NANOCOMPOSITE THIN FILM TiO$_2$/CdS ELECTRODES PREPARED BY THERMAL EVAPORATION PROCESS FOR PHOTOVOLTAIC APPLICATIONS

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Abstract. *The incorporation of cadmium sulfide (CdS) into TiO$_2$ nanoparticle thin films was investigated. The nanoparticle TiO$_2$ thin film onto an indium dopedtin oxide (ITO) substrate was deposited by Electron Beam Deposition (EBD) combined with thermal process. Then a CdS thin film was vacuum-deposited onto the pre-deposited TiO$_2$ film by a thermal evaporation technique. The obtained TiO$_2$/CdS was characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM). The TiO$_2$/CdS nanocomposite film was used in a photoelectrochemical (PEC) cell as a working electrode and a platinum electrode as a counter electrode. The electrolyte solution contains 1 M KCl and 0.1M Na$_2$S. The results show that the cell with TiO$_2$/CdS composite film electrode has significantly improved photoelectric capability in comparison with that of the pure TiO$_2$ thin films.*

I. INTRODUCTION

In recent years, an increasing interest has been devoted to the study of interparticle electron transfer between dissimilar semiconductor particles. Combining two semiconductor particles offers an opportunity to sensitize a semiconductor material having a large bandgap and energetically low-lying conduction band by another one having a small bandgap and energetically high-lying conduction band [1]. Charge injection from one semiconductor into another can lead to efficient and longer charge separation, which is anticipated to have potential applications in photocatalysis and solar energy conversion [2]. Nanoscale titania (TiO$_2$) is of great interest mainly due to its unique properties, such as high photoactivity, chemical stability and size dependent optical properties [3]. However, it is well known that the TiO$_2$ acts as a catalyst under ultraviolet excitation [4] due to its wide band gap (around 3.2 eV). To overcome this problem, various materials, like

dyes and metallic nanoparticles, have been used as sensitizer to increase the photoactivity of TiO_2 in the visible range.

Among the various semiconductors CdSe, CdTe, $CuInS_2$, InP etc., used as a sensitizer [5-8], CdS has shown much prospect as an effective sensitizer [9,10]. CdS belongs to the IIVI group, and it is typically sulfur deficient [11]. It is the most widely studied nano-crystalline semiconductor as a photoanode in PEC cells because of its suitable band gap, long lifetimes, excellent stability and easy fabrication [1214, 15]. In this study, CdS was used to sensitize TiO_2 nano-structures. In TiO_2/CdS nanocomposite, CdS acts as a visible sensitizer and TiO_2, being a wide band semiconductor, is responsible for charge separation which suppresses the recombination process. Hence, the prepared TiO_2/CdS nanocomposite thin films can effectively capture the visible light and quickly transfer the photogenerated electrons into the TiO_2 conduction band, and finally, the sensitization of CdS on ITO/TiO_2 strongly ameliorates the photoelectric performance of the TiO_2/CdS nanocomposite thin films.

There are numerous reports describing the fabrication of titania thin films using techniques such as EBD [16], doctor blading [17], magnetron sputtering [18], solgel processing [19], surfactant template self-assembly [20], pulsed laser deposition [21], and spray pyrolysis, etc. In this work, TiO_2 nanocrystalline thin films were obtained by evaporated Ti films by EBD method and then thermal treated. The CdS thin films have been made by a thermal evaporation technique. As compared with various techniques used for the deposition of CdS thin films in [22-26], EBD and thermal evaporation are relatively simple techniques for the large scale uniform coating to produce clean, dense and strong adhesion to substrate thin films.

II. EXPERIMENTAL

The optically transparent and electrically conductive indium tin oxide (ITO) coated glass substrate with a sheet resistance of 30 W/square was ultrasonically cleaned in a series of organic solvents (ethanol, methanol and acetone) and deionized water. A 300nm thick layer of Ti was deposited by EBD technique. In order to obtain TiO_2 nanoparticles, the Ti coated on the ITO substrate was annealed at $400°C$ in air for 8 h. Thin film of CdS with thickness of 30 nm was vacuum-deposited by thermal evaporation at pressure of 10^{-2} torr onto the pre-deposited TiO_2 films. The deposition rate was 0.2 nm/s and the thin film thickness was measured during deposition using conventional quartz crystal monitor. To obtain good crystallinity, the thin CdS films were annealed at $300°C$ in air for 1 hour. The surface morphology of the samples was investigated by using a "Hitachi" Field Emission Scanning Electron Microscopy (FE-SEM). The Ultravioletvisible (UVvis) absorption spectra were performed by using a Jasco UV-VIS-NIR V570 spectrometer, X-ray diffractograms were recorded on a Siemens D-5000 diffractometer using $CuK\alpha$ radiation with the wavelength 1.5406Å. In photoelectronic studies, a two-electrode Photoelectrochemical (PEC) cell was used. The PEC cell is composed of ITO/TiO_2 or ITO/TiO_2/CdS used as working electrode (working area is 0.6 cm^2) and a platinum electrode separated by an electrolyte containing 1 M KCl and 0.1M Na_2S. The photocurrent was measured on an Auto-Lab Potentiostat PGS-30. A halogen lamp was used as a light source.

III. RESULTS AND DISCUSSIONS

III.1. Morphology and structural characterizations of the TiO$_2$ thin film and the TiO$_2$/CdS nanocomposite film

The FE-SEM images of the surface of nc-TiO$_2$ film are presented in Fig. 1a. The surface of CdS film on the ITO/TiO$_2$ substrate is shown in Fig. 1b. From Fig. 1a it is apparent that the average TiO$_2$ particles size was found to be less than 20nm and a porous structure could be seen. As shown in Fig. 1b, a homogeneous CdS ?lm with good quality deposited onto ITO/TiO$_2$ substrate and good ?lm-to-substrate adhesion were observed. The vacuum deposition by thermal evaporation technique can effectively improve the distribution of CdS nanoparticles around TiO$_2$ nanoparticles and the porosity of the thin film. The XRD pattern of ITO/TiO$_2$/CdS thin film gives the enhancement in intensity of the peak at 2θ position of 26.80 corresponding to the (002) plane indicates preferential orientation in the (002) direction (Fig. 2). This result is in good agreement with literature [27-29].
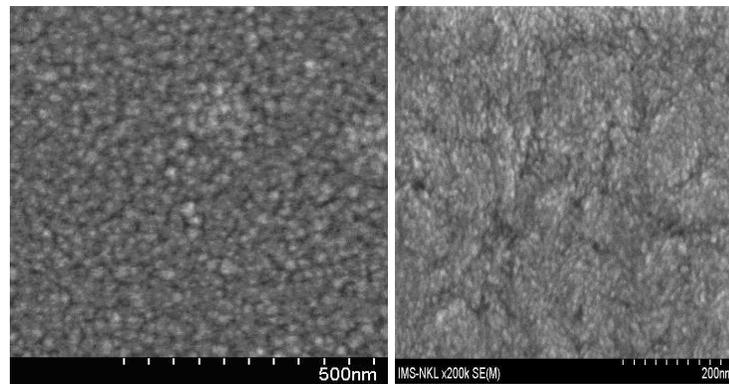

Fig. 1. FE-SEM images of the nc-TiO$_2$ film (a), TiO$_2$/CdS film (b)

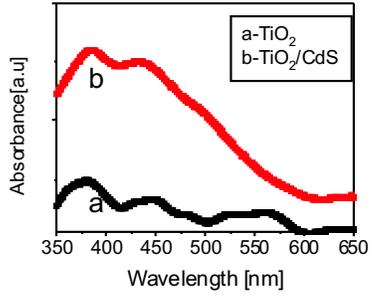### III.2. Absorption spectra of the TiO$_2$ and TiO$_2$ /CdS nanocomposite thin films

Fig. 3 shows the UV-vis absorption spectra of ITO/TiO$_2$ thin film (a) and CdS thin film on the ITO/ TiO$_2$ substrate (b). As it can be seen from Fig. 3, the TiO$_2$ thin film absorbs light mainly in the wavelength range from 380 nm to 420nm. The absorption intensity of the TiO$_2$/CdS nanocomposite film significantly increases. The main absorption edge for the CdS film on ITO/TiO$_2$ substrate is estimated to be about 550nm, which shifts toward visible region compared with the pure TiO$_2$ thin film. This is in good agreement with Hong-gang Fu et al. [9]. Therefore, the modification of CdS thin film for ITO/TiO$_2$ would effectively absorb the visible light of TiO$_2$/CdS nanocomposite thin films.

III.3. Photoelectronic performance of the TiO$_2$ /CdS nanocomposite film
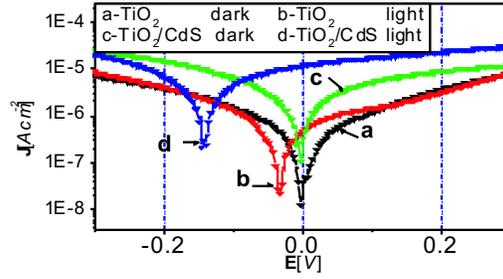
Fig.4 shows the photocurrent-potential behaviors of the photo-electrochemical cell with ITO/TiO$_2$ and ITO/TiO$_2$/CdS in turn under dark and illumination. Table 1 shows the open-circuit photovoltage (Voc) and the short-circuit photocurrent (Jsc) of the ITO/TiO$_2$
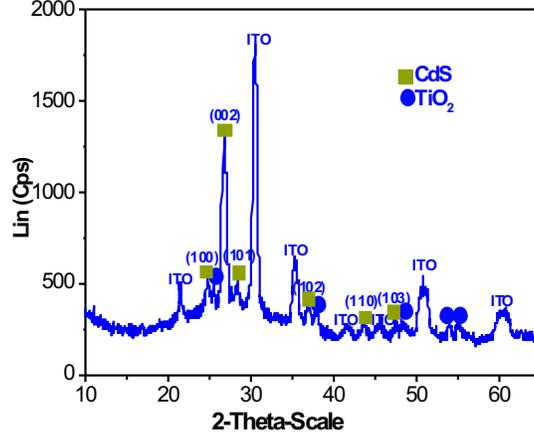
Fig. 2. XRD pattern of TiO_2/ CdS nanocomposite thin film on ITO substrate

**Fig. 3.** UV-vis absorption spectra of TiO_2 film and TiO_2 / CdS nano composite film.

Fig. 4. Photocurrent-potential behaviors of ITO/TiO_2 and the ITO/TiO_2 /CdS electrodes.

and ITO/TiO_2/CdS. It can be clearly seen that the photo-electrochemical cell made from films consisting only of TiO_2 has very low values of Voc and Jsc, whereas for the cell with coating a thin film of CdS, both Voc and Jsc increase dramatically. It is clear that the coupling CdS with TiO_2 ameliorates the photoelectric performance of the TiO_2/CdS nanocomposite films.

Table 1. The V_{oc} and J_{sc} of all samples used as working electrodes in the PEC cell

Sample	Voc (mV)	Jsc (μAcm^{-2})
TiO_2	32	0.5
TiO_2/CdS	143	11.5

It can be explained as the following: The electron affinity of the CdS is higher than that of the TiO$_2$. Therefore, according to Andersons model, a type-II heterojunction is formed between CdS and TiO$_2$ [30]. The light from the halogen lamp generates electron-hole pairs in CdS. The electrons from the conduction band of CdS are quickly transferred to the conduction band of TiO$_2$, as shown in Fig.5. Once the electrons diffuse into the conduction band of TiO$_2$, the probability of its decay is small, because there can be no free holes in TiO$_2$ under visible excitation. As a result, the electrons accumulate in the conduction band of the TiO$_2$ and the holes accumulate in the valance band of the CdS. In this way, the charge separation is achieved. The redox couple in the electrolyte, after reducing the oxidized dye, can be renewed in the counter-electrode, making the photoelectrochemical cell regenerative [17, 31]. It can be clearly seen that the coupling of TiO$_2$ with CdS can significantly enhance the separate of the electron and hole pairs. These results are promising for improving the efficiency of photovoltaic devices.
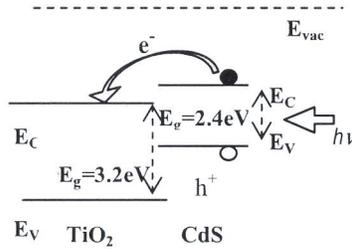
Fig. 5. Schematic diagram showing the charge transfer at TiO$_2$-CdS heterojunction interface

IV. CONCLUSIONS

TiO$_2$/CdS nanocomposite thin films have been successfully prepared by a thermal evaporation technique. X-Ray diffraction studies indicated that the CdS has preferential orientation in the (002) direction. The prepared TiO$_2$/CdS nanocomposite thin film has been possessed more excellent photoelectrochemical performance than that of ITO/TiO$_2$ film. It is believed that CdS thin films sensitizing TiO$_2$ microporus structures can be used in fabricating high efficiency photovoltaic devices. The differences in CdS layer thickness on the ITO/TiO$_2$ substrates will be investigated in our next study to find out a suitable one that has the best of values of VOC and JSC.

ACKNOWLEDGMENTS

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