

# Hydrogen Generation

## Using Integrated Photovoltaic and Photoelectrochemical Cells

Jin Z. Zhang<sup>1</sup>, Yiping Zhao<sup>2</sup>, Abraham Wolcott<sup>1</sup>, Wilson Smith<sup>2</sup>

<sup>1</sup>University of California, Santa Cruz

1156 High St.

Santa Cruz, CA 95064

Phone: 831-459-3776; fax: 831-459-2935

E-mail: [zhang@chemistry.ucsc.edu](mailto:zhang@chemistry.ucsc.edu)

<sup>2</sup>The University of Georgia, Athens

Athens, GA 30602

Phone: 706 542 7792; fax: 706 542 2492

E-mail: [zhaoy@physast.uga.edu](mailto:zhaoy@physast.uga.edu)

DOE Program Officer: Jane G. Zhu,

Phone: (301) 903-3811

E-mail: [Jane.Zhu@science.doe.gov](mailto:Jane.Zhu@science.doe.gov)

Subcontractors:

Jin Z. Zhang, University of California, Santa Cruz

Yiping Zhao, University of Georgia, Athens

### Objectives

*The primary objective of this project is hydrogen generation from water splitting using integrated photoelectrochemistry (PEC) and photovoltaic cells (PVC) based nanostructured materials. More specifically, various metal oxide nanostructures have been investigated to gain a better understanding of the many fundamental processes involved and photovoltaic (PV) as well as photoelectrochemical (PEC) properties towards water splitting. The emphasis has been on gaining deep insight into the effect of morphology, surface, doping, and sensitization using semiconductor quantum dots (QD) on basic processes such as electron transfer and transport as well as the PVC and PEC performances.*

### Technical Barriers

*Hydrogen generation at low cost and in an environmentally-friendly manner is a major challenge for its potential use as a clean fuel. PEC, in conjunction with PVC, based on low cost metal oxide nanomaterials is a promising approach for hydrogen generation from water splitting. Some of the technical challenges or barriers include the design and understanding of novel nanomaterial architectures for hydrogen generation from water splitting at high efficiency but low cost. Strategies based on QD sensitization and doping of 0-D, 1-D, and 2-D metal oxide nanostructures to produce inorganic nanocomposite materials for this purpose offer some intriguing alternatives to overcome some of these technical barriers by rationally engineering the electronic bandgap structure to enhance charge transfer and transport and thereby improved PVC and PEC performance.*

## Abstract

Investigation into integrated PEC/PVC for water splitting and light harvesting has focused on doping, QD sensitization and nanomaterials morphology. We have demonstrated, for the first time, PVC based on combined use of nitrogen doping and CdSe QD sensitization of nanocrystalline TiO<sub>2</sub> thin films with promising results for solar energy conversion. Such TiO<sub>2</sub>:N/CdSe PVC produced an incident-photon-to-current efficiency (IPCE) of 95% at 300 nm, a 27.7% fill factor (FF) and a power conversion efficiency of 0.84%. Many aspects of that system are still not optimized including nitrogen doping level, properties of CdSe QDs, and TiO<sub>2</sub> film morphology. PEC based on ZnO nanostructures produced via pulsed laser deposition (PLD), oblique angle deposition (OAD) and electron beam glancing angle deposition (GLAD) show differing morphological, photophysical and PEC characteristics due to each technique. A combination of HRSEM, UV-vis spectroscopy, XRD and photoelectrochemistry has been used to characterize the fundamental properties of the ZnO PEC. Hybrid nanorod structures of WO<sub>3</sub> and TiO<sub>2</sub> in a stacked configuration via the GLAD technique have also been studied for their light harvesting and water splitting abilities.

## Progress Report

To maximize the ability of TiO<sub>2</sub> to harvest photons and produce usable electrical current there have been two main strategies. Firstly, the most widely probed pathway is to exploit nanoporous TiO<sub>2</sub> by sensitizing the nanostructures with dyes to act as electron acceptor/injector pairs (Gratzel cell).<sup>1</sup> Doping has also been quite successful in narrowing the bandgap of metal oxides, most notably TiO<sub>2</sub> with N.<sup>2,3</sup> A modification of the dye sensitization has been to replace the organic dye with tunable semiconductor QDs.<sup>4</sup> A merger of both N doping and CdSe QD sensitization was found to be very advantageous and showed promising light harvesting PV characteristics.<sup>5</sup> While extensive wet chemical modifications of the TiO<sub>2</sub>:N thin films were performed, the use of nitric acid, hexamethyltetramine (HMT) and titanium iso-propoxide was the most efficient combination. TiO<sub>2</sub>:N thin films were thoroughly sensitized by CdSe QDs via the linking molecule thioglycolic acid (TGA). Nanocrystalline hybrid thin films of only 1.1 μm produced impressive initial results.

TiO<sub>2</sub>:N-TGA-CdSe thin films in this initial study showed a short circuit photocurrent ( $I_{sc}$ ) of 682 μA/cm<sup>2</sup>, an open circuit voltage ( $V_{oc}$ ) of -1.2V and a fill factor (FF) of 27.7%. With these characteristics it was found the hybrid thin films (1.1 μm) attained a 0.84% overall power conversion efficiency. Nitrogen doping level was determined using XPA to be in the range of 0.6-0.8% with HMT as the nitrogen precursor. Absorption of the TiO<sub>2</sub>:N was significantly red shifted from ~ 390 nm to an absorption onset of 600 nm, a bandgap narrowing of 1.14 eV (Figure 1). Due to the high extinction coefficient of CdSe QDs in the visible range, the majority of increased light harvesting was due to QD sensitization. Comparisons of power conversion efficiencies leads to the conclusion that the combination of doping and sensitization is greater than the simple sum of nitrogen doping (0.01%) alone or CdSe QD sensitization (0.73%) alone. Our assertion is that the valence hole recombination of CdSe QDs is aided, by the filled nitrogen doping energy level as viewed on the normal hydrogen electrode (NHE) scale at pH=0 (Figure 1). The two main processes are the electron injection from CdSe to TiO<sub>2</sub>:N, and the movement of nitrogen level electrons into the valence band of CdSe. Solid state TiO<sub>2</sub>:N-TGA-CdSe devices showed increased photo response and an IPCE of ~4.3% at the excitonic peak of the CdSe QDs at 600 nm (Figure 2). Light harvesting in the solid state device directly matched that of the 4.6 nm CdSe QDs utilized as electron donors. Immediate conversion optimization parameters include increasing nitrogen doping within the TiO<sub>2</sub> nanoparticles, and modifying the capping agent of CdSe from tetradecylphosphonic acid (TDPA) to pyridine. Added doping should increase hole mobility and light harvesting at the 600 nm absorption onset, and the smaller tunneling barrier of a pyridine coated CdSe QD will enhance the injection rate greatly by decreasing the tunneling barrier as indicated in previous studies.<sup>6</sup>

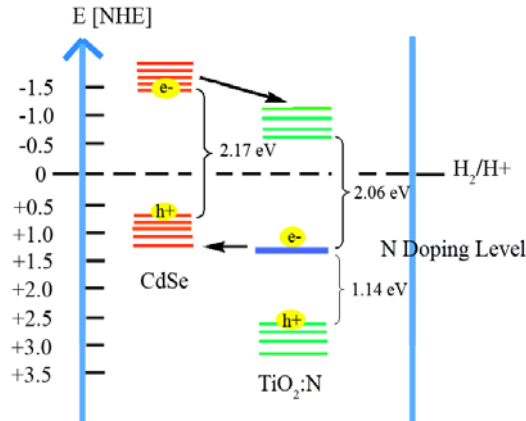


Figure 1. Illustration of the band structure of  $\text{TiO}_2:\text{N}$  and 3.5 nm CdSe QDs versus NHE. The two arrows represent electron injection from CdSe to  $\text{TiO}_2:\text{N}$  (top), and hole recombination from the nitrogen doping level to the CdSe valence band (bottom).

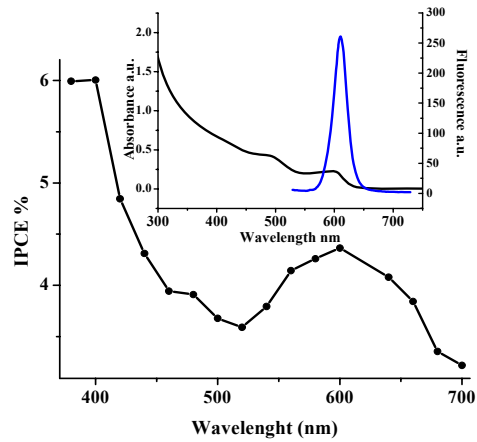


Figure 2. Solid state IPCE measurements of a  $\text{TiO}_2:\text{N}$ -TGA-CdSe thin film at AM 1.5 with 4.2% IPCE at 600 nm. Inset is the steady state PL and UV-vis measurements of 4.6 nm CdSe QDs used to sensitize the  $\text{TiO}_2:\text{N}$ .

In a comparative PEC study of ZnO thin films, three deposition techniques, including PLD, OAD and GLAD, were utilized to produce ZnO films with different morphologies. ZnO has been extensively studied for both PEC and PV applications using various wet chemical and deposition techniques.<sup>7-9</sup> A general illustration of PLD/OAD is shown wherein a high energy pulsed laser produces an adatom plume which deposits onto a substrate with a varying deposition angle  $\alpha$  (Figure 3). GLAD works in a similar fashion in that the substrate is tilted, but the adatom plume is produced by an accelerated electron stream instead and the substrate is also rotating at a specific rpm. All three techniques were found to produce very different morphologies and porosity as seen in HRSEM images (Figure 4).

PLD produced the densest films with a deposition angle  $\alpha = 0^\circ$  (Figure 4, top) and this resulted in a light brownish hue to the film that is indicative of defects in the crystal lattice of ZnO. Sintering of PLD thin films at 550 C° for 2 hours did not affect the overall color of these films. OAD ZnO thin films revealed a porous scale-like morphology at low resolution and a collection of interconnected nanoparticles of various spheroid shapes at increased magnification (Figure 4, middle). E-beam GLAD produced vastly different thin films made of 20-60 nm ZnO nanoparticles in a more classic nanoporous structure similar to  $\text{TiO}_2$ .<sup>10</sup> PEC measurement revealed good photoresponse for all ZnO films at AM 1.5 ( $\sim 100 \text{ mW/cm}^2$ ). The onset of photocurrent begins at 0V in comparison to the flat band potential of -0.28 V ( $V_{\text{FB}}$ ) indicating inefficient electron-hole separation at negative potentials (not shown). Flat band potentials of both OAD and GLAD ZnO were found by the potential intercepts of Mott-Schottky plots. The  $V_{\text{FB}}$  of GLAD ZnO

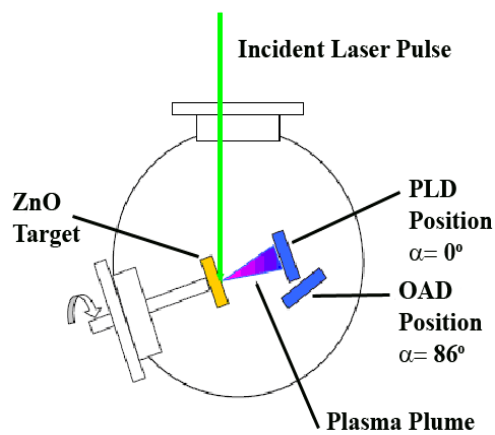


Figure 3. General illustration of a PLD ( $\alpha = 0^\circ$ ) and OAD setup ( $\alpha = 86^\circ$ ).

was found to be -0.22 V. Donor densities of OAD and GLAD ZnO samples were calculated to be  $6.6 \times 10^{13} \text{ cm}^{-3}$  and  $7.7 \times 10^{13} \text{ cm}^{-3}$  and space charge layer thickness was calculated to be 91 nm and 77 nm, respectively, based on the slopes of the Mott-Schottky plots. PEC comparisons thus far show varying degrees of photoresponse, and PLD ZnO samples were shown under AM 1.5 to have a photon-to-hydrogen efficiency of 0.92% (corrected for applied voltage) at an applied potential of +1.0V.<sup>11</sup>

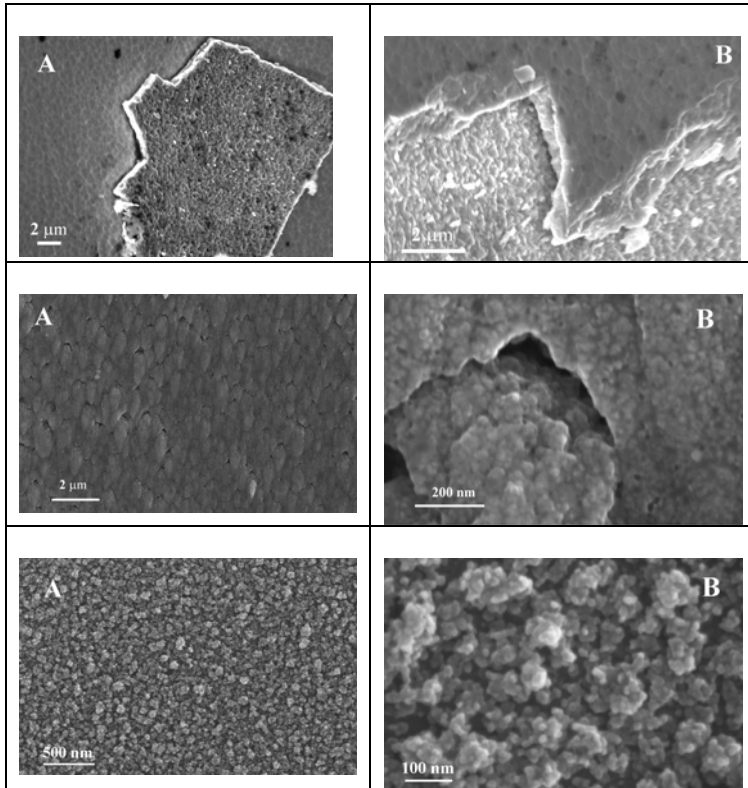


Figure 4. HRSEM images of PLD (top), OAD (middle) and E-beam GLAD (bottom) ZnO samples at various magnifications.

The structural and photocatalytic properties of multi-layered  $\text{WO}_3/\text{TiO}_2$  nanostructures were also investigated. Samples were made with a custom-built electron beam (E-beam) deposition system. Three hybrid structures were studied each with a layer of  $\text{WO}_3$  on the bottom, and a layer of the same morphology of  $\text{TiO}_2$  deposited on top. The average length of each segment was  $\sim 500\text{nm}$ . The first structure was deposited by positioning the substrate's normal parallel with the evaporation direction, and thin films created. For the second sample, the angle between the evaporation direction and the substrate normal was increased to  $>70^\circ$ , and a shadowing effect occurred called oblique angle deposition (OAD). A regular array of nanorods formed tilted in the direction of the incident vapor, shown in Figure 5(a).

When the obliquely angled substrate is rotated azimuthally during deposition, i.e. GLAD, and an array of vertically aligned nanorods is deposited. Figure 5(b) shows a SEM image of the multi-layered GLAD nanorod array.

The photocatalytic properties of each multi-layered sample were tested by their decay of an aqueous methyl blue solution. A 9 mm x 30 mm sample of each sample was placed in individual clear cuvettes, and then they were filled with the MB solution. The absorbance spectra for the solutions were measured with a UV-Vis spectrophotometer. Then, the samples were irradiated by UV light (366nm, 10mW) for 30 minutes intervals. To date, our results show that the GLAD multi-layered samples

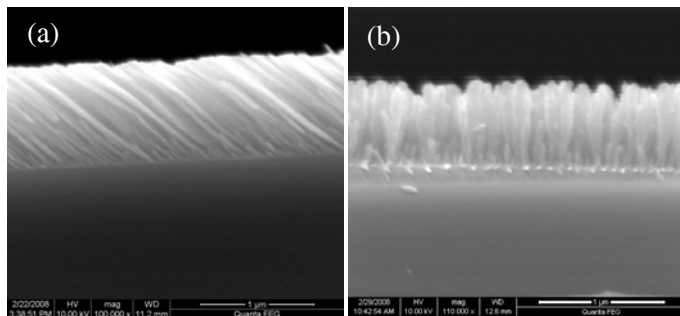


Figure 5 SEM image of the (a) multi-layered OAD nanorod array, and (b) multi-layered GLAD vertical nanorod array. The top layer of  $\text{TiO}_2$  was measured to be  $\sim 500\text{nm}$ , and the bottom layer of  $\text{WO}_3$  was also roughly  $\sim 500\text{nm}$ .

are able to degrade the MB solution much greater than both the thin films samples and the OAD samples, and also show great enhancement over a single layer of TiO<sub>2</sub>.

### Future Directions

Experimentation in the future for the PVC will include the optimization of the TiO<sub>2</sub>:N-TGA-CdSe system by increased nitrogen doping and modification of the CdSe QD ligand system. Ultrafast spectroscopy of both liquid and thin film TiO<sub>2</sub>:N-TGA-CdSe samples to deduce electron injection rates are also of prime importance to further justify our N doping level model. ZnO will continue to be studied in undoped and nitrogen doped capacities and evaluated for their PEC properties. Use of the GLAD system to produce hybrid nanorod systems of WO<sub>3</sub> and TiO<sub>2</sub> has already shown significantly improved photocatalytic activities and their PEC integration and characterization are already underway. Integration between PVC and PEC will be tested and optimized with respect to materials properties. Hydrogen generation efficiency will be determined quantitatively and as a function of the materials properties and device architectures.

### References

- (1) O'Regan, B.; Gratzel, M. *Nature* **1991**, *353*, 737.
- (2) Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science* **2001**, *293*, 269.
- (3) Burda, C.; Lou, Y. B.; Chen, X. B.; Samia, A. C. S.; Stout, J.; Gole, J. L. *Nano Lett.* **2003**, *3*, 1049.
- (4) Robel, I.; Subramanian, V.; Kuno, M.; Kamat, P. V. *J. Am. Chem. Soc.* **2006**, *128*, 2385.
- (5) Lopez-Luke, T.; Wolcott, A.; Xu, L.; Chen, S.; Wen, Z.; Li, J.; De La Rosa, E.; Zhang, J.Z. *J. Phys. Chem. B* **2007**.
- (7) Huynh, W. U.; Dittmer, J. J.; Teclerian, N.; Milliron, D. J.; Alivisatos, A. P.; Barnham, K. W. *J. Phys. Rev. B* **2003**, *67*.
- (8) Sobana, N.; Swaminathan, M. *Solar Energy Materials Solar Cells* **2007**, *91*, 727.
- (9) Vayssieres, L.; Keis, K.; Hagfeldt, A.; Lindquist, S. E. *Chem. Mater.* **2001**, *13*, 4395.
- (10) Wang, J. X.; Sun, X. W.; Yang, Y.; Huang, H.; Lee, Y. C.; Tan, O. K.; Vayssieres, L. *Nanotechnology* **2006**, *17*, 4995.
- (11) O'Regan, B.; Lenzenmann, F.; Muis, R.; Wienke, J. *Chem. Mater.* **2002**, *14*, 5023.
- (12) Wolcott, A. S.; W; Kuykendall, T.R.; Zhao, Y.; Zhang, J.Z. *Small* **2008**, *In Preparation*.

### Publications and Patents

- (1) Wolcott, A.; Kuykendall, T. R.; Chen, W.; Chen, S. W.; Zhang, J. Z. *J. Phys. Chem. B* **2006**, *110*, 25288.
- (2) Lopez-Luke, T.; Wolcott, A.; Xu, L. P.; Chen, S. W.; Wen, Z. H.; Li, J. H.; De La Rosa, E.; Zhang, J. Z. *J. Phys. Chem. C* **2008**, *112*, 1282.
- (3) Wolcott, A. Smith, W.; Kuykendall, T.R.; Zhao, Y.; Zhang, J.Z. *Small* **2008**, *in preparation*.
- (4) Wang, G.; Chen, D.; Zhang, H.; Nespurek, S.; Zhang, J.Z.; Li, J.; *J. Phys. Chem. C* in press, 2008.
- (5) W. Smith, Z.-Y. Zhang, and Y.-P. Zhao, *J. Vac. Sci. Technol. B* **25**, 1875-1881 (2007)
- (6) Y. P. He and Y.-P. Zhao, *J. Phys. Chem. C* **112**, 61-68 (2008)
- (7) Y.-P. He, Y.-P. Zhao, and J.-S. Wu, *Appl. Phys. Lett.* **92**, 063107 (2008)
- (8) W. Smith and Y.-P. Zhao, *Advanced Materials*, in preparation.
- (9) Nitrogen doped and CdSe QD sensitized thin films for photovoltaic (PV) and photoelectrochemical (PEC) cells, UC Santa Cruz, Patent Pending.