A Sonoelectrochemical Synthesis of Nanosized CdS on the TiO₂ Nanotubes Array for Highly Enhancing Photoelectrochemical Reactivity

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ABSTRACT

The nanoparticles of CdS were precipitated onto selforganized TiO₂ nanotube array photo-electrodes using sonochemical synthesis combining with constant current electrochemical deposition at 50 °C. The CdS nanoparticles, averaging 28.1 nm in diameter, were deposited on TiO₂ nanotubes. The prepared CdS nanoparticles were smaller in diameter and were better dispersed than when using plain electrodeposition. The sonochemical technique greatly reduced the temperature of electrochemical synthesis of CdS nanoparticles and the prepared CdS-TiO₂ nanocomposite possessed a stronger photocurrent response in both UV and the visible region. Additionally, a schematic diagram was proposed to illustrate the possible interaction between sonochemistry and electrochemical deposition.

Keywords: sonoelectrochemical synthesis, TiO₂ nanotube array, CdS nanoparticles, photoelectrochemical reactivity

1 INTRODUCTION

Highly ordered titania (TiO₂) nanotube arrays synthesized by anodic oxidation of titanium have been of great interest in recent years, due to the emergence of various attractive applications based on solar light conversion [1, 2]. Coupling TiO₂ nanotube array electrodes with a narrower band gap semiconductor seems to be a promising approach to extend their photo response in the visible region [3-6]. Cadmium sulfide (CdS) is one of the most important II-VI semiconductors used in various photo-electronic devices [7]. Previous methods of CdS preparation usually require high vacuum and/or high temperatures because it is necessary to produce gaseous precursor molecules or atoms to realize effective CdS synthesis [8-13]. Moskovits et al developed electrochemical fabrication of CdS nanowire or nanotube arrays in dimethyl sulfoxide (DMSO) by DC electrodeposition [1-17]. Although this method offers a simple and controllable way of synthesizing CdS nano-materials, the reaction temperature must be kept at 110 °C to enable elemental sulfur to dissolve in DMSO. High temperatures may result in the conglomeration and formation of larger particles, which decreases the photo response of CdS to sunlight. The use of ultrasound techniques in chemistry has developed rapidly in recent years and combining sonochemistry with electrochemistry has proven to be efficient in the preparation of various materials [18-20]. Ultrasound gives rise to high energy chemistry via the process of acoustic cavitations, making sonochemistry a unique interaction of energy and matter. However, little research has focused on the preparation of CdS nanomaterials using the sonoelectrochemical technique. We reasoned that the short energy bursts of high temperature ultrasound may allow the formation of CdS nanoparticles at lower environmental temperatures in the DMSO.

In this work, the nanoparticles of CdS were precipitated onto self-organized TiO₂ nanotube array photo electrodes by using sonochemical synthesis combined with constant current electrochemical deposition at 50 °C. The CdS nanoparticles, averaging 28.1 nm in diameter, were deposited on TiO₂ nanotubes. The prepared CdS nanoparticles were smaller in diameter and were better dispersed than when using plain electrodeposition. The sonochemical technique greatly reduced the temperature of electrochemical synthesis of CdS nanoparticles and the prepared CdS-TiO₂ nanocomposite possessed a stronger photocurrent response in both UV and the visible region.

2 EXPERIMENTAL

The highly ordered TiO_2 nanotube arrays (TiO_2NTs) were prepared by electrochemical anodic oxidation. A pure Ti sheet polished with Pt counter electrode was immersed in 0.5 wt% HF electrolyte, and polarized at 20 V for 20 min at room temperature. After fabrication, the samples were rinsed with DI water and dried in air. Subsequently, the samples were calcined at 450 °C in ambient air for 2 h with heating and cooling rates of 5 °C/min to induce anatase crystallization.

The CdS nanoparticle-modified TiO₂ nanotube arrays (CdS@TiO₂NTs) were prepared by sonoelectrochemical deposition method using a two-electrode system comprised of a Pt foil counter electrode and TiO₂ nanotube arrays work electrode (1 cm^2) under ultrasound. A mixed solution of 0.01 M CdCl₂ in dimethyl sulfoxide (DMSO) with saturated elemental sulfur was used as the electrolyte. Prior to sonoelectrodeposition, the mixed solution was bubbled with flowing N₂ for 30 min in order to remove O₂ within the solution. Then the CdS was cathodically deposited at the optimum constant DC density of 0.5 mA/cm² with ultrasonic intensities of 0.96, 1.2, 1.68, and 2.4 kW/m² for different times. After deposition, the photoelectrodes were immediately removed from the electrolyte and rinsed firstly

with hot DMSO, then with acetone, and lastly with doubledistilled water. The samples were finally dried in air at room temperature.

For reference, CdS@TiO₂NTs was also prepared by regular DC electrochemical deposition under the same conditions as the sonoelectrochemical deposition, except the temperature was $110 \,^{\circ}$ C.

The morphologies of the samples were observed by a LEO-1530 field emission scanning electron microscope (SEM). X-ray diffraction (XRD, Philips, Panalytical X'pert, Cu KR radiation) experiments were performed to determine the crystalline structure of the samples. X-ray photoelectron spectroscopy (XPS, VG, Physical Electrons Quantum 2000 Scanning Esca Microprob, Al K α radiation) combined with 4 keV Ar⁺ depth profiling was employed to analyze the elemental composition of the nanotube array films.

Photoelectrochemical measurements were carried out in $0.1 \text{ M } \text{Na}_2\text{SO}_4$ using a LHX 150 Xe lamp, a SBP 300 grating spectrometer, and an electrochemical cell with a quartz window. The wavelength-dependent spectral response was measured in a three-electrode configuration with a platinum wire counter electrode and SCE reference electrode at zero bias (VS SCE) in the range of 250-500 nm. The photoabsorption properties of the nanotube arrays were recorded with a diffuse reflectance UV-visible spectrometer (DRS) (Varian, Cary 5000).

3 RESULTS AND DISCUSSION

Highly ordered TiO₂ nanotube layers were grown in a 0.5 wt% HF solution using anodic oxidation, as previously described by the research groups of Grimes [1] and Schmuki [2]. Then the CdS nanoparticles were deposited into/onto the crystallized TiO2 nanotubes using the sonoelectrochemical method. For comparison, the CdS was also deposited on identical crystallized TiO₂ nanotube electrodes using the electrochemical method under the same conditions. The morphology of samples was examined using scanning electron microscope (SEM) images. The typical top and cross sectional views are shown in figure 1a and 1b, respectively. The TiO₂ layer consisted of an array of individual nanotube of 100 nm in diameter, with a wall thickness of 15 nm and a length of 400 nm. Figure 1c and 1d are SEM images of the prepared CdS modified TiO₂ nanotube layers after 2 min and 5 min of sonoelectrodeposition at 0.5 mA cm⁻², respectively. It can be seen that just a few CdS nanoparticles were deposited upon the TiO₂ nanotube arrays. Figure 1e is a SEM image of the CdS modified TiO2 nanotube layers after 10 min of sonoelectrodeposition. It is clearly indicated that the TiO₂ nanotube arrays were extensively covered with a relatively uniform layer of CdS nanoparticles with an average diameter of 28.1 nm. The corresponding cross-sectional SEM image (figure. 1f) shows that some CdS nanoparticles (marked with an arrow) were intercalated into the nanotubes.



Figure 1. SEM images of TiO₂ nanotube array electrodes (a, b) and CdS-TiO₂ nanotube array electrodes after CdS sonoelectrochemical deposition at 0.5 mA cm⁻² for 2 min (c), 5 min (d) and 10 min (e, f), respectively.



Figure 2. SEM image of CdS@TiO₂NTs electrodeposition at constant DC density of 0.5 mA cm⁻² for 5 min without ultrasonic irradiation.

Figure 2 is a SEM image of the as-prepared $CdS@TiO_2NTs$, showing a bigger diameter of CdS nanoparticles than those from the sonoelectrochemical method. Additionally, the CdS nanoparticles were also be deposited on metallic Ti at the same deposition rate for 10 min. The diameter distribution of CdS nanoparticles prepared using sonoelectrodeposition and plain electrodeposition indicates the diameter of particles was smaller with the sonoelectrodeposition.

The composition and structure of the TiO_2 nanotube and sonoelectrodeposited CdS nanoparticles were characterized by X-ray Photoelectron Spectroscopy (XPS) and X-ray Diffraction (XRD). Figure 3 shows a comparison of XRD patterns of TiO_2NTs and CdS@ TiO_2NTs . It is apparent that the anodized TiO_2NTs only exhibited an amorphous structure (curve 4a), while all calcined samples showed



Figure 3. Prepared TiO₂NTs respective XRD patterns of the (a) calcined TiO₂NTs in air at 450 $^{\circ}$ C (b) CdS@TiO₂NTs after 5 min (c) 10 min (d) electrodeposition. (A-anatase, C-CdS, T-titanium).

clearly the crystalline phase of anatase. The characteristic peaks corresponding to (002), (101), (102) and (110) crystal planes of CdS were detected from CdS@TiO_2NTs samples (curves 4c and 4d). These peaks can be indexed to a CdS hexagonal structure (JCPDs, No. 02-0549). The broad peaks associated with the hexagonal CdS phase suggest that the sizes of the CdS nanopaticles are very small. It can be seen that the deposited CdS was found to be inhomogeneous with the maximum CdS being deposited close to the surface, then exponentially decreasing with increasing depth inside the film. The result proved that CdS nanoparticles were loaded mostly on the surface of TiO_2NTs and a small quantity of CdS nanoparticles were deposited into TiO_2NTs. The result is consistent with the SEM observations.

Figure 4 investigates a comparison of the photocurrent spectra of plain TiO₂ nanotube array electrodes, a pure CdS layer on a Ti substrate and various prepared CdS-TiO₂ nanotube arrayelectrodes with different deposition times. It is apparent that the photocurrent of TiO₂ nanotube array electrodes modified by CdS nanoparticles was larger than those of either plain TiO₂ nanotube arrays or pure CdS layers in all wavelengths. Also, the CdS-TiO₂ nanotube array electrode prepared using the sonoelectrochemical method had a larger photocurrent and a broader photoresponse than the CdS-TiO₂ prepared by DC electrochemical method under the same deposition with conditions. It is noted that, 10 min sonoelectrodeposition, the photocurrent of CdS-TiO₂ was greater than that of either the plain TiO₂ nanotube array or the CdS-TiO₂ nanotube electrodes prepared using plain electrodeposition. Also, its photocurrent response light range increased from 280 nm to 475 nm. The experiments suggest that the CdS-TiO₂ nanotube layer is able to harvest light much more effectively than plain TiO₂ nanotube arrays under visible light illumination. The black curve in figure 4 shows the IPCE spectrum using TiO₂ nanotube array electrode, which indicates the external quantum

efficiency of the material is 9.82% when the incident light wavelength is 300 nm. The efficiency using CdS layer alone is 3.58% when the wavelength is 300 nm. For the CdS nanoparticle (sonoelectrodeposited for 2 min) sensitized TiO₂ nanotube array electrodes, the quantum efficiency is approximately 100% at the wavelength of 300 Additionally, for nm. the CdS nanoparticle (sonoelectrodeposited for 10 min) sensitized TiO₂ nanotube array electrodes, the quantum efficiencies are greatly enhanced at wavelengths from 280 nm to 475 nm, which suggests greatly enhanced overall efficiency.



Figure 4. Photocurrent spectra of TiO_2 nanotube arrays (black), CdS layer (green) and four types of CdS modified TiO_2 nanotube array electrodes, respectively.

This strong photo-response may be attributed to three major improvements. Firstly, smaller CdS nanoparticles were planted on TiO₂ nanotubes, and better dispersion was obtained. Secondly, increased light absorbability and better scattering was produced within the CdS-TiO₂ nanocomposite structure. Additionally, the photo-generated charge carriers in the CdS-TiO₂ nanotublar structure were separated more efficiently than the pure TiO₂ nanotube structure due to the favorable electron (e⁻) and hole (h⁺) transfer.

Accordingly, a possible precess can be proposed to illustrate the sonoelectrochemical synthesis of nanosized CdS on the TiO₂ nanotubes array. The deposition process would be composed of four steps: (a) dissolution of elemental sulfur; the effect of ultrasound in a liquid medium is primarily caused by cavitation, which promotes dissolution of elemental sulfur via local high temperature of ultrasound: (b) expelling air from nanotube-air in the nanotubes hinders inpouring of the electrolyte when TiO₂ nanotube electrodes were immersed in the electrolyte. In a push-pull regime, bubbles are formed from the dissolved gas and air in the nanotubes. Then the bigger bubbles can be effectively expelled from the electrolyte by oscillation of the entire system; (c) reduction of element sulfur to S^{2-} on the TiO₂ nanotube electrode; and (d) formation of CdS nanoparticles on TiO₂ nanotubes.

4 CONCLUSION

In conclusion, we have demonstrated that a simple and controllable way of preparing CdS nanoparticles deposited uniformly onto TiO₂ nanotube-array films at the lower temperature of 50° C has been developed using a sonoelectrochemical technique. In the coupled semiconductor system, the small band gap semiconductor CdS that can absorb light acts as a photo-sensitizer for the TiO₂. Through transfer of the photo-excited electron from CdS nanoparticle to TiO₂ nanotube, an enhanced photocatalytic reaction can occur. Thus, this photosensitization property of a coupled semiconductor system of CdS-TiO₂ provides a promising alternative approach in the design of highly efficient photocatalyzer of light.

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