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Improved performance of quantum dots sensitized solar cells using ZnO hierarchical spheres as photoanodes

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Abstract

In this study, the different sizes of ZnO hierarchical spheres (ZnO HS) based on the aggregations of nanoparticles were synthesized through hydrolysis of zinc acetate dihydrate in water and applied to photoanodes of quantum dots-sensitized solar cells (QDSSCs). Among these, ZnO HS with a main diameter of less than 1 μm could significantly extend the traveling distance of light within the photoanode films as the scattering centers and ZnO nanoparticles could prevent the decrease of specific surface area. CdS and CdSe quantum dots were deposited by successive ionic layer absorption and reaction (SILAR) method and chemical bath deposition (CBD) respectively. Field-emission scanning electron microscopy (FE-SEM), Transmission electron microscope (TEM) and X-ray diffraction (XRD) were used to identify the surface profile and crystal structure of ZnO HS photo-electrodes before and after depositing quantum dots. CdS/CdSe co-sensitized ZnO HS photoanodes demonstrated an overall power conversion efficiency of 4.13% under one sun illumination (100 mW cm^{-2}), which is higher than that of CdS/CdSe co-sensitized ZnO nanoparticles (ZnO NP) photoanodes.

Keywords: ZnO hierarchical spheres; CdS and CdSe quantum dots; ZnO nanoparticles; Quantum dots-sensitized solar cells

1. Introduction

The quantum dots sensitized solar cells (QDSSCs) is a new type of photo-electrochemical cell based on quantum dots (QDs) sensitized nanocrystalline electrodes as an alternative to organic-dye-sensitized solar cells [1–3]. Various narrow-band gap semiconductor QDs have been investigated as sensitizers such as CdS [4], CdSe [5], PbS [6], PbSe [7] and InAs [8]. The QDs were used to replace the organometallic or organic dyes and inject the excited electrons into a wide-band gap photoanode under illumination because of their outstanding optical properties and extraordinary electrical properties, for example, the tunable band gap energy, high extinction coefficients and the generation of multiple electron carriers under high-energy excitation [9,10].

In the construction of QDSSCs, the preparation of QDs loading on ZnO and TiO_2 photoanode surfaces has triggered extensive studies. Among the semiconductor QDs, CdS and CdSe have triggered widespread attention owing to their high potential in light harvesting. The conduction band edge of CdS is higher than that of ZnO and TiO_2, so it is benefits to photo-excited electrons inject into the photoanodes. The absorption range of CdS is limited below 550 nm because of its band gap (2.25 eV). The absorption range of CdSe can be extended to 720 nm (1.7 eV). So some scholars use the coupled QDs (CdS and CdSe) to sensitized ZnO and TiO_2 to extend the absorption rang and improve the power conversion efficiency (PCE). Recently, Yu et al. used CdS and CdSe to sensitize hierarchical TiO_2 sphere electrodes and got a PCE as high as 4.81% [11]. Santra et al. used the TiO_2 nanoparticles as photoanodes and demonstrated a remarkable value of PCE over 5% [12]. Lu et al. achieved a PCE of 3.23% by using CdS/CdSe co-sensitized ZnO nanocables [13].

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As the central component of QDSSCs, the photoanode plays a significant role in solar light harvesting which would affect the total light-to-electric conversion and the performance of the cell to a great extent. ZnO as photoanodes has attracted considerable interest during the past several years, because the energy band gap and the electron-injection process are similar to that of TiO_2. Additionally, ZnO has a bevy of outstanding qualities, like easier fabrication of the various nanostructures and modification of the surface structure compared with TiO_2. Recent studies on ZnO have mostly focused on one-dimensional nanostructures such as nanowires (NWs) and nanorods (NRs) [14,15]. One-dimensional nanostructures seem to have the direct electrical pathways that can ensure rapid collection of carriers and prevent charge recombination. However, the insufficient surface area of the one-dimensional nanostructures is a significant limitation which restricts the advance of conversion efficiency. So some scholars want to increase the light harvesting capability by utilizing optical enhancement effects, which can be achieved by introducing scatterers into the photoanode films. For instance, Zhang et al. reported hierarchically structured ZnO films as the photoanodes in DSSCs and achieved the PCE up to 5.4% [16]. This hierarchically structured ZnO aggregates were submicrometer-sized which consist of nanosized crystallites and, thus, could function as efficient light scatterers. Xu et al. applied the ZnO micro-flowers as scattering layer for ZnO-based DSSCs and an efficiency of 3.20% was achieved [17].

Herein we report hierarchically structured ZnO hierarchical spheres (ZnO HS) films as the photoanodes in QDSSCs for the enhancement of PCE due to the increasement of light-harvesting efficiency compared with ZnO nanoparticles (ZnO NP). ZnO HS are synthesized by the hydrolysis of zinc salt in water at 120 °C to obtain a relatively wide size distribution. This ZnO films possess the advantage of providing both a huge internal surface area for QDs adsorption and the submicrometer-sized aggregates as scatterers to enhance the light absorption. Compared with ZnO nanoparticles photoanodes, the ZnO HS has obviously improved conversion efficiency as high as 4.13%, which indicated that the film structure could result in a significant enhancement of the light scattering so as to promote the light-harvesting efficiency.

2. Experimental section

2.1. Materials

All reagents including zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), cadmium nitrate terahydrate [$Cd(NO_3)_2 \cdot 4H_2O$], sodium sulfide nonohydrate ($Na_2S \cdot 9H_2O$), triethanolamine [$(HOCH_2CH_2)_3N$, TEA], thiourea (CH_4N_2S), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), selenium pellets (Se), sodium sulfite (Na_2SO_3), cadmium acetate ($Cd(CH_3COO)_2$), ammonia solution ($NH_3 \cdot H_2O$), polyethylene glycol 2000 (PEG 2000), potassium chloride (KCl) and sulfur sublimed (S) were AR. Grade, purchased from Aladdin Chemical Reagent Co., Ltd, and used without further treatment.

2.2. Synthesis of ZnO HS

The ZnO HS was prepared via hydrolysis of 0.439 g of zinc acetate dihydrate in 20 mL of distilled water with 2.0 g PEG 2000 and 6 mL TEA at 120 °C for 2 h. Before hydrolysis, the solution ought to stir violently for 30 min until all reagents well combined. Reflux with water cooling was employed to prevent the solvent evaporating from start to finish. After the reaction, the products were cooled naturally and collected by centrifugation after washing with distilled water and ethanol several times. Being dried over night at 80 °C, the whole products were annealed at 450 °C for 30 min.

2.3. Preparation of the pastes for photoanodes

The typical procedure is as follows: 1.0 g of ZnO HS and 0.2 g of ethyl cellulose mixed well with 8.0 mL of ethanol and 2.0 mL of terpineo overnight. After that, the compound was evaporated for 3 h at 100 °C and concentrated to form the sticky ZnO HS paste. In the mean time, the commercial ZnO NP (with similar size at 30 ± 10 nm, purchased from Wuhan Geao Chemical Technology Company, China) was also used to prepare the pastes with the same process. ZnO HS and ZnO NP photoanodes for QDSSCs were prepared by coating the ZnO paste on the fluorine-doped tin oxide (FTO) with a doctor-blade technique [18] and annealing at 450 °C for 30 min to remove the organic matters. Before the fabrication, the FTO glasses were pretreated by sonication in ethanol and distilled water continuously and dried in atmosphere.

2.4. Fabrication of CdS and CdSe/CdS coupled QDs-sensitized photoanodes

The as-produced photoanodes were sensitized by using CdS QDs through SILAR method similar to previously reported approach [19]. Typically, the as-produced photoanodes were immersed successively in 0.1 M $Cd(NO_3)_2 \cdot 4H_2O$ ethanol solution and 0.1 M $Na_2S \cdot 9H_2O$ methyl alcohol solution for 2 min, respectively. Between each immersion process, the samples were rinsed with ethanol or methanol adequately to remove excessive amounts of ions. Such set-operation was one SILAR cycle and repeated up to 16 cycles. In the next step, CdSe was deposited on the CdS-coated ZnO film by using a CBD method twice. In a nutshell, 25 mL 10 mM aqueous $Cd(CH_3COO)_2$ solution, 25 mL 20 mM aqueous sodium selenosulfate (Na_2SeSO_3), and 0.075 mL $NH_3 \cdot H_2O$ were mixed well together, then the CdS-coated ZnO films were immersed into the solution for 1 h at 95 °C, as one cycle. The Na_2SeSO_3 solution was prepared by refluxing 0.395 g Se power in 50 mL aqueous solution of 2.4 g Na_2SO_3 at 70 °C for 8–12 h to obtain 0.1 M Na_2SeSO_3 solution, then diluted into 20 mM Na_2SeSO_3 solution. Finally, the ZnS passivated the photoanodes by twice dipping into 0.1 M $Zn(NO_3)_2 \cdot 4H_2O$ ethanol solution and 0.1 M $Na_2S \cdot 9H_2O$ methyl alcohol solution for 1 min alternately.