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A strategy to boost the cell performance of $CdSe_xTe_{1-x}$ quantum dot sensitized solar cells over 8% by introducing Mn modified CdSe coating layer

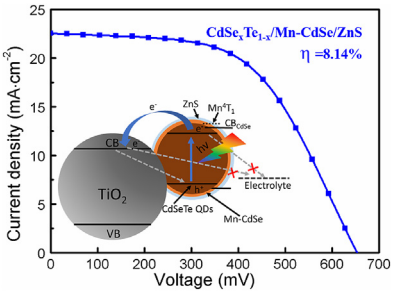
Guoshuai Wang [a], Huiyun Wei [a], Yanhong Luo [a], Huijue Wu [a], Dongmei Li [a, **], Xinhua Zhong [b, ***], Qingbo Meng [a, *]

[a] Key Laboratory for Renewable Energy (CAS), Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condense Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
[b] Key Laboratory for Advanced Materials, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China

HIGHLIGHTS

- Mn-doped CdSe interfacial modification layer is introduced into QDSCs.
- Up to 8.14% of efficiency obtained for $CdSe_xTe_{1-x}$ QDSCs.
- Enhancement of the deposition rate of Mn–CdSe QDs and light absorption.
- Charge recombination restrained by (Mn-)CdSe passivation layer.

GRAPHICAL ABSTRACT



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ABSTRACT

$CdSe_xTe_{1-x}$ alloyed colloidal quantum dots show great potential application on quantum dot-sensitized solar cells (QDSCs) due to its relatively wide light absorption range and high chemical stability. In this respect, a thin Mn modified CdSe layer is introduced into $TiO_2/CdSe_xTe_{1-x}$ alloyed QDs surface *via* a simple chemical bath deposition method (CBD) in order to further improve the cell performance. The power conversion efficiency of $CdSe_xTe_{1-x}$ QDSCs has been improved to 8.14%. Detailed investigation on the influence of this modification toward the $TiO_2/CdSe_xTe_{1-x}$ interface on the cell performance reveals that introduction of Mn into CdSe QDs is found to facilitate the Mn-doped CdSe deposition and improve the light absorption of the device. In the meantime, the existence of the (Mn-)CdSe layer can also work as a passivation layer to reduce charge recombination.

1. Introduction

Inorganic semiconductor quantum dots (QDs) offer some advantages, such as tunable band-gaps, high extinction coefficient and multiple exciton generation (MEG) [1,2]. Quantum dot solar cells have shown potential toward the third-generation solar cells

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: dmli@iphy.ac.cn (D. Li), zhongxh@ecust.edu.cn (X. Zhong), qbmeng@iphy.ac.cn (Q. Meng).

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due to low cost, easy fabrication and the possibility of boosting the power conversion efficiency (PCE) beyond traditional Shockley-Queisser limit for single-junction solar cells [3–5]. Currently, quantum dot solar cells based on two-component QDs (*i.e.* CdSe, PbS, CdTe and Sb_2S_3 *etc.*) or multi-component QDs (*i.e.* $CuInS_2$, $CdSe_xTe_{1-x}$ and $CuInSe_2$ *etc.*), have been widely investigated [6–12]. Typically, multi-component QDs have received particular attention since they can broaden light-response ranges and improve light absorption efficiency. For example, Cao et al. fabricated $Cd_{0.8}Mn_{0.2}Se$ QD-sensitized solar cell (QDSC) with a PCE of 6.33% [13]. Meng et al. reported 5.38% and 5.04% PCEs based on aqueous colloidal $CuInS_2$ and $CdSe_xTe_{1-x}$ QDSCs, respectively [10,14]. Zhong et al. reported QDSCs based on $CuInS_2$, $CdSe_xTe_{1-x}$, $CuInSe_2$ QDs derived from high-temperature environment, which presented as high as ~8% PCEs [12,15–17]. Still, due to serious electron loss resulting from charge recombination, the cell performance of QDSCs far lags behind conventional dye-sensitized solar cells (DSCs) [18] and newly popular perovskite solar cells [19].

For QDSCs, several important recombination processes often occur at the photoelectrode/QD/electrolyte interfaces, including the recombination of photo-generated electrons with oxidized species of the electrolyte or with oxidized QDs before injection, or back reactions of photo-generated electrons in TiO_2 with oxidized species of the electrolyte or with oxidized QDs [20,21]. Currently, several fruitful methods have been developed to restrain the above processes: (1) introducing ZnS passivation layer to the QDs'surface to reduce electron recombination at TiO_2/QDs/electrolyte interfaces [22,23]; (2) the treatment of wide-bandgap metal oxide thin layer (*i.e.* MgO, SiO_2) toward the TiO_2 surface to reduce electron losses [17,20]; (3) adopting a molecular dipole as the passivating ligand around QDs to alter their electronic structure [24]; (4) designing type II core/shell QD structure to realize the spatial charge separation and to suppress the recombination [25–27] and (5) developing new QD sensitizers with higher conduction band or introducing mid-gap states to facilitate charge extraction and retard interfacial recombination losses [13,27]. Anyway, interfacial modification is crucial to enhance the cell performance of the QDSCs in essence.

$CdSe_xTe_{1-x}$ alloyed QDs exhibit good crystalline quality and morphologies, well-defined particle sizes and size distribution. Moreover, their absorption edge can extend to near-infrared region and exhibit high chemical stability as well. 8.2% PCE has recently been reported for $CdSe_xTe_{1-x}$ based QDSCs [17]. Enhancing the light absorption to higher short-circuit photocurrent (J_{sc}) and reducing the recombination to higher the open-circuit photovoltage (V_{oc}) and fill factor (*FF*) are the key to further improve its cell performance. In this work, a thin Mn modified CdSe coating layer has been introduced into $CdSe_xTe_{1-x}$ based-QDSCs, which short-circuit photocurrent density (J_{sc}) and V_{oc} are enhanced, leading to the PCE improvement to 8.14%. Further investigation reveals that the existence of Mn can facilitate Mn-doped CdSe deposition on TiO_2/$CdSe_xTe_{1-x}$ surfaces, beneficial to the light absorption of the devices. Meanwhile, this Mn–CdSe coating layer can modify TiO_2/$CdSe_xTe_{1-x}$/electrolyte interfaces to suppress the recombination.

2. Experimental

2.1. Materials and reagents

Thioglycolic acid (TGA, 97%), oleic acid (90%), cadmium oxide (CdO, 99.99%), selenium powder (99.999%), and sodium nitrilotriacetate (AR, $N(CH_2COONa)_3$, 98+%) were purchased from Alfa Aesar Chemicals. Tellurium powder (200 mesh, 99.99%) was purchased from Aldrich. $Zn(CH_3COO)_2{\cdot}2H_2O$ (99+%), $Na_2S{\cdot}9H_2O$ (98+%), sulfur (99.5+%), $Mn(CH_3COO)_2{\cdot}4H_2O$ (99.0+%), $Cd(CH_3COO)_2{\cdot}2H_2O$ (98+%), Na_2SO_3 (97.0+%) and paraffin liquid were from Sinopharm Chemical Reagent Co. Ltd. Oleylamine (OAm, 80–90%) was from Aladdin. All the chemicals were used without further purification. The electrode substrate was fluorine-doped tin oxide conducting glass (FTO, thickness: 2.2 mm, Pilkington, sheet resistance: 14 Ω/square). Before use, FTO glass was first washed with mild detergent, rinsed with distilled water for several times, subsequently with ethanol in an ultrasonic bath, and finally dried under air stream.

2.2. Synthesis of $CdSe_xTe_{1-x}$ alloyed QDs

$CdSe_xTe_{1-x}$ alloyed QDs was prepared according to the literature with some modification [11,28]. In brief, 0.1 M Cd precursor solution (CdO dissolved in oleic acid and paraffin with 1: 3 volume ratio), 0.1 M Te and 0.1 M Se stock solutions (Te or Se powders were dissolved in TOP and paraffin (v/v, 1:3)) were mixed in a 50 mL three-necked flask with raw Cd: Se: Te molar ratio of 25: 4: 1. The mixture was heated to 320 °C under the protection of N_2 atmosphere and kept at this temperature for 5–6 min to get the QDs. Then, the reaction mixture was cooled down to 250 °C, followed by adding 2 mL OAm into the reaction system and kept at this temperature for 5 min, finally cooled down to the room temperature. The reaction procedure was monitored by fluorescence spectra. The aqueous colloidal QDs were obtained by the ligand exchange by following the literature [28]. 2.0 mmol of TGA was dissolved in 1.0 mL of methanol, which pH value was adjusted to 11 with 30% NaOH solution, subsequently added into ~10 mL of $CdSe_xTe_{1-x}$ QDs CH_2Cl_2 solution. The mixture was stirred for 2 h to afford the TGA-capped QDs precipitation, which were then extracted with 10 mL deionized water. $CdSe_xTe_{1-x}$ QDs aqueous solution was further purified by using acetone as precipitator. Finally, TGA-capped $CdSe_xTe_{1-x}$ QDs aqueous solution was obtained.

2.3. Characterization

The optical properties were obtained on UV–Vis spectrometer (Shimadzu, UV2550). Photoluminescence (PL) emission spectra were measured by using a fluorescence spectrophotometer (F97 Pro, Shanghai Lengguang Tech). Time-resolved photoluminescence decay spectra were obtained on a PL Spectrometer (Edinburgh Instruments, FLS 900), excited with a picosecond pulsed diode laser (EPL-445). The scanning electron microscopy (SEM) system (FEI XL30 S-FEG) equipped with an energy dispersive X-ray (EDX) spectrometer was employed to estimate the element content of the TiO_2/$CdSe_xTe_{1-x}$/Mn–CdSe film. The morphologies of TiO_2/$CdSe_xTe_{1-x}$ and TiO_2/$CdSe_xTe_{1-x}$/Mn–CdSe films were investigated by Transmission electron microscopy (TEM, FEI Tecnai F20 Super-twin). Typically, samples for TEM investigation were prepared by scraping the TiO_2 nanoparticles coated with $CdSe_xTe_{1-x}$ QDs from the FTO substrate and dispersed in ethanol, followed by transferring several drops of the suspension solution onto a carbon-coated copper grid.

2.4. Device fabrication

A double-layer TiO_2 film was deposited on FTO substrate by screen printing technique, consisting of a 12 μm-thickness transparent layer with P25 TiO_2 particles and a 6 μm-thickness light-scattering layer with the mixture of 300 nm rutile TiO_2 particles and 20 nm anatase TiO_2 particles [28]. The films were annealed at 500 °C for 30 min before use. 40 μL of $CdSe_xTe_{1-x}$ alloyed QDs aqueous solution was dropped onto the TiO_2 photoanode surface to make the TiO_2 film fully infiltrated overnight, which was rinsed first with deionized water, then with ethanol and finally dried in the air.