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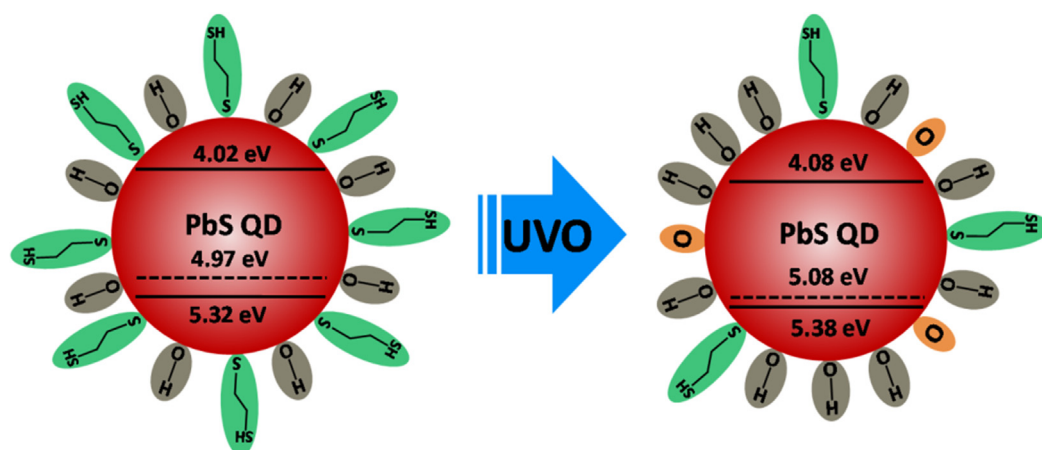
Photo-induced surface modification to improve the performance of lead sulfide quantum dot solar cell



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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 November 2017

Revised 9 March 2018

Accepted 14 March 2018

Available online 15 March 2018

Keywords:

Quantum dot

Solar cell

Hole transport layer

Doping

Surfactant

Thin film

ABSTRACT

The solution-processed quantum dot (QD) solar cell technology has seen significant advancements in recent past to emerge as a potential contender for the next generation photovoltaic technology. In the development of high performance QD solar cell, the surface ligand chemistry has played the important role in controlling the doping type and doping density of QD solids. For instance, lead sulfide (PbS) QDs which is at the forefront of QD solar cell technology, can be made n-type or p-type respectively by using iodine or thiol as the surfactant. The advancements in surface ligand chemistry enable the formation of p-n homojunction of PbS QDs layers to attain high solar cell performances. It is shown here, however, that poor Fermi level alignment of thiol passivated p-type PbS QD hole transport layer with the n-type PbS QD light absorbing layer has rendered the photovoltaic devices from realizing their full potential. Here we develop a control surface oxidation technique using facile ultraviolet ozone treatment to increase the p-doping density in a controlled fashion for the thiol passivated PbS QD layer. This subtle surface modification tunes the Fermi energy level of the hole transport layer to deeper values to facilitate the carrier extraction and voltage generation in photovoltaic devices. In photovoltaic devices, the ultraviolet ozone treatment resulted in the average gain of 18% in the power conversion efficiency with the highest recorded efficiency of 8.98%.

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1. Introduction

The size-tunable band gap of semiconducting quantum dots (QDs) has put them at the center stage of numerous optoelectronic research applications including photodetectors [1], light emitting diodes [2,3], transistors [4,5] and solar cells [6–12]. The passivation of unsaturated atoms on the QD surface plays crucial roles in maintaining the clean energy band gap [7,10], doping [9,13], air stability [9,10] and charge transport properties of QD solids [14]. Doping control in the high performance QD solar cells has been achieved by controlling their surface chemistry [14,15]. In the case of PbS QDs, iodine or halometallate ([PbI₃]) passivations have been reported to form air-stable n-type QD solids [9,10,16], whereas thiol passivation has resulted into p-type doping [17,18]. Recent progress in surface chemistry enables the one-step deposition of thick and electrically active QD layer [19–23], allowing us to do away with the time consuming and wasteful layer-by-layer deposition approach [7,9,24]. Solution phase surface passivation using halometallate ([PbI₃]) ligands [10,22,25] allows ordered deposition and tail state removal of PbS QD films to achieve record solar cell performance of 11.28% [10]. This recent advancement paves the way to develop production compatible ink for large-scale manufacturing of QD solar cells. The halometallate surface ligands, however, make the QD layer vulnerable to ionic ligands and polar solvents, thereby inducing additional restrictions on the choice of ligands and solvents for the top hole transport layer deposition. To date, n⁺-n-p device architecture with ZnO as a n⁺-type bottom layer, solution exchanged PbS QDs with the halometallate ligand as the n-type intermediate layer and PbS QDs treated with dilute concentration of (~0.01–0.02%) 1,2 ethanedithiol (EDT) as p-type top layer (PbS-EDT) have been explored in solar cell devices [10,25]. In this study, we have observed that common ligands like 3-Mercaptopropionic acid (MPA) or even higher concentrations of EDT ligand solution for top p-type PbS QD layers deposition, leads to flocculation and degradation of the intermediate n-PbS QD layer. Such restriction in chemical treatment undermines the desirable electronic properties of the hole transport layer.

Electron and hole transport layers play a crucial role in the filtration and transportation of opposite charge carriers toward their respective electrodes [17]. In the recent past efforts have been made to tune the energy band position of n⁺ ZnO layer [26] to aptly suit the purpose of photovoltaic processes. However, efforts to improve the properties of p-type PbS-EDT layer have been limited [27]. In the solar cells, p-type PbS-EDT layer forms the necessary n-p heterojunction with n-type PbS-[PbI₃] QD layer [17]. The Fermi energy difference between these layers controls the built-in voltage inside the device which acts as the driving force for the charge carriers in the depletion region of the solar cells. Doping control of PbS-EDT layer would help in tuning the Fermi energy difference with n-PbS layer and thereby improve carrier extraction and voltage generation in solar cell devices. Mild oxidation of PbS-EDT layer via ambient heat treatment has been shown to improve the p-type doping and passivation of QD surface [18,28,29]. Annealing in presence of oxygen may, however, be detrimental to n-type PbS-[PbI₃] layer as surface oxidation will alter the halometallate passivation and degrade their n-type properties.

Herein, we report facile and compatible ultraviolet ozone (UVO) treatment strategy to modify the electronic properties of PbS-EDT layer and implement it in improving the solar cell performances. We show that control UVO treatment leads to mild oxidation of the QD surface which modifies the Fermi energy to a deeper value and changes the energy band position of PbS-EDT layer in a favorable way. In solar cell devices, this helps to improve photovoltaic parameters (V_{oc} , J_{sc} , FF and PCE). Detailed analysis shows that recombination resistance, carrier lifetime and built-in potential

increases, whereas series resistance drops due to UVO treatment. This leads to superior performance in the solar cell devices.

2. Results and discussion

The PbS QDs are synthesized according to the reported method [29]. Transmission electron microscopy result shows that the average diameter of the PbS QDs is ~3.25 nm (Fig. S1). UVO treatment is carried out using a commercial UV ozone cabinet with 254 nm mercury lamp. PbS-EDT thin films are illuminated from the top for different time intervals for the UVO treatment. The detail of the device fabrication steps is given in the Supporting Information. The surface properties of PbS-EDT film with no UVO treatment (0s-UVO) and 15 s UVO treatment (15 s-UVO) are determined using X-ray photoelectron spectroscopy (XPS) measurement. Deconvolution of the O 1s spectrum of 0s-UVO (pristine) PbS-EDT film (Fig. 1a) shows peaks at 531.2 eV and 532.4 eV. The lower binding energy peak corresponds to Pb-OH and the peak at 532.4 eV corresponds to the organic component (COO) and adsorbed CO₂ [18,27,29]. An additional peak at 529.5 eV appears for 15 s-UVO treated film (Fig. 1b). This peak corresponds to the binding energy of Pb-O [18], implying the formation of lead oxide at the QD surface. It is further observed that the UVO treatment leads to an increase in the Pb-OH concentration along with a concomitant reduction in the COO and CO₂ contribution in the O 1s spectrum (supplementary information, Table S1). XPS analysis of the S 2p spectra (Fig. 1(c), (d) and Table S2) suggests that UVO treatment leads to the removal of bound thiol from the QD surfaces and increases the amount of unbound thiol in the film. The removal of bound thiol ligands from the QD surface could be due to the formation of Pb-O and Pb-OH components. The situations of the QD surface passivation for before and after UVO treatment are reconstructed from XPS data and are depicted-graphically at the insets of Fig. 1a and b respectively. The pristine PbS-EDT QD surface has a higher number of bound EDT ligands and contains no Pb-O component, whereas 15 s-UVO treatment leads to a decrease (11%) in bound EDT ligands and increase in Pb-OH (7%) and Pb-O (4.3%) components at the QD surface. The effect of UVO induced surface oxidation on the electronic energy levels of PbS-EDT layer is studied by ultraviolet photoelectron spectroscopy (UPS) [15]. He-I α radiation of energy 21.22 eV is used for the UPS measurement. High energy region of the UPS spectra is shown in Fig. 1e to highlight the secondary electron cutoff (SEC) energy. Fermi energy (E_f = 21.22 eV-SEC) for pristine and 15 s-UVO treated PbS-EDT layer is determined from their SEC to be 4.97 eV and 5.08 eV respectively, indicating a deeper shift of 0.11 eV in Fermi energy in the case of 15 s-UVO sample. The comparison of the UPS spectra in the low energy region (Fig. S2b) shows E_f moves closer to valence band edge (E_v) from 0.38 eV to 0.30 eV for the 15s-UVO PbS-EDT film. Further, 15 s-UVO shows a higher intensity count between E_f and E_v as shown in Fig. S2b. These results imply that higher numbers of electronic states are created between E_v and E_f by UVO treatment which leads to the increase in p-type doping in the film. The energy band gap of the QD films is determined from the first excitonic peak position of their optical absorption spectrum (Fig. 1f). A blue shift of 6 nm (~0.006 eV) for 15 s-UVO film indicates mild oxidation of the QD surface may actually increase the band gap and reduce the effective size of PbS QDs by a small margin [28].

We have sought to check the effect of UVO treatment in PbS-EDT layer and their performance in QD solar cells. The device architecture for the solar cell is shown in Fig. 2a. n-type PbS QD layer is prepared from the solution based ligand exchange approach using ligand solution of PbI₂ and ammonium acetate (AA) as developed

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