Study the Photocatalytic behavior of Nanocomposite CdS-TiO$_2$ Synthesized by Sonochemical Route

D D Sahoo$^1$, G S Roy$^2$

1. Mahanga puspagiri Mahavidyalaya, Erakana, Cuttack, Odisha
2. Principal, Bhadrak Autonomous College, Bhadrak, Odisha
gsroy2004@gmail.com

Abstract: Nanostructured colloidal semiconductors with heterogeneous photocatalytic behavior have drawn considerable attention over the past few years. This is due to their large surface area, high redox potential of the photogenerated charge carriers, and selective reduction/oxidation of different classes of organic compounds. In the present paper, we have carried out a systematic synthesis of nanostructured CdS-TiO$_2$ via Sonochemical method. The structural and microstructural characterizations of the as-prepared CdS-TiO$_2$ nanocomposites are determined using XRD and SEM-EDS techniques. The visible light assisted photocatalytic performance is monitored by means of degradation of phenol in water suspension.


Keywords: Nanocomposite, Nanocrystall, Surfactent

Introduction

Titanium dioxide is a material which has attracted lots of attention due to its importance in a variety of practical applications: catalysis, energy conversion, optics, sensing, etc. TiO$_2$ is biologically and chemically inert, abundantly available and cheap. This material is known to exist in several forms, among the most abundant are anatase, rutile and brookite [1]. The brookite phase is stable only at very low temperatures and hence is not so useful, practically. Rutile is obtained after high temperature calcinations and its fundamental properties, such as electrical, optical and thermal, are well studied [2, 3]. In contrast, the properties of the anatase form are not so well understood. The reason could be that the anatase, which is a comparatively low temperature stable phase, has gained significance only after nanostructure materials and their synthesis started playing a major role in materials science. Therefore, considerable effort has been focused on developing simple methods for synthesis of the TiO$_2$ layer with the desired morphology and improved performance. In order to maintain a sustainable environment, there is high demand to produce inexpensive renewable energy sources, so the development of low production cost solar cells is of particular interest among various potential applications of TiO$_2$ porous layers. In optoelectronic devices, the TiO$_2$ porous layer serves as the route for electron transport to the anode. Therefore the morphology of Ti thin films plays a crucial role in determining the efficiency of the devices. There are numerous reports describing the fabrication of Ti thin films using techniques such as Electron Beam Deposition (EBD) [4], doctor blading [5], magnetron sputtering [6], sol–gel processing [7], surfactant template self-assembly [8], pulsed laser deposition [9], spray pyrolysis, etc. In this work, various materials like dyes and metallic nanoparticles have been used as a sensitizer to increase the photoactivity of TiO$_2$ in the visible range. 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 [10]. 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 [11]. Among the various semiconductors, CdSe, CdTe, InP, etc, are used as sensitizers, CdS has shown much promise as an effective sensitizer. CdS belongs to the II–VI group, and is typically sulfur deficient. It is the most widely studied nanocrystalline semiconductor as a photoanode in photoelectrochemical cells because of its suitable bandgap, long lifetime, important optical properties, excellent stability and ease of fabrication. However it has not been much studied in the case of Dye-sensitized Solar Cells (DSCs). In this study, CdS was used to sensitize TiO$_2$ nanostructures. In a 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.
Preparation of CdS/TiO$_2$ by Sonochemical Method

A range of substrates were used for different purposes. For photo-electrochemical (PEC) cell testing, patterned ITO on glass was used. For XRD, FE-SEM samples, silicon substrates were employed. Optically transparent and electrically conductive indium tin oxide (ITO) coated glass substrate with a sheet resistance of 30 Ω per square and silicon substrates were ultrasonically cleaned in a series of organic solvents (ethanol, methanol and acetone) and deionized water. Initially the Micro emulsion is prepared. Microemulsion is a stable dispersion of one liquid phase into another, stabilized by an interfacial film of surfactant. This dispersion may be either oil in water or water in oil. Microemulsion is typically clear solutions as the droplet diameter is approximately 100 nanometers or less. This Microemulsion is divided into two parts. Titanium oxide is dispersed in one part of Microemulsion. Cadmium nitrate and sodium thiosulphate are added in the other part of Microemulsion. Then these two mixtures are added and kept in ultrasonic bath for 2 hours. Due to ultrasonic waves cavitation will be formed and chemical reaction takes place in high temp and atmospheric pressure. As a final product we will get the ceramic composite CdS/TiO$_2$ in powder form. We can use this for powder coating. This powder can be converted into sol by adding equal amount of pyridine and chloroform. Thin films on glass substrate can be prepared by dipping in the above sol.

Results and discussion

Figure 1. FE-SEM images of annealed TiO$_2$ thin film surfaces at (a) 300 °C, (b) 400 °C, (c) 450 °C and (d) 750 °C.

Figure 1 shows FE-SEM images of the annealed TiO$_2$ thin films (planar view) on silicon substrates at different temperatures. From the figure it is apparent that at annealing temperature of 300 °C the TiO$_2$ thin films have a nanoparticle structure, although conversion to TiO$_2$ may not be completed. The surface of the thin film is uniform and smooth with grain size less than 10 nm. The porous structure becomes visible after annealing at 400 °C. The average TiO$_2$ particle size was found to be less than 20 nm. The morphology and crystallinity are improved with increasing annealing temperature. The porous size is 5–10 nm and crystalline structure is anatase, which is crucial for application in solar cells. It is clearly seen from the figure that at an annealing temperature of 450 °C, the TiO$_2$ thin film is uniform with grain size in the range of 15–30 nm.

Figure 2 shows the XRD pattern of the TiO$_2$ thin films after annealing at 450 °C (figure 2(a)) and 750 °C (figure 2(b)), respectively. As can be seen from figure 2, the titanium films were completely transformed to TiO$_2$. In the figure, TiO$_2$ diffraction peaks can be assigned to the planes of the anatase and rutile phases according to the standard diffraction index.

Figure 2. XRD pattern of surfaces of TiO$_2$ thin films annealed at 450 °C (a) and 750 °C (b).

It is clear that anatase phase occurs and a small amount of rutile phase was observed at heating treatment of 450 °C. From figure 2(a) it is clearly seen that the diffraction peaks of TiO$_2$ annealed at 450 °C are large. It indicates that the TiO$_2$ films have a nanostructure. From figure 2(b), rutile peaks are found to be narrower, indicating that the TiO$_2$ thin film was crystallized in large grain size. The transformation from anatase phase to rutile phase was completed at 750 °C.

The XRD pattern of ITO/TiO$_2$/CdS thin film shows
that enhancement of the intensity of the peak at 2θ position of 26.8° corresponding to the (002) plane indicates preferential orientation in the (002) direction. This result agrees well with those of [11–13].

The UV-Vis transmittance spectral response for the pure TiO2 and CdS-50wt.% TiO2 nanocomposite is shown in Figure 4. The onset of transmittance starts below 350nm and a sharp transition occurred at around 380nm for the pure TiO2 anatase structure. Whereas for the case of CdS-50wt.% TiO2 nanocomposite prepared by sonochemical process, the spectral curve extends to the visible light region with the onset value corresponding to 490 nm. The absorption edge of TiO2 in CdS-TiO2 nanocomposites observed above 400nm indicates a significant “blue shift” of the bandgap energy compared to pristine TiO2. The quantum-sized effect of CdS in the nanocomposite structure seems plausible explanation for this “blue shift” effect. However, in the present study, the quantum CdS is not observed due to the coalescent or agglomeration of nanoparticles in the reverse micelle process. This may suggest that the nanocomposite coupled semiconductor (CdS-50wt.% TiO2) is expected to increase photogenerated charge carriers under the irradiation of visible light. It is noteworthy to mention that the absorption spectrum due to TiO2 is not present in the CdS-TiO2 nanocomposite films due to the different film thickness between TiO2 and CdS nanoparticles. Besides, the concentration of TiO2 also affects the optical absorption of CdS-TiO2 nanocomposites in the UV range.

Figure 3. FE-SEM images of the 70 nm (a) and 300 nm CdS (b) on TiO2 substrates.

Figure 4: UV-Vis spectral responses for pure TiO2 and CdS-TiO2 nanocomposite.

Conclusion

TiO2 thin films have been successfully prepared by sonochemical method combined with thermal process. At an annealing temperature of 300 °C, the TiO2 thin film has a nanoparticle structure with grain size around 10 nm. The porous structure appeared after annealing at 400°C with particle size less than 20 nm. At an annealing temperature of 450 °C, the TiO2 thin film is uniform with grain size in the range of 15–30 nm; the length of grains is from 100 to 300 nm. The surface-coated CdS and TiO2 anatase nanocomposite extends the absorption band edge in the visible region as observed from the UV-Vis measurements. The as-synthesized nanocomposite materials exhibit better photoactivity under visible light irradiation than that of pure TiO2.

References


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