

A strategy of combining SILAR with solvothermal process for In_2S_3 sensitized quantum dot-sensitized solar cells



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ABSTRACT

Pursuit of an efficient strategy for quantum dot-sensitized photoanode has been a persistent objective for enhancing photovoltaic performances of quantum dot-sensitized solar cell (QDSC). We present here the fabrication of the indium sulfide (In_2S_3) quantum dot-sensitized titanium dioxide (TiO_2) photoanode by combining successive ionic layer adsorption and reaction (SILAR) with solvothermal processes. The resultant QDSC consists of an In_2S_3 sensitized TiO_2 photoanode, a liquid polysulfide electrolyte, and a $\text{Co}_{0.85}\text{Se}$ counter electrode. The optimized QDSC with photoanode prepared with the help of a SILAR method at 20 deposition cycles and solvothermal method yields a maximum power conversion efficiency of 1.39%.

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1. Introduction

Quantum dot-sensitized solar cell (QDSC), a promising photoelectrochemical device directly converting solar energy into electricity, has attracted tremendous attention due to its easy fabrication and cost-effectiveness [1–3]. In comparison with the expensive sensitizers in dye-sensitized solar cells, the quantum dots (QDs) in QDSCs have triggered growing interests because of the tunable band gap and high molar extinction coefficient [4]. Furthermore, the theoretical power conversion efficiency of QDSC can reach as high as 44% according to the multiple exciton generation phenomenon due to the impact ionization effect [5]. In spite of those merits, the highest reported efficiency of QDSCs is limited at 8.55% [6], which is far behind the maximum efficiencies from dye-sensitized solar cells (13%) [7] and perovskite solar cells (20.1%) [8]. The preferred QDs for QDSC applications are highly toxic cadmium and lead chalcogenides (CdS [9], CdSe [2], CdTe [10], and PbS [11]). Although Cd-based and Pb-based QDSCs have higher power conversion efficiencies, their toxic elements may limit the large-scale applications. In this fashion, a prerequisite to develop commercial

devices is to replace the Cd-based and Pb-based QDs by nontoxic species.

As a typical III–VI group sulfide, indium sulfide (In_2S_3) with a bulk band gap of 2.0 eV has been extensively investigated in luminescence [12], photocatalysis [13], and Li-ion batteries [14]. Recently, In_2S_3 has been employed in QDSC as light absorber due to its excellent photoactivity, stable chemical and physical properties, high carrier mobility and low toxicity [15]. However, In_2S_3 sensitized solar cell demonstrates a quite poor photovoltaic performance [15–19]. Up to now, the fabrication of In_2S_3 QDs exploit some situ growth methods, such as successive ionic layer adsorption and reaction (SILAR) [19], solvothermal method [20] and electrodeposition technique [21]. In the current work, we present the synthesis of In_2S_3 QDs by combining traditional SILAR with solvothermal processes. SILAR synthesis shows good control over QD stoichiometry and size and can improve surface ligand coverage. However, devices fabricated using SILAR-synthesized materials suffer from QD corrosion, and lead to lower efficiencies than ex situ synthesized QD devices [22]. However, solvothermal synthesis is effective to obtain high-quality inorganic semiconductors [23]. In this fashion, the combination of SILAR and solvothermal processes is expected to optimize the uptake of In_2S_3 QDs and crystal structure. We employ $\text{Co}_{0.85}\text{Se}$ alloy as the counter electrode (CE), which has a superior catalytic performance for $\text{S}^{2-}/\text{S}_x^{2-}$ redox electrolyte [24]. In comparison with the QDSCs based on the photoanode prepared using

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SILAR in the current and previous reports [17], the QDSC adopting the photoanode prepared with SILAR at 20 deposition cycles (20C) combined with solvothermal method presents a power conversion efficiency of 1.39%.

2. Experimental

2.1. Fabrication of In_2S_3 sensitized TiO_2 photoanodes

The TiO_2 photoanode on an FTO glass substrate (sheet resistance $12\ \Omega\ \text{sq}^{-1}$) was fabricated according to the method in our previous report [25]. The In_2S_3 sensitized TiO_2 anodes were fabricated with a SILAR method. In details, the TiO_2 film was dipped into 0.034 M InCl_3 methanol solution for 1 min, rinsed with anhydrous methanol and then dried by N_2 flow, and subsequently dipped into 0.05 M Na_2S ethanol solution for 1 min, rinsed with anhydrous ethanol and then dried by N_2 flow. Each series of the two immersion processes was marked as one deposition cycle. Such deposition cycle was repeated several times to obtain the In_2S_3 sensitized TiO_2 anode, which subsequently suffered solvothermal reaction. The precursor solution for solvothermal reaction includes 1 mM InCl_3 , 4 mM sulfocarbamide ($\text{SC}(\text{NH}_2)_2$), and 6 mM citric acid trisodium salt ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$) in ethanol. When transferred the In_2S_3 sensitized TiO_2 anode into a 50 mL Teflon-lined autoclave with the FTO layer downward, the solvothermal reaction was performed at 120°C . After reaction for 4 h, the final photoanode was thoroughly rinsed with ethanol and dried by N_2 flow.

2.2. Fabrication of $\text{Co}_{0.85}\text{Se}$ CEs

A mixture aqueous solution consists of 0.0238 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.01 g Se, 7.5 mL hydrazine hydrate (85%) and 27.5 mL deionized water. After vigorous stirring for 10 min, the resultant solution was transferred into a 50 mL Teflon-lined autoclave holding a cleaned FTO glass substrate with FTO layer downward. After reacting at 120°C for 12 h, the substrate was taken out and rinsed with deionized water and then vacuum dried at 50°C .

2.3. Assembly of QDSCs

The typical sandwich configuration of a QDSC was illustrated in Fig. 1a. The liquid polysulfide electrolyte consisting of 1 M Na_2S and 1 M sulphur aqueous solution was injected into the cell through capillary force. The characteristic photocurrent–voltage (J – V) curves of the QDSCs were measured with an Electrochemical Workstation under AM 1.5G irradiation at $100\ \text{mW cm}^{-2}$. The active area of each QDSC was around $0.25\ \text{cm}^2$ defined by applying a black mask on the surface of the device. Due to the good matching of energy levels [26], as shown in Fig. 1b, the electrons can be excited from valence band of In_2S_3 to CB and then transfer to CB of TiO_2 .

2.4. Characterizations

The surface morphology of the In_2S_3 sensitized photoanode prepared using SILAR at 20C combined with solvothermal method was characterized using a scanning electron microscope (SEM, S4800). In order to detect the growth of In_2S_3 QDs on TiO_2 anode during the SILAR process, the In_2S_3 sensitized TiO_2 anodes after SILAR and solvothermal processes were subjected to UV–vis absorption at room temperature using bared FTO glass as a benchmark. The UV–vis diffuse reflection spectra were measured on an UV–vis spectrophotometer (Agilent 8453). The electrochemical impedance spectroscopy (EIS) measurements were scanned with a frequency range of 0.1 – $10^5\ \text{Hz}$ at an ac amplitude of 10 mV under dark condition.

3. Results and discussion

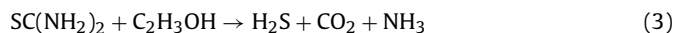
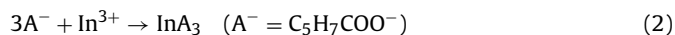
The morphology of the photoanode has a powerful influence on the photovoltaic performance of a QDSC. Typical top view SEM images in Fig. 2a and b show the nanoporous structure of In_2S_3 sensitized TiO_2 photoanode synthesized by SILAR at 20C combined with solvothermal method. From Fig. 2a and b, the photoanode has a homogeneous surface without aggregations and the average diameter of the In_2S_3 sensitized TiO_2 nanoparticles is $\sim 25\ \text{nm}$. The photoanode becomes more compact comparing with pristine TiO_2 in our previous report [25], suggesting that the TiO_2 nanoparticles have been covered densely by smaller In_2S_3 QDs and the nanoparticle structure of TiO_2 is retained. As references, the top-view SEM images of the photoanodes synthesized with SILAR at 8C or 24C combined with solvothermal are also provided in Fig. 2c and Fig. 2d, respectively. Top-view SEM photographs in Fig. 2c suggest a low coverage of In_2S_3 quantum dots with an average diameter of $\sim 20\ \text{nm}$ on dense TiO_2 film when In_2S_3 quantum dots are deposited for 8 cycles. With further increase in deposition cycle to 28 cycles (Fig. 2d), the TiO_2 surface has been completely covered by porous In_2S_3 quantum dots with a larger size ($\sim 50\ \text{nm}$). However, much thicker In_2S_3 layer on TiO_2 provides more interfaces for electron-transfer, therefore, the electron density at CB of TiO_2 nanocrystallite is expected to be decreased.

The In_2S_3 sensitized TiO_2 photoanodes are synthesized based on SILAR combined with solvothermal method. The whole reactions can be demonstrated as:

SILAR process:



Solvothermal process:



The SILAR process is used to deposit In_2S_3 on percolating TiO_2 film. At the very beginning of the solvothermal process, In^{3+} and A^- form InA_3 complexes. Then the S_2^{2-} ions released from $\text{SC}(\text{NH}_2)_2$ react with In^{3+} (released from InA_3 complexes) to form In_2S_3 under solvothermal treatment.

Fig. 3a shows the UV–vis absorption spectra of the In_2S_3 sensitized TiO_2 photoanodes prepared at various deposition cycles using pure TiO_2 photoanode as a benchmark. The typical absorption at around 340 nm is responding to the electron transition in In_2S_3 QDs between valence band and conduction band. Fig. 3b shows the UV–vis diffuse reflectance spectra of the resultant photoanodes, yielding a red shift of the band onset. This may be attributed to the increase of In_2S_3 loading and the increase of size of In_2S_3 QDs. Moreover, the photoanode prepared using SILAR at 20C combined with solvothermal method has the largest band span. In comparison with characteristic band at ca. 640 nm for bulk In_2S_3 [27], a distinct blue shift indicates that the size of In_2S_3 QDs is in the quantum confinement region [28].

The band gap (E_g) of the as-prepared photoanodes can be estimated according to the Kubelka–Munk theory [29]:

$$F(R) = \frac{(1 - R)^2}{(2R)} \quad (6)$$

where R is the diffused reflectance. As shown in Fig. 3c, the intercepts of the tangents from the plots of $[F(R)h\nu]^{1/2}$ versus $h\nu$ yield the E_g values of the photoanodes. The E_g are 3.13, 2.44,

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