

# FeS<sub>2</sub> Quantum Dots Sensitized Nanostructured SnO<sub>2</sub> Solar Cell: Photoelectrochemical and Photoinduced Absorption Spectroscopy Studies

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*Thin transparent films of SnO<sub>2</sub> semiconductor have been prepared from 3 nm diameter colloids and were used to prepare nanoparticulate electrodes. FeS<sub>2</sub> ultra fine particles were coated on a SnO<sub>2</sub> electrode by low temperature chemical reaction of iron pentacarbonyl with sulfur in xylene. Both the optical absorption and the photocurrent action spectrum of SnO<sub>2</sub> electrode were extended to visible region, upon coating with FeS<sub>2</sub> particles, by sensitization mechanism. Quantum size effect is manifested by the observation of a blue shift in both absorption and photocurrent action spectrum. PIA (Photoinduced absorption spectroscopy), 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 nanostructured electrode. Oxidized quantum dots can easily be obtained from the spectra of transient species, and their kinetics can be explored using time-resolved techniques. Incident-Photon-to-Current Efficiency about 22% has been obtained at 400 nm excitation.*

## 1. Introduction

A great effort is being done to obtain efficient and inexpensive organic and inorganic solar cells. The approach of using semiconductor colloids for the design of optically transparent thin semiconductor films is considered as the unique and the alternative for the amorphous silicon solar cells. Under this approach, films made from colloidal metal oxide semiconductors which have large band gap have retained a large attention. This is primarily because they are quite stable and because they predominantly absorb in the UV. The usefulness of these systems for solar cell applications was made possible by a basic principle namely, sensitization of their semiconductor surfaces into visible region either by organic dyes (dye sensitization)[1-4] or by inorganic

short band gap semiconductors also called quantum dots (QDs) (semiconductor sensitization) [5-8]. 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]. In the other hand, wide band gap semiconductors have been sensitized by short band gap (quantum dots) semiconductor materials (CdSe/TiO<sub>2</sub>[5], CdS/TiO<sub>2</sub>-SnO<sub>2</sub>[8]) as alternative to dye sensitization. Vogel and co-workers [6] have investigated the sensitization of nanoporous TiO<sub>2</sub>, ZnO, SnO<sub>2</sub>, etc..by quantum-sized CdS, PbS, Photocurrent quantum yields of up to nearly 80% and open circuit voltages up to 1 V range were obtained. In contrast with the dye sensitized solar cells, fundamental understanding for the factors controlling the interfacial electron transfer reactions is limited.

Short-band gap semiconductor FeS<sub>2</sub> (Pyrite) is another favorable candidate photosensitization material because of its environmental compatibility, high stability toward photocorrosion as well as very good absorption in the visible region of the solar spectrum. The pyrite polymorph of iron disulfide is of particular interest, and shows promise for solar energy conversion devices in both photoelectrochemical and photovoltaic solar cells[9,10] and solid state solar cells[11] due to its favorable solid state properties[12]. Ennaoui et al. have reported [12] interesting photoresponse of modified polycrystalline TiO<sub>2</sub> electrode with FeS<sub>2</sub> using CVD method. Y. Shen et al. have recently [13] reported a method of modification of TiO<sub>2</sub> large band gap (Degussa P25) by quantum sized FeS<sub>2</sub> particles by a similar procedure described originally by Chatzitheodorou [14]. They have reported an Incident-photon-to current efficiency of 25% at 400 nm excitation.

We reported, previously, the preparation of highly porous and transparent SnO<sub>2</sub> films on a conducting glass substrate by employing colloids of 3-5 nm diameter [2]. SnO<sub>2</sub> is a stable large bandgap semiconductor (E<sub>g</sub> = 3.6 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<sub>2</sub> films. But such films show poor affinity towards dye-adsorption. However, the semiconductor films prepared from colloids strongly adsorb both organic and 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.

In this work, we report a modification of SnO<sub>2</sub> metal oxide nanostructured films by quantum dots FeS<sub>2</sub> by a similar method described previously by Chatzitheodorou [14] on TiO<sub>2</sub> films. Our results will describe photoelectrochemical properties and photoinduced absorption spectroscopy of SnO<sub>2</sub> modified FeS<sub>2</sub> quantum dots.

## 2. Experimental:

### 2.1. Preparation of Nanostructured SnO<sub>2</sub> Films:

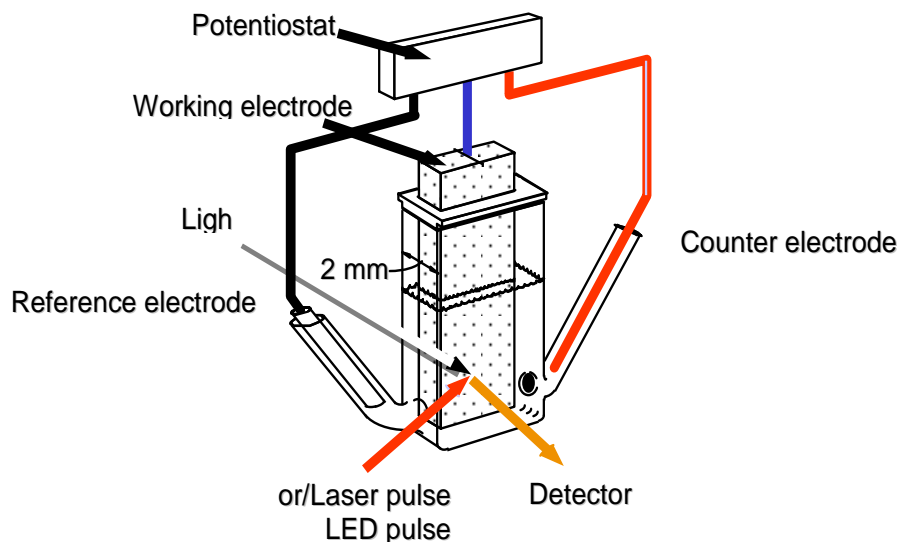
As described in a previous paper, Bedja et al [2], an aliquot of 1 mL of concentrated SnO<sub>2</sub> suspension was diluted with 97 mL of water and 2 mL of NH<sub>4</sub>OH. Addition of NH<sub>4</sub>OH was essential for controlling the stability of the colloids and improving the adsorption properties of the film. A small aliquot (usually 0.2 ml) of the diluted SnO<sub>2</sub> colloidal suspension was applied to a conducting glass surface of 0.8 x 2 cm<sup>2</sup> (TEC8, Pilkington) and was dried in air on a warm plate. The SnO<sub>2</sub> 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 (3-4 μm) was determined by profilometry.

### 2.2. Surface Modification of SnO<sub>2</sub> by Quantum Dots F2S2

SnO<sub>2</sub> metal oxide nano-structured films are modified by quantum dots FeS<sub>2</sub> by a similar method described previously by Chatzitheodorou [14] with a little change. The clean SnO<sub>2</sub> 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. 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.19]. Two electro-des were inserted consisting of a reference (Ag/-AgCl) and counter (Pt wire) electrodes.



**Fig. (1):** Tricompartimental Quartz photoelectrochemical Cell.

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 [15].

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 electrical 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<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 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.

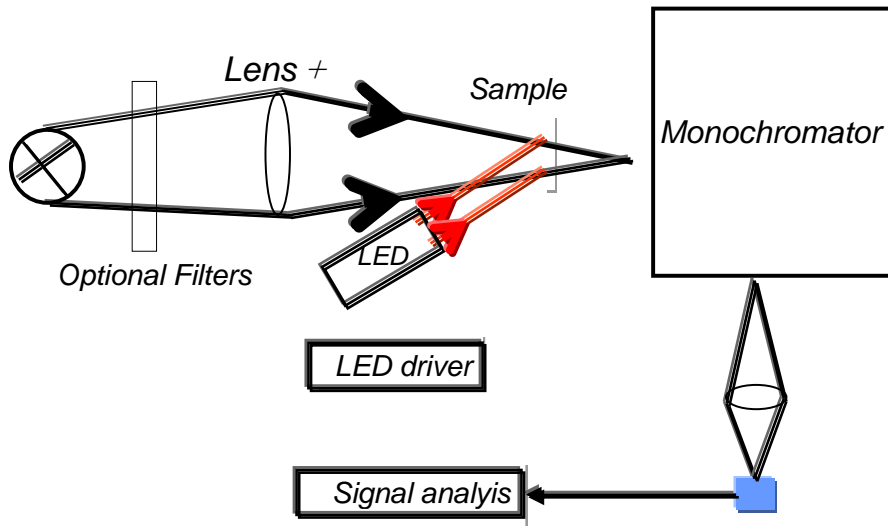


Fig. (2): Photoinduced Absorption Spectroscopy Set-up.

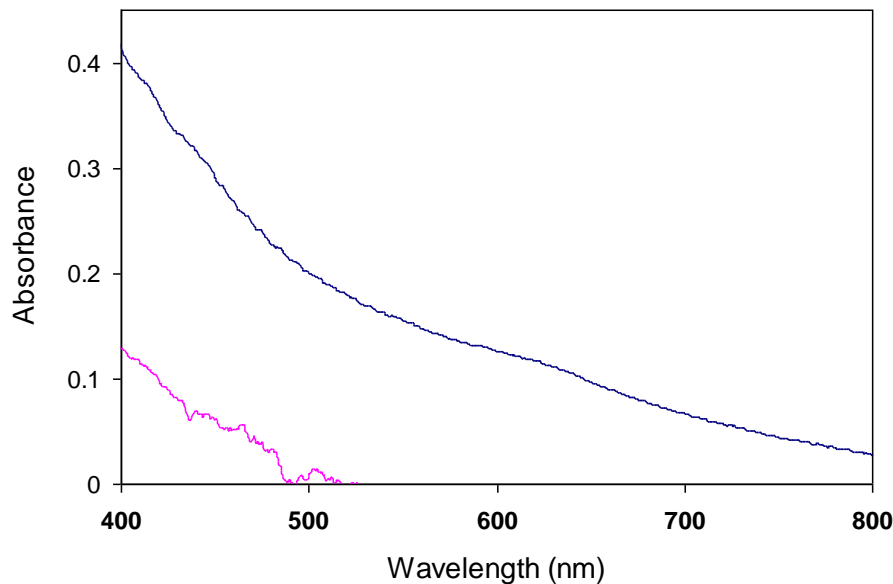
### 3. Results and Discussion:

In our previous work [2], we analyzed  $\text{SnO}_2$  film by X-ray powder diffraction (XRD). The XRD spectrum showed sharp and high-intensity peaks similar to those reported for crystalline  $\text{SnO}_2$ . This demonstrates a three-dimensional network of  $\text{SnO}_2$  nanocrystal-lites. Thus, the thin  $\text{SnO}_2$  film ( $\sim 3\text{-}4\ \mu\text{m}$ ) is highly porous. The diameter of these  $\text{SnO}_2$  particles was estimated to be less than  $50\ \text{\AA}$ . Since  $\text{SnO}_2$  mesoporous electrode possess larger inner surface than outer surface, it is reasonable that most of  $\text{FeS}_2$  particles are maintained in the pores. It has been estimated in a previous work [13] that large  $\text{FeS}_2$  particle is about  $8\ \text{nm}$ .

#### 3.1. IPCE and Absorption Spectra:

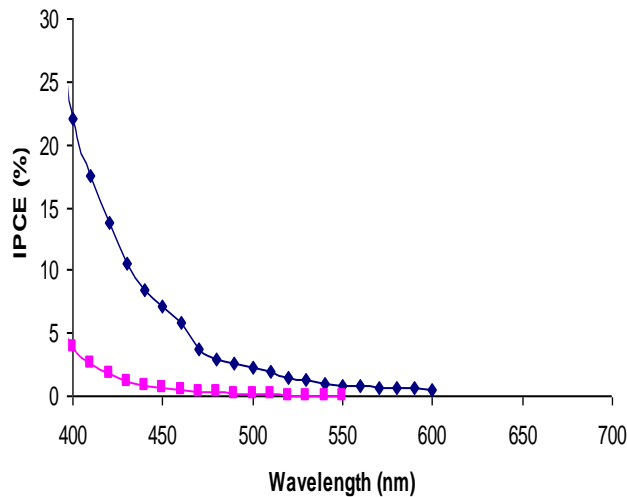
The absorption spectra of  $\text{SnO}_2$  film before and after modification with  $\text{FeS}_2$  are shown in Fig. (3 a and b). shows the absorption spectrum of nanoparticulate  $\text{SnO}_2$  film while figure 3b depicts the absorption spectrum of  $\text{FeS}_2$  modified  $\text{SnO}_2$  film showing a short wavelength absorption onset, although  $\text{FeS}_2$  bandgap is small around  $1\ \text{eV}$ . We would expect a large wavelength absorption onset near IR. This might be explained either in term of

non-stoichiometric pyrite present in the film or a quantum size effect of very small  $\text{FeS}_2$  particles which causes a bandgap energy rising. A separate work on  $\text{FeS}_2$  modified  $\text{TiO}_2$  under finalization showed XRD of a pyrite iron disulfide present in the film. We think the same would be present in  $\text{SnO}_2$  film. This significant blue shift of the absorption of ultra fine  $\text{FeS}_2$  particles compared to a bulk crystalline [17] is also observed in colloidal  $\text{FeS}_2$  particles in solution [18]. The low energy tail comes from large particles, while the high energy absorption shoulder of  $\text{FeS}_2 / \text{SnO}_2$  electrode comes predominately from small particles.



**Fig. (3):** Absorption spectra of (a)  $\text{SnO}_2$  particulate film and (b)  $\text{FeS}_2$  deposited on  $\text{SnO}_2$  film.

Figure (4) depicts the photocurrent action spectra of  $\text{SnO}_2$  electrode before and after modification with  $\text{FeS}_2$  particles. The photoresponse of  $\text{SnO}_2$  electrode (Fig. 4a) has been extended to the visible range after  $\text{FeS}_2$  modification (Fig. 4b). In addition, we can see the blue shift of the absorption spectrum of  $\text{FeS}_2 / \text{SnO}_2$  compared to a bulk  $\text{FeS}_2$ . This shift is understood in terms of the quantum size effect. Although the  $\text{FeS}_2 / \text{SnO}_2$  electrode shows a visible absorption in wavelengths longer than 580 nm, no photo-response was detected at these wavelengths which suggest that only small quantum-sized  $\text{FeS}_2$  particles play a dominant role in the spectral sensitization on  $\text{SnO}_2$  particles, while larger particles have less or no contribution.

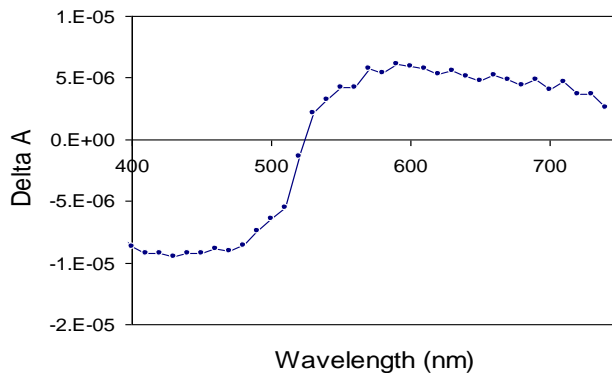


**Fig. (4):** Incident photon-to-current conversion efficiencies (IPCE) of SnO<sub>2</sub> particulate photoelectrode and (b) quantum dots FeS<sub>2</sub> adsorbed on SnO<sub>2</sub> photoelectrode. (electrolyte Na<sub>2</sub>S 0.1M, Na<sub>2</sub>SO<sub>4</sub> 0.01M)

### 3.2. Photoinduced Absorption Spectroscopy (PIA)

#### 3.2.1. PIA spectrum

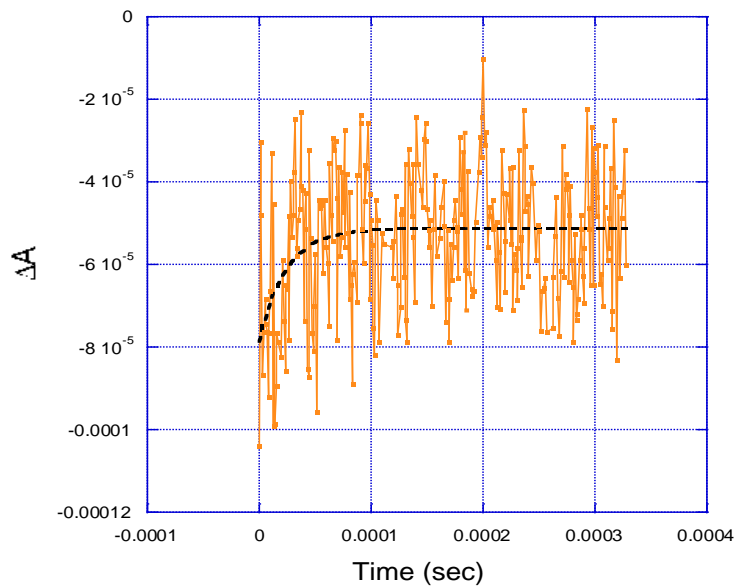
Figure (5) shows a PIA spectrum of FeS<sub>2</sub> modified SnO<sub>2</sub> without electrolyte (in air). The PIA spectrum clearly reflects the differential spectrum of FeS<sub>2</sub> upon formation injection of electrons to SnO<sub>2</sub>, with a bleach of the main absorption around 470 nm. The remaining hole in FeS<sub>2</sub> absorbs light and because valence band electrons are missing, an apparent increase in bandgap is seen (bleach, Moss-Burstein shift).



**Fig. (5):** Photoinduced absorption (PIA) spectrum of quantum dots FeS modified SnO<sub>2</sub> electrode in air. The spectrum was recorded using blue light (460 nm) excitation (42 mW.cm<sup>-2</sup>) with a modulation frequency of 9 Hz.

### 3.2.2. 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. The figure 6 shows such a PIA transient growth recorded at 550 nm. (Pseudo-) first-order rate constants for bleach (growth transient at 550 nm) is estimated at  $19 \mu\text{s}$  approximately, is due to hole-electron recombination and which does not follow simple first-order kinetic but is characterized by a range of recombination times. This has been explained by trapping of electrons. This relatively fast decay proves at least a well pore filling of SnO<sub>2</sub> film by ultra fine particles of pyrite.



**Fig. (6):** PIA growth transient absorption of quantum dots FeS<sub>2</sub> modified SnO<sub>2</sub> electrode after excitation with blue light (11 mW/cm<sup>2</sup>) recorded at 550 nm, using a sampling rate of  $10^3 \text{ s}^{-1}$  and averaged 100 times.

## 4. Conclusion:

The pyrite of iron disulfide (FeS<sub>2</sub>) shows promise for solar energy conversion devices in photoelectrochemical solar cells. 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.



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