

## Research Article

# Comparative Study between Dye-Sensitized and CdS Quantum-Dots-Sensitized TiO<sub>2</sub> Solar Cells Using Photoinduced Absorption Spectroscopy

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Two 8  $\mu\text{m}$  thick TiO<sub>2</sub> photoelectrodes have been sensitized separately by N719 dye molecules and CdS quantum dots for a comparison study. Photoinduced absorption (PIA) spectroscopy was employed to investigate the mechanistic properties of electrons under illumination conditions comparable to sunlight. The PIA spectrum of both electrodes (in the presence of electrolyte) is due to electrons in TiO<sub>2</sub> and iodine radicals I<sub>2</sub><sup>-</sup> in the electrolyte. In the absence of redox electrolyte, both electrodes show long-lived photoinduced charge-separation with lifetime in a millisecond range (8.5 ms for Q-dot-sensitized TiO<sub>2</sub> and 11.5 ms for dye-sensitized TiO<sub>2</sub>).

## 1. Introduction

Nanostructured solar cells sensitized by organic dyes (DSSCs) [1–6] or by inorganic short bandgap semiconductors (also called quantum dots, QDs) [7–10] have attracted a great deal of interest. They are capable to obtain efficient conversion of solar energy to electricity at a low cost comparative to conventional semiconductor photovoltaic devices [11, 12]. The approach of using semiconductor colloids for the design of optically transparent thin semiconductor films is considered as a unique and an alternative for the amorphous silicon solar cells. Using this approach, dye-sensitized solar cells based on bi- and polypyridyl ruthenium complexes have achieved solar-to-electrical energy conversion efficiencies of 10–11% under AM 1.5 irradiation [1–3]. On the other hand, wide bandgap semiconductors have also been sensitized by short bandgap quantum dots (CdSe/TiO<sub>2</sub> [6], CdS/TiO<sub>2</sub>-SnO<sub>2</sub> [10]) as alternative to dye sensitization. Vogel and coworkers [8] have investigated the sensitization of nanoporous TiO<sub>2</sub>, ZnO, and so forth by Q-sized CdS. Photocurrent quantum yields up to 80% and open-circuit

voltages up to 1 V range were obtained. In contrast with the dye-sensitized solar cells, fundamental understanding of factors controlling the interfacial electron transfer reactions in QD sensitized solar cells is limited.

In this paper, we report photoinduced absorption spectroscopy of an organic (N719 dye)-sensitized and inorganic (Q-dot CdS) semiconductor-sensitized TiO<sub>2</sub> (8  $\mu\text{m}$ ) photoelectrodes under illumination conditions comparable to sunlight in order to compare the mechanistic properties of electrons.

## 2. Experimental

**2.1. Preparation of Nanostructured TiO<sub>2</sub> Films.** We take care more about similarity in TiO<sub>2</sub> thicknesses in order to insure the same length of e-transfer from different sensitizer to external circuit. Before coating conducting glass ITO with TiO<sub>2</sub> nanoparticles, first we coated a blocking layer by immersing ITO plates into 0.02 M TiCl<sub>4</sub> solution at 70°C for 30 min. TiO<sub>2</sub> layer was made with EPFL paste by the Doctor Blade technique. Working electrodes were then sintered at

450°C for 30 min using heat gun and cooled down to room temperature.

**2.2. Surface Modification of TiO<sub>2</sub> by Quantum Dots CdS.** TiO<sub>2</sub> metal oxide nanostructured 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. Surface Modification of TiO<sub>2</sub> by N719 Dye.** The relatively hot (~80°C) TiO<sub>2</sub> nanostructured electrodes were immersed in a 0.5 mM ethanolic solution of N719 dye ((TBA)<sub>2</sub>-*cis*-Ru(Hdcbpy)<sub>2</sub>-(NCS)<sub>2</sub>, Solaronix, Switzerland) and left for about 2 hours only. (There was no need for overnight adsorption, just a reasonable adsorption to be able to investigate a good mechanistic study.)

**2.4. Characterization Methods.** UV-Vis spectra were recorded using a Hewlett-Packard 8453 diode array spectrometer. For PIA spectroscopy (Figure 1), excitation of the sample was provided by light from a blue LED (Luxeon Star 1 W, Royal Blue, 470 nm), which was square-wave modulated (on/off) by electronical 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. UV-Vis Absorption Spectra.** Figure 2 shows UV-Vis absorption spectra of bare TiO<sub>2</sub> film, CdS-sensitized, and N719-sensitized TiO<sub>2</sub> films. It is clear that CdS and N719 dye both have extended further the absorption into the visible up to 600 and 750 nm, respectively.

**3.2. PIA Spectroscopy of CdS/TiO<sub>2</sub> System.** Figure 3 shows typical PIA spectra of the CdS-nanostructured TiO<sub>2</sub> system. In the absence of the redox electrolyte, the PIA spectrum clearly reflects the differential spectrum of CdS upon formation of the oxidized CdS (or hole formation), with a bleach of the main absorption band at 470 nm. The PIA spectrum after the onset of 550 nm should reveal the spectrum of injected electrons into TiO<sub>2</sub> conduction band with a peak around 650 nm compared to CdS alone on ITO. In the later, large recombination occurs when it failed to be transported far away from the existing created holes. When the redox

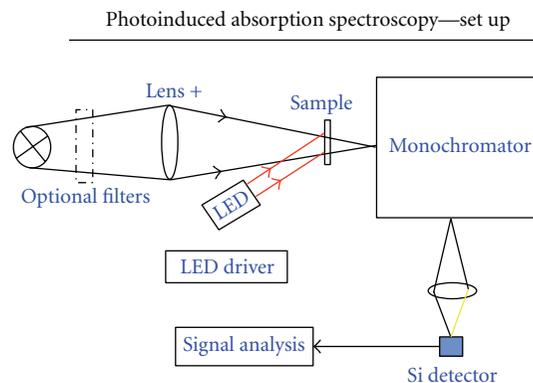


FIGURE 1: Schematic drawing of the photoinduced absorption spectroscopy setup.

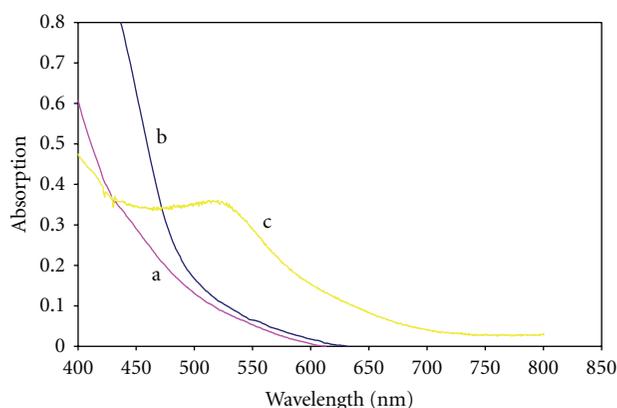


FIGURE 2: Absorption spectra of (a) TiO<sub>2</sub> particulate film, (b) CdS-adsorbed TiO<sub>2</sub> film, and (c) N719 dye-adsorbed TiO<sub>2</sub> film.

electrolyte is added, the PIA spectrum changes significantly. The oxidized CdS is rapidly reduced by the electrolyte, and thus little bleaching is observed under 530 nm. The broad absorption at wavelengths larger than 600 nm can be attributed to injected electrons in TiO<sub>2</sub>.

In Figure 4, PIA spectra of CdS-adsorbed TiO<sub>2</sub> electrodes in the presence of electrolyte and under open circuit are shown. When the redox electrolyte, composed of 0.7 M LiI and 0.05 M I<sub>2</sub> in 3MPN, is added, the PIA spectrum changes significantly. The absorption increases up to 600 nm and remains almost flat up to 800 nm. We attribute the PIA signals to electrons in nanostructured TiO<sub>2</sub> and iodine radicals (I<sub>2</sub><sup>-</sup>) [13]. Triiodide does not absorb at wavelengths larger than 600 nm, while I<sub>2</sub><sup>-</sup> exhibits a broad absorption peak at 750 nm with an extinction coefficient of 2200 M<sup>-1</sup> [14].

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 5 shows such a typical PIA transient decay recorded at 700 nm. Pseudo-first-order rate constant for e-injection from CdS conduction band to TiO<sub>2</sub> conduction band was about 8.5 ms approximately which does not follow simple first-order kinetic but is characterized by a range of injection times. This

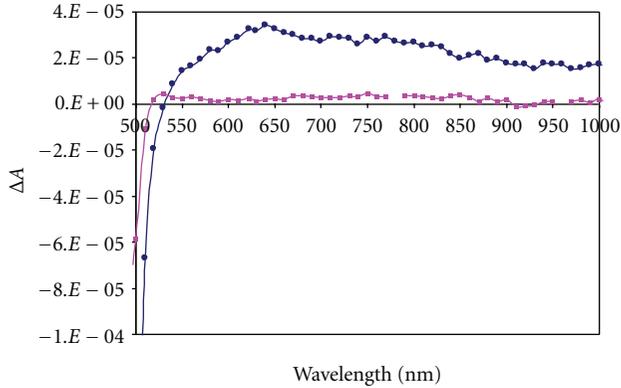


FIGURE 3: Photoinduced absorption (PIA) spectra of quantum dots CdS-modified  $\text{TiO}_2$ -NP electrode (circle) in air and CdS on conducting glass ITO (square). The spectra were recorded using blue light (460 nm) excitation ( $42 \text{ mW} \cdot \text{cm}^{-2}$ ) with a modulation frequency of 9 Hz.

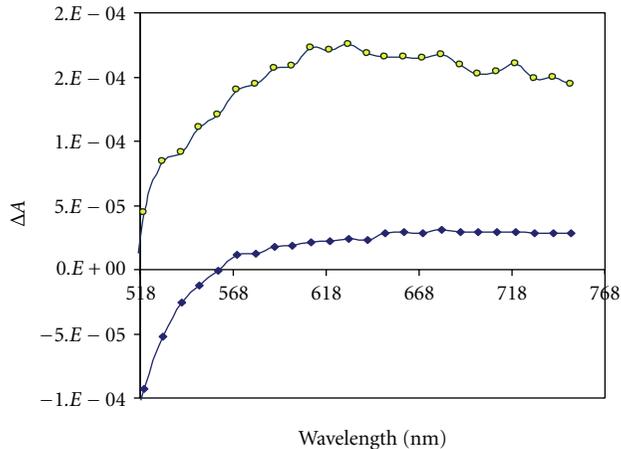


FIGURE 4: PIA spectra of CdS adsorbed at a nanostructured  $\text{TiO}_2$  film. Filled squares: in air; filled circles: in the presence of electrolyte. The spectra were recorded using blue light (460 nm) excitation ( $42 \text{ mW cm}^{-2}$ ) with a modulation frequency of 9 Hz.

relatively fast decay proves at least a well pore filling of  $\text{TiO}_2$  film by ultrafine CdS particles.

**3.3. PIA Spectroscopy of N719/ $\text{TiO}_2$  System.** Figure 6 shows typical PIA spectra of the dye-sensitized  $\text{TiO}_2$  system. In the absence of the redox electrolyte (Figure 6(a)), the PIA spectrum clearly reflects the differential spectrum of N719 upon formation of the oxidized dye, with a bleach of the ground state MLCT (metal-to-ligand charge transfer) main absorption band at 540 nm and an absorption peak at 780 nm (Figure 6(a)) which corresponds to MLCT transitions. Electrons in the  $\text{TiO}_2$  will also be present in the PIA. When the redox electrolyte composed of 0.7 M LiI and 0.05 M  $\text{I}_2$  in 3MPN is added (Figure 6(b)), the PIA spectrum changes significantly. The oxidized dye is rapidly reduced by

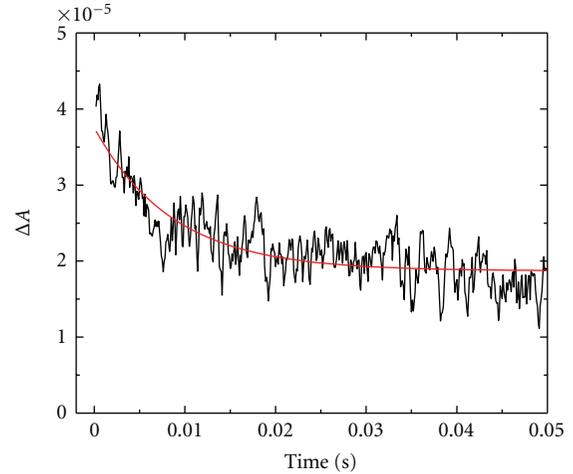


FIGURE 5: PIA decay transient absorption of Q-dots CdS-modified  $\text{TiO}_2$  electrode after excitation with blue light ( $11 \text{ mW/cm}^2$ ) recorded at 600 nm using a sampling rate of  $10^3 \text{ s}^{-1}$  and averaged 100 times.

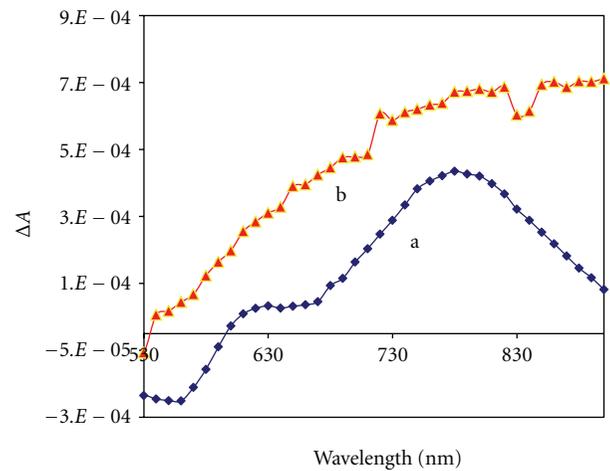
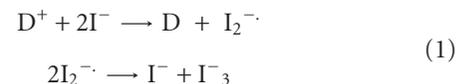


FIGURE 6: PIA spectra of N719 adsorbed at a nanostructured  $\text{TiO}_2$  film. (a) In air; (b) in the presence of electrolyte, 0.7 M LiI and 0.05 M  $\text{I}_2$  in 3MPN. The spectra were recorded using blue light (460 nm) excitation ( $42 \text{ mW cm}^{-2}$ ) with a modulation frequency of 9 Hz. With redox electrolyte (0.7 M LiI and 0.05 M  $\text{I}_2$  in 3MPN);  $f = 193 \text{ Hz}$ .

the iodide in the electrolyte, presumably according to the following reactions [15–17].



The resulting PIA spectrum should reveal the spectrum of electrons in  $\text{TiO}_2$  as well as triiodide in the electrolyte. The gradually increasing absorption with wavelengths larger than 600 nm can be attributed to electrons in  $\text{TiO}_2$  and iodine radicals ( $\text{I}_2^-$ ) [13]. Electrons in nanostructured  $\text{TiO}_2$  exhibit a very broad absorption and have an extinction coefficient of about  $1000 \text{ M}^{-1} \text{ cm}^{-1}$  at 800 nm [18]. Triiodide does not absorb at wavelengths larger than

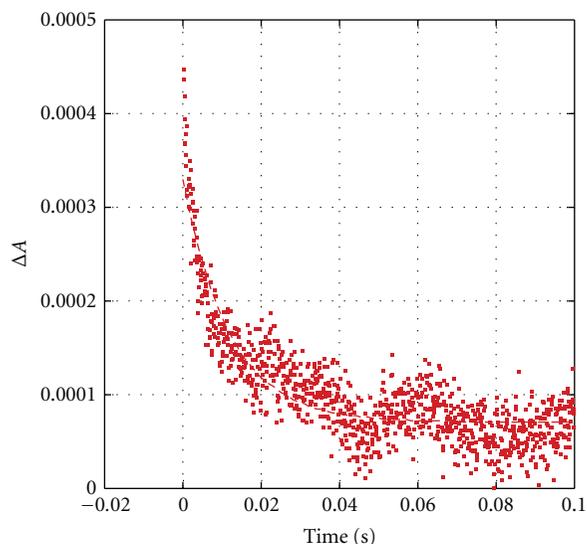


FIGURE 7: PIA decay transient absorption of N719 dye-modified  $\text{TiO}_2$  electrode in the absence of electrolyte after excitation with blue light ( $11 \text{ mW}/\text{cm}^2$ ) recorded at  $750 \text{ nm}$ , using a sampling rate of  $10^3 \text{ s}^{-1}$  and averaged 100 times.

$600 \text{ nm}$ , while  $\text{I}_2^-$  exhibits a broad absorption peak around  $750 \text{ nm}$  with an extinction coefficient of  $2200 \text{ M}^{-1} \text{ cm}^{-1}$ . Recently, it was shown in pulsed nanosecond laser studies that  $\text{I}_2^-$  is an important long-lived intermediate in the dye-sensitized solar cell [17, 19]. The PIA spectrum of Figure 6(b) has contributions of both electrons and  $\text{I}_2^-$  radicals.

Figure 7 shows typical PIA transient decay recorded at  $750 \text{ nm}$ . Pseudo-first-order rate constant for e-injection from dye excited state to  $\text{TiO}_2$  conduction band was about  $12 \text{ ms}$ . This does not follow simple first-order kinetic, but is characterized by a range of injection times. This has been explained by trapping of electrons within the  $\text{TiO}_2$  nanocrystals [16]. Similar pseudo-first-order rate constant of  $11 \text{ ms}$  has been measured using PIA transient decay for N719/ $\text{TiO}_2$  for electron recombination [20]. This relatively fast decay proves at least a well pore filling of  $\text{TiO}_2$  film by N719 dye molecules. The  $\text{CdS}/\text{TiO}_2$  system shows its first-order rate constant for e-injection of  $8.5 \text{ ms}$  which is relatively faster than that of the N719/ $\text{TiO}_2$  system ( $12 \text{ ms}$ ). This relatively faster kinetic process seen in  $\text{CdS}/\text{TiO}_2$  system may reflect its faster process of high kinetic processes in the range of picoseconds already observed with this system [21]. 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 oxidized dye molecules.

#### 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 cheaper compared to laser flash photolysis. The relatively faster kinetic process observed in  $\text{CdS}/\text{TiO}_2$  system compared to N719/ $\text{TiO}_2$  system could reflect its faster process of high kinetic processes in the range of picoseconds already observed.

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