

Energy Harvesting & Storage

Room: Lehua - Session EH-ThM

Nanotechnology & Energy

Moderator: Jin-Hyo Boo, Sungkyunkwan University, Korea

8:00am **EH-ThM1 Improving the Photoconversion Efficiency of Quantum Dots Sensitized TiO₂ Solar Cells Prepared by SILAR and Electrophoresis Method**, *I. Zarazua*, Centro de Investigaciones en Optica, Mexico, *D. Esparaza, A. Sanchez, A. Cerda, T. Lopez-Luke, Elder De la Rosa*, Centro de Investigaciones en Optica A.C., Mexico **INVITED** One of the most studied hybrid-type nanostructured solar cells is the Gratzel or dye sensitized solar cell (DSSC). DSSCs typically consist of TiO₂ NCs acting as a highly porous, wide bandgap semiconductor for electron collection, and dye molecules adsorbed onto the TiO₂ NCs surface acting as sensitizers to harvest solar light. An alternative to DSSC is the utilization of quantum dots (QDs), e.g., CdSe, CdTe, CdS, PbS, PbSe, Bi₂S₃, and InP, as sensitizers to replace the expensive ruthenium dyes. QDs have large extinction coefficients in the visible region and, after bandgap excitation, undergo charge separation, injecting electrons to the conduction band of the metal oxide

The quantum dots (QD) has been recently drawing great attention as a material for solar energy conversion. The quantum dots sensitized titanium dioxide (TiO₂) was synthesized by different chemical methods such as successive ionic layer adsorption and reaction (SILAR), and electrophoresis (EP). Titanium dioxide (TiO₂) films consisting of a 150 nm compact layer, a 6 μm layer made of 40 nm TiO₂ nanoparticles (NPs) and a 7 μm scattering layer made of 400 nm TiO₂ NPs, were composited with several QDs such as CdS, PbS, ZnS, and Bi₂S₃ by SILAR and EP. Multisensitized configurations as PbS/CdS/ZnS and CdS/Bi₂S₃/ZnS were analyzed obtaining a photoconversion efficiencies of 3.75% and 2.52% respectively. These efficiencies are due to high photocurrents (14.3 and 10.2 Ma/cm², respectively) obtained by the correct combination of near infrared and visible light photoabsorption. Photoconversion efficiency was increased to 5% by combining both sensitizers method in the appropriate way. It also was studied the effect of depositing Gold Nanoparticles (Au NPs) by electrophoresis in CdS SILAR sensitized solar cells, results show that Au NPs slightly reduces the photocurrent (from 8.7 to 7.4 Ma) by reducing the photoabsorption of the CdS QDs, but at the same time strongly increases the FF (from 51 to 58%) and Voc (from 510 to 560 Mv). Electrochemical measurements suggest that Au NPs help to prevent recombination processes in the solar cell. In this paper, a detailed analysis of charge transport on both configurations is presented; taking advantage of impedance spectroscopy (IES) a detailed analysis of each interface is also presented.

We acknowledge financial support from CONACYT through grant 134111, UC-MEXUS program, CEMIE-Sol (P28), and European Community Seven Framework Programme (FP7-NMP-2010-EU-MEXICO) and CONACYT under grant agreements 263878 and 125141, respectively. D. Esparza, Andrea Sánchez and Andrea Cerda acknowledge scholarship from CONACYT.

8:40am **EH-ThM3 Applications of pure ZnO and the Mn-doped ZnO on Dye Sensitized Solar Cells**, *P.X. Feng, Xiaoyan Peng, Y.M. Li*, UPR, Puerto Rico

Mn-doped ZnO nanopowders have been prepared by the sol-gel technique using zinc and manganese (II) acetates as precursors. The crystalline structural investigations reveal that as prepared nanostructures with low Mn doping concentration have single hexagonal phase and are grown along the preferred c-axis. The chemical bonding structure in Mn-doped ZnO nanopowders was examined using X-ray photoelectron spectroscopy techniques, which indicate substitution of Mn²⁺ ions into Zn²⁺ sites in ZnO lattice. Temperature-dependent Raman spectra of the nanocrystals displayed suppression of luminescence and enhancement in full width at half maximum in pure ZnO nanocrystals with increase in temperature, which suggests an enhancement in particle size at elevated temperature. Furthermore, the magnetic measurement of Mn-doped ZnO nanostructures exhibits the ferromagnetism at room temperature.

The characteristics of dye-sensitized solar cells (DSSCs) with pure ZnO and Mn-doped ZnO nanopowders have also been investigated. The enhancement of the performance of DSSCs achieved using Mn-doped ZnO nanopowders is attributable to the introduction of the spontaneous polarization direction of ferroelectric materials with the electric field which

will efficiently block the back transfer of electron from fluorine doped tin oxide to the I⁻/I₃⁻ redox couple.

9:00am **EH-ThM4 Infrared Spectroscopic Study of Adsorption of Carbon Monoxide and Other Surface Reactions at the Ruthenium Dioxide Particle Film Aqueous Solution Interface**, *Jim McQuillan, S. Aloi*, University of Otago, New Zealand

Ruthenium dioxide is renowned as a highly active oxidation catalyst as well as a material with supercapacitor properties. Its heterogeneous catalyst behaviour has been extensively studied in surface science using well-defined crystal faces under high vacuum conditions. These studies have led to a good understanding of its active sites and the roles they play in solid/gas interface reactions such as the oxidation of adsorbed carbon monoxide. At the same time, the importance of ruthenium dioxide as an electrocatalyst has led to many electrochemical studies of RuO₂ electrodes immersed in aqueous solutions. These studies, somewhat contrasting with those in surface science, have sought to elucidate the basis of the 'pseudocapacitor' behaviour of hydrous RuO₂ which must involve both faradaic and non-faradaic processes. In spite of extensive efforts the details of the electron and proton transfer processes at RuO₂ electrodes remain obscure and there have been few spectroscopic studies addressing questions about the molecular nature of processes at the hydrous RuO₂ interface.

We have used *in situ* attenuated total reflection infrared (ATR-IR) spectroscopy to examine hydrous RuO₂ particle films deposited on diamond and ZnSe prisms immersed in flowing aqueous solutions. The adsorption behaviour of oxalate has been shown to be very similar to that of oxalate adsorbing on TiO₂ involving bidentate chelation. Adsorbed carbon monoxide exhibits several peaks indicating a diversity of sites as previously observed in its adsorption to RuO₂ (110) under high vacuum. Adsorbed carbon dioxide/carbonate is formed from the oxidation of adsorbed CO. Both the adsorbed CO and adsorbed carbonate spectra are sensitive to the presence of CO and O₂ as redox agents in solution which suggests that surface ruthenium ions may undergo changes in oxidation state via redox species in solution. These novel *in situ* spectroscopic results are the first from the RuO₂ aqueous solution interface and will be discussed in comparison with those from surface science and electrochemistry.

9:20am **EH-ThM5 Effect of Different Synthesis Routes of NaTaO₃ and the Presence of Metal-Based Nanoparticles as Co-Catalyst on the Hydrogen Production**, *Leticia M. Torres-Guerra, I. Juarez-Ramirez, C. Gomez-Solis, D. Sanchez-Martinez, J.C. Ballesteros-Pacheco*, Universidad Autonoma de Nuevo Leon, Mexico **INVITED**

Significant attention has been paid on the investigations of new photocatalysts metal-oxides because of their ability to harness the sun energy to drive fuel-producing reactions, such as water splitting. The compound NaTaO₃ has been studied in the last 10 years as photocatalyst in this reaction. According to the results obtained by several authors, high activity on this reaction was found by using NaTaO₃ material prepared by solid state route. This result is associated with the high crystallinity of the powder. However, there are other factors that also influence the physicochemical properties of semiconductor material such as specific surface area, microstructure, optoelectronic properties among others. Therefore the synthesis of metal-oxides can be carried out by soft chemical methods in order to modify and control the morphology, which allows to increase sites for hydrogen evolution. In our research group we have explored the performance of sodium tantalate, NaTaO₃ and RuO₂/La:NaTaO₃ prepared by several synthesis methods such as solid state reaction, sol-gel, hydrothermal, ultrasonic, solvo-combustion on photoinduced reactions. The sodium tantalate phase with perovskite structure has been synthesized by solvo-combustion path at low temperature (180°C) and using nanoparticles of RuO₂ as co-catalyst. This material showed considerably high photocatalytic activity for hydrogen production around 9,800 μmol.h⁻¹.g⁻¹, twice greater than those results obtained when the material was prepared by solid state method. The activity is associated with the material high crystallinity and the presence of the second phase, Na₂Ta₄O₁₁ in small concentration after annealed at 600°C. The formation of nanosteps between NaTaO₃ nanoparticles also contributed to the reaction efficiency. In addition, it was found that the crystalline structure formed by chains enhances mobility among linked octahedra and separation of hole-electron pairs, which increases the photoactivity of the material in these processes. From photoelectrochemical study was proposed the reaction mechanism that occurs during the water splitting on NaTaO₃ single and doped phase. Additionally, experiments of the electrochemical impedance spectroscopy were realized in order to obtain Mott-Schottky plots to determine the flat band potential of NaTaO₃, RuO₂/La:NaTaO₃.

10:20am **EH-ThM8 Tailored Nanomaterials for Electrochemical Applications**, *Vojislav Stamenkovic*, Argonne National Laboratory

Research that is aimed to fundamental understanding of processes for electrochemical energy conversion and storage will be presented. Atomic scale insight at the topmost surface layer is essential in order to understand and control properties of catalytically active materials. Therefore, well-defined surfaces have been in focus of our research that is executed in ultra-high vacuum (UHV) systems merged with electrochemical cells. Properties such as surface structure, surface and bulk compositions, electronic properties and surface defects are established by UHV surface specific tools. Well-characterized surfaces are then transferred to the ambient pressure electrochemical cell under strictly controlled conditions, and formed electrified solid-liquid interface is being characterized in order to obtain direct correlation between fundamental properties of materials and electrochemical behavior.

Our recent work, has been demonstrated that fine tuning of surface properties can lead towards unprecedented improvements in their functional behavior [1]. This presentation will address unique approach that is capable of utilizing structure-function relationships in the design of multimetallic materials for electrochemical systems. The following topics will be discussed: 1) well-defined materials obtained by varying their surface structure, composition profile and electronic properties in UHV; 2) atomic/molecular insight into formation of the electrified solid-liquid interfaces; 3) identification of the active and the most vulnerable surface sites under reaction conditions; 4) insight into chemical nature between the surface atoms, reactants, and molecular species in the electrolyte; 5) design and synthesis of tailored nanomaterials with desired size, shape and composition profile [2,3]; 6) ex-situ and in-situ characterization of tailored electrochemical interfaces.

This synergistic approach encompasses highly diverse experimental methods that span from UHV to rational synthesis of nanomaterials, has been proven to serve as a foundation in the development of practical materials for electrochemical applications such as batteries, fuel cells and electrolyzers. Reaction rates and durability of tailored nanomaterials for the electrochemical oxygen reduction, hydrogen evolution and hydrogen oxidation are improved over 30-fold compared to state of the art catalysts.

References:

- [1] Stamenkovic et al. *Science* 315 (2007) 493.
- [2] Stamenkovic et al. *Nature Mat.* 6 (2007) 241.
- [3] Chen et al. *Science* 343 (2014) 1339.

10:40am **EH-ThM9 Photo-Electrochemical Energy Conversion and Storage**, *A. Hankin, Geoff Kelsall*, Imperial College London, UK

Global (mean) power demands of ca. 1.5×10^{13} W, projected to double by 2050, could be provided from the earth's ultimate power source, ca. 1.2×10^{17} W of incident solar radiation, if adequately efficient, robust and economic transducers are developed. However, the diurnal nature of solar power requires that such transducers are coupled to energy storage, preferably in chemical bonds for high specific energy / energy density, and to fuel cells for subsequent conversion to electrical energy. Such systems could decarbonise power sources, manage intermittency of renewable power sources and smooth the dynamics of electrical power demands. This can be achieved if electrons from photovoltaic panels are used, for instance, to electrolyse water to form (oxygen and) hydrogen, which can be oxidised subsequently in fuel cells. Alternatively, solar energy can be used directly, and potentially more cheaply, for photo-electrochemical reduction (and oxidation) of water in an environmentally benign route to hydrogen (and oxygen).

As in photovoltaic cells, a semiconducting material may be used to absorb solar photons with energies ($h\nu$) greater than the semiconductor's band gap, generating electrons in its conduction band (e_{CB}) and highly oxidising electron 'holes' in its valence band (h_{VB}). The semiconductor needs to be chosen judiciously, so that: (a) electrons at its conduction band edge have sufficient energy to reduce water to hydrogen, and (b) holes at its valence band edge are sufficiently energetic to oxidise water to oxygen. Though the feasibility of such processes is well established, practical reactor systems have yet to be deployed, because the semiconductors also need to be stable, well-matched to the solar spectrum and achieve acceptable photon-to-hydrogen energy conversion efficiencies. Unfortunately, no single material yet meets all these criteria, to enable such artificial photosynthetic reactors to be: efficient, robust and cheap, of which only any two properties are achievable at present.

200 nm thin films of n-type $\alpha\text{-Fe}_2\text{O}_3$ photo-anodes were produced by automated spray pyrolysis of iron(III) salts dissolved in ethanol onto F-doped SnO_2 coated glass or perforated titanium substrates heated to 450 °C and with an open area of ca. 17 %. These photo-anodes were deployed in laboratory-scale photo-electrochemical reactors, designed initially for photo-assisted electrolysis only, rather than spontaneous photo-electrolysis;

a metal cathode supported hydrogen evolution with an electrical energy input.

Results will be reported for the thermodynamic and kinetic constraints on such processes, together with the effects of experimental variables on H_2 production rates.

11:00am **EH-ThM10 Gate-Modulated Thermoelectric Characteristics of Silicon Nanowires on Plastic Substrates**, *Youngin Jeon*, Korea University, Republic of Korea, *J. Choi, K. Cho*, Korea University, *S. Kim*, Korea University, Republic of Korea

Recently, several novel concepts of thermoelectric technologies have been reported as a promising source of next-generation regeneratable energy. Moreover, silicon nanowire (Si NW) based thermoelectric devices are an attractive research area due to their advantages such as non-toxicity, abundance, and low-cost manufacturing, which can lead to new opportunities in broad areas of commercial electronics. The efficiency of energy conversion has been intensively studied by modulating the dimensionless thermoelectric figure of merit, $ZT = \sigma S^2 T / \kappa$, where σ is the electrical conductivity, S is the thermoelectric power (Seebeck coefficient), κ is the thermal conductivity, and T is the absolute temperature. Numerous studies indicate that the use of Si NW enables the improvement of ZT due to their low-dimensional properties. Nevertheless, it is still difficult to achieve high ZT value because σ , S and κ are interdependent. Therefore, the modification of these parameters in Si NW can enhance the thermoelectric properties. Among various methods, the field-effect modulation, applying electric fields on thermoelectric materials, may be one of the prominent ways to modulate the thermoelectric parameters. In this study, we fabricate a gated Si NW thermoelectric device constructed on a thermal-insulating plastic substrate, and examine the field-effect modulation of thermoelectric characteristics.

Figure 1 shows the optical image of our gated thermoelectric device on a plastic substrate. The structure of the device with a NW channel length of 50 μm is similar to a NW field-effect transistor. N-type Si NWs with a doped concentration of 10^{17} cm^{-3} are present between the electrodes and a gate electrode is located at the middle of the Si NWs. And a heater electrode is used as a heating source. We investigate the seebeck voltage variation of the gated thermoelectric device with the gate bias is applied. Figure 2(a) exhibits the seebeck voltage versus temperature variation characteristics of the device with V_{GS} from 0 to 5 V. Our device shows the good gate controllability of the channel potential, which implies the capability of the electrical conductivity modulation for the Si NWs. Thus, as V_{GS} decreases, the conductivity of the Si NWs also decreases accordingly, leading to the increase of the seebeck voltage with the same temperature variation. Therefore, as shown in Figure 2(b), the seebeck coefficient, defined as $- \Delta V / \Delta T$, is able to modulate with the gate voltage variation. Our study suggests that the gated thermoelectric device with n-type Si NWs on a plastic substrate reveals its potential use as a next-generation energy harvesting device.

11:20am **EH-ThM11 Transition Metals Ion Implantation into AlInN/GaN Thin Films**, *Abdul Majid*, University of Gujrat, Pakistan, *Zhu*, Chinese Academy of Sciences, Beijing

A lot of work has been done on Mn doping in III-V [1] but work on Mn and other TM ions doping in AlInN is still lacking. Out of III-Nitrides, AlInN is the only ternary alloy which is capable of lattice matching with GaN and is potential candidate for use as distributed Bragg reflectors, cladding layers and several other electronic /optoelectronic devices[2]. Like several other materials, the doping of AlInN with TM elements is expected to produce diluted magnetic semiconductors (DMS) based on it. Realization of AlInN based DMS will be exciting due to wide direct band gap and lattice matching capability at 17% indium content with GaN. This work is one of initial detailed reports on TM doping into AlInN. Transition metals ions of Cr, Mn, Co and V were implanted MOCVD grown wurtzite AlInN/GaN thin films at doses 5×10^{14} to 5×10^{16} ions/cm². The structural properties of the materials were studied by X-ray diffraction and Rutherford backscattering spectroscopy (RBS) techniques. XRD analysis revealed that GaN related peak for all samples remains at its usual Bragg position of $2\theta=34.56^\circ$ whereas a shift in AlInN peak taken place from its position of $2\theta=35.51^\circ$ for as-grown sample. RBS analysis provided interesting results with clear shift in position of indium related peak pointing to migration of indium atoms towards interface of heterostructures. Moreover this peak has observed to be splitted into two peaks which is indication of depth wise redistribution of indium atoms within the material. The measurements of magnetization versus temperature as well as applied magnetic field measured using SQUID magnetometer indicated room temperature ferromagnetism in the films. The density Functional Theory based calculations of Transition metals doped AlInN predicted that TM ions will preferably substitute In sites in the alloy. In order to model the experimental results and explore the mechanism of ferromagnetic exchange interactions in the materials, detailed density functional theory (DFT) based calculations

were performed. The electronic and structural properties of pure and TM doped AlInN were computationally investigated using ADF-BAND program which performs calculations using Kohn-Sham under Local Density Approximation. We modeled 64 atoms supercell with 3x3x3 mesh in the form Al₂₇In₅N₃₂ for pure AlInN and Al₂₇In₃Mn₂N₃₂ (2 Mn atoms substitutes 2 In atoms), Al₂₆In₅Mn₁N₃₂ (Mn substitutes Al) and Al₂₆In₅Mn₁N₃₂ (Mn substitutes Al) supercells for Mn doped AlInN. The literature suggests that Fermi level should lie within spin up Mn band predicting Mn:AlInN to be in half metallic state like other Mn doped III-Nitrides [3]. The calculated results indicate that Mn d band is partially filled for Al₂₇In₄Mn₁N₃₂ and Al₂₇In₃Mn₂N₃₂ whereas completely empty for Al₂₆In₅Mn₁N₃₂. It can be said that, either one or two Mn atoms substituting In sites produces expected half metallic AlInN whereas Mn substituting Al sites turns out to be unacceptable option. It is therefore concluded that Mn will preferably substitute indium in AlInN.

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[2]. A. Majid, G. Husnain, M. Usman, A. Shakoor, N. Hassan, J.J. Zhu, Physics Letters A 377, 2986 (2013)

[3]. T. Jungwirth, Jairo Sinova, J. Mašek, J. Kučera and A. H. MacDonald, Rev. Mod. Phys. 78, 809 (2006)

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