



Optimization of CdS/TiO₂ Nanotube-Array Composite Photocatalysts Prepared by Electrodeposition†

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Titania nanotube arrays were prepared by titanium anodizing, then CdS/TiO₂ nanotube arrays composite photocatalysts were prepared by an AC electrodeposition method for different times. The morphology and crystal structure of the CdS/TiO₂ composite photocatalysts were characterized by SEM and XRD. The photoelectrochemical properties of the composites were investigated by means of UV-visible absorption spectra and photocurrent measurements. The photocatalytic activity was evaluated by the degradation of methyl orange under UV-visible light irradiation. The results show that there is an optimum deposited time for the highest photocatalytic activity of the CdS/TiO₂ composite photocatalysts under UV-visible light irradiation and the optimum deposited time is determined to 3 min.

Keywords: CdS/TiO₂, Nanotube array, Composite photocatalyst, Electrodeposition, Methyl orange.

INTRODUCTION

Since Fujishima and Honda discovered the phenomenon of photocatalytic splitting of water on a titanium dioxide electrode under ultraviolet light in 1972¹, titania has become one of the most promising semiconductor materials due to its high chemical stability, excellent functionality, nontoxicity and relatively low price. because of its wide band gap (3.2 eV for anatase phase and 3.0 eV for rutile), it absorbs only ultraviolet light accounting for only about 4 % of the total solar energy, which limits its widespread uses.

An efficient measure to enhance the visible-light response of titania is to sensitize it with narrow bandgap semiconductors, such as PbS², CdTe³, BiFeO₃⁴ and CdS⁵. CdS has an ideal band gap energy (2.4 eV) which can be excited under visible light. Yet, CdS is light response material and can be photodecomposed by light in air and is usually not very active. With a combination of cadmium sulfide and titania, the electrons will feed into titania from cadmium sulfide and be captured by titania because of the wider forbidden zone of titania. As a result, the lifetime of the electron vacancy in cadmium sulfide particles will increase and the photodecomposition process of cadmium sulfide will be reduced, causing increased stability of CdS/TiO₂ composite.

In recent years, some CdS/TiO₂ composites have been fabricated by different methods, such as CdS/TiO₂ nano-bulk composite⁶, CdS/TiO₂ nanofilm⁷, TiO₂/CdS nanowire⁸ and CdS/TiO₂ nanotube array⁵. The TiO₂ nanotube array has better properties than others such as easy fabrication, more specific surface area and higher binding strength with CdS particles filled in the nanotubes due to unique dense nanotube arrays within the surface. However, the amount of cadmium sulfide on titania may affect the photocatalytic activity of CdS/TiO₂ composite photocatalyst. In this paper, TiO₂ nanotube arrays were prepared by titanium anodizing, then CdS nanoparticles were deposited on the TiO₂ nanotube arrays by an ac electrodeposition technique for different times. The characterizations, photoelectrochemical properties and photocatalytic activities of the CdS/TiO₂ composite photocatalysts for differently deposited times were carried out and evaluated.

EXPERIMENTAL

Preparation of samples: Details for the fabrication of titania nanotube arrays can be found in the literature⁹. To obtain nanotube arrays, a commercially pure titanium foil (99.9 % purity, 20 mm × 30 mm × 0.1 mm in size) was washed with acetone and distilled water in an ultrasonic cleaner. Then, the samples were etched in 60 % HNO₃ + 25 % HF + 15 % H₂O

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(vol.) solution for 30 s to remove the oxide layer on their surfaces, washed with distilled water and dried. The treated titanium foil with a working area of 20 mm × 20 mm was anodized using a direct-current power-supply system at 20 V for 1 h under ambient temperature, a pure titanium sheet with a working area of 30 mm × 30 mm as cathode and the solution of $\text{NH}_4\text{F}:\text{H}_2\text{O}:\text{glycerol}$ at a ratio of 1:20:79 wt % as electrolyte. A subsequent heating at 450 °C was applied to achieve the crystallization of the nanotube arrays before the cadmium sulfide deposition. The electrodeposition of cadmium sulfide on as-prepared titania nanotube arrays was carried out at 120 °C for 3, 6 and 10 min, respectively, in a non-aqueous electrolyte with 0.055 M CdCl_2 and 0.19 M elemental sulfur dissolved in dimethyl sulfoxide¹⁰. An AC 8 V potential with a frequency of 50 Hz was applied between the working electrode and the counter electrode of a Pt foil (2.5 mm × 30 mm in area). After the deposition, the samples were rinsed thoroughly with warm DMSO and distilled water in sequence and then subjected to annealing at 200 °C for 1 h followed by 450 °C for 1 h under N_2 flow.

Characterizations: The structures of samples were characterized by X-ray diffraction (Philips PC-APD) method using $\text{CuK}\alpha$ radiation. Surface morphologies were observed using scanning electron microscopy (HITACHI S-4700). UV-Visible absorption and transmittance spectra were measured on a spectrophotometer (UV-2550, Shimadzu) equipped with an integrating sphere.

Assessments of photoelectrochemical property: The photoelectrochemical test was conducted in a three-electrode system using an electrochemical workstation (CHI660B, China). A 0.5 M Na_2SO_4 was employed as the supporting electrolyte. The area of the working electrode was 1 cm^2 . A platinum plate was used as a counter electrode and a saturated calomel electrode as the reference electrode. The light source used was a 500 W Xe lamp. The photocurrent transient generated during irradiation was evaluated by amperometric *i-t* curve.

Measurement of photocatalytic activity: The photocatalytic experiments were carried out using a glass reactor with a magnetic stirrer and a 500 W Xe lamp (Shanghai Lansheng electron Co., Ltd., China). The reaction vessel (100 mL) has a double-walled with inlet and outlet tubes for cooling. Of the total radiated energy, approximately 40-48 % is in the ultraviolet portion of the spectrum and 40-43 % in the visible portion of the spectrum. A distance between the lamp and the top surface of the solution is 6 cm. The aqueous solution of methyl orange was used as a model pollutant for the degradation. TiO_2 nanotube array was used for comparison. A set of photocatalytic degradation experiments was performed with the following procedure: a CdS/TiO_2 nanotube array composite or TiO_2 nanotube array with an area of 4 cm^2 was placed in 50 mL of aqueous solution of methyl orange with an initial concentration of 10 mg/L; prior to the photoreaction, the reaction solution was magnetically stirred in the dark for 1 h to reach adsorption/desorption equilibrium; then the reaction solution with stirring was irradiated under the UV-visible light from the top to down vertically; during the photoreaction, samples were collected at regular intervals for measurement on a spectrophotometer (UV-2550, Shimadzu).

RESULTS AND DISCUSSION

Fig. 1 shows top-view SEM images of TiO_2 nanotube and CdS/TiO_2 composite photocatalysts by electrodeposition for different times. The compact, well-ordered nanotube arrays with an inner diameter of about 50-100 nm and a wall thickness of *ca.* 10 nm can be observed from Fig. 1a. For the deposition for 3 min (Fig. 1b), the CdS crystals were sparsely distributed within or between or on the nanotubes. With the increase in the deposition time to 6 min (Fig. 1c), most of the substrate area of the TiO_2 nanotube arrays was covered with aggregations consisting of CdS particles with a size of about 50 nm. Also, up to 10 min (Fig. 1d), a thicker layer of CdS aggregations was deposited on the substrate, nearly covered all the area. So, the electrodeposition time has a clear influence on the amount of CdS on the substrate, the longer the deposition time is, the more the amount of CdS on the substrate is.

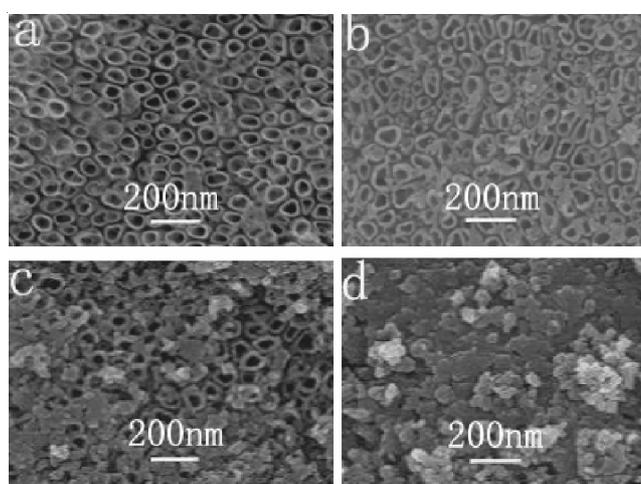


Fig. 1. Top-view SEM images of TiO_2 nanotube arrays and CdS/TiO_2 composites by electrodeposition for different times: (a) 0 min; (b) 3 min; (c) 6 min; (d) 10 min

Fig. 2 shows a comparison of XRD patterns of the annealed TiO_2 nanotube arrays with or without CdS crystal deposition. It is apparent that the titanium crystalline phase of the substrate metal can be clearly observed in the all samples. The characteristic peaks located at $2\theta = 25.3$ and 47.99° for all samples can be observed, which exhibits the crystalline phases of anatase TiO_2 . The characteristic peaks appeared at the diffraction angles of 24.8 , 26.49 and 28.2° can be assigned to the pure CdS hexagonal structure, which indicates CdS deposition on TiO_2 nanotube arrays. The peak of anatase TiO_2 at $2\theta = 25.3^\circ$ looks like being overlapped with the one of hexagonal CdS at $2\theta = 24.8^\circ$. So, after deposition for different times (3, 6 and 10 min), the structures on the substrate material in the samples are composed of hexagonal CdS and anatase TiO_2 crystalline phases. However, some differences can be observed that when the deposition time of CdS increases, the hexagonal CdS phase becomes clearer, whereas the intensities of anatase TiO_2 and Ti weaker. These XRD results confirmed the SEM observation.

Fig. 3 is the UV-visible absorption spectra of TiO_2 nanotube arrays and CdS/TiO_2 nanotube composites deposited for different times. The effect of CdS sensitization on TiO_2 can be

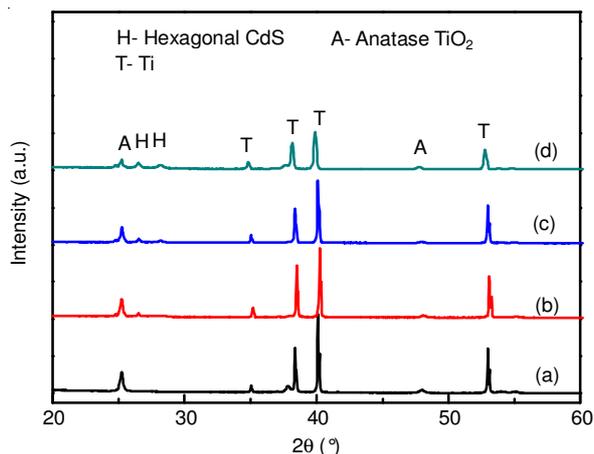


Fig. 2. XRD patterns of TiO₂ nanotube arrays and CdS/TiO₂ composites deposited for different times: (a) 0 min; (b) 3 min; (c) 6 min; (d) 10 min

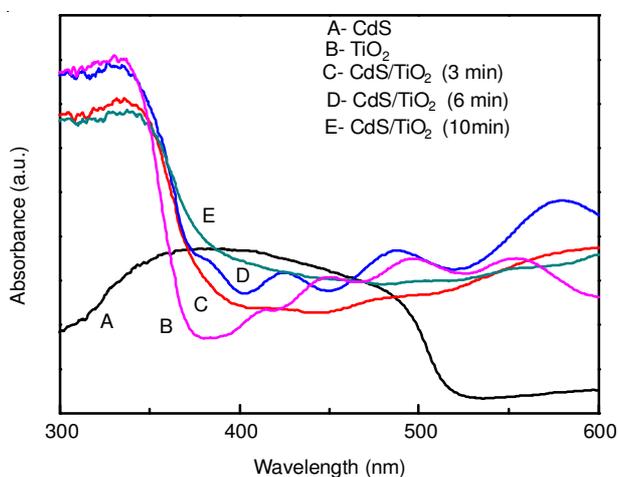


Fig. 3. UV-Visible absorption spectra of TiO₂ nanotube arrays and CdS/TiO₂ composites deposited for different times

easily noticed from the difference of absorption spectra. The most intensive absorption of hexagonal CdS appears in the wavelength zone in 350-500 nm and the absorption below 300 nm is very weak (curve A). The curve B is the UV-visible absorption spectrum of the pure anatase TiO₂. It can be observed that the UV-visible absorption spectra of the CdS/TiO₂ composite photocatalysts are red shifted clearly, compared with the pure anatase TiO₂. In addition, with an increase of deposition time from 3 to 10 min (curves C, D and E), the red-shift level also enhances. This result indicates that CdS in the specific wavelength range is mainly responsible for the red-shift of the UV-visible absorption band and the CdS deposition amount on the TiO₂ nanotube arrays affects the level of the red-shift of the UV-visible absorption band.

Fig. 4 is the amperometric i-t curves of transient photocurrent generated under UV-visible-light irradiation and in dark for TiO₂ nanotube array and CdS/TiO₂ composite electrodes deposited for different times. It can be seen that the photocurrents of all electrodes are nearly zero in dark and increase quickly upon illumination and reach a steady state after several seconds. Furthermore, it can be found that the regular photocurrent of the CdS/TiO₂ composite electrode deposited for 3 min is the highest up to about 1 mA/cm² in all samples,

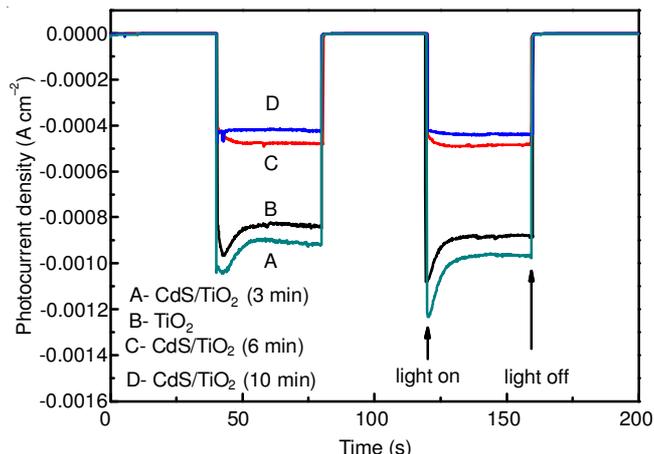


Fig. 4. Amperometric i-t curves of transient photocurrent generated under UV-visible light irradiation and in dark

whereas the one of the CdS/TiO₂ composite electrode deposited for 10 min is the lowest only about 0.4 mA/cm². The order of the photocurrent densities generated at UV-visible-light irradiation is A > B > C > D.

To evaluate the photocatalytic activities, the degradation of methyl orange in the presence of TiO₂ nanotube arrays and CdS/TiO₂ composite photocatalysts deposited for different times was carried out under UV-visible-light irradiation at room temperature. The experimental results are shown in Fig. 5. It is found that the rate of the degradation of methyl orange with the CdS/TiO₂ composite photocatalysts deposited for 3 min is the highest, the one with the CdS/TiO₂ composite photocatalysts deposited for 10 min is the lowest. This result indicates that the CdS deposited amount on the TiO₂ nanotube arrays affects the photocatalytic activity.

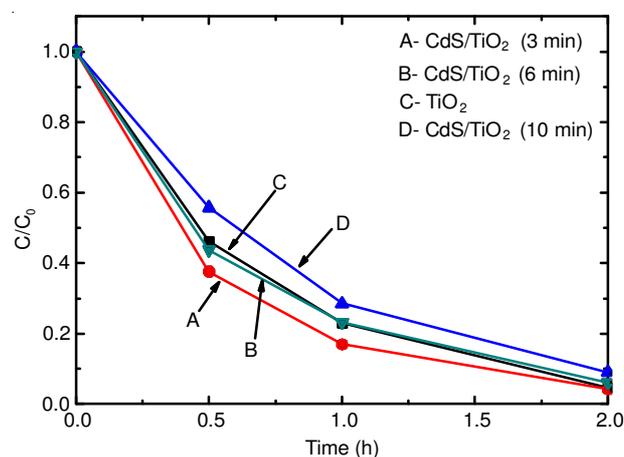


Fig. 5. Rates of degradation of methyl orange with TiO₂ nanotube arrays and CdS/TiO₂ composite photocatalysts deposited for different times under UV-visible-light irradiation at room temperature

From the view of above experimental results, It can be seen that the CdS/TiO₂ composite photocatalyst with a 3 min deposited time shows the best photoelectrochemical performance and photocatalytic activity under UV-visible light irradiation. That is to say, there is an optimum CdS deposited time of CdS/TiO₂ composite photocatalysts for the highest activity under UV-visible light irradiation, which is in agreement by Routhevitch *et al.*¹⁰.

When CdS nanoparticles were electrodeposited on the TiO₂ nanotube arrays, a good electro-contact heterojunction was formed between TiO₂ and CdS. The absorption intensity of CdS is relatively low in the UV area (Fig. 3), the electrons are excited into the CdS conduction band followed by a quick injection into the TiO₂ conduction band. The band-gap match between CdS and TiO₂ can efficiently increase the photoelectron-hole separation. Also, the formation of the heterojunctions strongly decreases the photogenerated carrier recombination. On the other hand, under illumination of the UV light, the electrons in the valence band of TiO₂ are excited into the conduction band. However, if the deposited amount of CdS on TiO₂ is too much, the TiO₂ nanotube arrays will be fully covered with CdS and can not absorb the UV light, which leads to decrease the photocatalytic activity. So there is an optimum CdS deposited amount of CdS/TiO₂ composite photocatalysts for the highest activity under UV-visible light.

Conclusion

Titania nanotube arrays were prepared by titanium anodizing, then CdS nanoparticles were deposited on the TiO₂ nanotube arrays by an AC electrodeposition technique for different times. The photocatalytic activity of the CdS/TiO₂ composite photocatalyst with a moderately deposited time is better than that of the naked TiO₂ nanotube arrays under UV-visible light irradiation, whereas the too long deposited time leads to decrease the photocatalytic activity of the CdS/TiO₂ composite photocatalyst. The reason is that when the CdS deposited time is too long, the TiO₂ nanotube arrays will be

fully covered with CdS and can not absorb the UV light. The optimum deposited time of the CdS/TiO₂ composite photocatalysts showed the highest activity under UV-visible light irradiation was determined to 3 min.

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