BRAIN. Broad Research in Artificial Intelligence and Neuroscience,
ISSN 2067-3957, Volume 1, October 2010,
Special Issue on Advances in Applied Sciences,
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PREPARATION AND CHARACTERIZATION OF TIO_2/CDS LAYERS AS POTENTIAL PHOTOELECTROCATALYTIC MATERIALS

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Abstract. The TiO_2/CdS semiconductor composites were prepared on indium tin oxide (ITO) substrates in different mass proportions via wet-chemical techniques using bi-distilled water, acetyl-acetone, poly-propylene-glycol and Triton X-100 as additives. The composite layers were annealed in normal conditions at the temperature of 450°C, 120 min. with a rate of temperature increasing of 5°C/min. The structural and optical properties of all the TiO_2/CdS layers were characterized by X-ray diffraction, UV-VIS spectroscopy, spectrofluorimetry and FT/IR microscopy. The microstructural properties of the deposited TiO_2/CdS layers can be modified by varying the mass proportions of TiO_2:CdS. The good crystallinity level and the high optical adsorption of the TiO_2/CdS layers make them attractive for photoelectrochemical cell applications.

Keywords: *Titanium dioxide; Cadmium sulphide; Photocatalyst*

2000 *Mathematics Subject Classification*: 74-XX

1. INTRODUCTION

Titanium dioxide (TiO_2) in the form of thin films is broadly used as a catalyst in photovoltaic and photocatalysis applications [1-7]. However, it is a semiconductor with a large band gap ($E_g \simeq 3.2$ eV) [8]. Although TiO_2 absorbs only 5% of the solar light reaching the surface of the Earth, the band gap of TiO_2 limits its absorption to the ultraviolet region of the solar spectrum [9]. In order to improve the performance of titanium dioxide, semiconductors such as CdS, CdSe, CdTe, PbS, Bi_2S_3, $CuInS_2$, which absorbs light in the visible wavelength region, can serve as sensitizers because they are able to transfer electrons to large band gap semiconductors such TiO_2 or ZnO [10]. Especially, considering that cadmium sulphide (CdS) is an important n-type semiconductor which has direct band gap ($E_g = 2.42$ eV), it finds applications in solar cell devices, thin film transistors for flat panel displays and optoelectronic devices [11]. Its energy levels can match with those of TiO_2 [10] therefore it expects that the sensitization of TiO_2 film with CdS can improve the photoelectric performance of TiO_2 electrodes. The absorption edge of pure TiO_2 is at about 380 nm and the absorption edge of pure CdS is at about 580 nm [10, 12]. Meanwhile, TiO_2/CdS semiconductor composites have attracted much interest because of synergistic effects on photoelectrochemical properties [13, 14] and photocatalytic activity [15] and have been extensively investigated for their applications in solar energy cells, catalysis, water purification and electrochromic devices [16-18]. In this work we have associated TiO_2 with CdS in order to prepare a mixed photocatalyst, aiming to improve photoelectrochemical properties and photocatalytic activity [19, 20]. TiO_2/CdS thin film heterojunctions were prepared on indium tin oxide (ITO) glass substrates resulting an improved photocatalytic efficiency both in UV-visible and visible light irradiation. The TiO_2/CdS semiconductor composites were prepared in different mass proportions (1:4, 2:3, 3:2 and 4:1, samples name: TC 1, TC 2, TC 3, respectively, TC 4) via wet-chemical techniques, using bi-distilled water, acetyl-acetone, poly-propylene-glycol and Triton X-100 as additives [21]. Titania P-25 (ca. 80% anatase, 20% rutile) was kindly supplied by Degussa AG, Germany. CdS was obtained by spray pyrolysis technique [22]. Acetyl-acetone (Merck, Germany), poly-propylene-glycol (Machery-Nagel, Germany) and Triton X-100 (Fluka, Switzerland) were used without any further purification. Bi-distilled water was used throughout all the experiments. A thin layer of a semiconductor composite TiO_2/CdS was deposited on ITO glass substrate,

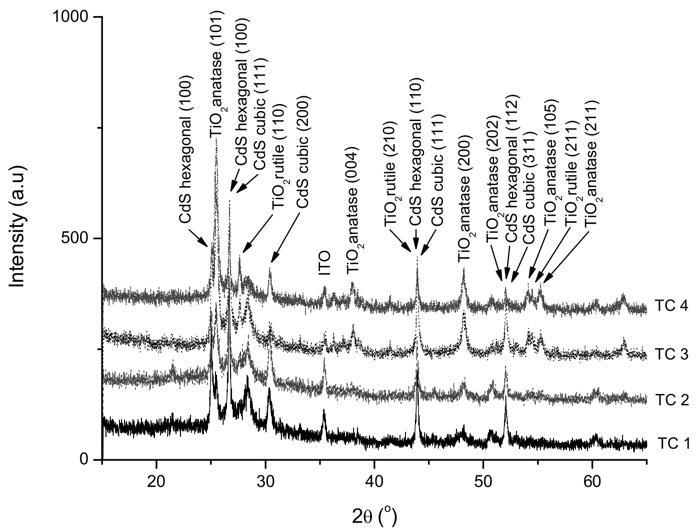

Figure 1: X-ray diffraction pattern for TiO_2/CdS composites samples

a conducting glass with a sheet resistance $\sim 30\Omega$ cm^{-2}. In order to establish the electrical contact among the nanoparticles and to form an ITO/TiO_2/CdS nanostructured film, the composite layers were annealed in normal conditions at the temperature of 450^{o}C, 120 min. with an increasing rate of temperature of 5^{o}C/min.

2. RESULTS AND DISCUSSION

The microstructural study of the TiO_2/CdS semiconductor composites has been investigated using X-ray diffraction and FT/IR microscopy. X-ray diffraction (XRD) measurements were performed using a BRUKER D8 Advance X-ray diffractometer, working at 45 kV and 45mA. The Cu$_{k\alpha}$ radiation was collimated with Soller slits and a germanium monochromator was used. FT/IR spectra of the materials were recorded using JASCO IRT - 3000 Irtron Infrared Microscope. Fig. 1 shows the X-ray diffraction pattern for TiO_2/CdS composites (sample TC 1, TC 2, TC 3 and TC 4). The diffraction pattern of the TiO_2/CdS composites exhibits the diffraction peaks owning to CdS phase (hexagonal and cubic). TiO_2 (rutile and anatase) phases were also detected.

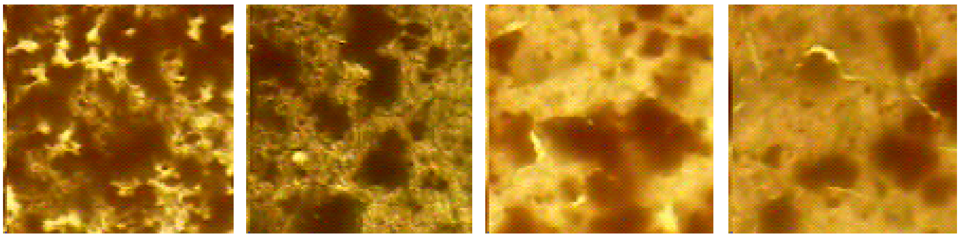

Figure 2: The FT/IR microscopy images of the TiO_2/CdS composites

The microstructural properties of the deposited TiO_2/CdS layers depend on the mass proportions of TiO_2:CdS. The proportion of CdS phase is direct proportional with the CdS powder used in the preparation process. The FT/IR microscopy images of the TiO_2/CdS composites upon annealing at high temperatures, are shown in Fig.2

The micrograph shows agglomerates with irregular morphology and size ranging from few micrometers down to hundreds of nanometer. The compositional contrast, shows the distribution of CdS-rich region (in dark) into the TiO_2 particles (in bright) suggesting that a part of the nanosized CdS particles coexist within a titanium oxide matrix. Optical properties of TiO_2/CdS semiconductor composites have been investigated using optical absorption and photoluminescence spectroscopy. UV-VIS absorption spectra of the as-prepared photocatalysts were taken on a JASCO V-550 spectrometer. The fluorescence spectra were obtained using an ABL&Jasco V 6500 spectrofluorimeter with xenon lamp. The optical studies of the TiO_2/CdS composites were performed using the absorption spectra observed in the wavelength range 200-900 nm. Fig. 3 shows the UV-Vis spectra of TiO_2/CdS samples.

The UV-Vis absorption spectra results shows that the absorption peak of the TiO_2/CdS composites shifts from the ultraviolet region to the visible region in comparison to that of the TiO_2 and CdS films [23, 24]. The absorption the mixed TiO_2/CdS shows an absorption plateau in the region 300-400 nm corresponding to the contribution of CdS to the absorption spectra. The level of the plateau increases with increasing CdS concentration. These results show that the coupled semiconductor can be excited by visible light. The influence of CdS on optical properties of the TiO_2/CdS nanostructured film can be also confirmed by photoluminescence (PL) spectroscopy, because CdS nanoparticles

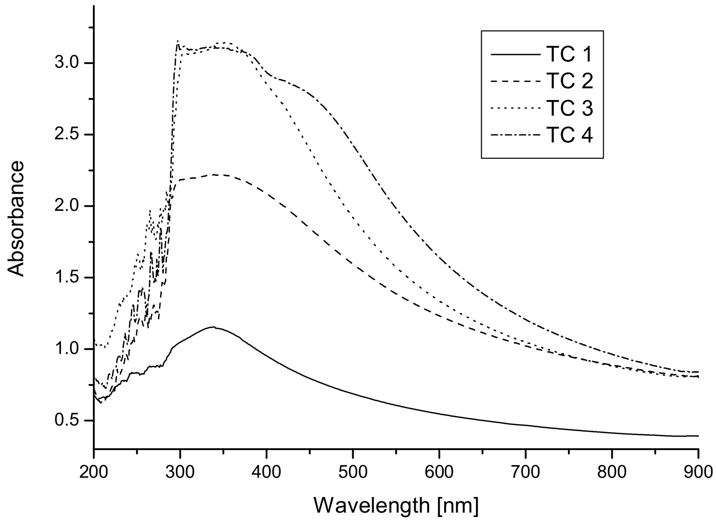

Figure 3: Absorption spectra of TiO_2/CdS composites samples with a different mass proportion

exhibit light-emitting behavior at a specific wavelength. Fig. 4 illustrates the fluorescence emission spectra of TiO_2/CdS nanostructured film at the exciting wavelength of 340 nm. The curves for TC 1, TC 2, TC 3 and TC 4 exhibited the clear photoemission peaks at about 375 nm, and compared with emission of bulk CdS (520 nm), 145 nm of blue shift was observed. These features indicate the quantum-confined effect of the TiO_2/CdS nanocomposite films [25].

3. Conclusions

TiO_2/CdS semiconductor composites were prepared on indium tin oxide (ITO) glass substrates by means of the wet-chemical techniques. XRD results have indicated the cubic and hexagonal phase of CdS nanoparticles were formed within/on the TiO_2 matrix. The FT/IR micrographs shows agglomerates with irregular morphology and size and confirm that a part of the nano-sized CdS particles coexist within a titanium oxide matrix. With the amount of Cd salt increasing, the size of CdS nanoclusters in the TiO2 matrix increased. Compared with TiO_2 and CdS bulk material, all the UV-VIS absorption and

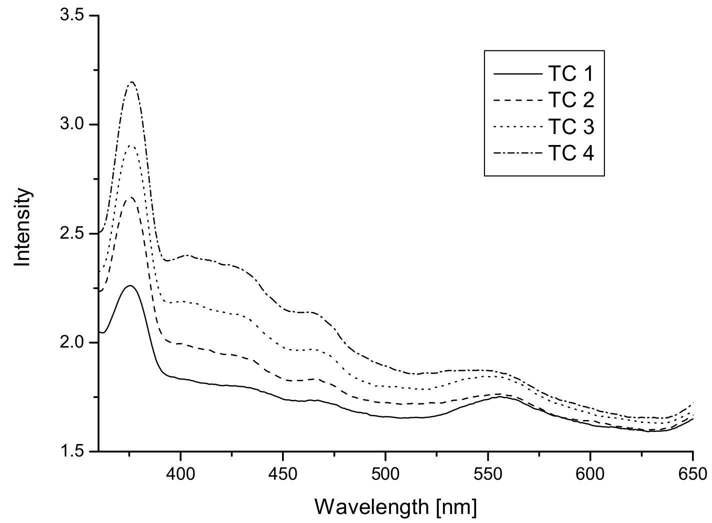

Figure 4: Spectrofluorimetric spectra of TiO_2/CdS composites samples with a different mass proportion

luminescence spectra had shown an explicit blue shift due to quantum confinement. The good crystallinity level and the high optical adsorption of the TiO_2/CdS layers make them attractive for photoelectrochemical cell applications.

ACKNOWLEDGMENTS

The present work was supported by the Ministry of Education and Research through PN 09-44N 02-06, PN II 71-047 and PN II 71-122 projects.

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