

# Integrating Photoelectrochemical (PEC) and Photovoltaic (PV) Cells Based on Nanomaterials for Hydrogen Generation



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Metal oxide nanostructures hold great potential for photovoltaic (PV), photoelectrochemical (PEC) and photocatalytic applications. While thin films of various materials of both nanoparticle and nanorod morphologies have been widely utilized, there have been few inquiries into nanodisc structures. Here we report the synthesis of ultrathin WO<sub>3</sub> nanodiscs (NDs) using a wet chemical route with polyethylene glycol (PEG) as a surface modulator. The WO<sub>3</sub> nanodiscs were thoroughly characterized using HRTEM, HRSEM, EDX, AFM and Cyclic Voltammetry. At potentials of -0.8 V there was observed generation of hydrogen gas from the surface of the PEC cell surface. Nitrogen doped TiO<sub>2</sub> is also investigated as a PEC/PV material, and was sensitized with CdSe QDs to increase the light harvesting capabilities of the thin film. TiO<sub>2</sub>:N/CdSe thin films of a thickness of 1.1 μm produced power conversion efficiencies of 0.84 %. We believe that the introduction of dopant produced energy levels in the TiO<sub>2</sub> crystal lattice aids in replenishing photoexcited holes in CdSe QDs adsorbed on the surface.

## Introduction

Dependence on fossil fuels and its fluctuating supply has arisen alarms that sustainable and alternative forms of energy are imperative. The increasing release of CO<sub>2</sub> in the atmosphere via combustion of fossil fuels is also showing detrimental signs of global climate change. Use of wind, solar, fuel geothermal and PEC cells as alternative energy sources are garnering a lot of attention.

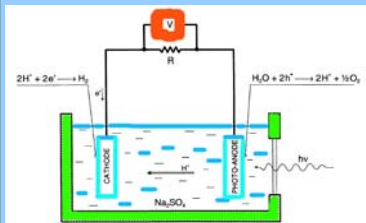


FIGURE 1

In PEC cells a substrate is illuminated with UV-visible radiation, and an exciton is formed. The photogenerated hole performs the oxidation of water at the surface. Electrons diffuse through the material and are collected at the back contact, and are utilized to reduce protons to H<sub>2</sub> gas (Figure 1).

## SEM and HRSEM of WO<sub>3</sub> Nanodiscs (NDs)

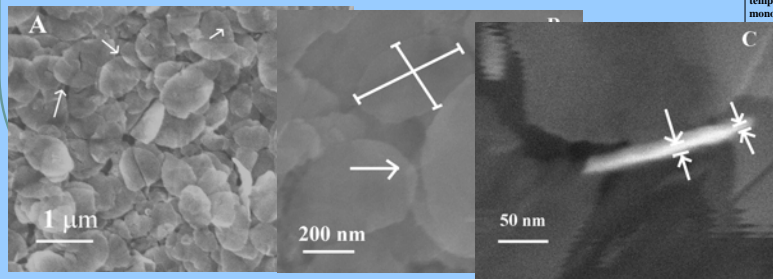


FIGURE 2. SEM and HRSEM images of WO<sub>3</sub> NDs revealing the ultrathin nature of the nanostructures. Arrows indicate areas of electron transparency, wherein multiple NDs can be seen overlapping with one another (A and B). The smallest WO<sub>3</sub> ND was 183 nm on the long axis and 6.7 nm (9 unit cells) at its thinnest point (C).

## HRTEM, SAED, EDX and XRD of WO<sub>3</sub> NDs

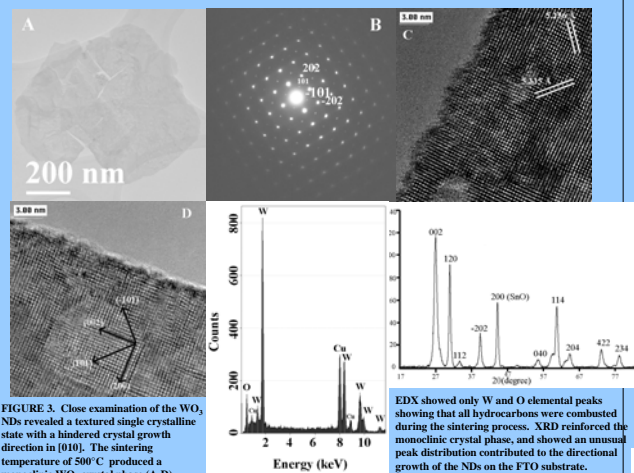


FIGURE 3. Close examination of the WO<sub>3</sub> NDs revealed a textured single crystalline state with a hindered crystal growth direction in [010]. The sintering temperature of 500°C produced a monoclinic WO<sub>3</sub> crystal phase (A-D).

EDX showed only W and O elemental peaks showing that all hydrocarbons were combusted during the sintering process. XRD reinforced the monoclinic crystal phase, and showed an unusual peak distribution contributed to the directional growth of the NDs on the FTO substrate.

## Cyclic Voltammetry and H<sub>2</sub> Generation

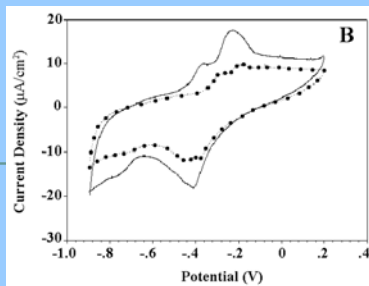


FIGURE 4. CV data showing the peaks of Na<sup>+</sup> and H<sub>2</sub> intercalation at -0.4 V and a reductive peak at -0.8 V which is indicative of proton reduction to H<sub>2</sub> gas. Unfortunately hydrogen production at the WO<sub>3</sub> surface damages the films.

## N Doped TiO<sub>2</sub> Sensitized with CdSe QDs

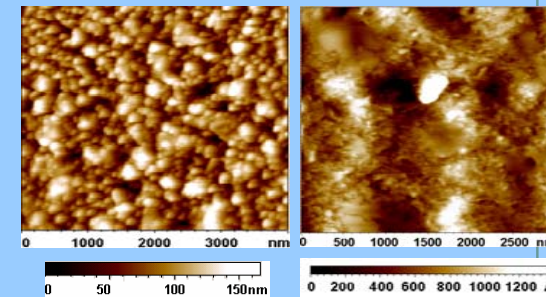


FIGURE 5. AFM images showing nitrogen doped TiO<sub>2</sub> thin films (left) and TiO<sub>2</sub>:N nanocrystalline thin films sensitized with CdSe QDs (right).

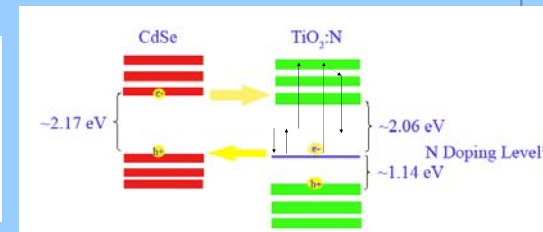


FIGURE 6. Energy diagram of CdSe QDs with a bandgap of 2.17 eV (3.5 nm QD), and TiO<sub>2</sub>:N with an overall bandgap of 3.2 eV, and a nitrogen dopant energy level of 1.14 eV (600 nm absorption edge). Arrows indicate the possible pathways of photoexcited electrons within the sensitized system.

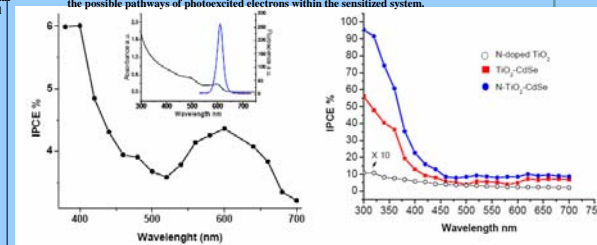


FIGURE 7. Incident-Photon-to-Current-Conversion-Efficiency (IPCE) under a solid-state environment without electrolyte for TiO<sub>2</sub>:N/CdSe thin films (left), and IPCE of various films within an electrolyte solution of Na<sub>2</sub>S illuminated by white light.

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