Photoinduced Absorption Spectroscopy as a Tool in the Study of Electron Injection and Recombination in CdS quantum Dots Sensitized ZnO Solar Cell

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Thin films of ZnO nanoparticulate films have been prepared and modified with CdS quantum dots via chemical bath deposition technique. Photoinduced absorption spectroscopy (PIA), where the excitation is provided by a square-wave modulated (on/off) monochromatic diode light source, is a multipurpose tool in the study of dye-sensitized solar cells. Here, we use PIA as a tool for the study of a quantum-dot modified metal oxide nanostructrued electrode. Oxidized quantum dots can easily be obtained from the spectra of transient species, and their kinetics can be explored using time-resolved techniques. ZnO based CdS photoelectrode has demonstrated best performances in both photoelectrical response and broadening response into visible with a maximum IPCE of 87% at 400 nm. Time constant for electron injection or hole transfer was relatively fast (44 μs) and proves at least a well pore filling of ZnO film by ultra fine CdS particles.

1. Introduction:

When used as electrodes in regenerative photoelectronchemical cells, wide band-gap nanostructured metal oxide (MO) semiconductor materials can serve as carriers of solar absorbers such as organometallic dyes [1-4] or inorganic narrow band-gap semiconductors (quantum dots: Q-dots) [5-8]. Power conversion efficiencies in the range of 8-12% in diffuse daylight have been obtained in the sensitization of highly porous TiO_2 film with only a sub monolayer required ruthenium complex. [1] In the other hand, wide band gap semiconductors have been sensitized by short band gap (Q-dots) semiconductor materials $CdSe/TiO_2$ [4], ZnO/ZnS[8] as alternative to dye sensitization. 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 can not migrate to MO. Thus, the two charges will be separated effectively.

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 work, we use photoinduced absorption spectroscopy (PIA) where on/off modulation of a light source is used. While PIA is a popular tool in the study of photoactive polymers [9,10], organic solar cells [11,12] and DSC (dye sensitized solar cells), there is, in our knowledge, no PIA published work on Q-dot sensitized MO solar cell. Here, we study photoelectrochemistry and PIA studies on CdS q-dots sensitized ZnO nanostructured electrodes.

2. Experimental:

### 2.1. Preparation of ZnO Nanostructured Films:

Colloidal ZnO was prepared as previously published [13]. 50 mmol (11g) of zinc acetate dehydrate was stirred in 100 ml absolute ethanol at room temperature and became an opaque suspension. 50 mmol (21 ml) of tetramethylam-monium hydroxide (TMAOH) in methanol was added. Then the obtained suspension was heated and refluxed (80 C) for about 30 min. During reflux, the solution became slowly white due aggregation of the colloids. Then, the suspension was left to cool down and settle overnight. After what, it is decanted and washed with ethanol. Using a rotary evaporator, ZnO was concentrated until visibly viscous. Gel-films were then obtained by doctor blading the colloidal solution onto SnO_2 doped-indium conducting glass (ITO) using adhesive tape (Scotch Magic) as spacer. The films were then fired in a hot–air stream at 350C for 30 min and the thicknesses were determined by profile-metry and were typically between 2-3 μm.

2.2. Surface Modification of ZnO by Quantum Dots of CdS:

ZnO metal oxide nanostructured electrodes were successively dipped into an aqueous solution of saturated $Cd(ClO_4)_2$ and 0.1 M Na_2S for 1 and 2 min, respecttively. 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 quartz cell similar to that in Fig. (1) [also in Ref.14]. Two electrodes were inserted consisting of a reference (Ag/AgCl) and counter (Pt wire) electrodes.
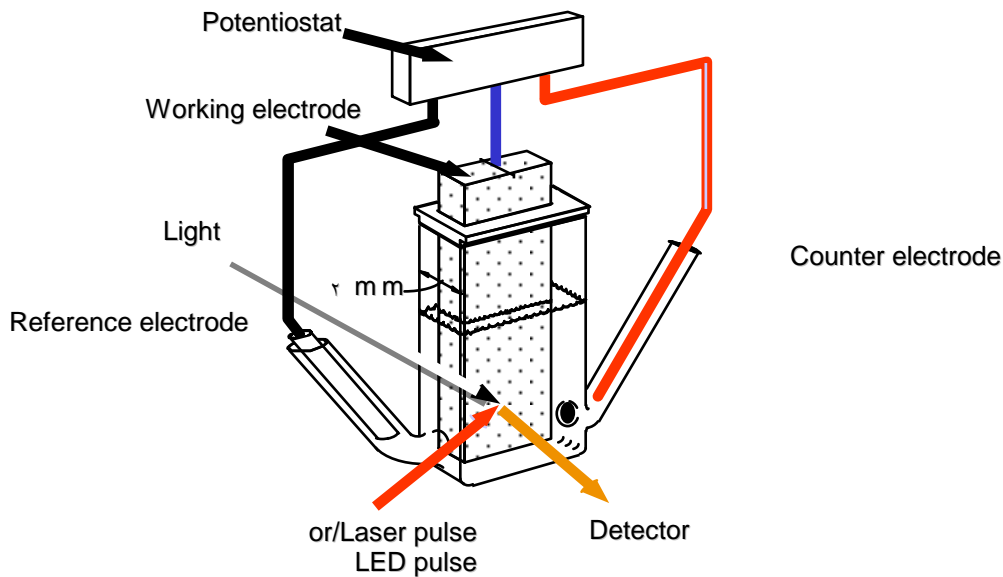
Fig. (1): Photoelectrochemical Cell (Quartz) [Bedja, Ph.D. Dissertation 1996]

A Princeton Applied Research (PAR) Model 173 and 175 universal potentiostats were used in electrochemical measurements.

For PIA spectroscopy (Fig. 2), excitation of the sample was provided by light from a blue LED (Luxeon Star 1W, Royal Blue, 470 nm), which was square-wave modulated (on/off) by electronical means using an HP 33120A waveform generator and a home- built LED driver system. The beam, with an intensity in the range of 0.5–30 mW/cm^2, excited a sample area of about 1 cm^2. 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 photo-diode, connected to a lock-in amplifier via a current amplifier (Stanford Research Systems models 830 and 570, respectively). 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.
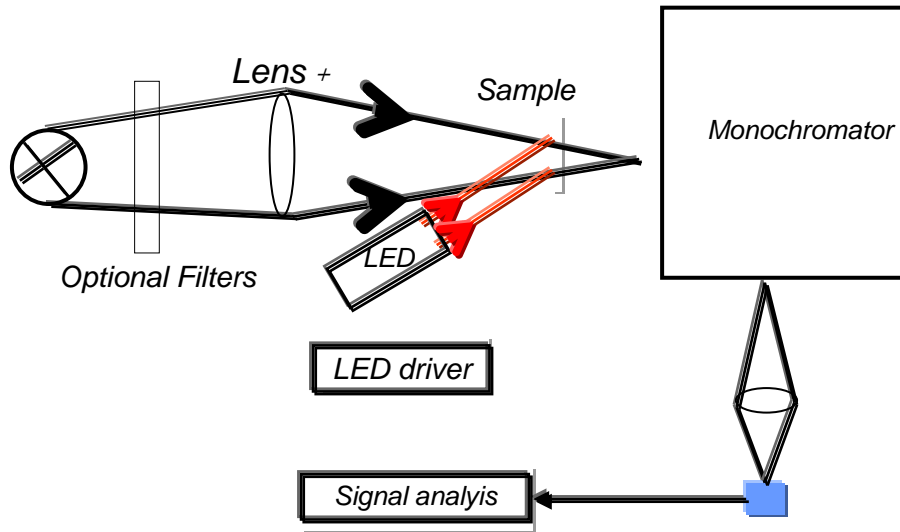
Fig. (2): Photoinduced Absorption Spectroscopy Set-up

3. Results and Discussion:

3.1. XRD Pattern

The X-ray diffraction (XRD) in figure 3 assess first the crystallinity of ZnO nanostruc-tured film (using Siemens D5000 apparatus) and shows clearly sharp and high-intensity peaks of CdS similar to those reported earlier by Y. Tak et al. [15].
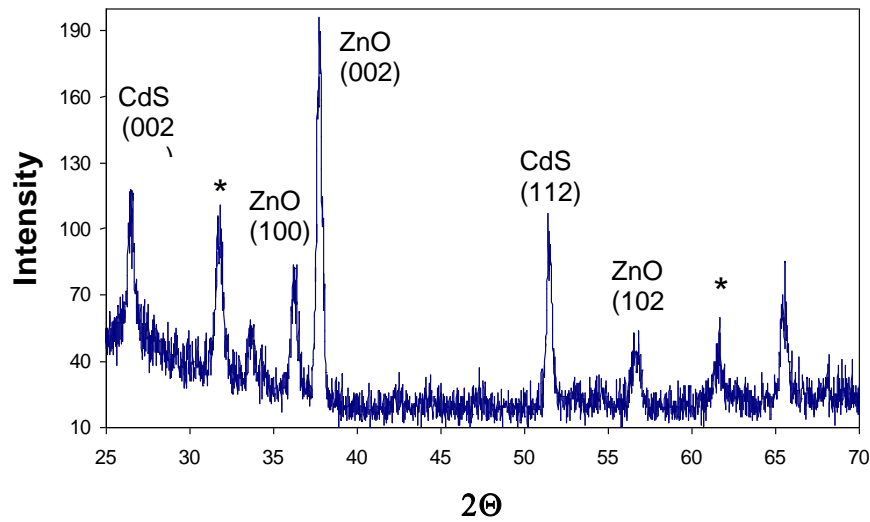

**Fig. (3):** XRD data of the as-prepared CdS/ZnO film. (*: SnO$_2$ substrate)

3.3. Absorption and IPCE Spectra:

Absorption spectra have been recorded for both ZnO film before and after CdS modification (Inset of Fig. 4). CdS sensitized ZnO samples could absorb visible light and the absorption range increased up to ~ 600 nm.

The photoelectrochemical response of the ZnO electrode, before and after modification with CdS, was evaluated by measuring the photocurrent of the electrode at va-rious excitation wavelengths. The incident photon-to-photocurrent efficiency (IPCE) was then determined from the expression (1) where I_{sc} is the short-circuit current (A/cm^2), I_{inc} is the incident light intensity

$$\text{IPCE (\%)} = 100 \times (1240 \times I_{sc})/(I_{inc}\lambda) \tag{1}$$

(W/cm^2), and λ is the excitation wavelength (nanometers). The onset of photocurrent of ZnO based electrode is seen at a wavelength below 430 nm. The photoresponse of ZnO electrode (Fig. 4A) has been extended to the visible range after CdS modification (Fig. 4b). High IPCE value have been mesasured (about 67% at 470 nm).
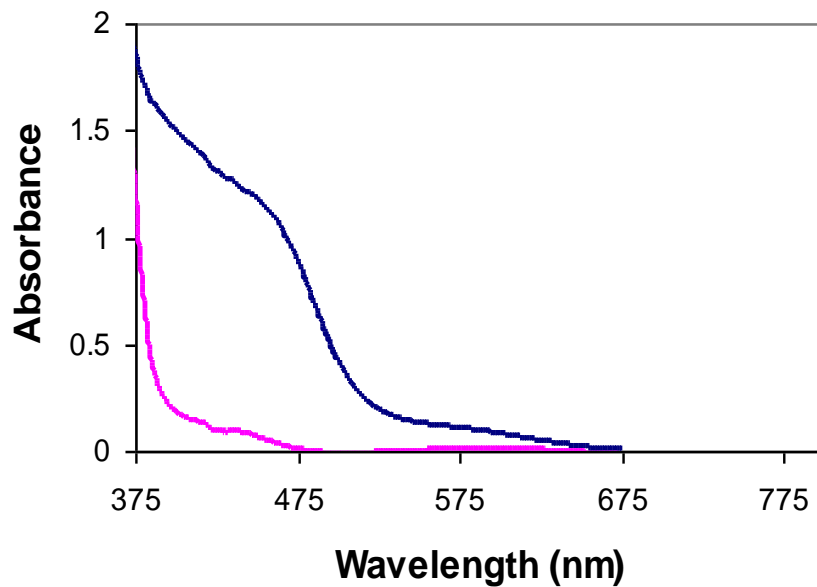
Fig. (4): Incident photon-to-current conversion efficiencies (IPCE) of ZnO Photo-electrode (A) before modification with CdS and (B) after modification with CdS. Inset: Absorption spectra of (a) ZnO particulate film and (b) CdS modified ZnO film. Electrolyte used was Na2S 0.1M, Na2SO4 0.01M.

Fig. (5) shows the anodic and cathode current behavior under dark and illumination of CdS sensitized ZnO electrode sample. The generation of anodic current is well representative behavior of an n-type semiconductor.
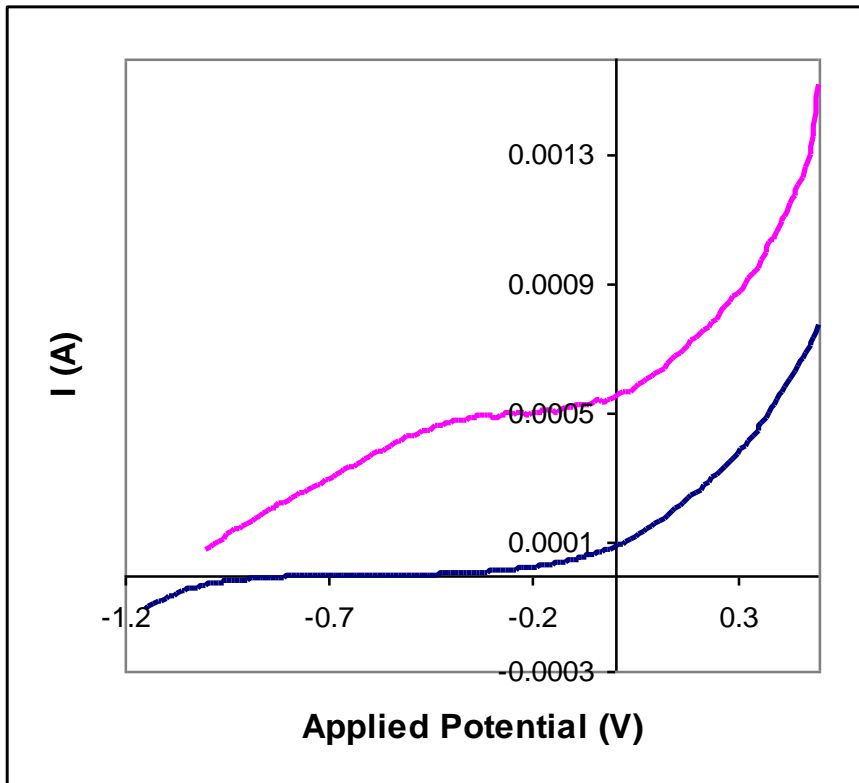

Fig. (5): Is the I-V characteristics of electrode: the traces were recorded in a dark and under 470 nm illumination. Electrolyte wasNa$_2$S 0.1M, Na$_2$SO4 0.01M

3.4. Photoinduced Absorption spectroscopy (PIA):

3.4.1. PIA spectrum

Fig. (6): shows a typical PIA spectrum of CdS modified ZnO film without electrolyte for comparison (in air). The PIA spectrum clearly reflects the differential spectrum of CdS upon formation injection of electrons into ZnO conduc-tion 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).
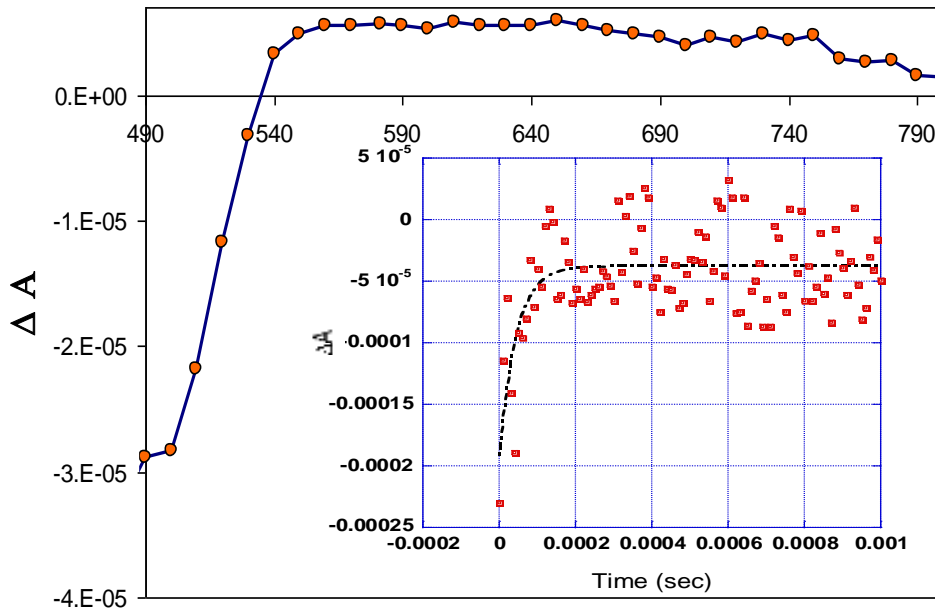
Fig. (6): Photoinduced absorption spectrum of CdS modified ZnO electrode without electrolyte (in air). The spectrum was recorded using blue ligh (460 nm) excitation (42 mW.cm^{-2}) with a modulation frequency of 9 Hz. Inset is a PIA transient absorption growth of a CdS modified ZnO electrode recorded at 500 nm.

3.4.2. 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. Inset of figure 6 shows such a PIA transient growth recorded at 500 nm. Fitting the transient growth gives a (pseudo-) first-order rate constant for bleach (growth at 500 nm) around 50 μs. This bleaching is due to hole-electron recombination which does not follow simple first-order kinetic but is characterized by a range of recombination times. This relatively fast growth proves at least a well pore filling of ZnO film by CdS particles. Contrarily to our relatively fast process that PIA has monitored, PIA can monitor even much slower processes like in the case of dye sensitized TiO$_2$ [16] and CdS sensitized TiO$_2$ in our different work submitted [17], recombination lifetimes are around 9 ms and 11 ms, respecttively. We may conclude that in our system case (CdS/ZnO) the lower recombine-tion process delays up to less than a millisecond. In the case of a dye (D719) sensitized TiO$_2$ compared to D719 sensitized ZnO electrodes [16], although TiO$_2$ and ZnO have quite different electronic structure of their respective

conduction band, it was observed identical recombination rates for both semiconductors. They concluded that the mole-cular state of the sensitized dye has a greater influence on the back-electron transfer on the kinetics than the conduction band electron state of the semiconductors. In our case, the same sensitizer on both ZnO (this work) and TiO$_2$ (submitted work ref.17) is an inorganic semiconductor (CdS). This latter seems has lower influence on the back-electron transfer on the kinetics than the conduction band electron state of the semiconductors.

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 lower costly compared to laser flash photolysis. Unlike dye molecule sensiti-zers, the conduction band electron state of ZnO or TiO$_2$ based photolectrode has greater influence on the back-electron transfer on the kinetics than the conduction band electron state of CdS semiconductor.

Aknowledgements:

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