

## Research Article

# CdS-Sensitized ZnO Nanorod Photoelectrodes: Photoelectrochemistry and Photoinduced Absorption Spectroscopy

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Thin films of ZnO semiconductor nanorods (ZnO-nr) of 6  $\mu\text{m}$  length and thin ZnO nanoparticulate films (ZnO-np) have been prepared and modified with Q-dots CdS for comparison study. PIA (photoinduced absorption spectroscopy), a multipurpose tool in the study of dye-sensitized solar cells, is used to study a quantum-dot-modified metal-oxide nanostructured electrode. Q-dot CdS-sensitized ZnO-nr (1D network) sensitized photoelectrode has demonstrated best performances in both photoelectrical response (IPCE max = 92%) and broadening response into far visible comparing to ZnO-np-based CdS solar cell. Preadsorbing ZnO-nr with ZnO-np does not bring further improvement. Time constant for electron injection into ZnO-nr conduction band was relatively fast decay of 6.5 ms, similar to TiO<sub>2</sub>-coated CdS, and proves at least a well pore filling of ZnO-nr film by ultrafine CdS particles. Unidirectional electron transfer mechanistic in ZnO-nr has played a major role in these performances.

## 1. Introduction

When used as electrodes in regenerative photoelectron-chemical cells, wide bandgap nanostructured metal oxide (MO) semiconductor materials can serve as carriers of solar absorbers such as organometallic dyes [1–5] or inorganic narrow bandgap semiconductors (quantum dots: Q-dots) [6–9]. Power conversion efficiencies in the range of 8–12% in diffuse daylight have been obtained in the sensitization of highly porous TiO<sub>2</sub> film with only a submonolayer required ruthenium complex [1, 2]. On the other hand, wide bandgap semiconductors have been sensitized by short bandgap (Q-dots) semiconductor materials CdSe/TiO<sub>2</sub> [6], CdS/TiO<sub>2</sub>-SnO<sub>2</sub> [9] as alternative to dye sensitization. Vogel and coworkers [7] have investigated the sensitization of nanoporous TiO<sub>2</sub>, ZnO by Q-sized CdS. Photocurrent quantum yields of up to nearly 80% and open-circuit voltages up to 1 V range were obtained. Under visible light irradiation, only the sensitizer is excited, and electrons transferred to their conduction band are injected to the inactivated MO semiconductor conduction band. If the valence band of the sensitizer is more cathodic than the valence band of MO, hole

generated in the semiconductor remains there and cannot migrate to MO. Thus, the two charges will be separated effectively.

Dye-sensitized solar cells (DSCs) based on one-dimensional (1D) ZnO nanostructures, which exhibit significantly higher electron mobility than that of both TiO<sub>2</sub> and ZnO-np films [10], have recently been attracting increasing attention [10, 11].

In contrast with the dye-sensitized solar cells, fundamental understanding for the factors controlling the interfacial electron transfer reactions in Q-dots-modified metal-oxide-based solar cells is limited. Photoinduced absorption spectroscopy is a suitable method to obtain spectral and kinetic information of the Q-dot-sensitized MO electrodes.

In this paper, we report QD-CdS-sensitized ZnO-np, ZnO-nr, and ZnO-nr preadsorbed with ZnO-np photoelectrodes. We described photoelectrochemical properties and for the first time photoinduced absorption spectroscopy for mechanistic study. We compare our results to those obtained recently on CdS-adsorbed TiO<sub>2</sub> using PIA measurements, in a separate paper submitted for publication.

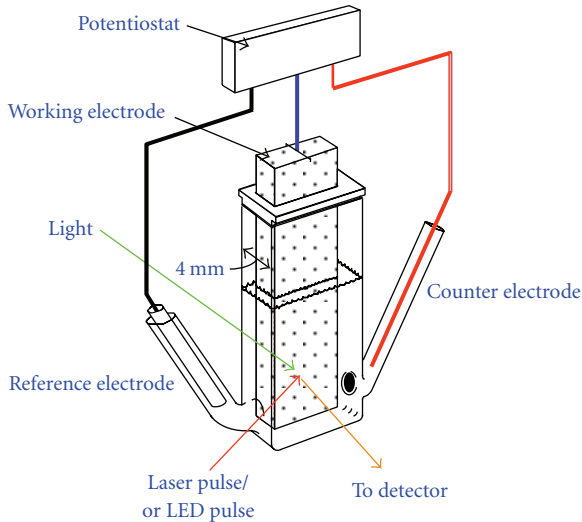


FIGURE 1: Photoelectrochemical cell (Quartz) [13].

## 2. Experimental Section

**2.1. Preparation of ZnO Nanorod (1D) Films.** Firstly, 300 nm ZnO seed layer was prepared on the optically conducting glass, indium-doped SnO<sub>2</sub> (ITO) substrate. Two drops of 5 mM solution of zinc acetate-dihydrate in ethanol absolute, rinsed in ethanol, and blow dried with nitrogen gas. This is repeated 4 times before sintering at 350°C in air for 30 min and cooled down to room temperature. This process is repeated twice [12].

Secondly, the deposited ZnO seed substrate was immersed into an aqueous solution of 25 mM zinc nitrate hexahydrate, 25 mM hexamethylenetetramine and 5 mM polyethyleneimine at 90°C for a hydrothermal reaction for a total of 12 hours. The solution was replaced by a fresh one every 4 hours. The obtained ZnO nanorods were rinsed with deionized water and dried in air at room temperature.

**2.2. Surface Modification of ZnO by Quantum Dots of CdS.** ZnO metal oxide nanostructured and ZnO nanorod electrodes were successively dipped into an aqueous solution of saturated Cd(ClO<sub>4</sub>)<sub>2</sub> and 0.1 M Na<sub>2</sub>S for 1 and 2 min, respectively. After each CdS layer deposition, the electrodes were heated at 125°C for 5 min.

**2.3. Characterization Methods.** UV-Vis spectra were recorded using a Hewlett-Packard 8453 diode array spectrometer. The photoelectrochemical measurements were carried out in a layer cell consisting of a 1 cm path-length quartz cuvette [13]. Two electrodes were inserted consisting of a reference (Ag/AgCl) and counter- (Pt wire) electrodes similar to that shown in Figure 1. A Princeton Applied Research (PAR) Model 173 and 175 universal potentiostats were used in electrochemical measurements. The setups for recording incident photon to current efficiency (IPCE) spectra and *I-V* curves have been described elsewhere [12].

For PIA spectroscopy (see described setup in Figure 2), excitation of the sample was provided by light from

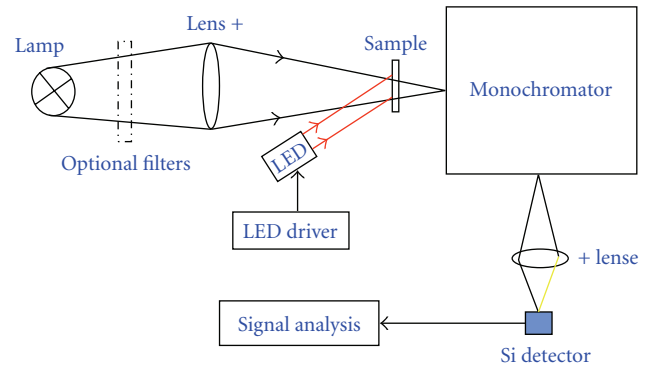


FIGURE 2: Photoinduced absorption (PIA) setup.

a blue LED (Luxeon Star 1 W, Royal Blue, 470 nm), which was square-wave modulated (on/off) by electrical means using an HP 33120 A waveform generator and a home-built LED driver system. The beam, with an intensity in the range of 0.5–30 mW/cm<sup>2</sup>, excited a sample area of about 1 cm<sup>2</sup>. White probe light was provided by a 20 W tungsten-halogen lamp. A cutoff filter (Schott RG715) was used to minimize excitation of the sample by the probe light where indicated. The transmitted probe light was focused onto a monochromator (Acton Research Corporation SP-150) and detected using a UV-enhanced Si photodiode, connected to a lock-in amplifier via a current amplifier (Stanford Research Systems models 830 and 570, resp.). For the time-resolved studies the output of the current amplifier was connected to a data acquisition board (National Instruments PCI-6052E). All PIA measurements were done at room temperature.

## 3. Results and Discussion

**3.1. Microstructure.** SEM image in Figure 3 shows a 1-dimensional network of ZnO nanorods about 6 μm length. The diameter of these nanorods was estimated to be less than 300 nm. Also in Figure 4 are SEM pictures of ZnO-nr films after modification with Q-dots CdS. Compared to ZnO-nr SEM alone, we clearly can observe a good adsorption of CdS particles around ZnO nanorods (see both Figures 4(a) and 4(b)).

**3.2. UV-VIS Absorption Spectra.** Absorption spectra have been recorded for both ZnO-nr films before and after CdS modification (Figure 5). Coating ZnO-nr film with CdS particles extends further its adsorption into the visible up to 700 nm.

**3.3. Incident Photon-to-Current Conversion Efficiency (IPCE) Spectra.** In Figure 6 is shown a comparison of photoreponses in the visible spectrum of the three-based ZnO network—CdS photoelectrodes, namely. High IPCE measurements have been found with all based ZnO network films using 1D ZnO network. 1D network of ZnO broadens the response to larger wavelengths compared to ZnO-np alone or ZnO-nr preadsorbed with ZnO-np. The broadening of

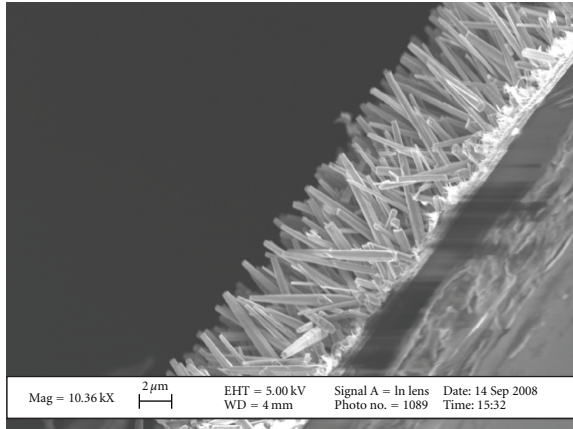


FIGURE 3: SEM cross-section picture of ZnO nanorod film.

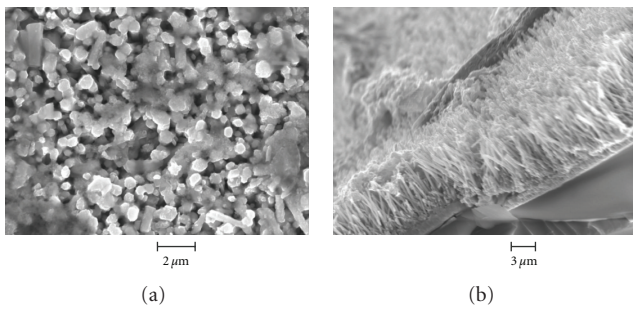


FIGURE 4: (a) SEM top picture of ZnO nanorod film modified with CdS. (b) SEM cross-section of ZnO nanorod film modified with CdS.

the response with ZnO-nr-based films may originate from the possible aggregation of some CdS particles between the nanorods, thus red-shifting in the absorption. By CdS aggregation we should observe lowering in IPCE response, but the fact that 1D ZnO network will enhance unidirectional e-transfer to the substrate will thus compensate the loss due to aggregation and keep the visible broadening higher. Regarding ZnO-nr preadsorbed with ZnO-np, this network design has not brought an enhancement to the simple ZnO-nr based cell, but on the contrary it lowers the response, and also the broadening into visible spectrum.

**3.4. PIA Spectroscopy.** Figure 7 shows a PIA spectrum of CdS-modified ZnO-nr and ZnO-np without electrolyte for comparison. The PIA spectrum clearly reflects the differential spectrum of CdS upon formation injection of electrons into ZnO conduction band, with a bleach of the main absorption around 470 nm. The remaining hole in CdS absorbs light, and because valence band electrons are missing, an apparent increase in bandgap is seen (bleach, Moss-Burstein shift). Almost negligible PIA signal is detected with ZnO-np preadsorbed with ZnO-np-based CdS solar cell. Both ZnO-nr- and ZnO-np-based CdS films depict different onset bleaching. Although they show similar PIA intensity above 670 nm, this difference in onsets is probably due to the broadening of visible absorption of CdS particles

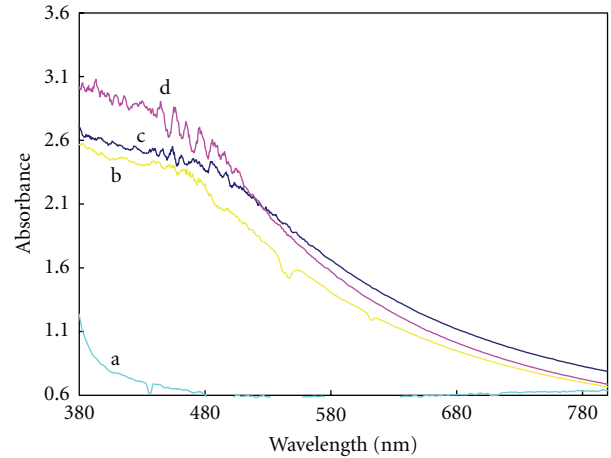


FIGURE 5: Absorption spectra of (a) ZnO-nr particulate film and (b), (c), and (d) different CdS coatings modified ZnO-nr particulate film.

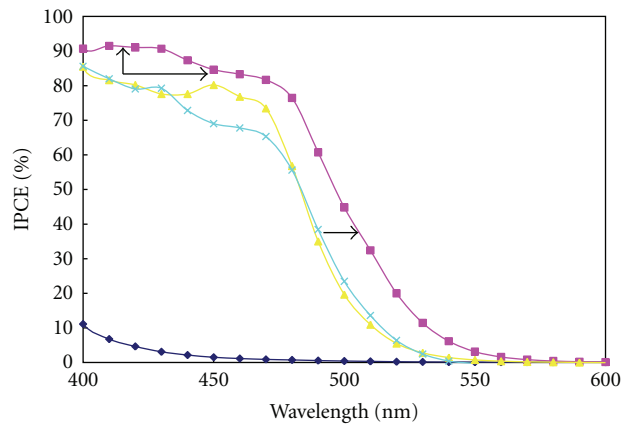


FIGURE 6: Incident photon-to-current conversion efficiencies (IPCE) of ZnO-nr photoelectrode before modification with CdS (dark blue square) and after modification with CdS (violet square); ZnO-np/CdS (cross) and ZnO-nr/ZnO-np/CdS (yellow triangle). Electrolyte was Na<sub>2</sub>S 0.1 M, Na<sub>2</sub>SO<sub>4</sub> 0.01 M.

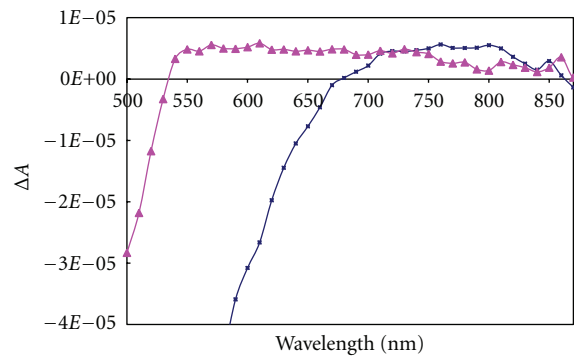


FIGURE 7: Photoinduced absorption (PIA) spectra of quantum CdS-modified ZnO-np (triangle) and ZnO-nr (square) electrodes in air. The spectra were recorded using blue light (460 nm) excitation (42 mW cm<sup>-2</sup>) with a modulation frequency of 9 Hz.

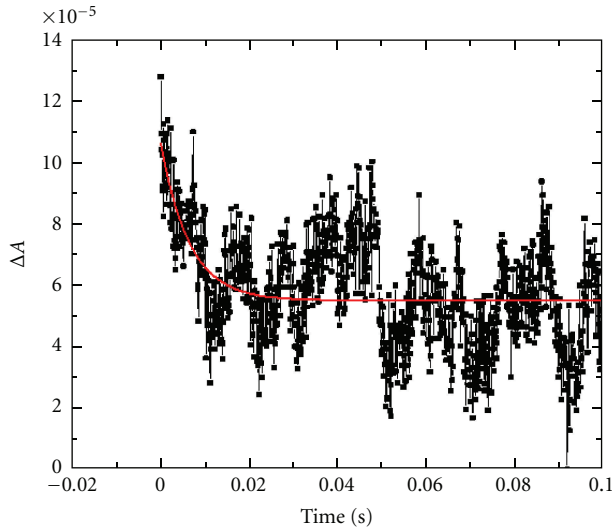


FIGURE 8: PIA decay transient absorption of quantum dots CdS-modified ZnO-nr electrode after excitation with blue light ( $11 \text{ mW/cm}^2$ ) recorded at 750 nm, using a sampling rate of  $103 \text{ s}^{-1}$  and averaged 100 times.

after aggregation between ZnO nanorods, thus red-shifting the PIA onset in the visible spectrum.

**3.5. PIA Kinetics.** Study of the kinetics in semiconductor sensitizing solar cells is not only feasible by laser flash photolysis but also possible using time-resolved PIA measurements.

Figure 8 shows an example of such PIA transient, here decay recorded at 750 nm for CdS-modified ZnO-nr. It is clear that the recombination yield between generated electrons and holes does not follow simple first- or even second-order kinetics but is characterized by a range of recombination times. Transport of electrons through ZnO-nr nanocrystals could also be one relation. For solar cell performance the pseudo-first-order rate constant under steady-state conditions is a relevant parameter as it can give direct information on possible recombination losses due to the reaction of electrons with holes. Analysis of the decay in Figure 8 during the first 1 ms (using a sampling rate of 1 MHz) gives a recombination lifetime of 6.5 ms approximately (similar to that found with CdS-coated  $\text{TiO}_2$ -np of 8.5 ms, in a separate article submitted for publication in Hindawi journals, 2011), which does not follow simple first-order kinetic but is characterized by a range of injection times. This relatively fast decay proves at least a well pore filling of ZnO-nr film by ultrafine CdS particles. Almost no transient decay has been observed for ZnO-nr preadsorbed with ZnO-np-based CdS films.

## 4. Conclusion

Photoinduced absorption spectroscopy where the excitation is provided by an on/off monochromatic light source can give direct information on electron-injection and hole-electron recombination rates using spectra of transient

species, and their kinetics can be explored using time-resolved techniques. PIA can monitor slow processes and is much cheaper compared to laser flash photolysis. ZnO-nr-(1D network) based CdS photoelectrode has demonstrated best performances in both photoelectrical response and broadening response into far visible comparing to ZnO-np-based CdS solar cell. Preadsorbing ZnO-nr with ZnO-np does not bring further performances, but on the contrary it lowers photoresponse and broadening to almost the same level as with ZnO-np-based cell. Unidirectional electron transfer mechanistic observed in ZnO-nr has played a major role in these performances.

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