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In_2S_3 sensitized solar cells with a new passivation layer

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ABSTRACT

In_2S_3 as a semiconductor sensitizer has the advantage of non-toxicity, good stability and high carrier mobility. In this paper, In_2S_3 sensitized solar cells were firstly prepared by a low cost chemical bath deposition methodology and then fully characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. The ZnS passivation layer modified the In_2S_3 sensitized TiO_2 photoanodes and resulted into enhanced J_{sc} and FF but a lowered V_{oc} compared with the original solar cell under AM1.5, 1 sun. More importantly, we have enhanced all FF, J_{sc} and V_{oc} when amorphous Y_2O_3 was used to passivate the In_2S_3 sensitized solar cells, achieving the highest FF of 65% among the reported similar solar cells.

1. Introduction

Dye-sensitized solar cells (DSCs) have been paid much attention in the past decades because of their low cost, relatively high efficiency and prosperous application future. The power conversion efficiency around 11.4% has been achieved using ruthenium complex as sensitizer together with I^-/I_3^- redox electrolyte of DSCs [1]. Porphyrin sensitized solar cells with $Co^{(II-III)}$ based redox electrolyte has reached 12.3% power conversion efficiency [2]. Very recently inorganic semiconductor quantum dots (QDs) which absorb light in the visible region, such as CdS [3,4], CdSe [5,6], InP [7], and Sb_2S_3 [8], have been used as sensitizers instead of organic dye in DSCs. QDs have strong absorption with high molar extinction coefficient than organic sensitizers. Further due to the quantum size effects, the absorption spectrum of QDs can be tuned by simply controlling the QDs' sizes or shapes. By using these unique advantages, the maximum theoretical power conversion efficiency of quantum dot sensitized solar cells (QDSSCs) is expected to be much higher than the DSCs [9], although the current benchmark work represents a very moderate efficiency.

In the majority of QDSSCs, the QD sensitizers employ toxic elements such as cadmium, lead, and arsenic, etc. [3,7,10] and there is a practical need to develop low toxic QD sensitizers. In_2S_3, a typical III–VI group sulfide, exists in three different structure forms: α-In_2S_3 (defect cubic structure), β-In_2S_3 (defect spinel structure) and γ-In_2S_3 (layered hexagonal structure). In fact, β-In_2S_3 is a well n-type photoactive semiconductor with a direct band gap about 2.0 eV, a relative large exciton Bohr radius approximately 34 nm [11–13] and a high carrier mobility [14]. Therefore β-In_2S_3 has been investigated as an inorganic semiconductor sensitizer in QDSSCs [15–17]. Arakawa et al. prepared In_2S_3 sensitized In_2O_3 solar cells with sulfidation of In_2O_3 thin film electrodes under H_2S atmosphere [15], while George et al. prepared In_2S_3 sensitized TiO_2 solar cells using atomic layer deposition with indium acetylacetonate ($In(acac)_3$) and H_2S as precursors [16]. In these efforts, the open circuit photovoltage V_{oc} is less than 0.3 V and the fill factor FF is less than 40%. Gan et al. reported the fabrication of a TiO_2–In_2S_3 core–shell nanorod array structure for QDSSCs and the In_2S_3 shell layer was prepared by using the low cost successive ionic layer adsorption and reaction (SILAR) method. However, the best FF (46%) of these devices is still low. Furthermore the reported V_{oc} is very modest as well therefore leading to a quite low energy conversion efficiency (much less than 1%) [17].

In order to enhance the solar energy conversion efficiency, the low V_{oc} and FF have to be increased which are mainly due to

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recombination of (i) electrons in TiO_2 and hole in β-In_2S_3 and (ii) electrons in TiO_2 and the oxidized electrolyte. The strategy used in the conventional DSCs to retard the recombination is to insert an insulation layer between TiO_2 and dye, such as Al_2O_3 layer [18]. In this paper, In_2S_3 sensitized solar cells were prepared by the robust and low cost chemical bath deposition (CBD) methodology. A ZnS passivated layer was inserted between the In_2S_3 sensitized TiO_2 photoanodes and the electrolyte. Based on these results, a further modified QDSSC, composing of amorphous Y_2O_3 shell passivated the In_2S_3 sensitized TiO_2 photoanodes was developed, which has not been reported previously. Interestingly, both cells represent very high V_{oc} and FF. More importantly, a 65% FF has been achieved on Y_2O_3 modified QDSSC, the highest value among similar QDSSCs and the V_{oc} achieved is also 73% higher than the very recent reports [15,16].

2. Experimental

2.1. Preparation of In_2S_3 sensitized TiO_2 photoanodes with passivation layers

The colloidal TiO_2 nanoparticles were prepared by hydrolysis of titanium tetraisopropoxide as described elsewhere [19,20]. The mesoporous TiO_2 photoanodes were obtained by screen printing TiO_2 paste on FTO glass (TEC-15, LOF), then sintering at 450 °C for 30 min in air. The TiO_2 film thickness was around 10 μm, which was determined by a profilometer (XP-2, AMBIOS Technology Inc., USA). For In_2S_3 deposition, the mesoporous TiO_2 photoanodes were immersed in a beaker containing a freshly prepared aqueous mixture of 0.05 M $InCl_3$ and 0.2 M thioacetamide. The beaker mouth was sealed with the Parafilm® M laboratory film, then maintained at 40 °C for 10 h in a thermostat water bath. After deposition, the mesoporous TiO_2 photoanodes were washed with water and dried in a vacuum drying chamber at room temperature. The ZnS passivation layer was prepared by SILAR process as described by Shen et al. and exhibited similar thickness [21,22]. The TiO_2/In_2S_3 film was coated with Y_2O_3 passivation layer by dipping the film in 0.1 M yttrium (III) acetate ethanol solution at room temperature for 30 min, followed by sintering at 400 °C for 5 min in Ar atmosphere.

2.2. QDSSC assembly

The platinized counter electrodes were prepared by spraying H_2PtCl_6 solution on FTO, followed by heating at 410 °C for 20 min [23]. The In_2S_3 sensitized TiO_2 photoanodes and Pt counter electrodes were assembled into a sandwich cell by heating with a 60 μm thermal adhesive film (Surlyn, DuPont). An I^-/I_3^- redox electrolyte solution of 0.05 M I_2, 0.1 M LiI, 0.6 M 1-propyl-2,3-dimethylimidazolium iodide (DMPII) in 3-methoxypropionitrile was filled from a hole made on the counter electrode, which was later sealed by thermal adhesive film and a cover glass. The active area of QDSSC was 0.5 cm × 0.5 cm = 0.25 cm^2 [24,25].

2.3. Characterization and measurements

The structure and crystallinity of the sample were investigated by X-ray diffraction (XRD, Rigaku, Japan). The composition and chemical state of $TiO_2/In_2S_3/Y_2O_3$ film was confirmed by X-ray photoelectron spectroscopy (XPS, Thermo Electron Corp., USA). Scanning electron microscopy (SEM) was used to examine the morphology of TiO_2/In_2S_3 film (Sirion200, FEI, Netherlands) and the transmission electron microscopy (TEM) was operated to observe the crystallinity and arrangement of TiO_2, In_2S_3 and Y_2O_3 (JEOL-2010, Japan). The absorbance of In_2S_3 sensitized TiO_2 film was recorded on a UV–vis spectrophotometer (U-3900H, Hitachi, Japan). The current density–voltage (J–V) characteristics of the QDSSCs were measured under AM 1.5 (100 mW/cm^2) illumination which was provided by a solar simulator (Oriel, USA), and recorded using a Keithley model 2420 digital source meter (Keithley, USA). Incident-photon-to-current efficiency (IPCE) curves were operated with a QE/IPCE measurement kit (Newport, USA) using a 300 W Xe lamp and a monochromator.

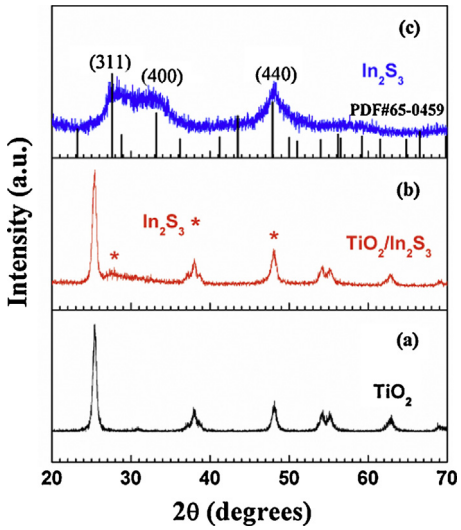

Fig. 1. XRD patterns of (a) pure TiO_2 nanoparticles, (b) TiO_2/In_2S_3 film and (c) pure In_2S_3 powder.

3. Results and discussion

3.1. Microstructure characterization of the In_2S_3 sensitized photoanodes

The powder X-ray diffraction (XRD) patterns of pure TiO_2 nanoparticles and In_2S_3 sensitized TiO_2 nanoparticles were shown in Fig. 1. It can be seen that the two samples show similar patterns except some small peaks in the sample of In_2S_3 sensitized TiO_2. In order to identify these small peaks, the pure In_2S_3 particles were prepared by the similar CBD method under the same condition. The XRD patterns of the single In_2S_3 particles were matched with that of cubic β-In_2S_3 (JCPDS#65-0459), indicating these weak peaks in the In_2S_3 sensitized TiO_2 belong to β-In_2S_3. Due to the relatively low quantity, only the most intense peak were observed and the peak width was large. The peaks at 2θ values of 27.6°, 33.2° and 47.8° are attributed to the (3 1 1), (4 0 0) and (4 4 0) planes of β-In_2S_3, respectively. The Y_2O_3 was not observed in the XRD patterns of Y_2O_3 coated TiO_2/In_2S_3 film, either due to high dispersed Y_2O_3 or amorphous phase.

The scanning electron microscopy (SEM) images of In_2S_3 sensitized TiO_2 mesoporous films were shown in Fig. 2. Obviously, although the porous structure of TiO_2 film was remained after the In_2S_3 deposition, the In_2S_3 coverage was relatively homogenous and a flake form of In_2S_3 was also exhibited. After the TiO_2/In_2S_3 film was coated with Y_2O_3 layer, there was an apparent change of surface morphology (Fig. 2b): the agglomeration and rearrangement of adjacent isolated In_2S_3 grains lead to surface smoothing of TiO_2/In_2S_3 films [26]. The significant morphology change was due to the annealing process at 400 °C for 5 min which is the last procedure during Y_2O_3 layer coating experiment. In fact, it will exhibit almost the same surface morphology as Fig. 2b if the TiO_2/In_2S_3 film is only annealed at 400 °C for 5 min without any extra coating procedure.

In order to get more information on the morphology of Y_2O_3, In_2S_3 sensitizer and their arrangement on TiO_2 surface, the TEM