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CdSe nanocrystal sensitized ZnO core-shell nanorod array films: Preparation and photovoltaic properties

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ABSTRACT

ZnO/CdSe core-shell nanorod array films were synthesized via a two-step method. ZnO nanorod array films were first grown on a TCO substrate, and then CdSe nanocrystals were deposited on the nanorods to form core-shell structured films. The resulting films were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and UV–vis absorption spectroscopy. Especially, dark-field images and transmission electron diffraction of the TEM were used to study the morphology and the chemical nanostructure of the ZnO/CdSe core-shell nanorods in detail. We investigated the photovoltaic performance of the resulting ZnO/CdSe core-shell nanorod array films as solar cell photoanodes. Parameters, such as the length of the ZnO nanorods, the shell phase structure and the deposition time of the CdSe nanocrystals were found to affect the photovoltaic performance of the solar cell. This study provides a facile method to prepare nanocomposite photoanodes of solar cells, and gives some insight about the fundamental mechanisms that improve the performance.

1. Introduction

One-dimensional (1D) ZnO nanorods with a wide gap have been applied to nanostructured solar cells because of their specific opto-electronic properties [1]. The ZnO nanorod array provides a direct path from the point of photogeneration electron to the conducing substrate and greatly enhances their surface area, leading to improved light harvesting and overall efficiencies [2].

Inorganic semiconductor nanocrystals sensitized nanostructured metal oxides such as ZnO have attracted significant attention as photoanodes in low-cost photovoltaic devices [3,4]. As we all know, the photosensitizer plays an important role in determining the stability [5], light harvesting capability and also the total cost of the dye-sensitized solar cells (DSSCs). At present, despite the success of DSSCs using ruthenium dyes [6], researching cheaper alternative panchromatic sensitizers is still needed in order to improve the performance and reduce the cost of solar cell.

Relatively low band-gap semiconductors such as CdS [7,8], PbS [9,10], Bi_2S_3 [11], CdSe [12,13] and InP [14] have been explored to serve as photosensitizers because of their advantages over dyes that can provide the ability to match the solar spectrum better and generate multiple electron–hole pairs per photon [13,15]. Among these materials, nanocrystalline CdSe has a reasonable band gap (1.7 eV), which matches the solar visible spectrum well and offers new opportunities to harvest light energy in the entire visible region of solar light. There has been an increasing effort to obtain a uniform deposition of CdSe nanocrystal sensitizers on the nanostructured or porous n-type materials such as TiO_2, ZnO, SnO_2 by different techniques, including chemical bath deposition (CBD) [12,16,17,18], sonochemical method [19], electrodeposition [20], and chemical vapor deposition [21]. Among them, CBD is a simple and low-cost method to fabricate composite films. Recently, a small number of investigations have been reported on CdSe sensitized 1D ZnO structured photoanodes. For instance, Norris et al. reported CdSe QDs sensitized ZnO nanowires solar cell [13]. In their studies, CdSe QDs were firstly synthesized by utilizing the injection of organometallic precursors into a hot coordinating solvent, and then assembled on ZnO nanowires via bifunctional linker molecules to aim at increasing the coverage of CdSe QDs. The higher coverage of CdSe on each ZnO nanowire could make the better use of the nanowire-shaped structures of ZnO. Tena-Zaera and co-workers [22] prepared CdSe nanocrystal sensitized ZnO nanoarray solar cells through the electrochemical deposition of a CdSe coating layer on ZnO samples. However, electrochemical deposition process easily results in a thick CdSe layer on the top of the pores between ZnO nanorods.

In this work, CdSe nanocrystal sensitized ZnO core-shell structured nanorod array composite films were successfully obtained by a low-cost and simple two-step method. First, ZnO nanorod array films were grown on a fluorine-doped SnO_2-coated glass (TCO)

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substrate via a hydrothermal method, and then CdSe nanocrystals were deposited on the ZnO films through a CBD method without linker molecules. The chemical nanostructure of the CdSe nanocrystals sensitized ZnO core-shell nanorod array and their photovoltaic performance were investigated. The well-covered thin absorber of CdSe nanocrystals on the ZnO nanorods is beneficial both for light absorption and for charge separation, which are two critical steps in solar-to-electric energy conversion. The combination of ZnO and CdSe shifts the absorption characteristics of the material architecture into the visible light spectrum. Also we investigated how different parameters, such as the length of the ZnO nanorods, the phase structure transformation and the layer thickness of the CdSe nanocrystals affected the performance of the solar cell devices and ultimately got a 0.34% power-conversion efficiency with a short-circuit photocurrent density (J_{sc}) of 3.10 mA/cm^2 and an open-circuit photovoltage (V_{oc}) of 0.43 V correspondingly for the annealed ZnO/CdSe core-shell film.

2. Experimental

2.1. Preparation of ZnO nanorod array films

ZnO nanorod array films were grown on a TCO substrate (resistivity: 10–15 Ω/square, Asahi Company) pre-coated with ZnO seed layers. For preparing the ZnO seed layer, the TCO substrate was first rinsed ultrasonically using acetone, ethanol, and distilled water in sequence. Subsequently, a thin ZnO sol layer was coated on TCO by a dip-coating method. The synthesis of the ZnO precursor sol has been described in detail elsewhere [23]. A ZnO seed film was finally obtained after being annealed at 500 °C for 30 min. The precursor aqueous solution for the preparation of ZnO nanorod array films was composed of 0.1 mol/L $Zn(NO_3)_2$ and $(CH_2)_6N_4$ in a 1:1 molar ratio. The pH value of the solution was adjusted to 8.6 by the addition of ammonia. The precursor solution (60 mL) was then transferred to a Teflon-sealed autoclave comprising substrates pre-coated with a ZnO seed layer. The reaction was run at 95 °C for 3, 4, 8 and 16 h, respectively, to synthesize nanorod array films comprising ZnO nanorods of different length. Finally, the resulting films were rinsed with distilled water and dried at 300 °C for 30 min.

2.2. Preparation of ZnO/CdSe core-shell nanorods array films

CdSe was deposited on a ZnO substrate by the CBD method with $N(CH_2COOK)_3$ (denoted as NTA) as the complex and $NaSeSO_3$ as the Se source. An aqueous $NaSeSO_3$ solution was prepared by refluxing 0.02 mol Se powder with 0.05 mol Na_2SO_3 at 70 °C for 7 h. The above-obtained ZnO nanorod array film was placed vertically into a beaker containing a solution of 80 mmol/L $CdSO_4$, 80 mmol/L Na_2SeSO_3 and 120 mmol/L NTA at 2 °C in the dark. The solution was continuously stirred to achieve a homogenous distribution of the chemical components during the deposition. After deposition for different times, the films were rinsed with deionized water. The annealing process of the composite film was performed in a tubular furnace at 400 °C under a N_2 atmosphere.

2.3. Characterization

The morphology of the samples was characterized using field-emission scanning electron microscopy (SEM, JEOL 6700F). Transmission electron microscopy observations (mainly including electron diffraction patterns and dark-field images) were performed using transmission electron microscopy and selected area electron diffraction (TEM/SAED, JEOL 2010F). A PerkinElmer Lambda35 spectrometer UV–vis system was used to obtain the absorption spectra of the samples over a range of 350–650 nm.

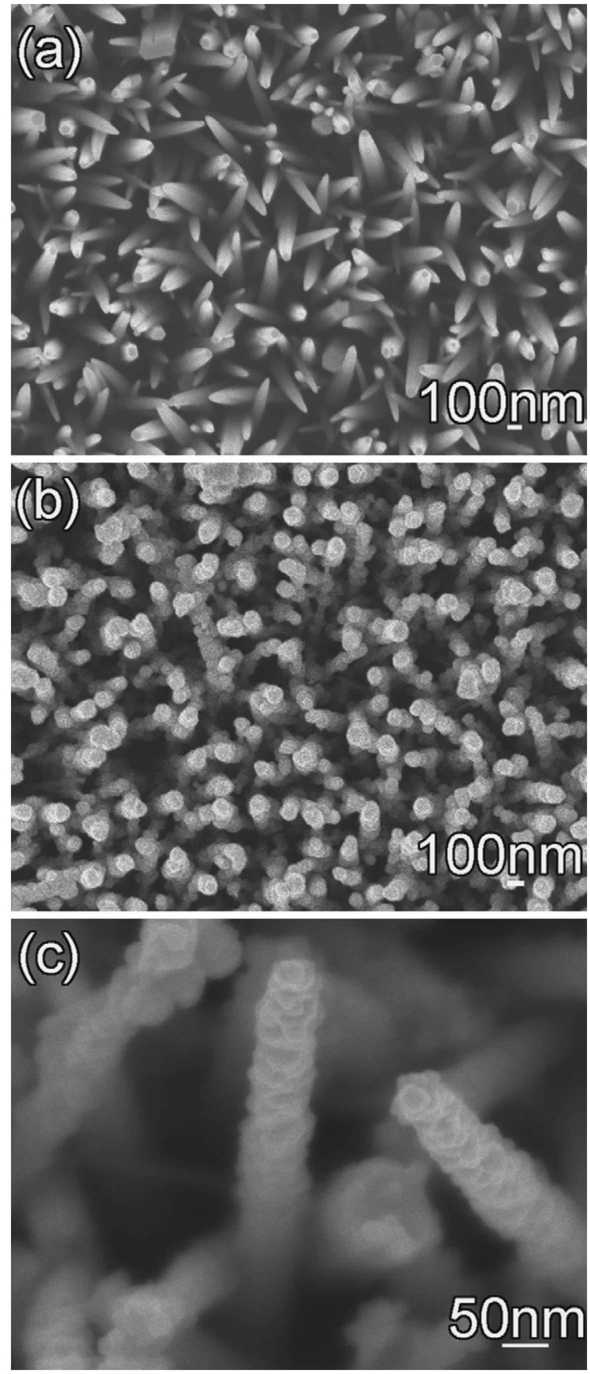

Fig. 1. SEM images of (a) ZnO nanorod array film, (b) ZnO/CdSe core-shell nanorod array film at low magnification and (c) at high magnification.

2.4. Photovoltaic measurements

We assembled CdSe nanocrystals sensitized ZnO nanorod array solar cells by placing the ZnO/CdSe core-shell nanorod array photoanode face-to-face with a TCO photocathode coated with a thin layer of Pt (100 Å). The space between the electrodes was filled through capillary action with the electrolyte (0.03 mol/L I_2 and 0.3 mol/L LiI in propylene carbonate). The photovoltaic experiments were performed under irradiation from the back of the core-shell film to the Pt film with an Oriel 91192 AM 1.5 solar simulator as light source (calibrated for AM 1.5 illumination with a light intensity of 100 mW/cm^2). The active areas were typically 0.1 cm^2. The current density–voltage (I–V) response of the devices was recorded