Energy Frontiers Focus Topic
Room: 106 - Session EN2+TF-WeA

Thin Films for Solar Fuels
Moderator: A.J. Muscat, University of Arizona

4:00pm **EN2+TF-WeA7 N-doped $SrTiO_3$(100) Epitaxial Films for Fundamental Studies of Visible Light Active Photocatalysts**, ***T. Luttrell***, *M. Batzill*, University of South Florida

N-doping of photocatalysts, in particular TiO_2, has been extensively studied for its ability to increase visible light activity. However, the solubility of N in TiO_2 is limited to ~ 2% and thus limits the visible light absorption. One reason for the low solubility of nitrogen is the different preferred charge state of nitrogen (3-) compared to the substituted oxygen (2-) anions. Here, we investigate the less studied perovskite $SrTiO_3$, which has similar photocatalytic activity to TiO_2. Because a wide range of oxides crystallize in the perovskite structure, we anticipate that charge compensating co-doping in N:$SrTiO_3$ can be more easily accomplished than in TiO_2. Such co-doping may result in a higher achievable N-concentration. In our studies, the stability of N-doping in $SrTiO_3$ and the effect of co-doping have been investigated in thin films. High quality pure and N-doped epitaxial films of $SrTiO_3$ have been grown on $LaAlO_3$(100) substrates by pulsed laser deposition (PLD). The structural and electronic properties have been investigated, by x-ray and UV photoemission spectroscopy (XPS and UPS) and ex-situ atomic force microscopy (AFM). N-doping was accomplished by deposition in an ammonia atmosphere. N^{3-} ions are substituting for O^{2-} ions in the $SrTiO_3$ matrix and thus cause a charge imbalance that is compensated for in pure films by formation of oxygen vacancies. To avoid this defect formation, substitution of the quadrivalent cations in $SrTiO_3$ by co-doping with La^{5+} is investigated. La co-doping allows a higher nitrogen solubility in $SrTiO_3$. Nitrogen doping causes a band gap narrowing due to formation of filled N-2p states at the top of the valence band and thus an increase in visible light adsorption. The UV and visible light photocatalytic activity is assessed by decomposition of methyl orange.

4:20pm **EN2+TF-WeA8 Photoelectrochemical Water Splitting by Hematite Nanostructures Prepared by Chemical Bath Deposition**, ***R. Morrish***, Colorado School of Mines, *M. Rahman*, *J.M.D. MacElroy*, University College Dublin, *C.A. Wolden*, Colorado School of Mines

Hematite (a-Fe_2O_3) is a promising material for sustainable generation of H_2 due to its low cost, widespread availability, chemical stability, and ability to absorb a significant fraction of visible light. However numerous challenges remain in order for this material to approach its theoretical potential of 15% solar to hydrogen efficiency. Nanorod geometries are an ideal configuration for this material, decoupling the different length scales required for photon absorption and efficient carrier transport. Unfortunately such structures have historically yielded poor photoelectrochemical performance (<5 mA/cm^2).[1] We recently demonstrated that nanorods synthesized by chemical bath deposition (CBD) could be activated through the use of appropriate annealing treatments.[2] Photocurrents >500 mA/cm^2 were achieved at 1.23 V versus RHE, and the photoanodes displayed low onset potentials. These changes were correlated with significant amount of tin diffusion from the underlying FTO substrate into the Fe_2O_3 matrix occurs during high temperature annealing process. The benefits of this process may include enhanced conductivity as well as improvement of the FTO/ Fe_2O_3 interface. Despite these advancements, significant room remains for further improvement. In this paper we describe a number of strategies to reach this goal. First, the nanostructure of the hematite can be further improved. This is explored by varying the CBD chemistry, optimizing the post-deposition annealing conditions, and through subtractive processing. A second issue is electron transport at the hematite/FTO interface, and this is explored through the use of novel treatments of the FTO prior to deposition. Finally, the addition of an electrocatalyst can further reduce the onset potential. Each of these three strategies has demonstrated enhanced photocurrent over our previous results. We plan to integrate these advancements in order to maximize performance. Detailed characterization of the structure, composition, and electrochemical changes observed with these processes will be used to provide fundamental insight into the mechanisms underlying the improvements.

References

[1] N. Beermann, L. Vayssieres, S.-E. Lindquist & A. Hagfeldt, "Photoelectrochemical Studies of Oriented Nanorod Thin Films of Hematite", 2456-2461, (2000).

[2] R. Morrish, M. Rahman, J. M. D. MacElroy & C. A. Wolden, "Activation of hematite nanorod arrays for photoelectrochemical water splitting", 474-479, (2011).

4:40pm **EN2+TF-WeA9 Nanostructured Thin Films for Solar Water Splitting**, ***K. Sivula***, Ecole Polytechnique Federale de Lausanne, Switzerland **INVITED**

Solar energy can be converted to chemical energy stored in hydrogen through water splitting using a photoelectrochemical device. However, decades of research have failed to identify one semiconducting electrode material that can perform the water splitting reaction with adequate efficiency, stability and material cost. Here I present a system that overcomes the limitations of conventional materials to afford direct solar hydrogen production by taking inspiration from natural photosynthesis and using two photosystems in tandem. In addition, to reach the terawatt energy scale needed to have a global impact, I describe the use of abundant and inexpensive semiconducting materials. Specifically, progress developing hematite (Fe_2O_3) photoanodes and cuprous oxide (Cu_2O) photocathodes will be presented. I will show that our water splitting tandem cell, using these materials and inexpensive processing techniques, is capable of solar-to-hydrogen conversion efficiencies of over 5 % at standard conditions. I will further detail how the progress in developing the electrode thin films has been enabled by exploiting recently developed techniques like aerosol–assisted chemical vapor deposition and atomic layer deposition.

5:20pm **EN2+TF-WeA11 TiO_2 N-doped Nanofibers Deposited by Electrospinning for Photocatalytic Applications**, *D. Di Camillo, F. Ruggieri*, ***L. Lozzi***, *S. Santucci*, University of L'Aquila, Italy

Titanium dioxide (TiO_2), thanks to its interesting properties as nontoxicity, low cost and high chemical stability, has been extensively investigated for several application in which, following light absorption, the generated charges can be usefully applied, as for photovoltaic applications or for photocatalytic devices. However, due to the wide intrinsic energy gap of TiO_2 (between 3.0 and 3.2 eV, depending on the crystalline structure), only a small fraction of the solar spectrum can be used to promote the light absorption [6]. In the photocatalytic devices one of the most important goal of the recent research is to be able to prepare photocatalyst which can be active by absorbing the visible light, in order to increase the application of TiO_2-based system in poor regions (where it could be difficult to use UV light sources) or to reduce the application cost . In order to increase the fraction of the solar spectrum that can be absorbed, different approaches have been used, mainly by doping TiO_2 with metals or anions.

One of the most studied doping is using nitrogen. TiO_2 doped with nitrogen atoms can be prepared in different ways, as powders, as thin films by sol-gel or reactive sputtering.

In this paper we will show the photocatalytic results obtained depositing TiO_2 N-doped nanofibers (NF) prepared by means of electrospinning (ES) and near-field electrospinning (NF-ES) techniques for the photo-degradation of methylene blue (MB) in water under visible light. The ES preparation technique allows a quick deposition of fibers on wide surfaces using a cost-effective system. Instead NF-ES method allows the growth of a well ordered NF net, with a spacing lower then few microns.

The NFs were deposited using different deposition and post-deposition parameters (solution composition, annealing temperature and atmosphere) and have been characterized by using X-ray photoemission spectroscopy (XPS), X-ray diffraction (XRD) and Secondary Electron Microscopy (SEM). The photocatalytic properties have been studied recording the variation of the optical absorption of MB when the sample is illuminated by an halogen lamp (visible spectrum).

The annealing process determines a partial loss of nitrogen and the formation of the Anatase crystalline phase. The TiO_2 N-doped NFs have shown interesting degradation properties, which are much better than those observed when TiO_2 NFs are used.

5:40pm **EN2+TF-WeA12 Fabrication of Palladium Nanoscale Structures for Hydrogen Sensing Applications**, *D. Rodríguez-Vindas*, University of Puerto Rico at Río Piedras, *C. Ortiz, V. Pantojas*, University of Puerto Rico at Cayey, ***W. Otaño***, University of Puerto Rico at Cayey and Institute for Functional Nanomaterials

Palladium (Pd) metal is one of the most prominent materials studied for the detection of hydrogen gas. Hydrogen rapidly dissociates on its surface and diffuses into subsurface layers forming palladium hydride with consequent changes in optical, mechanical and electrical properties that are easily detected. Materials with nanoscale morphologies are promising to improve sensor performance as they provide large surface areas for adsorption, and smaller crystallite size reducing the time needed for "bulk" diffusion. The amount of sites available for hydrogen adsorption per Pd atom is also higher in the surface and subsurface layers resulting in higher sensitivity. In this project, Pd nanoribbons and nanoshells are prepared by magnetron sputtering deposition on top of the mat of polymer fibers, which act as a template that shapes the morphology of the palladium being deposited while providing support to the metallic scaffold that is created. Sputtering is a line-of-sight deposition process and the fibers become a variable angle-substrate for the incoming Pd flux. A larger amount of palladium is deposited on top of the fiber where the incoming flux is perpendicular to the surface compared to the sides where the flux is incident at a glancing angle. The top and sides of the fibers shadow their bottom parts closer to the substrate preventing any substantial deposition there. The end result of the deposition is the formation of Pd nanostructures, thicker in the middle region than at the edges, with a large void network. Process parameters such as deposition time, sputtering pressure, and power can be used to produce nanoshells with different thickness and crystallinity. The high sensitivity and response time shown to 1% or less of hydrogen in nitrogen is understood to result from the reduced dimensions combined with this unique nanostructure. A description will be given of the conductance changes with hydrogen concentration as result of the competing mechanisms of percolation and scattering. This work shows the use of nanotechnology combined with unique processing approaches to produce new sensor geometries with different behavior and morphology than simple thin film or wire approaches.

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