

Photochemical (PEC) Hydrogen Production and Solar Harvesting Utilizing Metal Oxide Nanomaterials

Abraham Wolcott,^Σ Tevye R. Kuykendall^Δ, Wilson Smith^Ω, Tzarara Lopez-Luke ^Σ Yiping Zhao^Ω and Jin Zhang ^Σ

^Σ University of California, Santa Cruz, Department of Chemistry and Biochemistry

^ΔThe Molecular Foundry, Lawrence Berkeley National Laboratory

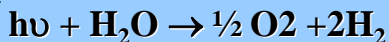
^Ω University of Georgia Athens, Department of Physics and Astronomy



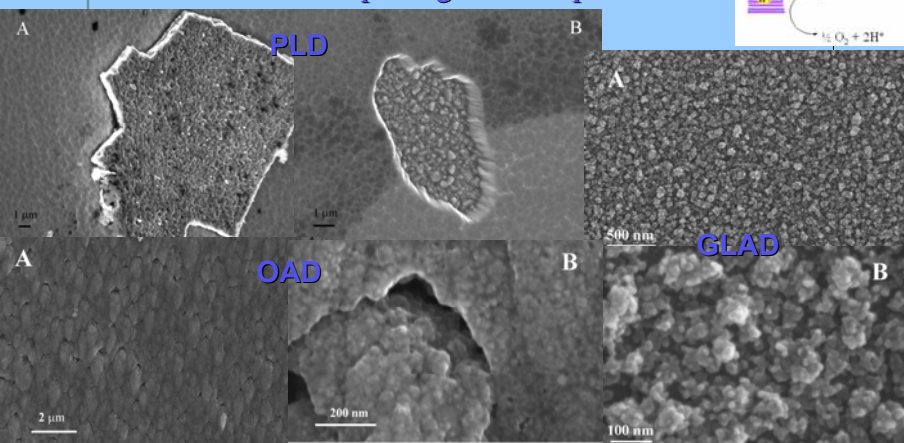
Due to ever increasing petroleum prices and growing evidence connecting the effects of CO₂ levels to global climate change, the pressure for sustainable alternative energy (SAE) production has grown. Hydrogen production via light driven water splitting (photolysis) is a promising field of research which can offset the need for methane reforming and nuclear power driven electrolysis for hydrogen generation. ZnO PEC cells produced by pulsed laser deposition (PLD), oblique angle deposition (OAD), and glancing angle (GLAD) were characterized by HRSEM, XRD, UV-vis and PEC techniques. Water splitting efficiency of the PLD ZnO samples was shown to achieve a photon-to-hydrogen efficiency of 0.92% with a 1 V potential bias. Solar harvesting using photovoltaic (PV) devices is also a widely investigated technology, and here we combined for the first time the use of nitrogen doped nanocrystalline TiO₂ with CdSe nanoparticle sensitization. The thin film TiO₂:N/CdSe devices had a nitrogen doping level of 0.8%, a fill factor (FF) of 27% and a power conversion efficiency of 0.84%. We believe the addition of the nitrogen level may aid in the recombination of photo generated holes in the valence band of the CdSe QDs leading to higher efficiencies.

Photo Driven Water Splitting

The splitting of water on n-type metal oxide PEC cells occurs due to the photogeneration of electrons and holes (exciton). In our setup, the oxidation of water to produce O₂ resides at the photoanode and the reduction of protons to hydrogen gas (H₂) occurs at a Pt coiled cathode. After photoexcitation electrons migrate into the bulk of the ZnO PEC cell, while the holes migrate to the surface. Electrons that diffuse to the back contact are then collected as photocurrent, and holes act as oxidizing centers for adsorbed water molecules. Reduction of recombination pathways such as surface traps, electron scavenging by dissolved oxygen and photocorrosion, should be minimized to increase efficiency. Fundamental PEC characteristics are collected here to compare and further understand the differences in the three deposition techniques examined.

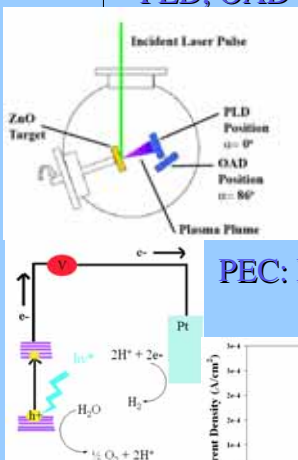


SEM and HRSEM: Morphological Comparison



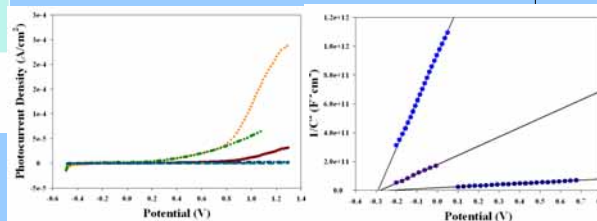
SEM and HRSEM images of PLD (top), OAD (bottom) and GLAD ZnO PEC cells

PLD, OAD and Ebeam GLAD Deposition

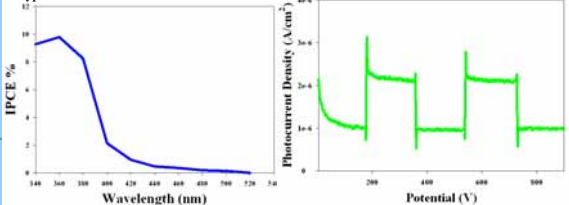


Deposition is performed in an ultra high vacuum (UHV) chamber where upon a Nd:YAG (355 nm) pulsed laser is incident upon a ZnO target, and produces an adatom plume. The plume is deposited onto a substrate at angle (α) where $\alpha = 0^\circ$ is PLD and $\alpha = 86^\circ$ is OAD. GLAD utilizes an electron beam with a tilted and rotating substrate.

PEC: Linear Sweep, Mott-Schottky and IPCE Measurements



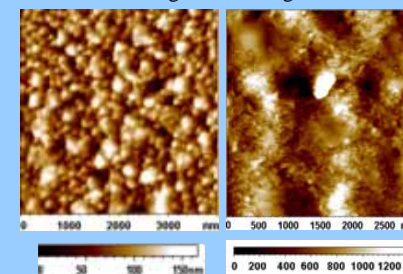
(Left): Linear sweep voltammograms in PB buffered 0.5 M NaClO₂. ZnO PLD (dotted) shows the best photoresponse at 0.3 mA/cm² at 1.3 V, than ZnO (dot-line) OAD and ZnO GLAD (solid line) samples performed the poorest. (Right) Mott-Schottky plots show the flatband potential (V_{fb}) to be -0.29 V for ZnO PLD (blue), -0.28 V for ZnO OAD (purple), and -0.23 V for GLAD ZnO (dark purple) with positive slopes which are characteristic of n-type metal oxide semiconductors.



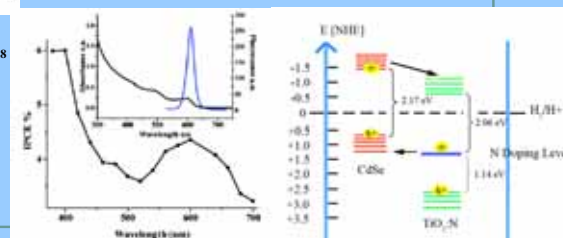
(Left): Incident-photon-to-current-conversion efficiency (IPCE) action spectra of a 500 nm thick ZnO OAD PEC cell. On/Off light cycles at AM 1.5 of a ZnO PLD PEC cell at 1V showing immediate photoresponse and a decrease in I_{ph} over time revealing an increase in electron-hole recombination after initial illumination.

Nitrogen Doped Nanocrystalline TiO₂ Sensitized with CdSe QDs for PV devices

Hexamethyltetramine (HMT) was the nitrogen precursor source of the TiO₂ and achieved a 0.8% doping level. CdSe QDs were bound to the surface of the TiO₂:N by thioglycolic acid (TGA). 1.1 μ m TiO₂:N-TGA-CdSe thin films had a fill factor (FF) of 27%, and a power conversion efficiency (η) of 0.84%. Increasing nitrogen doping, and performing a ligand exchange of tetradecylphosphonic acid (TDPA) for pyridine should increase light harvesting efficiencies.



AFM images of nanocrystalline TiO₂:N thin films before (left) and after (right) incorporation of 3.5 nm CdSe QDs via the linking molecule TGA.



(Left) IPCE action spectra of a solid state TiO₂:N-TGA-CdSe device with a precise photoresponse that matches that of the CdSe QDs excitonic peak position in solution (inset). (Right) Schematic energy level diagram versus the normal hydrogen electrode (NHE) of TiO₂:N with a sensitizing 3.5 nm CdSe QD. We believe the increase in power conversion efficiency of the simultaneously doped and sensitized system could be due to an enhanced electron-hole recombination from the nitrogen doping level (TiO₂:N) to the valence band in CdSe.

