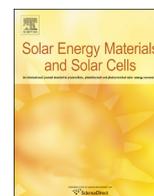




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## Solar Energy Materials &amp; Solar Cells

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# Tailoring band structure of ternary $\text{CdS}_x\text{Se}_{1-x}$ quantum dots for highly efficient sensitized solar cells



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## ARTICLE INFO

## Article history:

Received 9 October 2015

Received in revised form

28 March 2016

Accepted 28 April 2016

Available online 13 May 2016

## Keywords:

Solar cells

Ternary quantum dot

Graded band structure

Interfacial defects

## ABSTRACT

Instead of employing numerous binary quantum dots (QDs), engineering ternary alloyed ones has been emerging as a promising approach to tailor their optical and electronic properties. In this paper, composition-tunable  $\text{CdS}_x\text{Se}_{1-x}$  QDs have been explored and demonstrated to be efficient sensitizers for quantum dot-sensitized solar cells (QDSCs). The optical bandgap and the corresponding band edges could be varied by controlling the component ratios of the ternary QDs while keeping the particle size constant, and a moderate bandgap was attained to deliver broad light harvesting and ideal band alignment. The successful balance of these two requirements resulted in a power conversion efficiency (PCE) of 3.58% for  $\text{CdS}_x\text{Se}_{1-x}$  QD-sensitized  $\text{TiO}_2$  solar cells. When the engineered  $\text{CdS}_x\text{Se}_{1-x}$  interlayer was further incorporated between CdS core and CdSe shell layers, a superior PCE of 5.06% has been reached for the graded  $\text{CdS}/\text{CdS}_x\text{Se}_{1-x}/\text{CdSe}$  structure, which appreciably outperforms the conventional  $\text{CdS}/\text{CdSe}$  one ( $\eta=4.41\%$ ). The incorporation of  $\text{CdS}_x\text{Se}_{1-x}$  interlayer offers two benefits, (1) the construction of a favorable stepwise band structure, facilitating desired charge injection, and (2) the passivation of the interfacial defects and interphase strain, contributing to suppressed charge recombination. This work highlights the broad prospect of ternary alloyed QDs for developing highly efficient QDSCs.

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## 1. Introduction

The pressing demand of cost-effective and highly efficient solar devices for clean and sustainable energy, to partially replace fossil fuels has been intensified with an increasing concerns of environmental pollution and climate change all over the world [1,2]. Inorganic semiconductor quantum dot-sensitized solar cells (QDSCs) with rapid enhanced power conversion efficiency recently have received revitalized attention as third generation photovoltaic cells due to the versatile advantages of quantum dots (QDs) compared to the conventional dye sensitizers, such as tunable bandgap by controlling their size, large extinction coefficient, multi-excitation generation, and high stability toward water and

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oxygen [3–18]. A theoretical power conversion efficiency (PCE) up to 44%, beyond the traditional Shockley and Queisser limit of 32% for semiconductor solar cells, has encouraged researchers to develop QDSCs with the use of a variety of QDs as sensitizers for light harvesting, including CdS [13], CdSe [14], CdTe [16], PbS [17], PbSe [18], etc. Compared to the metal halide perovskites as light harvesters, which have stunned the photovoltaic community with a PCE exceeding 20% but suffered from moisture-sensitive nature, inorganic QDs show impressive stability to ambient conditions [1]. Among kinds of the QDs developed, the fascinating CdS/CdSe co-sensitization system has been shown to demonstrate the excellent power conversion efficiencies (PCEs) over 5% employing mesoporous  $\text{TiO}_2$  films [6,19,20]. Our previous work also report an outperforming PCE of 6.33% for CdS/Mn-CdSe sensitized  $\text{TiO}_2$  solar cell [19].

In QDSCs, the optical bandgap of the QDs and the alignment of their bands with the underlying oxide semiconductor are critical for broad light harvesting and efficient charge separation [21]. However, these two requirements are not easily fulfilled simultaneously. Although the utilization of QDs with large size or narrow bandgap can expand the light absorption spectrum, the low conduction band edge of those QDs may prevent the effective

injection of photo-generated electrons from the QD sensitizer into oxide semiconductor. This explains the relatively low PCEs of narrow bandgap QDs (such as PbS and Ag<sub>2</sub>S) sensitized solar cells, which possessed broad light harvesting, but suppressed electron injection [22,23]. Therefore, under such circumstance, the tuning of optical and electronic properties of QDs purely by changing the particle size could be limited. Fortunately, instead of employing binary QDs, tailoring ternary QDs through alloying has emerged as a promising approach to pursue desired bandgap while keeping the particle size constant [24]. The optical bandgap and the corresponding band edges can be feasibly varied by altering component ratios of the alloyed QDs at a fixed size. In other words, in addition to size, ternary QDs provide composition as an additional dimension for tailoring their optical and electronic properties. Hence, employing composition-tunable alloyed QDs as sensitizer enables us to improve the optical absorption without overly impeding the subsequent charge injection from QDs to oxide semiconductors [25]. However, in contrast to the use of numerous binary QDs, the attempts to explore ternary alloyed ones as sensitizers in liquid-junction QDSCs to manipulate the band structure have been relatively rare [9,21,26–29].

Cd<sub>x</sub>Se<sub>1-x</sub> alloyed semiconductors belong to ternary chalcogenide compounds, and the bandgap can be engineered between the bulk CdS (2.45 eV) and CdSe (1.75 eV), over a wide visible wavelength range [29]. Moreover, CdS and CdSe are considerably miscible in view of their small lattice mismatch, leading to the formation of Cd<sub>x</sub>Se<sub>1-x</sub> (0 ≤ x ≤ 1) solid solution with almost zero enthalpy change [30]. Not surprisingly, the excellent ternary alloyed QDs attracted significant interest in the potential photovoltaic application. Up to now, much work has been committed to the preparation of different morphologies of ternary Cd<sub>x</sub>Se<sub>1-x</sub>, such as colloidal QDs [24], thin film [29], nanobelt [31], etc., and the optical and electrical properties have been extensively studied. Hossain et al. reported a PCE of 4.05% based on Cd<sub>x</sub>Se<sub>1-x</sub> sensitized TiO<sub>2</sub> solar cell, rivalling the well-studied cascaded CdS/CdSe photoelectrodes [21]. Sung et al. synthesized complete composition-tuned Cd<sub>x</sub>Se<sub>1-x</sub> layer sensitized TiO<sub>2</sub> nanowire arrays, and employed as efficient photoelectrodes for hydrogen generation [29].

In this work, Cd<sub>x</sub>Se<sub>1-x</sub> QDs with controlled composition were prepared as the sensitizers for QDSCs by successive ionic layer adsorption and reaction (SILAR), instead of the high-temperature thermal vapor transport or hot injection methods [24,29]. SILAR allows the Cd<sub>x</sub>Se<sub>1-x</sub> layer to successively grow in a reproducible and controllable manner [13]. Aiming to engineer novel band alignment facilitating charge separation and impair the interfacial defects and interphase strain for suppressed charge recombination in the multilayered QDSCs, Cd<sub>x</sub>Se<sub>1-x</sub> interlayer was further incorporated into CdS/CdSe co-sensitization system between CdS core and CdSe shell for enhanced photovoltaic performance. Such an idea is similar to that of boosting the luminescence quantum efficiency by gradually changing the shell composition in multi-shell structures [32,33]. Ultimately, the graded CdS/CdSe/CdSe structure delivers a superior PCE of 5.06% under simulated AM 1.5 100 mW cm<sup>-2</sup> illumination, which turns out to outperform the conventional CdS/CdSe QDSCs (η=4.76%) prepared under the same manufacturing procedures.

## 2. Experimental

### 2.1. Chemicals and materials

Titanium oxide (TiO<sub>2</sub>, Degussa, P25), α-terpineol (C<sub>10</sub>H<sub>18</sub>O, 96%, Sigma Aldrich), ethyl cellulose [(C<sub>6</sub>H<sub>7</sub>O<sub>2</sub>(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>n</sub>, 48.0–49.5% (w/w) as ethoxyl, Sigma Aldrich), cadmium acetate dihydrate (Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, 98%, Sigma Aldrich), sodium sulfide nonahydrate (Na<sub>2</sub>S·9H<sub>2</sub>O, ≥98.0%, Sigma Aldrich), sulfur (S, purified

by sublimation, Sigma Aldrich), sodium sulfide anhydrous (Na<sub>2</sub>SO<sub>3</sub>, 99.1%, Italy), trisodium salt of nitrilotriacetic acid (N(CH<sub>2</sub>COONa)<sub>3</sub>, ≥98.0%, Aldrich), zinc acetate dihydrate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, ≥99.0%, Aldrich), selenium powder (Se, 99.5%, Alfa Aesar), brass foil (alloy 260, 0.3 mm thick, Alfa Aesar), hydrochloric acid (HCl, 37%, USA), methanol (CH<sub>3</sub>OH, ≥99.5%, Sigma Aldrich), and ethanol (CH<sub>3</sub>COOH, ≥99.5%, Decon) were all used as received.

### 2.2. Preparation of mesoporous TiO<sub>2</sub> films

Commercially available F-doped tin oxide (FTO) glass was used as transparent conducting substrates to prepare TiO<sub>2</sub> photoelectrodes. To prepare TiO<sub>2</sub> paste, 0.5 g Degussa P25 mixed with 0.25 g ethyl cellulose and 1.75 g α-terpineol were first dispersed into 5.0 mL ethanol, and then sonicated for 30 min to form a slurry after removing the ethanol under stirring. Mesoporous TiO<sub>2</sub> films were prepared by doctor blading of TiO<sub>2</sub> paste on the clean FTO substrate, followed by sintered at 500 °C for 30 min in air with a heating rate of 5 °C/min. The thickness of the TiO<sub>2</sub> film, measured from the cross sectional image of SEM, was ca. 16 μm, as shown in Fig. S1 (ESI<sup>†</sup>). The active area of the TiO<sub>2</sub> films was approximately 0.36 cm<sup>2</sup> (0.6 cm × 0.6 cm square).

### 2.3. In situ assembling of QDs

For in situ assembling of QDs by both successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD) processes, the films were immersed into the as-prepared precursor solutions to allow the ions of the reactants to penetrate into the mesoporous film and incorporate into the interior of mesopores, leading to the formation of one layer of QDs. Specifically, the SILAR processes for Cd<sub>x</sub>Se<sub>1-x</sub> QDs deposition were all conducted inside a glove box under N<sub>2</sub> atmosphere. TiO<sub>2</sub> films were first dipped into cation ion precursor, i.e., 0.1 M Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O methanol solution for 1 min, rinsed with methanol and dried under N<sub>2</sub> atmosphere for several minutes. Subsequently, the dried films were then dipped into anion precursors for another 1 min to allow S<sup>2-</sup> and Se<sup>2-</sup> to react with the pre-adsorbed Cd<sup>2+</sup>, leading to the formation of the desired ternary Cd<sub>x</sub>Se<sub>1-x</sub> QDs. The above anion precursors were prepared by dissolving different amount of Se powder into a concentration-fixed 0.1 M Na<sub>2</sub>S solution containing water and methanol (volume ratio, v/v=1/1) under vigorous stirring. The feed Se molar concentrations were 0, 0.00625, 0.0125, 0.025 and 0.05 M, respectively, i.e., Se/S varied from 0/16, 1/16, 2/16, 4/16 to 8/16. The Se<sup>2-</sup> generated in this process could stay stably for a period of time in alkaline Na<sub>2</sub>S solutions. One deposition cycle was completed by further rinsing and drying. The two-step dipping procedure is termed as one SILAR cycle. A certain number of SILAR cycles were employed to obtain a desired amount of QDs loaded on the TiO<sub>2</sub> films. As follows is a brief description of CBD procedure for the deposition of CdSe: 0.1 M Na<sub>2</sub>SeSO<sub>3</sub>, 0.1 M Cd(CH<sub>3</sub>COO)<sub>2</sub>, and 0.2 M N(CH<sub>2</sub>COONa)<sub>3</sub> aqueous solution were mixed together with a volume ratio of 1/1/1, and then the TiO<sub>2</sub> films were vertically immersed into the solution for the assembly of a CdSe layer under dark condition at 24 °C for 3 h. Na<sub>2</sub>SeSO<sub>3</sub> solution was prepared by dissolving Se powder in an aqueous solution of Na<sub>2</sub>SO<sub>3</sub> at 70 °C for ca. 1 h under vigorous stirring. For the preparation of CdS seed layer, 4 SILAR cycles were conducted, employing 0.1 M Cd(CH<sub>3</sub>COO)<sub>2</sub> in methanol and 0.1 M Na<sub>2</sub>S in a mixture of methanol and water (volume ratio, v/v=1/1) as the cation and anion source, respectively. Finally, all the photoelectrodes were coated with 2 SILAR cycles of ZnS passivation layer, by dipping alternatively into 0.1 M Zn(CH<sub>3</sub>COO)<sub>2</sub> and 0.1 M Na<sub>2</sub>S solutions for 1 min/dip. The deposition of ZnS serves as a tunnel barrier for back charge

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