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# Effect of CdS layers on opto-electrical properties of chemically prepared ZnS/CdS/$TiO_2$ photoanodes

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ABSTRACT

In the present work, CdS nanoparticles as a sensitizer were grown on the spin coated nanoporous $TiO_2$ film by repeated cycles of a Successive Ionic Layer Adsorption and Reaction (SILAR) method. ZnS layer was coated on the CdS/$TiO_2$ anodes to act as a protection layer on CdS. The crystallite size of CdS nanocrystals is calculated to be 3 nm from XRD spectra. The optical band gap of the film determined from transmittance spectra decreases from 3.46 to 2.15 eV with the increase in the number of CdS SILAR cycles. SEM and TEM analysis depict the enabled penetration of CdS (1 1 1) nanoparticles into the nanoporous $TiO_2$ (1 0 1) structure. EDX study confirms the presence of all the elements (Ti, Cd, S, Zn and O) found on the photoanode. The attachment of cubic structured CdS on anatase phase of $TiO_2$ in the photoanode is verified using Raman spectra. Photoluminescence (PL) study shows that the emission peak corresponding to $TiO_2$ has been slightly blueshifted due to the interaction of CdS nanoparticles in $TiO_2$ nanoporous structures. The electrical measurement shows that the dark and light illuminated resistivity of the preferred photoanode is 7.91 and 5.65 Ω cm respectively.



## 1. Introduction

A sensitized solar cell is one of the current fields of research and can be considered as a low cost alternative to existing photovoltaic (PV) technology. In a sensitized solar cell, light is generally absorbed by the sensitizer, photo generated electrons are then rapidly injected into the conduction band of the coupled semiconductor which lead to an electron–hole separation and this property is essential for sensitized solar cells. Porous $TiO_2$ film is a vital material for the photoanode of solar cells which has a high surface area substrate for sensitizer and a conductor of photo generated electrons from sensitizer to anode [1,2]. Among the three phases, anatase phase of $TiO_2$ is much preferred because its energy band gap is greater than that of rutile phase. Again, the anatase phase provides better electron transport rate, higher diffusion coefficient and more sensitizer loading capacity than rutile and brookite $TiO_2$ phases [3] which can obtain energy either directly from sunlight or from light sensitizers, causing electrons to be excited to conduction band creating positive holes in valence band for effective charge separation in solar cell [4]. In recent years, inorganic nanomaterials have been developed as another light harvester for solar cells. Sensitizers such as CdS, CdSe, PbS, PbSe and InP were used as thin film semiconductor absorbers in solar cells [5]. Among these materials cadmium sulfide (CdS) is one of the most important II–VI group semiconductor with direct band gap energy of 2.42 eV which has been widely used as a photoanode sensitizer [6,7]. Sensitizers have several advantages over organic dyes such as tunable absorption bands, higher absorption coefficients and the generation of multiple electron–hole pairs by a single incident photon [5].

Most common routes used to deposit a sensitizer on a porous metal oxide semiconductor are direct growth by chemical bath deposition or the Successive Ionic Layer Adsorption and Reaction (SILAR) method and deposition of pre-synthesized sensitizer using bi-functional organic linkers

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[8]. The disadvantages of using the latter method are inefficient charge separation due to organic linkers and poor surface coverage of sensitizer on the mesoporous metal oxide surface, which can lead to low conversion efficiency [9]. In the SILAR method, cationic and anionic precursors ($Cd^{2+}$ and $S^{2-}$ ions) are dissolved in appropriate solvents and separately placed in two beakers. Then the substrate was dipped into the cationic precursor solution followed by rinsing in the corresponding solvent to remove the excess chemical residuals from the surface followed by drying. Again, the same substrate was dipped into the anionic precursor solution followed by rinsing and drying. The two-step dipping is considered as one SILAR cycle [8]. Solvents such as ethanol and methanol are preferred over water because it shows better penetration into the nanopores of the oxide film ($TiO_2$) and more homogeneous deposition are also observed due to low surface tension and low viscosity property. Furthermore, better light absorbance and higher energy conversion efficiencies are also obtained [10]. But, CdS nanoparticles would be easily corroded in a solar cell system due to solar light illumination or interaction with electrolyte. So protective layer coating is more important for corrosion protection of CdS. For this, a wide band gap semiconducting material is commonly used as a protective layer on the surface of CdS/$TiO_2$. Thus, a high band gap semiconductor, ZnS (band gap, 3.8 eV) was coated on CdS/$TiO_2$ as a protection layer via SILAR method [11].

Stability is one of the main challenges as poor photostability has initially limited many applications of CdS semiconductor material. However, ZnS has been investigated as the most compatible passivating material for CdS [6]. ZnS coated over on the CdS-assembled $TiO_2$ film is also demonstrated to improve the overall energy conversion efficiency of the cell because the conduction band of ZnS is higher than the CdS which leads to effective energy barrier and passivation effects [12]. The combination of these two semiconductors (CdS and ZnS) allow band gap tuning in a significant range of the visible spectrum [1]. The superior performance of CdS-sensitized solar cell is obtained due to the following combined effect; energetically favoured electron injection from sensitizer to $TiO_2$ conduction band due to the upward shifted energy levels of sensitizer, favorable electron injection to $TiO_2$ and suitable surface modifications like ZnS coating to inhibit electron recombination [13]. The PV performance of the solar cell is closely related with the strategies of sensitization to the photoanode [14].

Here, we report the synthesis of nanoporous $TiO_2$ thin films by spin coating technique and subsequent deposition of CdS as a sensitizer using the SILAR method. ZnS is coated as the top layer on the CdS/$TiO_2$ photoanode for preventing corrosion and to facilitate photocarriers transportation to $TiO_2$.

## 2. Experimental details

### 2.1. Materials

Titanium tetraisopropoxide (TTIP, 97%), ethanol, methanol, hydrochloric acid (HCl) and polyethylene glycol (PEG 300) were purchased from Sigma-Aldrich. Cadmium nitrate tetrahydrate ($CdNO_3)_2 \cdot 4H_2O$, 99%), sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 98%) and zinc nitrate hexahydrate (Zn $(NO_3)_2 \cdot 6H_2O$, 96%) were purchased from Merck.

### 2.2. Preparation of nanoporous $TiO_2$ films

The nanoporous $TiO_2$ thin films were prepared at room temperature by chemical route using spin coating technique [15]. In a typical synthesis route, a precursor solution was prepared by mixing appropriate ratios of ethanol, hydrochloric acid (HCl) and titanium tetraisopropoxide (TTIP), and then stirred for 2 h at 50 °C. The molar ratio of the ingredients TTIP/HCl/Ethanol was 0.1: 0.05: 15. After stirring for two hours, a small amount (~20 μl) of PEG 300 was added to the mixture because the decomposition of PEG is responsible for the generation of porous structure in the films [16]. The pH value of the prepared $TiO_2$ sol ranged from 3 to 4 which was measured using a pH meter. Then the solution was stirred for 12 h at room temperature in order to increase the porosity of the film. The obtained solution is spin coated onto the cleaned glass substrate rotated at 1000 rpm for 2 min. After each coating, the coated film was dried at 200 °C for 2 min in ambient atmosphere. The coating procedure was repeated up to 15 times. Finally the coated films were annealed at 400 °C for 1 h in air.

### 2.3. Deposition of CdS on nanoporous $TiO_2$ films

For CdS deposition, the precursors used were cadmium nitrate tetrahydrate ($CdNO_3)_2 \cdot 4H_2O$) and sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$). CdS as a sensitizer was deposited on the prepared nanoporous $TiO_2$ films using the SILAR method [2]. The source of $Cd^{2+}$ ion was prepared from 0.3 M $Cd(NO_3)_2$ ethanol solution and the $S^{2-}$ source from 0.3 M $Na_2S$ methanol/distilled water (1:1 by volume) solution. A single SILAR cycle having a two-step dipping process consists of 5 min dip-coating of $TiO_2$ photoelectrode into the cationic precursor solution followed by thoroughly rinsing in the corresponding solvent for 2 min and dried in air. Again, the same substrate was dipped (5 min) into the anionic precursor solution followed by rinsing (2 min) and drying. Up to 12 SILAR cycles were carried out in order to obtain the desired samples. Finally, it was annealed to improve the film crystalline quality, light-harvesting ability and current transportation property. For CdS, suitable annealing temperature is more important because it can easily be damaged due to overheating. Many researchers have reported that the favorable annealing temperature for CdS is 300 °C [5]. Hence, all the films were annealed at an ideal temperature of 300 °C for 20 min.

### 2.4. Deposition of ZnS coating on CdS/$TiO_2$ films

The source of $Zn^{2+}$ ion was coated on CdS/$TiO_2$ photoelectrode using 0.05 M zinc nitrate (Zn $(NO_3)_2 \cdot 6H_2O$) and the $S^{2-}$ source was 0.05 M $Na_2S$ aqueous solution via SILAR method [11]. The CdS/$TiO_2$ film was immersed in zinc nitrate for 30 s followed by rinsing in the corresponding solvent for 10 s and subsequently dried in air. Again, the same substrate was dipped (30 s) in $Na_2S$ solution followed by rinsing (10 s) and drying. Three ZnS SILAR cycles have been performed for all the electrodes prepared by the above process. The prepared ZnS coated photoanode was annealed at 300 °C for 10 min in air. The prepared photoanodes are labeled as ZnS/$y$CdS/$TiO_2$ where the value of $y$=2, 4, 6, 8, 10 and 12 correspond to number of SILAR cycles of CdS. The