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Fabrication and characterization of CdSe quantum dots sensitized TiO_2 nanotubes films and their photovoltaic properties

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TiO_2 nanotubes (NTs) were synthesized by hydrothermal method. The TiO_2 NTs applied to make photoelectrode for CdSe quantum dots (QDs) sensitized solar cells. CdSe QDs sensitized TiO_2 nanotubes were successfully prepared by successive ionic layer adsorption and reaction (SILAR) technique. The morphology, structure and properties of prepared samples were characterized by X-ray powder diffraction (XRD), transition electron microscopy (TEM), scanning electron microscopy (SEM) and UV-Vis absorption spectroscopy. The decorated CdSe QDs expanded the photoresponse range of TiO_2 NTs from ultraviolet region to 540-640 nm and the CdSe/TiO_2 NTs prepared by SILAR deposition of 6 cycles exhibited the highest visible photocurrent.

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1. Introduction

The photosensitization of nanocrystalline TiO_2 by an adsorption of a dye was pioneered by O'Regan and Grätzel and investigations continued during the past three decades because the potential as a low cost alternative to conventional silicon solar cells [1-3]. In this system, a very large surface-to-volume ratio of nanocrystalline TiO_2 is used for coverage of the dye onto a TiO_2 surface. The decrease of electron diffusion coefficient in the nanocrystalline particles of TiO_2 can be a consequence of the presence of electron traps that occur in the grain boundaries at the contacts between these nanoparticles. Thus, the use of TiO_2 in the form of nanorods, nanowires and especially nanotubes (NTs) may be an interesting approach to improve electron transport [4-7].

Quantum sized semiconductor materials such as CdS, PbS, InP, CdSe have recently been reported for possible use as a photosensitizer absorbing photons on TiO_2. Considerable interest has developed regarding quantum dots because of their unique electronic and optical properties. The use of quantum dots as sensitizers have advantages compared to organic dyes that are an adjustable band gap or band edge, effective light harvesting, and their possible stability under sun light. Most quantum dots for use as sensitizers can be produced by in situ-precipitation on the TiO_2 [1-3]. CdSe QDs (Eg =1.7 eV) as semiconductor sensitizer is the most widely investigated light absorber in semiconductor-sensitized solar cells owing to its wide absorption spectrum. As a result of recent reports, CdSe QDs as a sensitizer for TiO_2 solar cells are being widely investigated [1-3]. In current study, one dimensional TiO_2 NTs synthesis by hydrothermal method. The SILAR method was applied for sensitization of TiO_2 NTs by CdSe QDs. Then this photoelectrode used for fabrication of solar cell and its photovoltaic properties were characterized.

2. Experimental

2.1. Synthesis of TiO_2 NTs

In a typical synthesis, 5 g TiO_2 P25 nanoparticles (Degussa) entered into a Teflon autoclave of 500 ml capacity. Then, the autoclave was filled with 80 ml NaOH (10 M) aqueous solution, sealed into a stainless tank and maintained at 140 °C for 16 h. Then the autoclave was naturally cooled to room temperature and the obtained sample was filtered, washed with distilled water for several times. Finally the products were collected and washed with 0.1 M HCl aqueous solution and subsequently washed with distilled water for several times. At last, the products were calcinated at 500 °C in air for 30 min.

2.2. Preparation of TiO_2 NTs Film

The 4 g of TiO_2 NTs was ground in a mortar with 8 ml of distilled water, 20 µl of acetylacetone (Merck) and 10 drops of Triton X-100 (Aldrich) to break up the aggregate into a dispersed paste. TiO_2 NTs thin film was coated using doctor blade technique onto F-doped SnO_2 glasses (Solaronix) which the electrodes subjected to $TiCl_4$ (Merck) treatment at 70 °C for 30 min before and after

coating of TiO_2 layer. All electrodes were sintered at 500 °C for 30 min.

2.3. Preparation of CdSe QDs sensitized TiO_2 NTs

The prepared TiO_2 NTs films were sequentially sensitized with CdSe QDs by using SILAR technique. First, 0.01 M NaHSe was synthesized by mix the selenium powder (0.01 M) (Merck) with $NaBH_4$ (0.08 M) (Merck) in deionized water at 60 °C and stirred for 10 min. Second, the TiO_2 NTs films was dipped in 0.01 M $CdCl_2$ solution (Merck) at 60 °C for 10 min and rinsed in deionized water. Then, it was immersed in 0.01M NaHSe solution at 60 °C for 10 min and then washed with deionized water. The two-step dipping procedure was termed as one SILAR cycle. In this paper, cycles of 2, 4, 6, 8 were done to specify the optimum condition for synthesis of CdSe-sensitized TiO_2 NTs films.

2.4. Solar cell fabrication

Solar cells fabricated of CdSe QDs sensitized TiO_2 NTs films as a working electrode and Pt-sputtered glass was used as the counter electrode. The cells were sealed with thermoplastic (DuPont Surlyn®, Solaronix). A drop of an iodide electrolyte solution (Solaronix) was infiltrated into the cells. I-V characteristics were measured using a potentiostat (CHI 604C, CH Instruments) and a solar simulator (1 sun, Am 1.5).

2.5. Characterization

The phase compositions of samples were determined by X-ray diffractometer (XRD, D5000 model) equipped with graphite monochromatized Cu KD radiation. The morphology and composition of the prepared sample was observed using scanning electron microscopy (SEM, Philips XL30 model), transmission electron microscopy (TEM, Tecnai™ G2 F30 model) and Energy-dispersive X-ray spectroscopy (EDX). UV-Vis diffuse reflectance spectra (DRS) were recorded on a UV-4100 UV-Vis spectrophotometer.

3. Results and discussion

3.1. Characterization of TiO_2 NTs

The crystal structure is confirmed by the X-ray diffraction (XRD) analysis. Fig. 1 shows the XRD pattern of the TiO_2 NTs synthesized sample. All the relatively sharp peaks could be indexed as anatase TiO_2 with crystalline cell constants a = 3.783Å and c = 9.51Å, which indicated they obtained TiO_2 had relatively high crystallinity, and these peaks are basically in agreement with the reported values Joint Committee on Powder Diffraction Standards (JCPDS) card No. 04-0477.

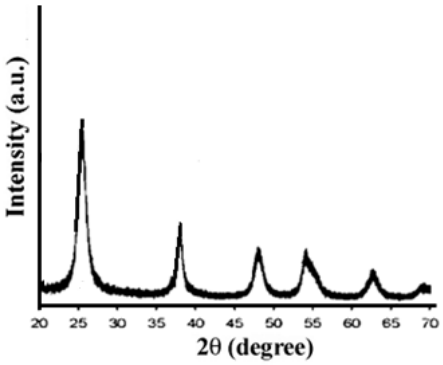

Fig. 1. X-ray diffraction pattern of the as-synthesized anatase TiO_2 NTs.

The TiO_2 NTs were obtained after hydrothermal synthesis, showing very clear morphology and well-defined structure (Fig. 2a). TEM images (Fig. 2b) demonstrate that NTs grow extensively with the length of several hundred nanometers with quite clean and smooth tubular surfaces. No TiO_2 particles exist around the NTs, proving high yield conversion of TiO_2 synthesized powder to NTs under experiment conditions.

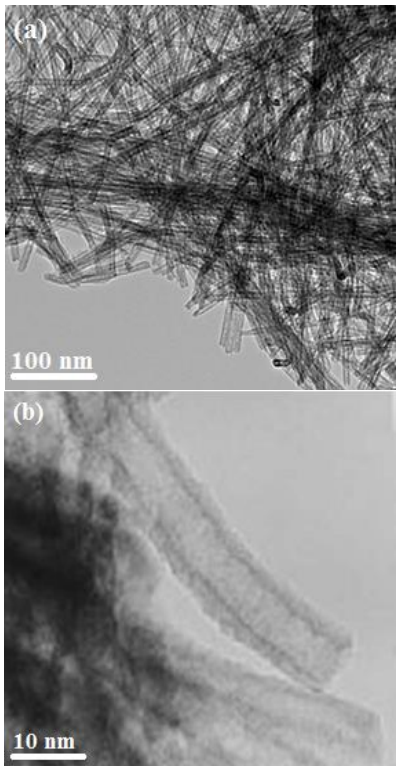

Fig. 2. (a, b) TEM image of TiO_2 NTs were obtained after hydrothermal synthesis.

3.2. Characterization of CdSe QDs sensitized TiO_2 NTs films

The crystal structures and compositions of both the electrodes prepared by SILAR were explored by the X-ray diffraction experiment. Fig. 3 Shows the XRD pattern of CdSe QDs sensitized TiO_2 NTs prepared by 6 cycles SILAR.

As showed in Fig. 4 a, b, the SEM image top-view of the CdSe sensitized TiO_2 NTs with 6 cycles indicates that the SILAR process does not damage nanostructured and the CdSe QDs are uniformly distributed in the TiO_2 NTs. Fig. 4b shows the EDX spectrum of the TiO_2 nanotubes after CdSe deposition, the present of the Ti, O, Cd, and S is clearly showed and the ratio of the Cd:Se = 0.975, which is close to the atom ratio of CdSe composition, confirming that the CdSe is deposited in the film.

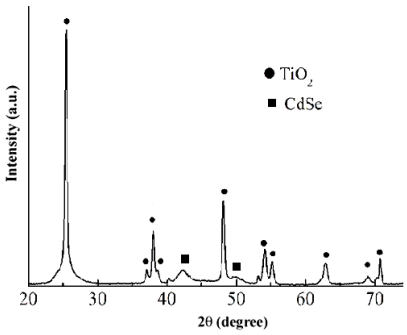

Fig. 3. X-ray diffraction patterns of photoelectrode (TiO_2 NTs / CdSe QDs).

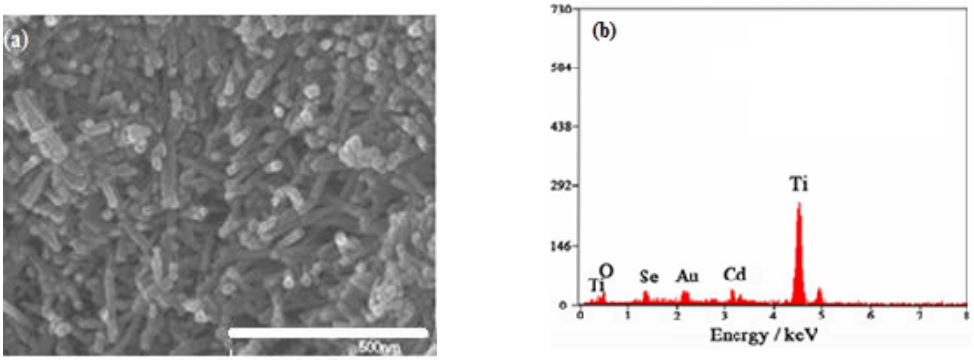

Fig. 4. SEM images of top-view CdSe/ TiO2 NTs, (b) EDX spectrum.

Fig. 5 gives the UV-Vis absorption spectra of the CdSe QDs sensitized TiO2 NTs for different SILAR cycles. The bare TiO_2 NTs show the absorption edge at 392 nm, which corresponds to 3.2 eV band gap. After the deposition of CdSe QDs in the film, the absorption spectra show that the absorption edges are shifted significantly toward the visible region. It was observed that with the SILAR cycles increasing, the absorption peaks transform from approximately 540 nm to 640 nm and the absorption peaks are stronger and stronger. This is due to the increase of the loaded amount of CdSe QDs with the increased SILAR cycles.

Fig. 6 shows the I–V characteristics of the TiO_2 NTs before and after modification with CdSe QDs. The original TiO_2 NTs don't show any photocurrent density under visible light illumination, and photocurrent increases with the increasing of SILAR cycles because of the amount of CdSe quantum dots loaded on the TiO_2 NTs are increasing. However, when the SILAR cycles increased to 8, the photo-current under visible light is smaller than that of 6 cycles. This may too many CdSe QDs are clogged on the nanotubes, which limit the effective transfer of photoelectron and decrease the conversion rate.

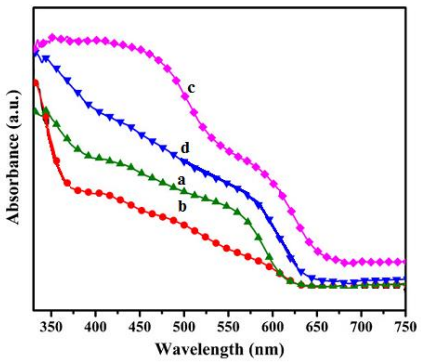

Fig. 5. UV–Vis spectra of the CdSe QDs sensitized TiO_2 NTs (a) CdSe (2), (b) CdSe (4), (c) CdSe(6), (d) CdSe (8).

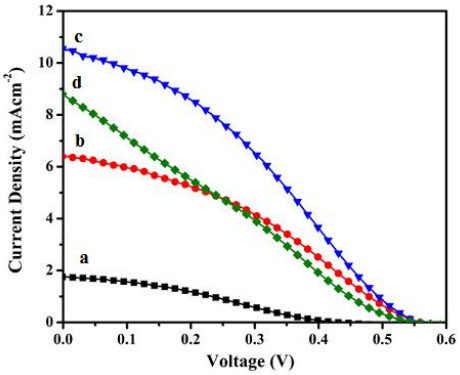

Fig. 6. The I–V characteristics of (a) CdSe(2)/TiO_2 NTs, (b) CdSe(4)/TiO_2 NTs, (c) CdSe(6)/TiO_2 NTs, (d) CdSe(8)/TiO_2 NTs.

4. Conclusions

TiO_2 NTs were successfully produced with hydrothermal method and then applied in quantum dots sensitized solar cells. In summary, CdSe/TiO_2 NTs were successfully fabricated via SILAR deposition of uniform CdSe QDs on the TiO_2 NTs. For the CdSe/TiO_2 NTs film with 6 cycles, the conversion efficiency showed the best result. The most excellent photoelectrochemical performances and the enhanced photoelectrochemical properties can be attributed to the extended absorption in the visible light region and the effective separation of photo-generated carriers in this photoelectrode.

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