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Improved performance of CdSe/CdS co-sensitized solar cells adopting efficient CuS counter electrode modified by PbS film using SILAR method

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ABSTRACT

In this paper, CuS film was deposited onto fluorine-doped tin oxide (FTO) substrate using a facile chemical bath deposition method, and then modified by PbS using simple successive ionic layer absorption and reaction (SILAR) method with different cycles. These CuS/PbS films were utilized as counter electrodes (CEs) for CdSe/CdS co-sensitized solar cells. Field-emission scanning electron microscopy equipped with an energy-dispersive X-ray spectrometer was used to characterize the CuS/PbS films. The results show that CuS/PbS (10 cycles) CE exhibits an improved power conversion efficiency of 5.54% under the illumination of one sun (100 mW cm^{-2}), which is higher than the CuS/PbS (0 cycles), CuS/PbS (5 cycles), and CuS/PbS (15 cycles) CEs. This enhancement is mainly attributed to good catalytic activity and lower charge-transfer and series resistances, which have been proved by electrochemical impedance spectroscopy, and Tafel polarization measurements.

1. Introduction

Quantum-dot-sensitized solar cells (QDSSCs) are the most promising candidate for the development of next generation solar cells, due to their potential properties such as their versatile properties of high molar extinction coefficient, multiple exciton's generation, tunable band gaps by particle sizes and low cost [1–5]. So far, various inorganic semiconductor materials with narrow-band gap have been investigated as sensitizers in QDSSCs such as CdS, CdSe, PbS, InAs, PbSe and $CuInS_2$ [6–13]. Among these QD sensitizers, CdS and CdSe are widely studied together for QDSSCs due to their suitable band gap of 2.25 and 1.70 eV in bulk, and CdSe/CdS co-sensitized solar cells exhibited a higher performance over 5% [14,15].

As an indispensable part of QDSSCs, the counter electrode (CE) is also attracting much research attention [16]. Platinum (Pt) counter electrode is widely used in DSSCs for high electroanalytical activity in organic iodide/triiodide (I^-/I_3^-) redox electrolyte, however, the sulfur-containing polysulfide electrolyte in the QDSSCs will adsorb to Pt surfaces and decrease the surface activity and conductivity of the Pt electrodes and then shorten the lifetime [17,18]. Therefore, various Pt-free CEs have been reported as alternatives, such as CuS, Cu_2S, CoS, NiS, and PbS [19–23]. Meanwhile, some composite electrodes including, Cu_2S/carbon, CoS/NiS, CuS/CoS, Cu_2ZnSnS_4 and Cu_2S/RGO were also investigated [24–28].

Among inexpensive metal sulfides, CuS and PbS have been used as CEs for QDSSCs and photoelectrochemical cells due to their low resistance and high electrocatalytic activity for the redox reaction of polysulfide electrolyte [29,30]. It is imperative to investigate the photovoltaic performance of the combination of CuS and PbS, which is an attempt to boost the catalytic activity and reduce the inner energy loss [31]. Recently, M. Eskandari et al. prepared CuS/PbS CE by the successive ionic layer absorption and reaction (SILAR) deposition method and enhanced the efficiency from 1.17 (CuS CE) up to 2.22% (CuS/PbS CE) [32]. S. Arabzade et al. introduced the sequential deposition method to deposit CuS/PbS CEs. For the CdS/CdSe QDs sensitized cells, the efficiency is enhanced to 3.58%, and an higher fill factor is obtained as 0.53 [33].

Here, we fabricated a novel composite CuS/PbS CE using chemical bath deposition (CBD) and SILAR. In our work, CuS film is compact and uniform deposited onto fluorine-doped tin oxide (FTO) by CBD method, which is benefit to contact with the FTO and CuS film. Subsequently, CuS film was modified by PbS by SILAR method with different cycles. Through the regulation of cycles, CuS/PbS (10 cycles) CE-based CdSe/CdS co-sensitized solar cell showed a higher power conversion efficiency of 5.54%.

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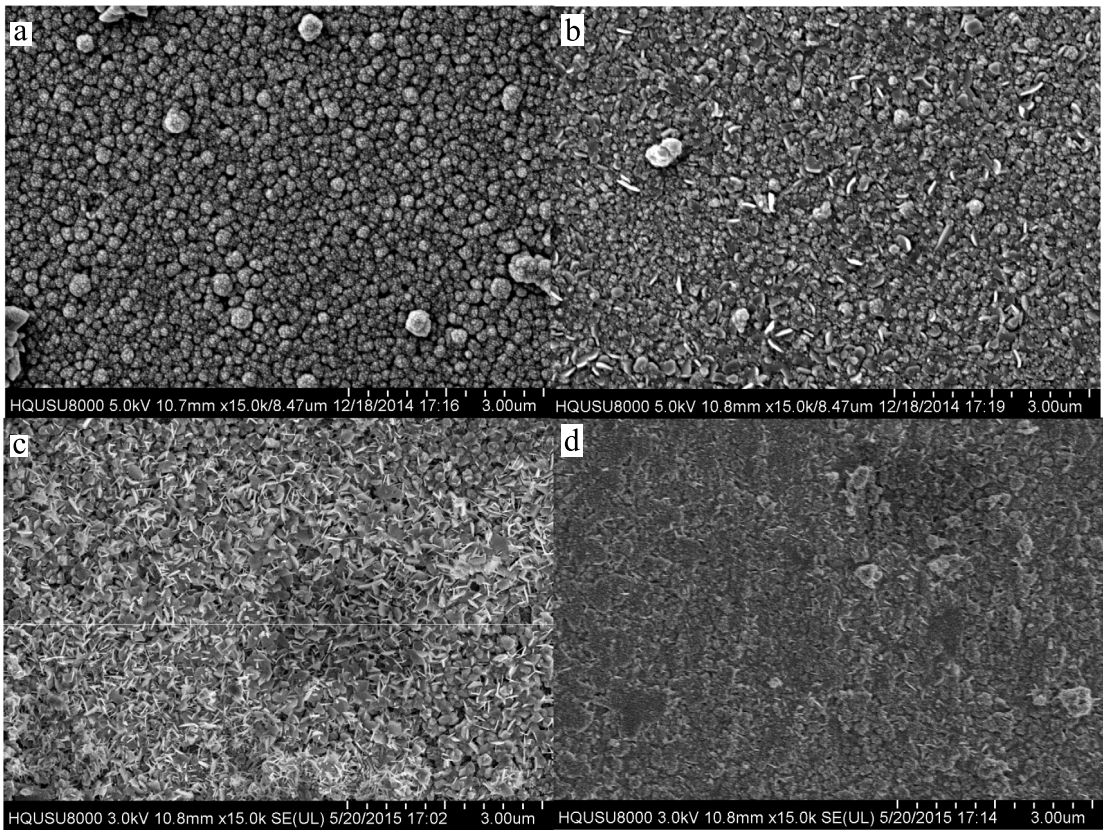

Fig. 1. FE-SEM images of CE1(a), CE2(b), CE3(c) and CE4(d) films.

2. Experimental

2.1. Fabrication of CuS and CuS/PbS CEs

CuS CEs were deposited on FTO substrate using the facile CBD method. Before preparing CEs, the FTO glass substrates were pretreated by sonication in deionized water, acetone, isopropyl alcohol, and ethanol continuously. To fabricate the CuS CEs, cleaned FTO substrates were immersed in a compound containing cationic and anionic precursors of cupric (II) chloride dihydrate, thioacetamide, which act as sources of Cu^{2+} and S^{2-}. Ammonia and triethanolamine were added as reagents, subsequently the mixture was transferred to the water-bath at 80 °C for 30 min. After the procedure was repeated twice, CuS counter electrodes were obtained. The CuS/PbS electrodes with different cycles were fabricated using SILAR method as follows. The as-prepared CuS CEs were immersed into a 0.05 M $Cd(NO_3)_2$ aqueous solution for 1 min. After washed with water and ethanol, the CEs were steeped into a 0.05 M Na_2S aqueous solution for another 1 min to allow S^{2-} to react with the preceding Pb^{2+}, followed by another rinsing with water and ethanol continuously. All procedure was called one SILAR cycle. The CuS/PbS (0 cycles), CuS/PbS (5 cycles), CuS/PbS (10 cycles) and CuS/PbS (15 cycles) CEs were prepared and were denoted as CE1, CE2, CE3 and CE4 respectively.

2.2. Assembly of QDSSCs

TiO_2 film photoanodes were prepared by successive doctor-blade method, containing a transparent layer (9.5±0.5 μm) with the use of TiO_2 nanoparticles paste and a light-scattering layer (7.5±0.5 μm) using 1–1.5 μm TiO_2 microspheres as previous procedure [34]. CdS and CdSe QDs were assembled onto TiO_2 photoanodes using SILAR method as follows. TiO_2 photoanodes were alternately dipped into 0.1 M $Cd(NO_3)_2$ solution and 0.1 M Na_2S solution for 2 min respectively. After 10 cycles, the CdS sensitized electrodes were obtained. For the deposition of CdSe, the CdS sensitized electrodes were immersed into 0.1 M $Cd(NO_3)_2$ solution and 0.1 M $NaSeSO_3$ solution for 5 min alternately. $NaSeSO_3$ aqueous solution was prepared by refluxing Se powder and Na_2SO_3 at 100 °C; for 8 h and the electrodes were sensitized with 8 cycles. Finally, a ZnS passivation layer was deposited on the CdSe/CdS/TiO_2 electrodes by 2 cycles with 0.1 M $Zn(NO_3)_2$ solution and 0.1 M Na_2S solution for 1 min alternately. The QDSSCs were assembled by injecting a redox electrolyte into the aperture between the sensitized photoanodes and the above four kinds of counter electrode. The redox electrolyte consisted of 0.5 M sodium sulfide, 2 M sulfur and 0.2 M potassium chloride in a mixture solution of methanol/water (7:3 by volume).

2.3. Characterizations

The superficial morphologies of CE1, CE2, CE3 and CE4 were characterized by a field emission scanning electron microscopy (FESEM, SU8000, HITACHI) equipped with an energy-dispersive X-ray (EDX) spectrometer. EIS (frequency range of 100 kHz to 100 mHz) with a perturbation amplitude of 5 mV and Tafel polarization (scan rate of 10 mV s^{-1}) were performed using an electrochemical workstation (IM6, Zahner, Germany) with a symmetrical cell of four kinds of counter electrodes in dark conditions. The photovoltaic properties of QDSSCs were measured under white light irradiation of 100 mW cm^{-2} (AM 1.5 G) from the solar simulator (XQ-500 W, Shanghai Photo-electricity Device Company, China).

3. Results and discussion

The surface morphologies of different counter electrodes of CE1, CE2, CE3 and CE4 are shown in Fig. 1a–d, respectively. Fig. 1a shows the SEM images of as-prepared CuS films on FTO glass (CE1). With modified by PbS, the CuS counter electrodes are covered with sheet PbS film.