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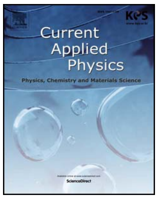

ZnO/TiO_2 core–shell heterojunction for CdS and PbS quantum dot-cosensitized solar cells

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ABSTRACT

ZnO nanorods (NRs) with regular morphology were prepared through hydrothermal method, and the TiO_2 shell was assembled onto the surface of ZnO NRs by spin coating to the ZnO/TiO_2 core–shell heterojunction. CdS and PbS quantum dots (QDs) were used to cosensitize the ZnO/TiO_2 nanostructure by direct adsorption (DA) and successive ionic layer adsorption and reaction, respectively. SEM, TEM, and HRTEM images show that the samples possessed a rough surface and four lattice fringes indicating the successful synthesis of the ZnO/TiO_2/CdS/PbS composite structure. The ZnO/TiO_2(10T)/CdS/PbS sample showed a high absorption intensity at a broad range of wavelength to visible light region. The ZnO/TiO_2(10T)/CdS/PbS photoelectrode with QDSSCs showed the highest IPCE of 36.04% and photoelectric efficiency (η) of 1.59%; these values increased by approximately 550% and 150% compared with those of unsensitized ZnO (0.29%) and ZnO/TiO_2(10T) (1.04%) and about 146% and 120% compared with those of ZnO/TiO_2(10T)/CdS and ZnO/TiO_2(10T)/PbS, respectively. The fill factor was 0.36, and the photocurrent density (J_{sc}) and open circuit voltage (V_{oc}) reached the maximum values of 9.73 mA cm^{-2} and 0.46 V, respectively.

1. Introduction

Quantum dot-sensitized solar cells (QDSSCs) are similar to dye-sensitized solar cells (DSSCs) and are composed of working electrode, electrolyte, and counter electrode; QDSSCs are a promising material for transformation of solar energy to electric energy at a low cost [1,2]. In general, semiconductor metal oxide materials with wide band gaps (E_g), such as ZnO (E_g of approximately 3.3 eV) [3] and TiO_2 (E_g of approximately 3.2 eV) [4,5], exhibit superior properties and electronic structures for transferring charge carrier but cannot absorb visible light and infrared solar photon. Various promising semiconductor QDs with narrow E_g exhibit distinct optical and electrical properties; these QDs include CdS [6,7], CdSe [8,9], PbS [10,11], cadmium telluride [12], and InAs [13]. QDs are mainly characterized by (1) quantum size effect, (2) surface effect, and (3) multiple exaction excitation effect. Semiconductor QDs sensitizing TiO_2 or ZnO can broaden their absorption of the solar spectrum. Therefore, multiple semiconductor QDs with narrow E_g have been used for sensitizing TiO_2 or ZnO to enhance electrical conduction in the composite structure.

Scholars have extensively studied the fabrication and application of ZnO and TiO_2 nanostructures [14–18]. TiO_2 is the earliest and most widely studied photocatalytic material. TiO_2 nanoparticles have attracted considerable research interest because of their high photocatalytic activity, acid–base resistance property, resistance to photochemical corrosion, low cost, non-toxicity, and other advantages [19,20]. ZnO semiconductor materials possess higher electron transport capacity than traditional TiO_2 semiconductor materials and thus can better inhibit the electronic composite and improve the photoelectric properties of the equipment [21]. However, single ZnO nanomaterials with wide band E_g are prone to chemical etching [22], and their light absorption is limited to wavelength ultraviolet light ($\lambda < 387$ nm), thereby limiting the availability of sunlight. To overcome these limitations, researchers have focused on synthesis of ZnO/TiO_2 core–shell heterostructure composites. The ZnO/TiO_2 core–shell heterojunction not only can broaden the range of light absorption wavelength of ZnO nanomaterials but can also prevent or slow down material corrosion caused by the external environment (such as acid, alkali solutions, or organic dyes) to a certain extent. Coating a layer of ZnO led to superior chemical stability and extended service life of the material. Among developed QDs, CdS is the semiconductor material of direct band-gap. Compared with that of TiO_2 (approximately 3.2 eV), the E_g of CdS (approximately 2.4 eV) is more negative. Therefore, electrons produced by the excitation are transmitted rapidly to the conduction band of TiO_2, thereby preventing the recombination of photogenerated electrons and hole pairs. Several studies reported that the photoelectric conversion efficiency of QDSSCs can be further improved if they are

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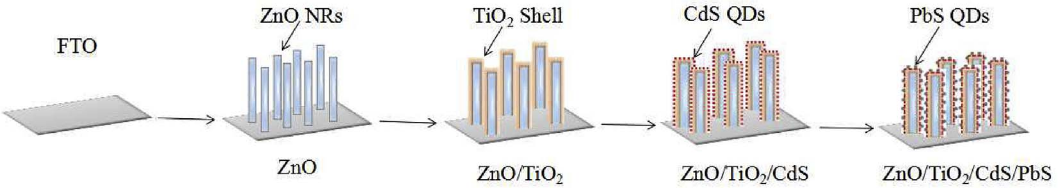

Fig. 1. Schematic of experimental process for ZnO/TiO$_2$/CdS/PbS composite structure.

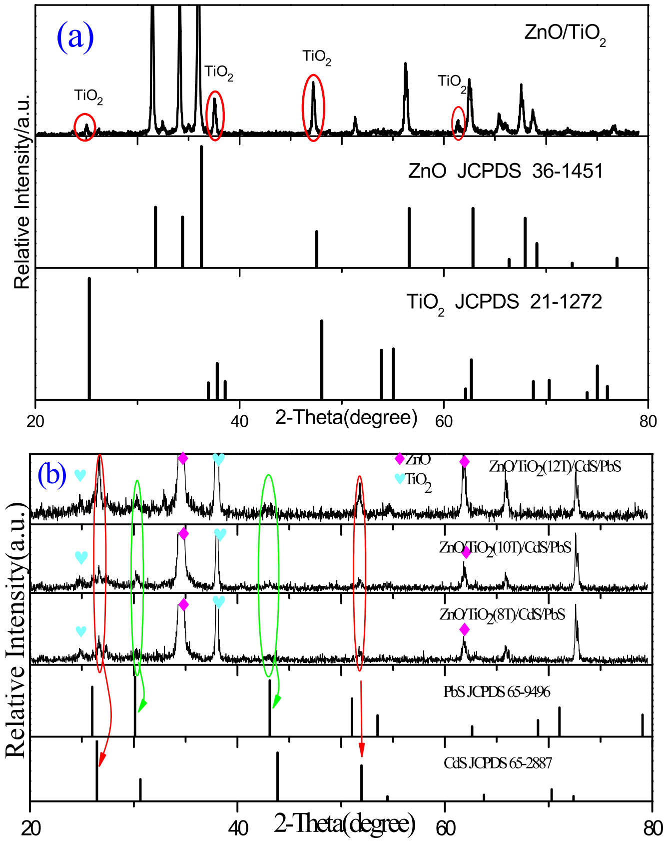

Fig. 2. XRD patterns of ZnO/TiO$_2$ core–shell nanocables(a) and ZnO/TiO$_2$/CdS/PbS composite structure coatings different times(b).

sensitized by multiple QDs [23,24]. Moreover, the light absorption range of PbS can be extended to the near infrared region of the solar spectrum to produce numerous photogenerated carriers [25]. Researchers prefer PbS because of its multiple exciton generation effects [26,27].

In this work, CdS QDs were used to sensitize ZnO/TiO$_2$ nanostructure by direct adsorption (DA). PbS QDs were assembled onto the surface of the samples via successive ionic layer adsorption and reaction (SILAR).

2. Experimental

2.1. Preparation of CdS QDs and PdS QDs

CdS QDs were synthesized by one-step aqueous phase process. A solution of 0.02 M $CdCl_2 \cdot 2.5H_2O$ (analytical reagent (AR) grade) and thioglycolic acid (AR) were added into a 250 mL three-necked flask and stirred constantly. The pH of the solution was adjusted by adding an alkaline solution. The aqueous solution was added with 0.02 M $Na_2S \cdot 9H_2O$ (AR) and refluxed at 100 °C for 5 h.

Aqueous solutions of 0.1 M $Pb(NO_3)_2$ (AR) and 0.1 M $Na_2S \cdot 9H_2O$ (AR) were prepared for growing PdS QDs onto the samples.

2.2. Preparation of ZnO/TiO$_2$ core-shell heterojunction

Fluorine-doped tin oxide (FTO, 10 Ω/cm^2) sheet glass was used as substrate, cleaned ultrasonically by deionized water and alcohol for 30 min, and dried at room temperature. ZnO seed layer was prepared on the FTO glass substrate by dipping it into the solution with 0.05 M zinc acetate and 0.05 M diethanol amine ethyl alcohol for 10 s. ZnO nanoparticles were obtained by annealing at 400 °C for 2 min and used as seed layer. ZnO NRs were prepared on the FTO substrates via one-step hydrothermal method. The two substrates were immersed into a Teflon bottle with autoclavable screw caps and filled with 40 mL of aqueous solution, with the conductive side facing down. The aqueous solution contained 12 mL of ammonia (25%) and 240 mL of 0.1 M zinc acetate. The bottle was heated at 90 °C for 180 min. The samples were removed and dried in air at room temperature.

TiO$_2$ layer was prepared as a shell of the ZnO NRs via a sol–gel process after dissolving titanium isopropoxide [$Ti(OC_3H_7)_4$] in 2-methoxy ethanol. The acid was used to catalyze the hydrolysis of $Ti(OC_3H_7)_4$. The TiO$_2$ layer was spin-coated on the surface of ZnO NRs at 2000 rpm. The TiO$_2$ layer was spin coated for 8, 10, and 12 times to obtain different numbers of surface coating layers, and the samples were labeled ZnO/TiO$_2$(8T), ZnO/TiO$_2$(10T), and ZnO/TiO$_2$(12T), respectively. Finally, the substrate was placed in a furnace and calcined at 500 °C for 2 h to form ZnO/TiO$_2$.

2.3. Preparation of QD-sensitized ZnO/TiO$_2$ core–shell heterojunction

CdS QD-sensitized ZnO/TiO$_2$ nanostructure by DA: the above samples were immersed in CdS QDs solution for 6 h at 60 °C and dried in air at room temperature.

PdS QDs were grown on the samples by SILAR. First, CdS QD-sensitized ZnO/TiO$_2$ core–shell samples were placed on a watch glass with 0.1 M $Pb(NO_3)_2$ aqueous solutions for 3 min. The samples were removed, washed with deionized water, and dried in air. Secondly, the samples were dropped on a watch glass with 0.1 M $Na_2S \cdot 9H_2O$ aqueous solution for 3 min and washed by deionized water. These steps are circulates of SILAR. In this work, PdS QDs were treated for three repeated SILAR cycles.

Fig. 1 shows the flow chart of experimental reaction.

2.4. Characterization

X-ray powder diffraction (XRD) patterns were recorded using a Rigaku/Dmax-2500 system. The morphology, microstructure, and high-resolution transmission electron microscopy (HRTEM) images of the samples were characterized by a JEOL-2100F scanning electron microscope. UV–visible (UV–vis) absorption was obtained by UV-2501PC (Lambda 950). A Keithley 2400 source meter was used to measure the photovoltaic performance (*J–V* curves) of the cell devices under an AM 1.5 G solar simulator illumination. The system was equipped with saturated Ag/AgCl as reference electrode, Pt as counter electrode (CE), and 0.5 M Na_2S and 0.7 M Na_2SO_3 as polysulfide electrolyte. The power of the simulated light was regulated to 100 mW/cm^2 by using an NREL standard Si solar cell. Incident photon-to-current conversion efficiency (IPCE) was recorded on a Zolix electrochemical station using a Zolix LSH-X150 150-W Xe lamp decorated with a monochromator.