One-pot hydrothermal synthesis of thioglycolic acid-capped CdSe quantum dots-sensitized mesoscopic TiO$_2$ photoanodes for sensitized solar cells

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ABSTRACT

In this work, colloidal CdSe QDs capped with a short chain thiol ligand thioglycolic acid (TGA) were prepared using a one-pot synthesis route in aqueous medium. This method integrates colloidal QDs synthesis and assembly of QDs in a single step due to the use of TGA, which serves as a stabilizer to control the formation of QDs and a linker to tether CdSe QDs to TiO$_2$ during the synthesis of QDs, and it could achieve high surface coverage of high-quality QDs on TiO$_2$ electrodes. The hydrothermal temperature is found to play an important role in determining the size of CdSe QDs and photovoltaic properties of the resulting TiO$_2$/CdSe photoanodes. To further improve the fill factor and efficiency of solar cells, PbS/CuS films were prepared with chemical bath deposition method and used instead of the usual Pt as counter electrodes (CEs). PbS/CuS CEs show superior electrocatalytic activity for the reduction of polysulfide than Pt. An optimized TiO$_2$/CdSe based QDSSC in combination with the PbS/CuS CEs achieved a champion PCE of 4.18% under one sun illumination (100 mW cm^{-2}).

1. Introduction

As a new type of photovoltaic technology, quantum dots sensitized solar cells (QDSSC) have attracted considerable attention over the past few years. QDSSC resemble their counterparts, dye-sensitized solar cells (DSSC), but use narrow band gap quantum dots (QDs), rather than organometallic dyes as sensitizers. Advantages of using QDs as sensitizers include higher molar absorption coefficient, tunable band gaps, and multiple exciton generation characteristics [1–3], and all of these are particularly suitable for light absorbers in solar cells.

Apart from the difference in sensitizer, it is noteworthy that QDSSC is a truly aqueous device that uses water as the only solvent for the S^{2-}/S$_n^{2-}$ redox mediator in the electrolyte, while DSSC usually employ liquid electrolytes based on organic solvents, such as acetonitrile and methoxypropionitrile [4,5], which are toxic and hazardous to human health. Truly aqueous electrolyte could ensure the realization of inexpensive and environmentally friendly solar cells. In recent years, tremendous research efforts have been devoted to developing aqueous DSSC, and a record cell efficiency of ~ 6% has been reported with the effort of Lin, Bella, and Barolo et al. [4–9], while the maximum efficiency of aqueous QDSSC has reached 12.07% [10].

In order to further improve the performance of QDSSC, simultaneous engineering of the photoanode and counter electrode (CE) is highly desirable in terms of achieving high coverage of QDs on mesoporous TiO$_2$, improving electron injection efficiency, and reducing charge recombination. These factors have a close relationship with the synthesis and sensitization strategies of QDs. At present, high quality QDs are usually synthesized with the organometallic high-temperature synthesis method, in which QDs are synthesized in organic solvents and capped with long-chain molecules [11]. The synthesized QDs are then assembled onto TiO$_2$ by direct adsorption [12], electrophoretic deposition [13], or linker assisted assembly method [14]. Bisquert, Kamat, and Bandara fabricated TiO$_2$/CuInS$_2$ or TiO$_2$/CdSe photoanode by adopting these methods and obtained encouraging results [13,15–17]. However, the lack of an anchoring functional group on capping agents of as-synthesized QDs for coupling to the TiO$_2$ often resulted in low surface coverage and agglomeration of QDs, and the long-chain capping agent may hinder interfacial charge transfer at QDs/TiO$_2$ interface. In 2012, Zhong's group developed an ex situ ligand exchange route for assembling colloidal QDs onto TiO$_2$ [10,18–20]. The organic ligand with long-chain was replaced with a short-chain molecular with a free carboxyl group, which facilitates the binding of QDs to TiO$_2$ and charge transfer. Then the modified QDs and TiO$_2$ were bridged through the carboxyl group. High surface coverage can be obtained via this route, resulting in the PCE as high as 12.7% [10]. Nevertheless, this approach requires three complicated steps including

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QD synthesis, ligand exchange and assembling QDs onto TiO_2, involving harsh synthetic condition (oxygen and water-free) and a complex ligand exchange process. To address this issue, it needs to develop a fast and efficient sensitization strategy to assemble colloidal QDs onto TiO_2 surface.

Counter electrode (CE) is an important component in QDSSC, which collects electrons and regenerate the hole scavenger by catalyzing the reduction of the oxidized species in the electrolyte. As a conventional CE, Pt is not only expensive, but also incompatible with polysulfide electrolyte due to the chemisorption of the sulfur species on the Pt surface (so-called poisoning effect) [21], which suppresses its electrocatalytic activity, resulting in poor interfacial electron transfer at CE/electrolyte interface. Therefore, efforts have been made on the substitution of Pt, such as metal chalcogenides (PbS [22], Cu_2S [21], CuS [23], CoS [24], CuSe [25]), carbon-based CE (graphene/PbS [26], MoO_3/C [27], RGO/Cu_2S [21], Cu_2S/carbon [28]), ITO/Cu_2S [29], and ZnO/PbS nanorods arrays CEs [22]. Composites CEs successfully combined the merits of each component, leading to superior catalytic activity and stability. Therefore, these composite CE-based QDSSC obtained a PCE of greater than 5%, which demonstrated their potential in constructing high-performing QDSSC. However, most of these composite CEs suffer from limitations such as long reaction times, harsh reaction condition, using of expensive equipment during processing. As a result, new kinds of composite CEs, especially using facile and low cost methodologies for fabrication are still in need.

For metal sulfide CEs, CuS showed superior catalytic activity toward reduction of polysulfide. However, CuS may suffer from continuous corrosion, leading to the instability of the QDSSC [30]. PbS has similar catalytic activity to CuS but with better stability [31,32]. Therefore, the composite CuS/PbS CE may exhibit the synergy effect between the intrinsically high electrocatalytic activity of the CuS and the stability of the PbS.

Compared with organometallic high-temperature synthesis method, aqueous synthesis is simple and cost effective. However, the reports on the use of water-based QDs sensitizer are relatively scarce [33,34]. In this study, colloidal CdSe QDs were synthesized in aqueous solution by a facile hydrothermal method, and the prepared QDs capped with a short-chain bifunctional linker, thioglycolic acid (TGA), obviating the need for ligand exchange. Most importantly, this method integrates colloidal QDs synthesis and assembly onto TiO_2 in a single step due to the use of TGA, thereby simplifying the QDs loading process. It can achieve high coverage of CdSe QDs within TiO_2, as well as afford greater control over the size of CdSe. To further enhance the efficiency, CuS/PbS composite CEs were prepared on FTO substrates using chemical bath deposition method to improve the catalytic activity of CEs. Notably, QDSSC assembled with the optimized CuS/PbS CEs and TiO_2/CdSe photoanode achieved a PCE of 4.18%, superior to the one assembled with Pt (2.2%), under one sun irradiation.

2. Experimental

2.1. Fabrication of TiO_2/CdSe photoanodes

Mesoporous TiO_2 electrodes were prepared via screen-printing of the commercial P25 paste on the FTO substrate, and its thickness and area was 10 μm and 5 mm × 5 mm, respectively. The mesoporous TiO_2 was then sensitized with colloidal CdSe QDs via hydrothermal method. The CdSe precursor solution was prepared via the reaction between Cd^{2+} and KHSe solution. KHSe solution was prepared by reacting KBH_4 with selenium powder (3:1 M ratio) in aqueous solution at 95 °C for 10 min. Cd precursor solution was prepared by mixing a solution of $CdCl_2$ and TGA as stabilizer in deionized water, and then the pH value of the solution was adjusted to 11.5 with NaOH. 1 ml of 0.2 M freshly prepared KHSe solution was injected into the Cd^{2+} precursor, and the molar ratio of Cd^{2+}:Se^{2-}:TGA was fixed at 10:1:25. As illustrated in Scheme 1, 40 ml of the resulting CdSe precursor solution was loaded

into a Teflon-lined autoclave of 50 ml in capacity. Then, the mesoporous TiO_2 films were immersed into the autoclave and incubated in an oven at 90–210 °C for 12 h to promote the growth and assembly of CdSe on TiO_2. After the hydrothermal reaction, the autoclave was cooled to room temperature, and the TiO_2 electrodes were taken out and washed with deionized water, followed by N_2 blow-drying. All of TiO_2/CdSe photoanodes were then thermal-treated at 400 °C for 2 min to remove the TGA molecular and enhance the electronic coupling between TiO_2 and CdSe QDs. The obtained CdSe QDs were precipitated by adding isopropanol and centrifuged at 4000 rpm, and then were dried in vacuum at 60 °C for further characterization.

2.2. Preparation of CuS/PbS and Pt CEs

Chemical bath deposition method was applied to prepare the CuS/PbS CEs. First, 12.5 mmol Pb(CH_3COO)_2, 50 mmol NaOH, 20 mmol thiourea and 10 mmol triethanolamine (TEA) were dissolved in 400 ml deionized water under vigorous stirring and denoted as solution A. Second, 3.75 mmol $CuCl_2$ and 8 mmol TEA were dissolved in 100 ml deionized water and denoted as solution B. Then solution A was added to solution B slowly. Some cleaned FTO substrates with a pre-drilled hole were inserted into the solution, and the beaker with the reactive solution was placed on heating magnetic agitator. The deposition of PbS/CuS films is based on the slow release of Pb^{2+}, Cu^{2+}, and S^{2-} ions in the solution, which are then condensed on to the FTO substrates. The FTO were subsequently taken out of the chemical bath after different dipping time: 1, 2, and 3 h, respectively, rinsed with distilled water and dried. For easy identification, these samples were labeled as PbS/CuS-1, PbS/CuS-2, and PbS/CuS-3, respectively. The compact Pt CEs were prepared by sputtering ~ 100 nm thick layer of Pt on FTO glass. The gray precipitate found in the growth solution was separated by centrifugation and finally dried under vacuum overnight at 60 °C and kept for further characterization.

2.3. Fabrication of solar cells and symmetric dummy cells

The liquid-junction QDSSC were fabricated by assembling the TiO_2/CdSe photoanodes and CuS/PbS CEs with a 50-μm Surlyn spacer. Then, polysulfide electrolyte consisting of 2 M Na_2S, 2 M S, and 0.2 M KCl in water was injected into the cells by vacuum back-filling through a hole predrilled in the CE, which was then sealed with a cover glass after filling. For electrochemical impedance spectroscopy (EIS) and Tafel measurements, symmetric dummy cells were fabricated by assembling two identical PbS/CuS or Pt CEs face-to-face and filling the polysulfide electrolyte. The detailed characterization of the synthesized materials and solar cell device is presented in the Supporting information.

3. Results and discussion

As demonstrated in previous reports [35], TiO_2 has a strong affinity for the carboxylate group of the TGA molecules. Thiol groups, on the other hand, bind strongly to CdSe QDs. Therefore, TGA-capped CdSe precursor with a free carboxyl group could bind chemically to the TiO_2 surfaces and form TiO_2/CdSe photoanodes, and CdSe precursor that was not adsorbed onto TiO_2 formed CdSe QDs after hydrothermal reactions (Scheme 1). TGA molecular plays two important roles during the growth and assembly of the QDs. Firstly, it serves as capping agent to control the growth of CdSe QDs. Secondly, it acts as a linker to attach CdSe QDs onto the TiO_2 during the growth of CdSe. The ion-scale dimension of QDs precursor make them could diffuse into deeper regions of the TiO_2 films, which guarantee the high coverage of the CdSe QDs on the TiO_2 film.

Fig. 1 shows the surface morphologies of the bare TiO_2 and TiO_2/CdSe photoanodes prepared with different hydrothermal temperatures. It can be observed that in Fig. 1a that the as-prepared TiO_2 film exhibited a highly mesoporous structure, which favors an easy