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FeS_2-QUANTUM DOTS-AND DYE-SENSITIZED SnO_2 SOLAR CELLS: PHOTOVOLTAIC PERFORMANCE AND DYNAMIC COMPARATIVE STUDIES

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Two 4μm thick SnO_2 photoelectrodes have been sensitized separately by N719 dye molecules and FeS_2 quantum dots for a comparison study. PIA (photoinduced absorption spectroscopy), a multipurpose tool in the study of dye-sensitized solar cells, is also used to study quantum-dot based solar cells. PIA was employed to investigate the mechanistic properties of electrons under illumination conditions comparable to sunlight. PIA transient decays of both electrodes (in air) are attributed to hole-electron recombination or dye regeneration and does not follow simple first-order kinetic but is characterized by a range of recombination times. Incident-**(**Pseudo-) first-order rate constants for bleach at 420 nm and 550 nm are of approximately 0.15 ms and 19 us for N719 and FeS_2 based solar cells, respectively. Photon-to-Current Efficiencies (IPCE) at 400 nm and 540 nm are 20 and 22%, respectively. Both short recombination rates constants and lower performances of both cells can be explained by the lower valence band of SnO_2 electrodes and the presence of FeS_2 phases other than the photoactive pyrite phase.

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1. Introduction

Nanostructured solar cells sensitized by organic dyes (DSSC)[1-4] or by inorganic short band gap semiconductors (also called quantum dots, QDs)[5-8] have attracted a great deal of interest because of their efficient conversion of solar energy to electricity at a low cost compared to conventional semiconductor photovoltaic devices. 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. With this approach, DSSC's based on bi- and polypyridyl ruthenium complexes have achieved solar-to-electrical energy conversion efficiencies of 10-11% under AM 1.5 irradiation [1]. On the other hand, wide band gap semiconductors have also been sensitized by short band gap quantum dots ($CdSe/TiO$[4], CdS/TiO_2-SnO_2[8]) as alternative to dye sensitization. Vogel and co-workers[6] have investigated the sensitization of nanoporous TiO_2, ZnO, etc 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.

We reported, previously, the preparation of highly porous and transparent SnO_2 films on a conducting glass substrate by employing colloids of 3-5 nm diameter[2]. SnO_2 is a stable large bandgap semiconductor (Eg = 3.2 eV) and has been widely used in many practical devices (e.g., electrochromic thermal windows). Although it does not respond to visible light excitation, it can be sensitized with organic dyes. Chemical vapor deposition technique has been the choice for the deposition of thin SnO_2 films. But such films show poor affinity towards dye-adsorption. However, the semiconductor films prepared from colloids strongly adsorb both organic and

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inorganic sensitizers. This is because of their highly porous nature as well as its ability to interact with dye molecules from solution. Such dye-modified films have important applications in developing photoelectrochemical cells.

Contrary of our work done previously[2], instead of using laser flash photolysis for fast kinetics studies, we are reporting in this work for the first time a study of slow kinetic processes on ruthenium complex (N719) and FeS_2 Q-dots modified SnO_2(4µm) electrodes, separately, employing photoinduced absorption spectroscopy (PIA) under illumination conditions comparable to sunlight in order to compare the mechanistic properties of electrons. The study will include photoelectrochemical measurements too.

2. Experimental details

2.1 Preparation of Nanostructured SnO_2 Films

As described in a previous paper (Bedja et al.)[2], an aliquot of 1 mL of concentrated SnO_2 suspension was diluted with 97 mL of water and 2 mL of NH_4OH. Addition of NH_4OH was essential for controlling the stability of the colloids and improving the adsorption properties of the film. A small aliquot (usually 0.2 ml) of the diluted SnO_2 colloidal suspension was applied to a conducting glass surface of 0.8 x 2 cm^2 (TEC8, Pilkington) and was dried in air on a warm plate. The SnO_2 colloid-coated glass plates were then annealed at 450 °C for 1 h. The semiconductor thin films annealed at 450 °C adhered strongly to the glass surface and were stable in the pH range 1-13. Film thickness (4 µm) was determined by profilometry.

2.2 Surface Modification of SnO_2 by Quantum Dots FeS_2

SnO_2 metal oxide nanostructured films are modified by quantum dots FeS_2 by a similar method described previously by Chatzitheodorou[9] with some little changes. The clean SnO_2 electrode was dipped in the solution of sulfur (0.02 M) in xylene, followed by immersion in a solution of iron pentacarbonyl (0.01M) in xylene at the temperature close to 139 °C. The whole experiment was carried out under a nitrogen atmosphere. This procedure was repeated several times until a clear dark color appears. The new in this procedure is the heating of the electrodes at 125 °C for about 5 min after washing with xylene solvent between two immersions.

2.3 Surface Modification of SnO_2 by N719 dye

The method employed for the modification of the SnO_2 electrode with $Ru(dcby)_2(NCS)$ was similar to that employed for the modification of TiO_2 particulate films with the derivatives of a ruthenium complex.[3] Warm SnO_2 plates (70°C) were immersed overnight in an ethanolic solution of $Ru(dcby)_2(NCS)$. The electrodes were then washed with acetonitrile and used in photoelectrochemical measurements. The yellow orange coloration of the film confirmed the adsorption of the dye.

2.4 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 Figure (1) [alsoin Ref.10]. Two electrodes were inserted consisting of a reference (Ag/-AgCl) and counter (Pt wire) electrodes. 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.[2]

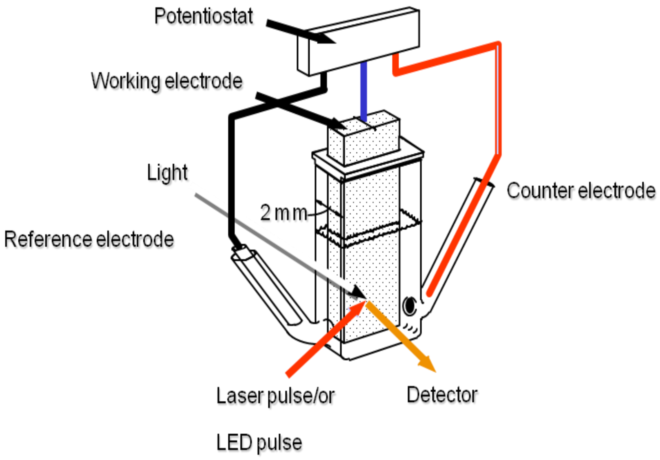

Fig. 1 Tricompartimental Quartz photoelectrochemical Cell.

For PIA spectroscopy, 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 electronically 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 amplifiervia 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.

3. Results and discussion

3.1 UV-VIS Absorption Spectra

Figure 2 shows UV-Vis absorption spectra of bare SnO_2 film, FeS_2-sensitized and N719-sensitized SnO_2 films. It is clear that FeS_2 and N719 dye both have extended further the absorption into the visible up to 600 and 750 nm, respectively. The low energy tail in FeS_2 absorption (Figure 2b) may come predominately from larger particles. However, the high energy absorption shoulders are probably originated from ultra-small particles. Because FeS_2 has a small band gap around 1 eV,[11] we would expect a larger wavelength absorption onset near IR. This can be explained in a separate work[10] where it has been found that FeS_2 presents indirect bandgap of energy between 1.6 and 2.0 eV, higher energies which are particular of ultra-fine particles of FeS_2.

To mention, during deposition of FeS_2 onto SnO_2 film, the appearance of the electrode changed from white or transparent to a brown / grey color, which clearly indicates FeS_2 adsorption as confirmed by the XRD study on FeS_2 adsorbed TiO_2 powder in our previous work.[10] In that work, a number of much smaller and rather poorly resolved peaks also appeared. Possible origin of these peaks are FeS_2 that exists in a cubic phase (pyrite) and an orthorhombic phase (marcasite). Furthermore hexagonal FeS (troilite), FeO etc., may also exist.

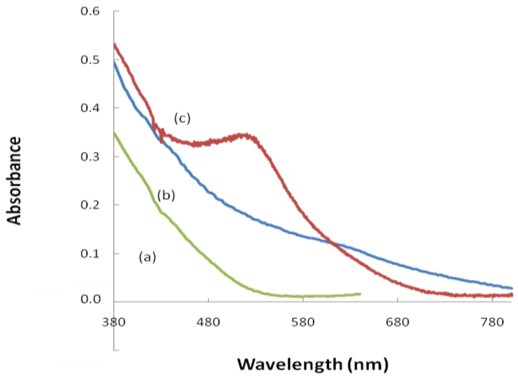

Fig. 2 Absorption spectra of (a) SnO_2 particulate film and (b) FeS_2 sensitized SnO_2 films and (c) N719 dye sensitized-SnO_2 film

3.2 Photocurrent Action Spectra

The photoelectrochemical response of the SnO_2 particulate film was evaluated by measuring the photocurrent of FeS_2 or N719 adsorbed FTO/SnO_2 at various excitation wavelengths. The incident photon-to-photocurrent efficiency (IPCE) was then determined from the expression (1)

$$IPCE\ (\%) = 100x(1240I_{sc})/(P.\lambda) \qquad (1)$$

Where I_{sc}, is the short-circuit current (A/cm^2), P is the incident light power intensity (W/-cm^2), and λ is the excitation wavelength (nanometers).

Similarly, IPCE spectra (Figure 3) show essentially the same trend as the absorption spectra. The photoresponse of SnO_2 film has been extended to the visible range after FeS_2 and N719 dye modification. Although the FeS_2/SnO_2 electrode shows strong visible absorption in wavelengths longer than 580 nm (Figure 2b), no photoresponse (IPCE) was detected at these wavelengths (Figure 3), which suggest that only small quantum-sized FeS_2 particles play a dominant role in the spectral sensitization on SnO_2 particles, while larger particles have less or no contribution.

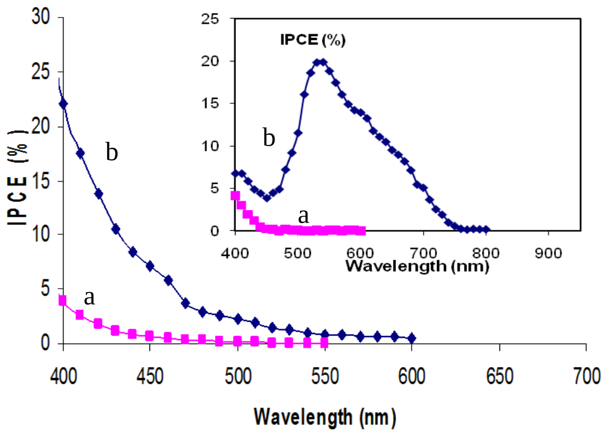

Fig. 3 Incident photon-to-current conversion efficiencies (IPCE) of (a) SnO_2 particulate photoelectrode and (b) quantum dots FeS_2 adsorbed on SnO_2 photoelectrode. Inset is IPCE of (a) SnO_2 particulate photoelectrode and (b) N719 dye adsorbed on SnO_2 photoelectrode (electrolyte Na_2S 0.1M, Na_2SO_4 0.01M)

The lower performance of the electrode can be explained by the presence of FeS_2 phases other than the photoactive pyrite phase, as evidenced from XRD study in our separate work on TiO_2.[10] A maximum IPCE of 20% was observed for N719/SnO_2 based cell. If we account for the unabsorbed light (-50%) the photon conversion efficiency is likely to be twice the observed value. This lower IPCE obtained compared to TiO_2 based cell[1,2] is due probably to lower Voc (due to lower Fermi Level by 0.5 V) and also to difficulty of obtaining a thick particulate SnO_2 film.

3.2PIA Spectroscopy of FeS_2 and N719 sensitized SnO_2 Systems

Figure 4 shows a typical PIA spectrum of the FeS_2–nanostructured SnO_2 system. In the absence of the redox electrolyte, the PIA spectrum clearly reflects the differential spectrum of FeS_2 upon formation of oxidized FeS_2 (or hole formation), with a bleach of the main absorption band at 460 nm. The PIA spectrum after the onset of 550 nm should reveal the spectrum of injected electrons into TiO_2 conduction band with a peak around 600-650 nm. This positive absorption at large wavelengths prove that photogenerated electrons have been well injected into SnO_2 conduction band and this bleaching does not come from relaxation process because the transient decay given by Figure 5 is in the order of micro-to millisecond. Relaxation processes usually happen in nanosecond time scales

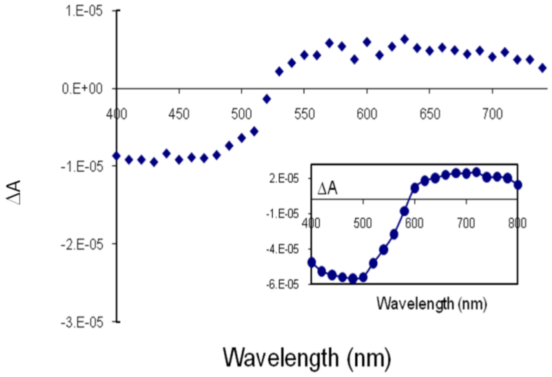

Fig. 4 Photoinduced absorption (PIA) spectrum of quantum dots FeS modified SnO2 electrode in air. Inset: PIA spectrum of quantum dots N719 modified SnO2 electrode in air. The spectra were recorded using blue light (460 nm) excitation (42 mW.cm-2) with a modulation frequency of 9 Hz

It has to be noted that despite low absorption magnitude of FeS_2 on very thin SnO_2 film, still we could measure PIA spectrum while using low laser energy diode. This means a large density of electrons could decay freely, in contrary with trapped ones or in presence of large number of boundaries. Figure 4 Inset shows a PIA spectrum of the N719 dye–sensitized SnO_2 film. Similarly to PIA spectrum of FeS_2 on SnO_2 film (Figure 4), here, a bleach of the ground state MLCT (Metal-to-ligand charge transfer) main absorption band is swell identified at 540 nm and an absorption peak at 780 nm (Figure 4 inset) which corresponds to MLCT transitions. For both FeS_2 and N719 dye, the remaining holes in oxidized species absorb light and because valence band electrons are missing, an apparent increase in bandgap is seen (bleach, Moss-Burstein shift) .Electrons in nanostructured SnO_2 film exhibit a very broad absorption, similar to that in TiO_2.[10]

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 a typical PIA transient decay recorded at 420 nm for N719 sensitized SnO_2 system. Fitting the transient growth gives a (pseudo-) first-order rate constant for the bleach (growth at 420 nm) of about 150 µs. For solar cell performance the pseudo-first-order rate constant under steady-state conditions is a relevant parameter, as it can give a direct information on possible recombination losses due to the reaction of electrons with oxidized dye molecules. This bleaching is due to electron recombination with oxidative dye which does not follow simple first-order kinetic but is characterized by a range of recombination times, which is due to existence of trapping sites in SnO_2. This relatively fast growth proves at least a well pore filling of SnO_2 film by N719 molecule. This decay time measured is well in the order of recombination or dye regeneration times in ruthenium based DSSC cells.[11] A much higher pseudo- first-order rate constant of 11 ms has been measured using PIA transient decay for N719/TiO_2 for electron recombination.[12] This difference with N719-SnO_2 system lifetime decay of electron recombination by almost two-fold times is most probably due to more positive energy position of SnO_2 valence by 0.5V.

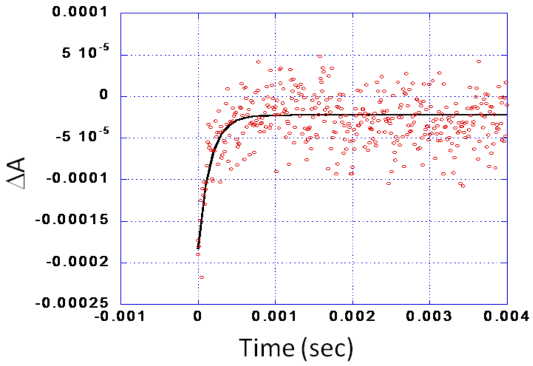

Fig. 5 Photoinduced absorption transient decay of N719 dye sensitized- SnO_2 electrode in air. The spectrum was recorded using blue ligh (460 nm) excitation (42 mW.cm^{-2}) with a modulation frequency of 9 Hz.

Figure 6 shows a typical PIA transient decay recorded at 550 nm for FeS_2 sensitized SnO_2 system. Fitting the transient growth gives a **(**pseudo-) first-order rate constant for bleach (growth at 550 nm) of about 19 µs**.** Similarly to N719**,** this bleaching is due to electron-hole recombination which does not follow simple first-order kinetic but is characterized by a range of recombination times, due to existence of multiple trapping sites. This fast growth proves at least a well pore filling of SnO_2 film by FeS_2 nanoparticles.

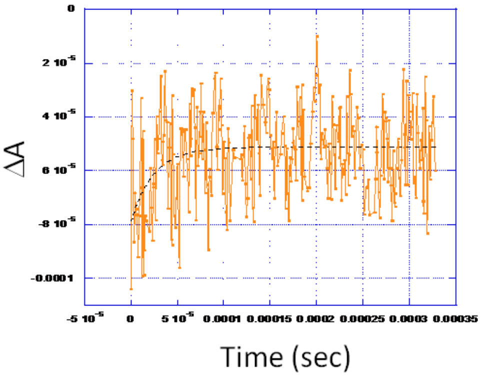

Fig. 6 PIA decay transient Absorption of quantum dots FeS_2 modified SnO_2 electrode after excitation with blue light (11 mW/cm2) recorded at 780 nm, using a sampling rate of 10^3 s^{-1} and averaged 100 times.

4. Conclusion

Photoinduced absorption spectroscopy where the excitation is provided by an on/off monochromatic light source can give direct information on 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 cheaper compared to laser flash photolysis. Both short recombination rates constants and lower performances of both cells can be explained by the lower valence band of SnO_2 electrodes and the presence of FeS_2 phases other than the photoactive pyrite phase for FeS_2-SnO_2 system.

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