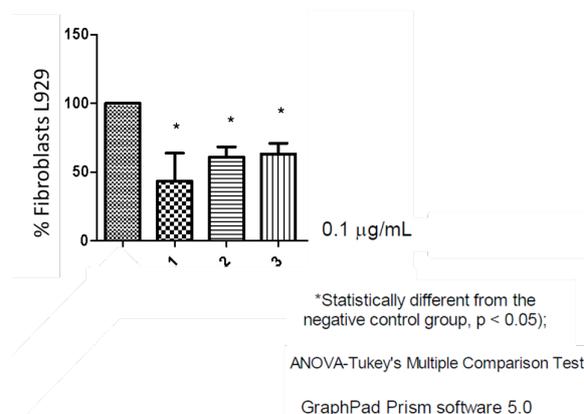


Figure 1: Figure of natural compound nanoparticles cytotoxicity in a different controlled delivery system, at 0.1 ppm concentrations. Samples: 1- PLA-natural compound 0.5%; 2- PCL- natural compound 1%; 3- PLA- natural compound 1%.

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Sol-Gel Production and Electrochemical Characterization of Free-Standing Metal Oxide/MWCNT Nanocomposite Anodes for Li-Ion Batteries

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Abstract: Lithium ion batteries (LIBs) are one of the most promising candidates for electrochemical energy conversion and storage devices, in the scientific and industrial fields, with one of the best energy densities (Wang *et al.*; 2006). Zinc and tin dioxide based materials are being used as active anode materials for rechargeable lithium batteries, because the theoretical capacity of ZnO (978 mAhg^{-1}) and SnO₂ (1491 mAhg^{-1}) has been estimated to be superior to that of graphite (372 mAhg^{-1}) (Guler *et al.*; 2014, Ning *et al.*; 2008). High capacity anodes such as zinc and tin based usually suffer severe capacity fading, because of the quick aggregation of metal particles and the huge volume expansion during Li⁺ insertion/extraction cycles (Huang *et al.*; 2011). To prevent the pulverization of the anodes and electrical detachment of active materials, MWCNT buckypaper substrates are considered as a buffer material during the battery applications (Guler *et al.*; 2014). In this work, ZnO/MWCNT and SnO₂/MWCNT buckypaper nanocomposite films were prepared as free-standing anode materials by sol-gel spin coating. Structural properties and electrochemical performances of metal oxides/MWCNT nanocomposite anodes were investigated and compared. As can be seen from Figure 1, it was aimed to accommodate the stresses arisen from the volume increase during charging process by using highly porous MWCNT network that coated with a thin layer of the metal oxides (MO). The structural properties of free-standing buckypaper composite film anodes were characterized by FEG-SEM (Field Emission Gun - Scanning Electron microscopy), TEM (Transmission Electron Microscopy), EDS (Energy Dispersive X-ray Spectroscopy) and XRD (X-ray Diffraction) techniques. Electrochemical performance tests, CV (Cyclic Voltammetry) and EIS (Electrochemical Impedance Spectroscopy) analyses of free-standing anodes of CR2016 type Li-ion batteries were also performed. The cells were charged and discharged at 25 °C between fixed voltage limits (2.5 V to 0.2 V).

Keywords: Li-ion battery applications, metal oxide/MWCNT nanocomposite anodes, sol-gel synthesis, spin coating method, structural and electrochemical characterization.

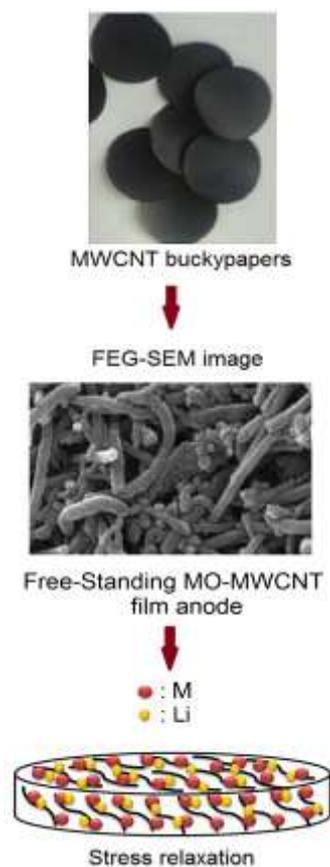


Figure 1: The illustration of the production of free-standing Metal Oxide/MWCNT anodes.

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The Effect of Different Solvent Combination of LiBF₄ Electrolyte on Free-Standing SnO₂/MWCNT Nanocomposite Anode Capacity for Li-ion Batteries

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Abstract: Owing to their high energy density, lithium-ion batteries are widely used in portable electronics (Xiang *et al.*; 2009). With a wide optical band gap (3.6 eV) tin dioxide is an n-type semiconductor material. For rechargeable lithium batteries, tin and tin oxide based materials are being used as active anode materials (Kose *et al.*; 2013). However, during Li⁺ insertion/extraction cycles, anodes of such high capacity usually suffer severe capacity fading resulting from both the huge volume change and the quick aggregation of tin particles (Zhang *et al.*; 2009). MWCNT buckypaper substrates are considered as a buffer material during the battery applications in order to prevent the pulverization of the anodes and electrical detachment of active materials (Kose *et al.*; 2013). For commercial Li-ion cells, the typical non-aqueous electrolyte is a solution of LiPF₆ in linear and cyclic carbonates such as dimethyl carbonate and ethylene carbonate, respectively (Kerr *et al.*; 2003). Compared with LiPF₆, LiBF₄ has some advantages such as better thermal stability and lower sensitivity toward environmental moisture and its solution provides lower charge-transfer resistance, especially at low temperatures (Zhang *et al.*; 2006). In this work, free-standing SnO₂/MWCNT nanocomposite was used as anode, metallic Li as cathode and 1 molal LiBF₄ solution as electrolyte. It was aimed to determine the optimum ratio of Ethylene Carbonate (EC):Dimethyl Carbonate (DMC) solvents in 1 molal LiBF₄ electrolyte solutions for high capacity SnO₂/MWCNT buckypaper anode. Different EC : DMC (2:1, 1:1 and 1:2) solvent combinations were prepared in a glove box. For these electrolyte solutions, conductivity tests were applied. Structural properties and electrochemical performances of SnO₂/MWCNT nanocomposite anodes prepared by sol-gel spin coating method (Figure 1) were investigated. The structural properties of free-standing buckypaper composite anode was characterized by SEM (Scanning Electron microscopy), TEM (Transmission Electron Microscopy) EDS (Energy Dispersive X-ray Spectroscopy) and XRD (X-ray Diffraction) techniques. Electrochemical performance tests, CV (Cyclic Voltammetry) and EIS (Electrochemical Impedance Spectroscopy) analyses of free-standing anodes of CR2016 type Li-ion batteries were also performed. The cells were charged and discharged at 25 °C between fixed voltage limits (2.5 V to 0.2 V).

Keywords: Li-ion battery applications, LiBF₄ electrolyte, ethylene carbonate, dimethyl carbonate, SnO₂/MWCNT nanocomposite anodes, sol-gel synthesis, spin coating method, structural and electrochemical characterization.

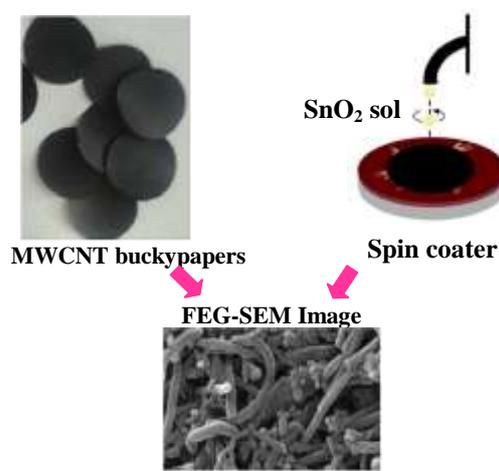


Figure 1: The representation of the production of free-standing SnO₂/MWCNT anodes.

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Photocatalytic Activities of ZnO and ZnO/ZnS Synthesized by Microwave-Hydrothermal Method

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Abstract: Because of the diffusing of toxic and coloured wastewater into water sources, dyes have a bad effect on the nature of water like inhibiting sunlight penetration and reducing photosynthetic reaction. (Hu *et al.*; 2011). The techniques which are used for the treatment of dye waste effluents are usually are usually inefficient, non-destructive and costly. (Jia *et al.*; 2013). Heterogeneous semiconductor photocatalysts such as ZnO have an important role for the removal of dye pollutants from water. ZnO semiconductor has a wide bandgap energy of 3.37 eV and a relatively large exciton binding Energy (60 meV), thus can absorb only UV light with the wavelength equal to or less than 385 nm. But solar spectra contain only approximately 3%–5% UV light; therefore, the great mass of solar photons is useless for ZnO photocatalyst, which greatly limits its environmental applications (Ma *et al.*; 2011). The photocatalytic performance of ZnO can be improved by modification due to inhibit recombination of photogenerated electron-hole pairs. The band gap of ZnS (3.68 eV) is larger than that of ZnO, experimental results have demonstrated that the combination of these two wide bandgap semiconductors could yield a novel composite with the photo excitation threshold energy lower than those of the individual components (Ma *et al.*; 2013). In the present study, ZnO/ZnS nano photocatalysts were synthesized by microwave-hydrothermal method using different precursors as Sulfur source. The prepared photocatalysts were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and UV–visible (UV–vis). The photocatalytic activities samples and undoped ZnO have been studied for the degradation of dye, and have also been compared with together.

Keywords: Synthesis, photocatalyst, ZnO/ZnS, degradation

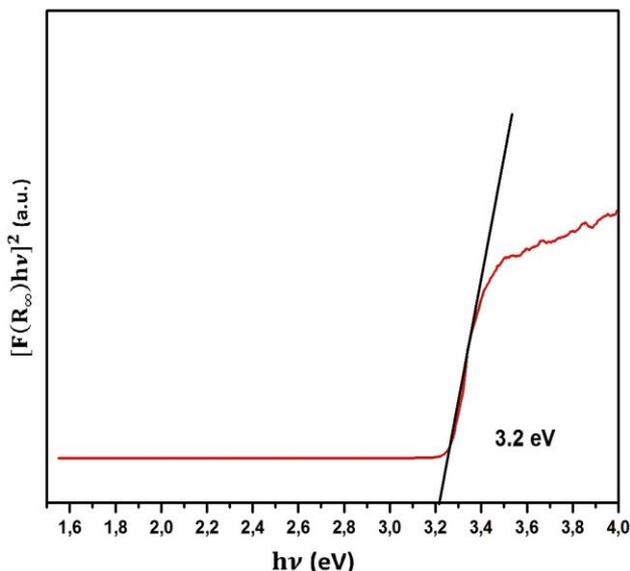


Figure 1: Kubelka-Munk transformed reflectance spectra of ZnO/ZnS

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Polystyrene Micro/Nanofibers and its Application in the Removal of Crude Oil Spills

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Abstract: Water pollution by crude oil has major environmental impact worldwide (M. Al-Azab *et al.* 2005). The great concern of the global community on the unfavorable and longstanding effects of spilt oil on ecosystems, created a vital need to develop materials for effective oil spill clean-ups (Xia, Y. Q *et al.* 2010). This work aimed to study the effectiveness and applications of PS polymer in clean-up of crude oil from oil spills.

Molecular weights of the fibrous polystyrene precursors, were in the range of 100,000 – 350,000 Dalton. Fibers were used for the removal of crude oil spills in seawater. Due to the hydrophobic nature of both the fibers and the crude oil, the later was instantly absorbed onto the fibers achieving a maximum sorption capacity of 220 g of crude oil per each gram of fiber.

Nano/Microfibers of polystyrene was prepared by electrospinning technique (Haitao Zhu *et al.* 2011). Fibers with a size range of 500 nm- 8 μ m in diameter and below 100 m²/g in surface area were prepared after a thorough optimization of the electrospinning process. Fibers prepared were tested for their oil absorption efficiency as a function of absorbent weight, time of absorption, and initial concentration of the polymer solution prior its conversion to fibers. Results showed an initial sorption capacity of a range of 60-200 g/g with microfibers prepared from 20% PS solution.

The surface area of the produced fibers varied based on fiber size distribution, which depends on variations in the electrospinning parameters. Hence, optimizations of the process were studied to achieve consistency in the fiber size distribution, and the surface area of the fibers as well. Results showed the importance of the high surface area and interconnectivity of the porosities within the PS microfibrinous sorbent for the removal of the oil, making the microfibrinous PS sorbents an excellent candidate for crude oil spill cleanup.

Keywords: nanofibers, polystyrene, crude oil, electrospinning

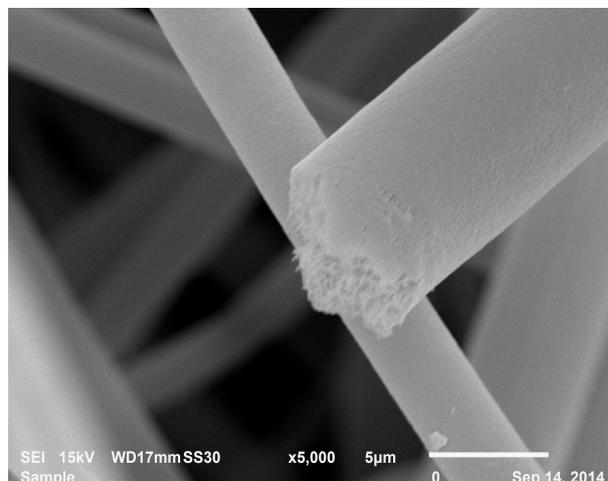


Figure 1: SEM image for electrospun PS fibers with mesoporosity and different size distribution. Polystyrene was dissolved in the proper solvent forming solutions of 20, 30, and 40 wt%. Electrospinning process conditions were optimized at a voltage of 20 kV, a feeding rate of 10 ml/hr, and a distance of 15 cm. Due to the high viscosity of the crude oil, their flow within the fibrous sorbent during the process of removal will be limited and requires macroporosity for a more efficient sorption and impregnation within the fibrous sorbent. The produced microfibers contained macroporosity by virtue of the interlocking between the fibers within the electrospun fibrous mesh.

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Effects of biopolymer nano coils on sand dune stabilization and dust controlling

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Abstract

Despite the large history and popularity of sand/dune stabilization in exploratory research, a unique method with large-scale applications has yet to be realized. The main impediments reside in the methods of the stabilizations currently in use, at the moment (a) no specific technology is available, (b) a particular stabilizer is necessary for each specific condition, (c) most products just stabilize the surface of sand dunes and (d) most applications require a long time to be fixed in large quantities in a predetermined and controllable fashion. Designing biopolymeric networks with controlled size and desirable properties is the best way to fix sand dune and dust. Thus we hereby describe a novel view and simple method to stabilize sand/dunes by designing a novel aqueous biopolymer coils system to spray on the sand/dune surface in order to make a network with sand/dune agents by penetration of aqueous biopolymer into the sand dune.

Carboxymethyl-nanocellulose: a versatile raw-material in coating industry

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Abstract: Cellulose is the most abundant polysaccharide and widespread biopolymer in nature. For this reason, cellulose and its derivatives are very attractive for the manufacture of sustainable biobased materials. Unlike cellulose, functionalized cellulose with carboxymethyl groups (CMC) is water soluble exhibiting a multitude of applications as gelling agent in food industry, as paint thickeners in coating industry and film packaging in food and paper industry (Klemm et al., 2005). Aside from its mechanical and water retention properties, the biocompatibility exhibited makes CMC a promising option as a support of biomolecules with chemical and biological activity for the development of biosensors and wound dressings (Carlsson et al., 2014). However, commercially available CMC powders have high degrees of substitution (DS) ranging between 0.5-1.2 and a high density of anionic charged groups by the presence of surface carboxylic groups. The high surface negative charge has a deleterious impact on the stability of the incorporated biomolecules (Carlsson et al., 2014) and even affecting the release behavior of incorporated drug (Valo et al., 2013).

In this study, we have synthesized CMC with various degrees of substitution (DS) using environment-friendly aqueous conditions. The functionalized CMC pulp with DS<0.2 was submitted to ultrahomogenization resulting in high quality carboxymethyl nanocellulose (NC) suspensions (over 90% of nanofibrils) through a energy-efficient process (energy reduction of >60% compared to unmodified NC). The carboxymethyl-NC films prepared by solvent casting exhibited improved optical and morphological properties whilst retaining the mechanical properties in the temperature range (-50 to 200°C) studied. Preliminary results obtained by electrochemical impedance spectroscopy (EIS) using functionalized nanocellulose in solution and as additives to protective coatings have shown improved anti-corrosion performance in coated substrates. The increased hydrophobicity and zeta potential of prepared CMC suspensions reveal great potential for industrial coating and will be further explored on the adsorption of molecules for biomedicine applications.

Keywords: carboxymethyl cellulose, transparent films, corrosion inhibitors, biomedical applications.

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Acknowledgements

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Graphene Reinforced Concrete

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Abstract:

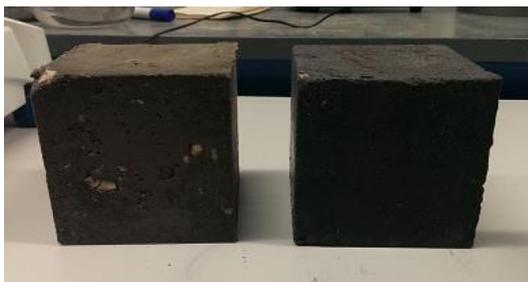
This work presents the revolutionary idea of bridging the international research on nanoscience with traditional construction material concrete. The aim of the project is to introduce graphene - an one atom thick layer of graphite with two-dimensional properties, within the chemical matrix of cement. The stand-out mechanical properties of graphene such as very high ultimate tensile strength and retaining initial size after strain make it suitable for applications in the construction industry. There are two main liquid exfoliation methods of producing surfactant-stabilized graphene dispersions in aqueous environment [2],[3]. The first one uses sonication energy principles for breaking down layers of graphite and the addition of surfactant (Sodium Cholate) preserves all of their properties in water [3]. The second uses high-shear exfoliation machine which uses laws of turbulent forces to achieve even better quality flakes with more consistent rate of dispersion [2]. The resultant solution from 48h of sonication is mixed with Ordinary Portland Cement (OPC), sand and aggregate to prepare standard 10x10x10cm concrete cubes for testing compressive strength. The results show that the addition of only 2.1mg/ml of graphene flakes increase the compressive strength by 9.8% when compared to cubes mixed with normal tap water, after 28days of curing time. The outcomes of the experiments prove the hypothesis that wonder nanomaterial alter the hydration crystals of the cementitious paste and the enhanced hydration reaction in the curing period of the concrete leads to many improvements [1]. The graphene reinforced concrete can revolutionize the construction industry and change the face of future infrastructure by introducing a very environmental friendly product.

Keywords: graphene, concrete, liquid exfoliation, cement, hydration reaction, compressive strength

Figure 1: Two cubes above show the comparison between normal (tap water) concrete on the left and graphene reinforced one on the right. The addition of nanomaterials enhances the main chemical reaction during the hardening of concrete and this leads to increased compressive strength of the construction material.

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Quantum Dot Sensitized Solar Cells with Cuprous Sulfide Counter Electrode

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Abstract: Although, solution processing is a promising route for the realization of low-cost, large-area devices with short energy payback time and high specific power, low-temperature fabrication conditions and good atmospheric stability while maintaining a high efficiency remains a major technical challenge. However, the recent report of a certified efficiency of 8.55% for a ZnO/PbS Quantum dot (QD) solar cell (SC) achieved by engineering the band alignment of the QD layers through the use of different ligand treatments promises the possibility of new approaches towards the goal of high-performance air-stable solar cells compatible with simple solution processes (Chuang et al, 2014). CdSe QDs with an absorption onset in the red or near infrared are equally promising (Kamat, 2008). In this work, QDSCs based on a mesoporous structure of TiO₂ and a polysulfide redox electrolyte, were prepared by adsorption of colloidal CdSe QD absorbers onto the photoanode, with and without linkers. CdSe/ZnS QDs were synthesized within aqueous pools of reverse micelles, based on standard wet chemistry methods, while alkylphosphine oxide (TOPO) functionalized CdSe QDs were prepared by reactions of organo-metallic precursors at high temperature. A chlorine surface treatment performed on TiO₂ prior to sensitisation improved QD adsorption on the photoanode. An electrochemically deposited Cu₂S/conducting glass (CTO), which has a higher tolerance to polysulfide electrolyte, was used as the counter electrode. The Cu₂S film, composed of interconnected nanoflakes, showed good catalytic activity with the best SCs (effective area 0.16 cm²) showing up to 2.13% conversion efficiency under AM1.5 illumination. The photovoltaic characteristic of the solar cells was measured using a calibrated solar simulator with 100 mW/cm² irradiation (AM 1.5). The colloidal QDSC performance was primarily limited by a low fill factor of 0.45, which is believed to arise from charge transfer of photogenerated electrons to the aqueous electrolyte. This work was supported by the MATEPRO - NORTE-07-0124-FEDER-000037 and the European Commission through NanoCIS project (FP7/PIRSESGA-2010-269279), both of which are gratefully acknowledged.

Keywords: CdSe, quantum dot, solar cell, TOPO, Cu₂S

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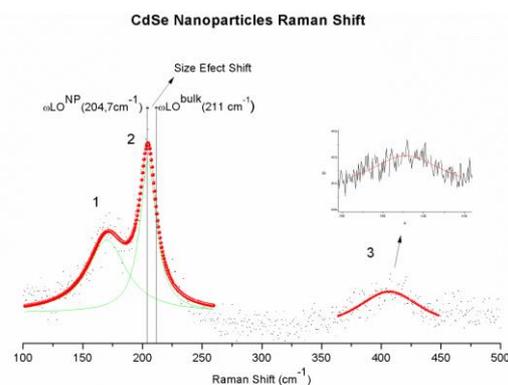


Figure 1: Resonance Raman spectrum of CdSe nanoparticles (NP) deposited on glass, excited at laser wavelength 514 nm. (1)-TO (170.3 cm⁻¹); (2)-LO (204.7 cm⁻¹); (3)-2LO (408.8 cm⁻¹).

Laser intensity of <9.32 kW/cm² was used to minimize a possible local heating. Red and green depict the spectral deconvolution to the vibrational modes. The inset shows the amplified Raman shift' at (3). LO phonon mode shift and asymmetric broadenings towards low-frequency (2,3) in comparison with Bulk CdSe are explained by the contribution of different phonon modes and are an indication of the phonon confinement effect, which is a consequence of the nano size of the CdSe particles. The presence of transverse modes at (1) is an evidence of the non spherical symmetry of the NP's.

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Reduced graphene oxide on TiO₂ nanorods and nanotubes photo-anode for solar hydrogen evolution

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Abstract: The solar hydrogen evolution process via water splitting is a carbon free technology for next generation. Many researchers and energy departments are expecting that minimum efficiency for commercialization is about ~10% of solar to hydrogen conversion efficiency (STH). However the world STH efficiency doesn't reach yet. Splitting water into hydrogen and oxygen has been occurred by stages, i) absorption of light, ii) electron-hole excitation, iii) charge transfer to reactive sites, iv) redox reaction. Among these stages, charge transfer stage is most important to lead the redox reaction of water. Graphene has been considered a new approach to improve the charge transfer rate without direct or indirect recombination. In this work, we demonstrated that improved charge transfer and collection in PEC system by using a reduced graphene oxide sheets. Reduced graphene oxide sheets were chemically synthesized by improved Hummer's method. TiO₂ nanotubes and nanorods were synthesized by anodizing and hydrothermal method respectively. Subsequently, These TiO₂ photo-anodes were directly immersed into solution involving reduced graphene oxide. After several minutes in immersed state, the graphene oxide on TiO₂ nanotubes were chemically reduced by adding hydrazine solution as a reducing agent. The microstructural features of RGO/TiO₂ nanotubes photo-anode were investigated by FE-SEM, TEM, XRD, Raman spectroscopy. Furthermore solar hydrogen production test was characterized in the PEC cells. Consequently graphene decorated TiO₂ nanotubes and nanorods were revealed superior photocatalytic activity because the graphene sheets led to increase the mobility of charge carriers and recombination time.

Keywords: Reduced graphene oxide(RGO), Titanium dioxide(TiO₂), Solar hydrogen evolution

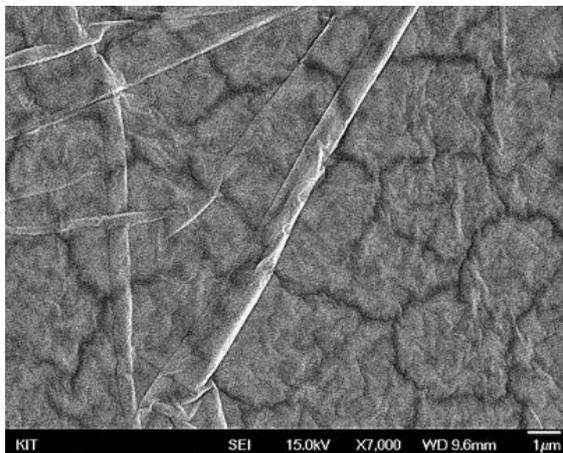


Figure 1: FE-SEM image of a graphene oxide coated TiO₂ nanorods.

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Silicon Nanowire as an Effective Absorber for Solar Cell Application: Fabrication and Numerical Simulation

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Abstract: Silicon nanowires (Si-NWs) have been considered widely as a perfect light absorber with strong evidence of enhanced optical functionalities. Here we report finite-difference time-domain simulations for Si-NWs to elucidate the key factors that determine enhanced light absorption, energy flow behavior, electric field profile and exciton generation rate distribution. To avoid further complexity, a single Si-NW of cylindrical shape was modelled on c-Si and optimized to elucidate the aforementioned characteristics. Light absorption and energy flow distribution confirmed that Si-NW facilitates to confine photon absorption of several orders of enhancement whereas the energy flow is also distributed along the wire itself. With reference to electric field and exciton generation distribution it was revealed that Si-NW possesses the sites of strongest field distributions compared to those of flat silicon wafer. To realize the potential of Si-NWs-based thin film solar cell, a simple process was adopted to acquire vertically aligned Si-NWs grown on c-Si wafer. Further topographic characterizations were conducted through SEM and TEM-coupled EDS.

Keywords: Fabrication, FDTD simulation, photovoltaic solar cell, Silicon nanowires.

One dimensional Si nanostructures, such as, Si nanowires (Si-NWs) have been emerged as an extremely

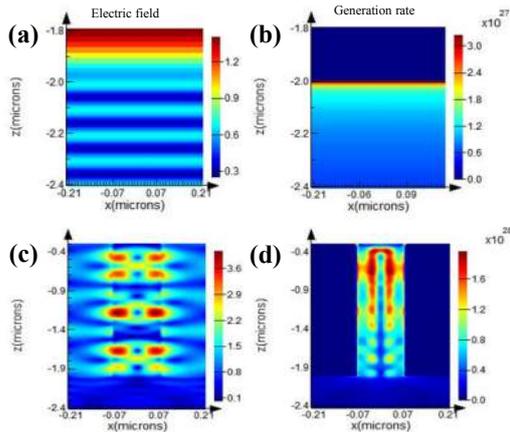


Fig. 1 Electric field and generation rate profile at 740 nm wavelength. (a) Fabry-Perot mode like electric field distribution in c-Si slab, (b) generation rate distribution in c-Si slab, (c) confined and enhanced electric field distribution in Si-NW on c-Si slab and (d) confined exciton generation rate distribution along the Si-NW length.

attractive candidate due to their unique properties. Apart from low-cost, Si-NWs have strong optical absorption in the solar spectrum, i.e., less than 1% equivalent of Si materials in Si-NWs can achieve the same amount of absorption absorbed by traditional planar wafer-based PV devices. Si-NWs-based solar cells with radial p-n junctions offer a short collection length for charge carriers, thus allowing the use of lower-quality Si materials. Si-NWs can be produced with excellent electrical characteristics. These advantages may substantially reduce the production cost of Si-NW-based solar cells while retaining efficiencies competitive with planar multicrystalline Si solar cells.

Vertically aligned Si-NWs were fabricated on c-Si wafer. The process was consisted of four simple steps, viz. i) ultrathin layer of Au coating on c-Si wafer, ii) sintering to turn the film into Au nanoparticles, ii) CVD to grow Au nanoparticles-assisted Si-NWs and iv) removal of Au nanoparticles. SEM and TEM measurements confirmed a variety of lengths (eg. few microns) and diameters (eg. 50 to 200 nm) of Si-NWs.

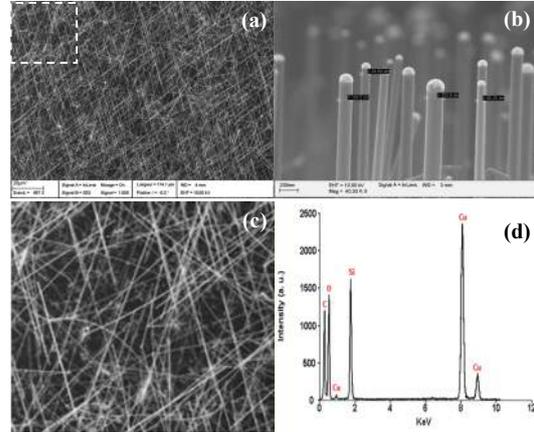


Fig. 2 SEM micrographs. (a) wide view of as-fabricated Si-NWs on c-Si wafer, (b) close-view of individual as-fabricated Si-NWs showing different dimensions in length and diameter, (c) Magnified images of the small area marked by white square in Fig. 2a and (d) TEM-coupled EDS to confirm the elemental composition of as-fabricated Si-NWs on c-Si wafer.

Details will be presented and explained in full report. Acknowledgement: The authors are thankful to Center of Research Excellence in Renewable Energy (CoRERE), King Fahd University of Petroleum and Minerals, KSA.

Environmentally Friendly Design of Tailor-Made Nano-porous Polymeric Gas Adsorbents

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Abstract: More than 80% of the worldwide commercial energy supply is based on fossil fuels. The heavy use of fossil fuels as energy source has led to two major drawbacks. The first is environmentally related problem due to the large amounts of greenhouse gas (GHG) emissions, especially carbon dioxide (CO₂) whereas the second problem is related to the continual depletion of the fossil fuel resources. Eliminating the dependency on fossil fuel as a source of energy and searching for alternative sources for energy use such as hydrogen is, therefore, a crucial step. Conventionally, gases of a natural gas mix are separated using cryogenic distillation, which is an energy intensive process as well as a damaging one to the environment since it involves the consumption of large amount of fossil fuel to generate the required energy for the liquefaction and distillation processes. Hence, there is an urgent need for gas separation using a novel cost-effective material that consumes lower energy. (McKeown, Budd, & Book, 2007; Xu et al., 2014) A range of nanoporous polyimide polymers were synthesized using a two-step poly-condensation reactions as shown in Figure 1 of bis (carboxylic anhydride) with various aromatic diamines designed to investigate their effect on both the pore sizes and pore size distribution for gas storage application. This reaction ended with the formation of polymers of intrinsic micro-porosity (PIM), which are known to comprise rigid backbone due to their lack of rotational freedom along the polymeric backbone. (McKeown & Budd, 2010) The polymers exhibited high surface area as determined by nitrogen adsorption and high thermal stability as determined by TGA. The high surface area was further validated using molecular simulation techniques. Structural modifications of the diamines have resulted into a variety of nano-porous polymeric structures. The chemical structures were confirmed using FTIR, NMR and GPC techniques. BET isotherms of the resultant polymers were carried out to evaluate their physical characteristics. The results showed that the fractional free volume and the Connolly surface of the PIMs had greater values resulting from the inability of the rigid and contorted structures of the PIMs to pack space efficiently and thus creating interconnected nano-channels throughout the polymeric structures as shown in Figure 2.

Keywords: Carbon dioxide, Hydrogen, Polymers of Intrinsic Micro-porosity (PIMs), Two-step poly-condensation, interconnected nano-channels, gas adsorbents.

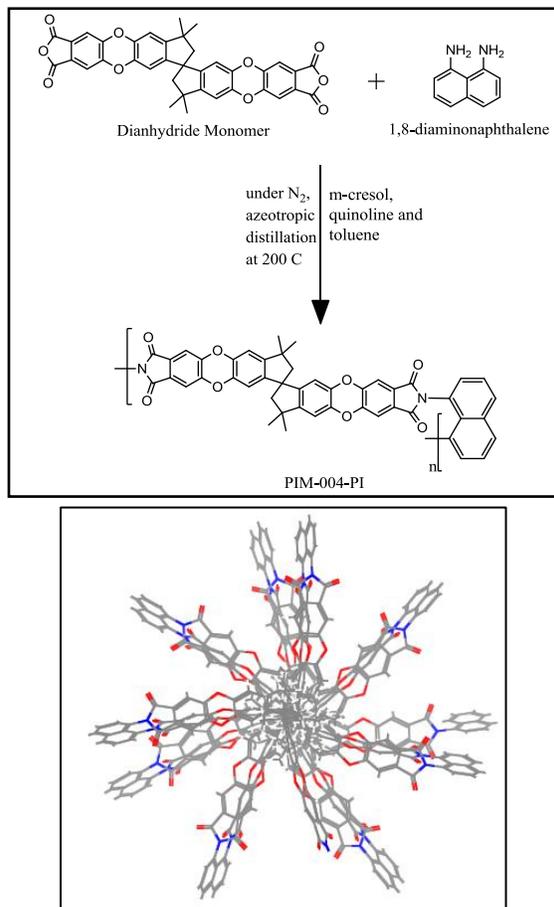


Figure 1 Synthesis of Nano-Porous Polyimide using Two-Step Poly-condensation.

Figure 2 PIM-004-PI Porous Structure.

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Silica-based nanocoating and LDHs sensors for enhancement of paperboard barrier properties

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Abstract: Conventional solutions to enhance paperboard barrier properties for packaging are limited essentially to film coating by synthetic polymers that hinder end-of-life disposal or recycling (Han *et al.*, 2010). Sol-gel methods are proven and convenient for organic-silica nanocoating since silica particles are generated *in situ* and randomly dispersed on the paper surface thus forming an impermeable interface between three-dimensional silica network and cellulose fibers (Han *et al.*, 2010; Sequeira *et al.*, 2007)

Tetraethyl orthosilicate (TEOS) is often used as silica precursor, individually or mixed with other alkoxidederived precursors. For instance, dimethyldiethoxysilane (DEDMS), 3-aminopropyltriethoxysilane (APTES) and octyltriethoxysilane (OTES) can be used to improve barrier properties due to their polarity. Similarly, Zn(2)-Al-NO₃ type layered double hydroxides (LDHs) can be added to the formulation and used as anion/water sensors (Tedim *et al.*, 2011). The silica-coated paperboard were characterized by scanning electron microscopy (SEM-EDS). Water vapor transmission rate (WVTR) was measured by the “desiccant method” (ASTM E 96-95, 1995) and oxygen permeation (J_{O_2}) measurements were performed using air in one side of paperboard and nitrogen flow on the other side and measuring $p(O_2)$ in the N₂ flow (Yaremchenko *et al.*, 2007).

Keywords: Nanocoating, paperboard, silica-based formulations, layered double hydroxides, sol-gel process, barrier properties.

SEM images (Figure 1) of paperboard transversal cuts (delimited by dashed lines) reveal the position of silicon (red areas) on the side where the formulation was applied (ca. 2 g/m²). Silica (red color) remains mostly at the outer surface.

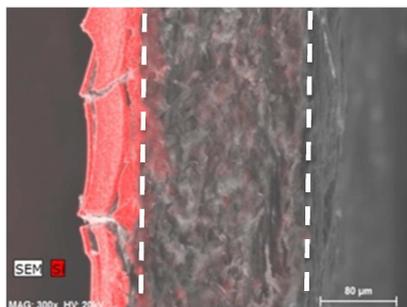


Figure 1: SEM image of TEOS_OTES formulation (2g/m²) applied on the paperboard surface (left side).

Table 1. Barrier properties of paperboard before (uncoated) and after coating with various silica based formulations.

	WVTR (g m ⁻² day ⁻¹)	J_{O_2} (m ³ m ⁻² day ⁻¹)
Uncoated	548.83 ± 21.05	1.512
TEOS	300.20 ± 4.87	0.677
TEOS_LDHs	269.59 ± 3.25	1.037
TEOS_DEDMS	230.98 ± 3.33	0.562
TEOS_DEDMS_LDHs	199.25 ± 2.98	0.936
TEOS_APTES	221.96 ± 4.04	0.490
TEOS_APTES_LDHs	132.35 ± 2.95	0.778
TEOS_OTES	225.60 ± 3.54	2.578
TEOS_OTES_LDHs	131.37 ± 2.90	1.915

Generally the incorporation of a secondary silica precursor improves barrier properties (WVTR and J_{O_2} decrease) (Table 1). For example, in comparison with the uncoated the TEOS_APTES coating decreased WVTR approximately 60% and J_{O_2} about 67%. The incorporation of LDHs caused an increase in J_{O_2} (ca. 60%) and diminished WVTR (ca. 10-40%) when compared with initial formulations. The best results were obtained with the formulation TEOS_APTES. Considering the anionexchange properties of LDHs they can act as nanosensors but also as water scavengers.

Conclusion: Silica coated paperboards exhibit good barrier properties when mixed silica alkoxide precursors are used. The incorporation of LDHs is very promising.

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