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Preparation and photoelectrochemical properties of TiO_2 hollow spheres embedded TiO_2/CdS photoanodes for quantum-dot-sensitized solar cells

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ABSTRACT

A novel process was developed by introducing TiO_2 hollow spheres (THS) into TiO_2 nanoparticles film as light scattering centers to improve the light harvesting of CdS sensitized TiO_2 (TiO_2/CdS) photoanodes for quantum-dot-sensitized solar cells (QDSCs). The THS in TiO_2 nanoparticles film can largely enhance the light scattering due to the multi-reflection among or within the THS, leading to the increase of optical path length in TiO_2 film. Furthermore, the THS in TiO_2 particles favors the penetration of CdS nanocrystals in the porous TiO_2 film. As a result, the photocurrent is significantly improved with THS embedding in TiO_2/CdS photoanodes. The experiment results suggest that an optimal content of THS is highly desired, too high content of THS in the photoanode will degrade the light to electricity conversion efficiency due to the strong back-scattering in the interfacial area of TiO_2 film and the conducting glass, penetration of excess and large CdS nanocrystals, and poor charge transfer between TiO_2 particles. The photoelectrochemical measurement shows that the highest photocurrent of 2.4 mA/cm^2 was obtained with 10% THS in the TiO_2/CdS photoanode, which is nearly four times higher than that of the TiO_2/CdS photoanode without THS (0.5 mA/cm^2).

1. Introduction

Quantum-dot-sensitized solar cells (QDSCs) are considered as a promising low-cost alternative to existing photovoltaic technologies such as crystalline silicon and thin inorganic films, due to the versatile properties of semiconductor quantum dots (nanocrystals), such as tunable band-gap, high absorption coefficient, generation of multiple electron carriers under high energy excitation and delivery of hot electrons without thermalization [1–3]. Porous TiO_2 film is a key material for the photoanode of QDSC, which serves as a high surface area substrate for semiconducting nanocrystals sensitizer and a conductor of photogenerated electrons from the sensitizer to the anode. Up to now, TiO_2 nanostructures in different shapes, such as nanoparticles, nanorods, nanotubes, hollow spheres, have been employed to tailor optical and electronic properties of photoanodes [4–7]. TiO_2 hollow spheres (THS) with low bulk density, high specific surface area, and good surface permeability [8–12] are considered as novel nanostructures for photoanodes in QDSCs and dye-sensitized solar cells (DSSCs). In DSSCs with porous TiO_2 based photoanodes prepared by either embedding THS in the TiO_2 particle films or coating THS on the TiO_2 films or conducting glass [8,13–19], the THS have been proved to benefit the utilization of light due to the enhancement of light scattering. However, few reports focused on the photoanodes for QDSCs based on THS [20]. In a recent report [20], Wang et al. introduced a THS scattering layer in QDSCs and achieved a 10% improvement of solar-to-electric conversion efficiency. As the size of semiconductor nanocrystals sensitizer in QDSCs is much larger than dye molecules, penetration of nanocrystals into high aspect-ratio TiO_2 nanostructure is more difficult than the case in DSSCs [21]. Therefore, it is of great interesting to investigate the effect of THS embedding in TiO_2 particles film as scattering centers on the optical and photoelectrochemical properties of the semiconductor nanocrystals sensitized TiO_2 photoanodes for QDSCs.

In this paper, THS embedded TiO_2 nanoparticles films were prepared by doctor-blade method. In succession, CdS nanocrysals were deposited on the TiO_2 films by a successive ionic layer adsorption and reaction (SILAR) method. The influence of THS embedding on the deposition of CdS, the optical and photoelectrochemical properties of TiO_2/CdS films was studied. The experiment results show that the TiO_2/CdS photoanode with 10% THS exhibited the best photoelectrochemical performance due to the enhanced light scattering of the THS as well as the facile penetration of CdS nanocrystals in the porous TiO_2 films.

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2. Experimental

2.1. Synthesis of THS

According to the Ref. [22], particles could efficiently scatter light with wavelength less than double size of the particles. To enhance the light scattering in visible light region in range from 400 to 700 nm, the appropriate size of THS should be around 350 nm. THS were synthesized using SiO_2 sphere template method [23]. Firstly, SiO_2 sphere templates with a uniform size of 300 nm were prepared using a modified Stöber method. Then, TiO_2 shell of about 50 nm in thickness were deposited on the SiO_2 templates by a sol–gel method to obtain SiO_2@TiO_2 core–shell structure. In succession, the SiO_2 cores were removed from the obtained core–shell spheres by using hydrothermal treatment in NaOH solution. The finally obtained amorphous THS were dispersed in ethanol to prepare a suspension with a density of about 4.2 mg/ml.

2.2. Fabrication of TiO_2/CdS photoanodes with THS

Eighty milligram TiO_2 nanoparticles (P25, 20–30 nm, Degussa AG), 10 mg ethyl cellulose and 130 mg terpineol were mixed in ethanol. Then, the ethanol was evaporated to obtain a TiO_2 nanoparticles doctor-bladeing paste. To prepare paste with different content of amorphous THS, 1 ml, 2 ml and 3 ml of THS ethanol suspension was added to the same amount of mixture of P25 TiO_2 nanoparticles, ethyl cellulose, terpineol and ethanol, before the ethanol-evaporating process. The mass percentages for THS in TiO_2 were 5%, 10% and 15%, respectively. The pastes with and without THS were doctor-bladed on the fluorine-doped tin oxide (FTO) glass and sintered at 500 °C for 1 h to crystallize THS into antase phase. The finally obtained TiO_2 films (~10 μm thick) were denoted as THS-0%, THS-5%, THS-10% and THS-15%, respectively.

For the deposition of CdS nanocrystals, a SILAR method was used. Briefly, the TiO_2 film was firstly dipped into 0.05 M $Cd(NO_3)_2$ aqueous solution for 5 min, rinsed with deionized water, and then dipped for another 5 min into 0.05 M Na_2S aqueous solution, and rinsed again with deionized water. Ten cycles, the two-step dipping procedure is termed as a cycle, were applied to ensure the deposition of enough CdS nanocrystals. The CdS sensitized TiO_2 films with different content of THS are referred to THS-0%/CdS, THS-5%/CdS, THS-10%/CdS and THS-15%/CdS, respectively.

2.3. Characterization

The morphology and microstructure of the samples were examined by a JEM-2100 transmission electron microscope (TEM), and a Hitachi S-4800 field emission scanning electron microscope (SEM), coupled with an energy dispersive spectroscopy (EDS). The transmittance, reflectance, and incident photon-to-current conversion efficiency (IPCE) spectra were taken using Zolix Solar Cell QE/IPCE Measurement System (Zolix Solar cell Scan100) equipped with an integrating sphere. For IPCE measurement, 0.2 M Na_2S aqueous solution and platinum foil were served as redox couple and counter electrode respectively. A 300 W Xe lamp equipped with gratings was used to generate a monochromatic beam, and the incident light intensity was calibrated by a standard silicon photodiode. The photoelectrochemical performance of the TiO_2/CdS photoanodes is investigated by conducting the photocurrent density vs. potential (J–V) measurements in the three electrodes cell configuration with platinum as counter electrode, saturated calomel electrode (SCE) as reference electrode and 0.2 M Na_2S aqueous solution as electrolyte; 150 W xenon lamp was used as the light source.

3. Results and discussion

3.1. Characterization of the as-prepared THS

Fig. 1 shows the SEM and TEM images of the as-prepared THS. In this case, the THS prepared without any calcination treatment are amorphous phase [18]. The SEM images (Fig. 1a and b) show that the THS exhibit good spherical morphology with a uniform size of about 350 nm in diameter. The occasionally observed broken spheres demonstrate the formation of hollow spheres. The TEM image in Fig. 1c further indicates the hollow structure with a shell thickness of about 50 nm.

3.2. Morphologies of TiO_2 films embedded with THS

The cross-sectional view SEM images in Fig. 2 shows the porous structure of the TiO_2 films with different contents of THS after calcination at 500 °C for 1 h. XRD measurement (not shown) confirms that the amorphous THS have been crystalized into anatase phase [23]. It is obvious that most of the THS embedding in the TiO_2 nanoparticles remain good spherical morphology even after the calcination at 500 °C. And, the THS are uniformly dispersed into the TiO_2 nanoparticles in samples THS-5% and THS-10%, while some of THS aggregate into larger particles in THS-15% due to the high content of THS.

3.3. Optical properties of TiO_2/CdS photoanodes

Fig. 3 shows the optical transmittance (Fig. 3a and b) and reflectance (Fig. 3c and d) spectra of the TiO_2 photoanodes with and without CdS sensitization. As shown in Fig. 3a, the transmittance of the TiO_2 film gradually decreased with the increase of content of THS, indicating the enhancement of light trapping property of the THS embedded films. A similar trend is observed after the deposition of CdS nanocrystals, as shown in Fig. 3b. The lower transmittance in the range of 400–530 nm for TiO_2/CdS photoanodes compared to that of the pristine TiO_2 film is ascribed to the light absorption of CdS nanocrystals. The absorption onsets deduced from the reflectance spectra could be qualitative determined by linear extrapolation from the inflection point of the curves toward the baseline, as indicated with dashed lines in Fig. 3b. The CdS sensitizing in TiO_2 film extends the optical absorption into the visible region. Furthermore, the absorption edge of the curves shifted to long wavelength region as the content of THS in the TiO_2 film increases. The absorption edge in visible region is related to the band-gap of CdS nanocrystals, which is tuned by the size of the nanocrystals. So, we can conclude that higher content THS embeded in the TiO_2 film facilitates the formation of larger size CdS nanocrystals.

Normally, in a porous TiO_2 structure with small pore size, the surface tension of water suppress the penetration of ions into the porous film and hence restrict the penetration of CdS nanocrystals [24]. However, in this case, the introduction of THS of 350 nm in diameter in the TiO_2 particles film results in a wider pore size distribution for effective CdS penetration in TiO_2 film [25]. With the increasing content of THS, more and lager CdS nanocrystals form within the TiO_2 porous film, resulting in the improved visible light absorption and the red-shift of the absorption onset. The facilitated penetration of CdS nanocrystals into THS embedded TiO_2 film is also confirmed by the measurement of CdS content along the cross-section of the TiO_2/CdS photoanode. The SEM image in Fig. 4 provides an entire cross-sectional view of the microstrucure of the THS-10%/CdS film, which is about 10 μm in thickness. EDS spectra at the top (A), middle (B) and bottom (C) position in the cross-section reveal the penetration of CdS nanocrystals even at the deep region of the film. The sligtly reduced percentage of Cd and S (shown in the right of Fig. 3) indicates a gradual reduction of CdS nanocrysals deposition from the top to the bottom of the film. Therefore, the THS embedding results in an excellent penetration depth and an increased amount of CdS nanocrystals loading in TiO_2 film.

The enhanced light scattering of the incoming radiation in THS embedded TiO_2 film is revealed by the reflectance spectra, as shown in Fig. 3c. The reflectance in the visible region (from 425 to 700 nm) increases with the increasing content of THS. The result is in consistent with P. Stamatakis's report that particles could efficiently scatter light with wavelength less than double size of the particles [22]. Considering the scattering and multi-reflection of light among or within the THS [9], optical path length of the visible light in the THS embedded TiO_2 films would be extended and the light absorption of the CdS nanocrystals are enhanced (Fig. 3d). However, it should be mentioned that the reflected light also covers back-scattered light resulting from the light scattering of THS near the conducting glass. The back-scattering, which becomes stronger with the increasing content of THS, is negative for the light harvesting of the photoanodes [15].