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In situ synthesis of binary cobalt–ruthenium nanofiber alloy counter electrode for electrolyte-free cadmium sulfide quantum dot solar cells

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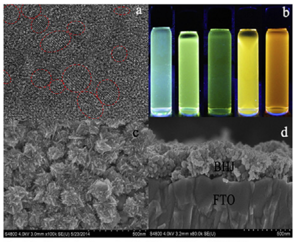
HIGHLIGHTS

- A binary nanofiber alloy CE-based quantum dot solar cell was prepared.
- An enhanced power conversion efficiency of 3.04% is achieved.
- Lower charge transfer resistance and better diffusion current density are revealed.
- Red-shifts are observed for quantum dots by varying the loading of precursors.

GRAPHICAL ABSTRACT



The efficient electrolyte-free Quantum Dot Solar Cells assembled by colloidal CdS Quantum Dots/TiO_2 bulk-heterojunction(BHJ) and Co-Ru alloy nanofiber counter electrode have been demonstrated.

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ABSTRACT

A facile, low-cost and low-temperature fabrication approach of counter electrode is essential for pursuing robust photovoltaic devices. Herein, we develop a hydrothermal in situ growth of Cobalt–Ruthenium (Co–Ru) alloy nanofiber electrode for quantum dot solar cell (QDSC) applications. Colloidal CdS QDs with tunable absorption band edge are synthesized and used as light absorber. After optimizing the QDs with the highest photoluminescence quantum yield accompanied by considerable solar light absorption ability, QDSC based on Co–Ru alloy electrode delivers a much higher power conversion efficiency than its counterparts, i.e., either pure Co or Ru metal electrodes. In detail, Co–Ru alloy electrode exhibits high specific area, excellent electrical behavior, intimate interface contact, and good stability, thus leading to notable improved device performances. The impressive robust function of Co–Ru alloy with simple manufacturing procedure highlights its potential applications in robust QDSCs.

1. Introduction

Since the first pioneering work in 2005, solution-processed quantum dot solar cells (QDSCs) have attracted continuing interest as a candidate device for third-generation thin-film solar cells over the last decade, due to the potential to be manufactured at low cost as well as the promising solution to global energy and environmental problems [1–3]. As a relatively newly emerging hotspot, it remains a challenging task to attain the desirable efficiency for electrolyte-free QDSCs. Most of the QD-based solar cells, either liquid-junction or all-solid state ones, deliver a power conversion efficiency (PCE) of typically around 3% [4–7]. A typical QDSC consists of three components: quantum dot-sensitized bulk-heterojunction (BHJ), hole/electron extraction layer (PEDOT:PSS), and

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counter electrode (CE). The CE is an indispensable component in QDSC, which transports electron/hole generated from the photoactive layer and directs charge carriers to external circuit. The metal materials with low resistance have been widely used in QDSCs as counter electrodes. Usually, these metal CEs are prepared by cost-intensive thermal evaporation under vacuum, which requires high consumption of energy. Moreover, most of the CEs fabricated by the above-mentioned methods exhibit poor mechanical properties and complicate morphologies, thus leading to poor contact between CE and the photoactive layer due to the weak interactions and adhesion between the boundaries of particles [8–10].

Alloy CEs are promising candidates for efficient QDSCs by controlling the electronic structure or surface strain of nanoparticles to enhance the interactions between the boundary particles, which have become an important strategy to tune and optimize the device performances [11–13]. In recent years, various inorganic compounds have been utilized as CEs to develop the photovoltaic (PV) devices, such as selenide [14,15], sulfides [16] and carbides [17] etc., which show good electric activity. Among these, the synthesis of alloy nanocrystals, which bears low-cost, scalable, and solution-processable features, arouses great impetus to the researchers [18–20]. As an important class of photoelectrocatalysis, Cobalt–Ruthenium (Co–Ru) alloy materials have drawn scientific and industrial interests due to their distinctive electronic properties, interesting electrochemical behaviors, and a wide variety of potential applications [21–23]. In detail, ruthenium has shown excellent photocatalytic abilities mainly due to its high electron affinity [24–27]. Introducing Ru metal can offer additional pathways to trap charge carriers and increase the lifetime of the charge carriers, which will benefit the charge collection of the CE. Besides, cobalt supported on alloy material has attracted much attention and has shown much enhanced catalytic activity [19,28]. It has been reported that the Fermi level of the semiconductors can be tuned effectively after introducing Co and there often exists an enhanced charge transfer across the interface [29]. Inspired by these incentives, we synthesize Co–Ru alloy CE for QDSC applications and expect that the desired synergetic effect can improve the photovoltaic performances of solar cells. Herein, we for the first time develop an alternative strategy for the self-assembly formation of Co–Ru alloy by hydrothermal method to enhance the photoelectric properties of QDSCs without any post-treatments. Then the alloy acting as CE was applied to QDSCs and the resultant Co–Ru alloy CE demonstrates intrinsic electrical activity for the electron/hole extraction, charge-transfer ability, better interface contact and low expensiveness, thus making it superior to the single Co or Ru metal CE. This work demonstrates that Co–Ru alloy is indeed a promising support to improve charge transfer activity and durability for practical QDSC applications.

2. Experimental

2.1. Preparation of the counter electrodes

The Co–Ru nanofiber alloy CEs were prepared by a minor modification of the hydrothermal method [14]. 1 mL of 0.020 M $RuCl_3$ aqueous solution and 1 mL of 0.015 M $Co(NO_3)_2$ aqueous solution that were dissolved in deionized water were added to a 10 mL Teflon-lined autoclave in sequence, and then 1.5 mL of $N_2H_4 \cdot H_2O$ was added under vigorous stirring for 20 min. Fluorine-doped tin oxide glass (FTO, sheet resistance 8 Ω cm^{-2}) was turned on its side and then righted itself in the autoclave. The autoclave was sealed and maintained at 200 °C for 12 h. For the preparation of either pure Ru or Co metal CE, the FTO glass was vertically immersed in a mixing aqueous solution consisting of 2 ml of either 0.020 M $RuCl_3$ solution or 0.015 M $Co(NO_3)_2$ solution and 1.5 ml of $N_2H_4 \cdot H_2O$ that was dissolved in deionized water, followed by being deposited at 200 °C for 12 h by hydrothermal method. Finally, the resultant CEs were kept in vacuum oven for further experiments.

2.2. Synthesis of colloidal CdS quantum dots

For the synthesis of S precursor, 1.95 g Sodium sulfide dissolved in 250 mL deionized water was prepared at room temperature under nitrogen gas atmosphere. Under vigorous stirring, the colorless S source was formed.

The aqueous colloidal CdS QDs were prepared in the presence of glutathione as stabilizing agent [30,31]. 20 mL of 0.02 M cadmium chloride as source of Cd was diluted to 100 mL in a three-necked flask in the presence of 60 μL glutathione, the pH solution is adjusted to 10 by adding a few drops of 0.01 M NaOH aqueous solution. The mixture was degassed at 100 °C for 1 h under vacuum. The solution was then heated for an additional 20 min to 100 °C under nitrogen gas atmosphere. After adjusting the solution to a desired temperature, an appropriate amount of S precursor was rapidly injected into the hot solution. Under vigorous stirring for 1 h, the CdS QDs were formed, followed by being purified and precipitated twice in absolute alcohol, dried with nitrogen flow and stored with solid form in a nitrogen-filled glove box.

2.3. Preparation of nanocrystal TiO_2 colloidal

The colloidal TiO_2 was prepared according to our previous reports [32–34]. In brief, tetrabutyl titanate (10 mL) was added to distilled water (100 mL) under stirring, then transferred to a mixed solution (150 mL) containing nitric acid (1 mL) and acetic acid (10 mL) at 80 °C, followed by an ultrasonic stirring for 30 min. Finally, the mixture was hydrothermally treated in an autoclaved at 200 °C for 24 h. Subsequently, the P25 (1 wt.%) were added in TiO_2 colloid by repeating crystallization at 200 °C for 12 h. At last, The PEG-20000 (2 wt.%) and a few drops of the Triton X-100 emulsification reagent were added. Finally, an even and stable TiO_2 colloid was produced.

2.4. Fabrication of electrolyte-free QDSCs

A layer of acceptor colloid with a thickness of about 250 nm was prepared by coating the TiO_2 colloid on FTO glass by spin-coating, followed by sintering in air at 450 °C for 30 min. Then the acceptor film was soaked in a 10 mg/mL aqueous colloidal CdS QDs for 12 h to form BHJ. Next, the colloidal CdS QDs were spin-coated onto BHJ. Then, the poly (3, 4-ethylenedioxylenethiophene)-polystylene sulfonic acid (PEDOT:PSS) aqueous solution at concentration of 3 wt.% was injected into the interspace between the BHJ and CE. Finally, the holes on the back of the CEs were sealed with a Surlyn film covered with a thin glass slide by heating process under vacuum. Note that the active area of our solar cell device is about 0.25 cm^2.

2.5. Characterizations

The microstructure of the CdS QDs was investigated by high-resolution transmission electronic microscopy (HR-TEM), which was carried out by using a TEM (JEM-2010, JEOL Ltd.) working at 200 kV. Samples for HR-TEM were firstly ultrasonically dispersed, followed by being placed on carbon-enhanced copper grids, and dried in air. The morphologies of the TiO_2 acceptor layer and the cross-section of BHJ were characterized by using a field emission scanning electron microscope (FE-SEM, Hitachi S4800). The photoluminescence (PL) spectrum was measured by using a spectrophotometer (FLS920, Edinburgh), in which a xenon lamp and a