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Improved stability of depletion heterojunction solar cells employing cation-exchange PbS quantum dots

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ABSTRACT

PbS colloidal quantum dots (QDs) have emerged as one of the most promising photovoltaic solar cells material. The synthesis of PbS QDs generally uses TMS_2S as sulfur source. However, the volatile and environmentally unfriendly properties of TMS_2S will limit its industrial applications. This paper presents a new method of synthesizing PbS QDs employing a CdS QDs/ODE solution as the sulfur precursor by exploiting a cation exchange reaction. The resulting QDs show a performance comparable with previous work for solar cells. Through optimizing the architecture of the photoactive layer, excellent stability in air is achieved. An efficiency of 7.89% is retained in air after 110 days.

1. Introduction

PbS quantum dots (QDs) have attracted increasing attention for photovoltaic applications because of their quantum-size-effect-tuning matching their absorption with the sun's broad spectrum [1,2]. The power conversion efficiency has experienced a rapid increase to more than 10% over the past decade as a result of advances in QD surface passivation and improvements in device architecture [3]. For examples, Lan incorporated high amounts of iodide on CQDs to achieve improved passivation and deliver a certified efficiency of 10.6% [4]. Meanwhile, Liu presented a new solution-phase ligand-exchange method that enable closely packed CQDs films with flat energy landscapes, with a certified power conversion efficiency of 11.28% [5]. From early PbS QD Schottky junction solar cells to recent depleted heterojunction (DH) solar cells (such as a rectifying junction of TiO_2, ZnO, CdS with PbS QDs film) [6–8], the photovoltaic performance has been significant improved [9].

While broad efforts have been dedicated to improve the device architectures [10,11], the surface chemistry is another major factor that affects the photovoltaic performance [12,13]. The well-known short-chain-organic ligand exchange process has been tuned to optimize inter-dots distance to enhance carrier transport and to passivate those high-density trap states attributed to a large amount of surface dangle bonds [14]. Recently, halide surface passivation treated PbS QDs have shown a great improvement in photovoltaic performance as a result of a lower density of trapped carriers than in their organic

ligands counterparts [15]. Furthermore, halide ion balances the excess charge caused by the nonstoichiometric ratio during the synthesis of the QDs [16].

In the synthesis of PbS QDs, an optimum size between 3 and 4 nm is desired for photovoltaic devices in general. And a lot of efforts have been made to the synthesis of PbS QDs [17,18]. In previous research, bis (trimethylsilyl) sulfide (TMS_2S), a reactive sulfur source, was commonly injected into a Pb precursor solution to form PbS QDs [19]. The resulting QDs have good mono-dispersity and stability, and the size is suitable for solar cells. However, the TMS_2S is volatile, toxic and expensive, which limit its industrial applications for solar cells. Sulfur powder is of particular interest in some chalcogenide (such as CdS, ZnS) QDs [20] due to its less toxicity, low price and good stability. However, it is not capable to achieve monodisperse PbS QDs with diameters smaller than 4 nm attributed to a relatively low nucleation threshold in Pb precursor system. Whereas, cation exchange techniques provide a powerful synthetic tool to overcome the limitations of traditional colloidal syntheses [21,22]. A typical example is to apply a two-step reaction process to covert CdS QDs/NRs to PbS QDs/NRs in a Cu_2S structure [23]. Zhang *et al.* and Kim *et al.* also developed a direct cation exchange synthesis method to obtain PbSe QDs employing pre-synthesized CdSe and ZnSe QDs as raw materials. These PbS QDs offer a power conversion efficiency exceeding 6% with improved air stability [24,25].

In this paper, a direct pathway toward PbS QDs using CdS QDs as starting material via a cation exchange reaction is presented. In a

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comparatively green synthetic environment employing sulfur powders as anion source, CdS QDs of desired sizes are produced by injecting a sulfur/ODE solution into a cadmium oleate/ODE mixture. Then the pre-synthesized CdS QDs in ODE are injected into a $PbCl_2$/OLA mixture to form PbS QDs. This method produces chloride-terminated (in situ) PbS QDs, preventing the QDs from oxidative attack and balancing excess charge from nonstoichiometric surface termination. These QDs are applied to an improved architecture in DH solar cells. PbS-TBAI exchanged QDs film serve as the main photoactive region whereas PbS-EDT exchanged one serve as the electron-blocking layer. This improvement results in a high power conversion efficiency (PCE) of 7.89% and a J_{sc} of 30.96 mA/cm^2, the highest of PbS QDs heterojunction solar cells.

2. Experimental details

2.1. Synthesis of CdS QDs

In a typical synthesis, CdO (0.28 g) and oleic acid (OA 1.5 ml) were loaded into a 50 ml three-neck round-bottom flask with 18 ml of octadecene (ODE). The mixture was heated to 300 °C under vigorous stirring and argon bubbling, yielding a yellowish brown homogeneous solution. Then 0.032 g sulfide powers in 10 ml ODE solution was injected into the flask. Before the injection of sulfur precursor, the heating mantle was removed and the solution was cooled down to room temperature naturally.

After the synthesis, the CdS QDs were purified through a method that was reported in a previous work [26]. The isolation procedure was repeated by using hexane, ethanol, and acetone, CdS QDs were sedimented through centrifugation and were dried in an oven in following steps. Butylamine was added in the first extraction step to enhance the ability to remove the fatty acid and carboxylate salts into ethanol and chloroform was added in the precipitation step to retain the non-polar liquid [26].

2.2. Synthesis of PbS QDs via cation exchange

$PbCl_2$ (0.773 g) and oleylamine (9.2 ml) were mixed to a three-neck round-bottom flask and degassed under vacuum at 80 °C for 30 min. The flask was then heated to 140 °C by bubbling with argon and was maintained at this temperature for another 30 min. Then 200 mg CdS QDs in 6.67 ml ODE solution were injected swiftly into the reaction flask at a temperature range from 80 °C to 160 °C. The solution changed to a brownish color immediately as the evidence of the formation of PbS QDs. After the injection, the heating mantle was removed and the reaction was stopped naturally. At 75 °C, 9.3 ml toluene and 7.4 ml OA were added to purify QDs solution to replace the weakly bound oleylamine (OLA) at 40 °C followed by vigorous stirring for 20 min. Then the PbS QDs were purified several times using toluene and acetone, finally dispersed in toluene for device fabrication.

2.3. Device fabrication

Commercial conducting FTO/glass substrates were cleaned ultrasonically with emulsifier, acetone, ethanol, and deionized water sequentially. After drying in nitrogen, a TiO_2 compact layer was deposited on the well-cleaned FTO substrate. 0.2 M titanium diisopropoxide bis (acetylacetonate) ethanol solution was spin-coated on the clean substrate followed by sintering at 500 °C for 30 min, followed by immersion in a 40 mM $TiCl_4$ aqueous solution for 30 min at 70 °C and drying at 500 °C for another 30 min 5–6 layers of PbS-TBAI exchanged QDs films were spin-coated onto the TiO_2 layer. Onto the multiple TBAI layers, two layers of PbS-EDT exchanged QDs films were deposited. Finally, Au electrode was deposited by thermal evaporation at a rate of 0.02–0.03 nm/s under a pressure of $1-5\times10^{-5}$ Torr to a thickness of 150 nm. An active size was defined by the mask as 0.09 cm^2.

2.4. Device characterization

The morphologies and crystal structures of the QDs were analyzed by using a JEM-2100 high-resolution transmission electron microscope. Optical absorption spectra were measured by using a Shimadzu UV–VIS–NIR 3600 spectrophotometer. X-Ray diffraction patterns were recorded with a Rigaku D/MaxrB diffraction using Cu Kα radiation with a wavelength of 0.1540 nm. The sectional view of the device was analyzed by a SU8020 field-emission scanning electron microscope. Photocurrent density-voltage (J-V) curves were conducted with a Keithley 2636 sourcemeter under N_2 atmosphere using a xenon lamp solar simulator equipped with an AM 1.5 filter as the light source. IPCE was tested by using a Zolix spectrograph, the light source was also provided by a xenon lamp, and a standard silicon cell (OPRC185Si. QG-CAL S/N #1138) was used as a reference.

3. Results and discussion

The typical transmission electron microscopic (TEM) images of the as-synthesized CdS and PbS QDs are shown in Fig. 1a-b. It is clear from the images that the particles are monodisperse particles with similar shapes. The mean size of CdS QDs is ~2.7 nm, while the PbS QDs size is ~3.5 nm. The high-resolution TEM (HRTEM) image of a single CdS QD, as shown in Fig. 1c, demonstrates a single crystal with a high crystallinity. A single crystal PbS QD with an injection temperature of 150 °C is shown in the Fig. 1d. There is not an apparent structural defect in the QD and the continuous fringes are well-resolved. It is an indication that the elevated temperature provides sufficient thermal energy to remove any lattice stress or disorder that may be generated in the ion exchange reaction and CdS QDs are fully converted to PbS QDs in a directed cation exchange reaction. The cation-exchange process depends on the thermodynamic driving force and the activation barrier. The solvation of cations plays an important role in determining the thermodynamics of the reaction, and which could be controlled by varying the solvent environment. On the other hand, many factors (for instance, the anion sublattice structure, the iconicity of the cation-anion interaction, and the structural difference between the reactant and product phases) would impact on the activation barrier for the diffusion and exchange of the cations. In our experiments, the cation exchange reaction was triggered by using $PbCl_2$ in oleylamine. Based on above-mentioned facts, the solvent environment could provide enough thermodynamic driving force for the reaction, which would be caused by that the $CdCl_2$ is easier to solvation in oleylamine than $PbCl_2$. And being as a support, the similar results have been also reported in the reference [27]. Furthermore, the observed 0.336 nm and 0.296 nm fringe spacing in the HRTEM image correspond to the separation of the (111) and (200) lattice plane of zinc blende CdS QDs and rock salt PbS QDs.

An absorption spectrum of toluene dispersions of CdS QDs is shown in Fig. 2a. The sharp first excitonic absorption peak is an evidence of a narrow size distribution of the QDs, in a good agreement with the TEM image. It has been reported that a uniform CdS QDs size is beneficial to the formation of reasonable monodisperse PbS QDs [27]. Typical absorption spectra of PbS QDs with various CdS/ODE injection temperatures are shown in the Fig. 2b. It can be found that the position of the first excitonic absorption peak is shifted from 850 nm to 1202 nm (red) with the increase of injection temperature from 80 °C to 160 °C, an evidence of that a higher injection temperature results in larger PbS QDs. It is attributed to an increased width of the reaction zone and the increase of the diffusion rate of the cation with temperature. A narrow size distribution is achieved in lower injection temperature and a slow red-shift is observed. With the increase of injection temperature, a large red-shift occurs accompanied by a broad size distribution, which means that the QDs grow rapidly at a high