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| Description  |                                                                                                                                                                                                                                                                                                                                      |



# Effect of diamine treatment on the conversion efficiency of PbSe colloidal quantum dot solar cells

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## **ABSTRACT**

Polymer-free photovoltaic devices were fabricated via a solution process using PbSe colloidal quantum dots (QDs) and an organic semiconductor (tetrabenzoporphyrin, BP) that can be prepared *in situ* from a soluble precursor. The device structure was ITO/PEDOT/BP:QD/QD/Al, where BP:QD and QD layers correspond to a bulk heterojunction and a buffer layer, respectively. The buffer layer was treated with ethylenediamine (EDA) to crosslink the QDs. As a result, the energy conversion efficiency of the EDA-treated device was superior to that of an untreated device, mainly due to an increase in the short-circuit current density.

**KEYWORDS:** A. Quantum dot; A. Nanoparticle; B. Crosslink; C. Solar cell

**PACS:** 72.40.+w, 73.63.Kv, 81.07.Pr, 84.60.Jt

## 1. Introduction

Quantum dot solar cells (QDSCs) are good candidates among various organic solar cells to improve the energy conversion efficiency [1-5]. Although wide-gap semiconductor (e.g. CdSe and InP) quantum dots (QDs) have been used as acceptor materials in QDSCs, they exhibit very little absorption at infrared (IR) wavelengths. Type IV-VI semiconductors, such as PbS, PbSe and PbTe, are narrow-gap semiconductors and, as QDs in solar cells, are expected to improve the coverage of the solar spectrum. In addition, a PbSe QDSC may attain a maximum energy conversion efficiency of up to 60 % due to carrier multiplication [6]. Based on these expectations, several groups have proposed QDSCs consisting of PbSe QDs and conjugated polymers [3-5]. Recently, we reported a solution-processed polymer-free photovoltaic devices consisting of PbSe colloidal QDs and tetrabenzoporphyrins that has higher carrier drift mobility and higher durability compared with polymeric semiconductors [7]. In that study, flat heterojunction (FHJ) and bulk heterojunction (BHJ) structures were fabricated and the current-voltage characteristics of the devices under near-IR illumination were studied. Consequently, the energy conversion efficiency of the BHJ device was found to be much higher than that of the FHJ device. However, the photovoltaic performance of the BHJ device (ITO/PEDOT/BP:QD/Al) was still low ( $1.8 \times 10^{-3}$  %). The low conversion efficiency was thought to be due to the poor electrical contact between the QDs and BP (or between QDs) because of long-chain ligands (oleic acid) which are present on the surface of the QDs, and the low rectifying properties of the cell due to the direct contact between the BP and Al cathode caused by the roughened surface of the active layer.

In this Letter, we exchanged the oleic acid surface ligands for butylamine ligands to improve the electrical contact between the QDs and BP, and introduced a buffer layer consisting of PbSe QDs onto the composite layer (BP:QD) to avoid the direct contact between BP and Al cathode. In addition, the QD buffer layer was treated with ethylenediamine to crosslink the PbSe QDs and increase the conductivity of the buffer layer.

## 2. Experiments

### ***Synthesis of PbSe QDs.***

PbSe QDs were synthesized according to a previously reported method [7]. Briefly, 4.0 mmol of lead(II) oxide (purity 99.999%, Aldrich), 10.0 mmol of oleic acid (90%, Aldrich), and 12.3 g of 1-octadecene (90%, Aldrich) were placed in a three-necked flask and the temperature raised to 180 °C under argon. 25.24 g of trioctylphosphine (TOP) solution containing Se (5 wt%) and diphenylphosphine (DPP, 0.55 mmol) was then rapidly injected into the flask. After the injection of the DPP/Se/TOP solution, the reaction temperature was maintained at 150 °C and PbSe QDs were grown for 1 min. After the reaction, PbSe QDs were separated from the matrix by centrifugation. Then, the surface ligands of QDs were immediately exchanged from oleic acid (OA) to butylamine (BA). The IR spectrum of BA-capped QDs shows a clear peak in the 3250–3400  $\text{cm}^{-1}$  region which corresponds to the N–H stretching vibration of the amino group, indicating that the ligands were exchanged (data not shown). Figs. 1(a) and 1(b) show the transmission electron microscopy (TEM) images of the OA-capped and BA-capped PbSe QDs, respectively. The mean diameter and standard deviation of the size distribution were 5.2 nm and 8%, respectively for both types. The mean surface-to-surface interparticle distances between QDs were 3.8 nm for the OA-capped QDs and 1.4 nm for the BA-capped QDs. Fig. 1(d) shows the absorption spectra of PbSe QDs and BP. The first exciton absorption peak was found at 1550 nm.

### ***Device fabrication.***

Indium tin oxide (ITO) coated glasses were used as the bottom anodes. The ITO anodes were washed sequentially with Extran (Nacalai Tesque), pure water, acetone, and isopropanol. The ITO anodes were then dried in a vacuum for 30 min at 120 °C. A hole injection layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (100-nm-thick) was coated on the ITO anodes, and baked at 150 °C for 30 min under nitrogen. After baking the PEDOT:PSS layer, a chloroform solution of the precursor for tetrabenzoporphyrins, 1,4:8,11:15,18:22,25-Tetraethano-29H,31H-tetrabenzo[b,g,l,q]porphine (CP), and BA-capped QDs (40:60, vol:vol) was spin-coated onto the PEDOT:PSS layer. It was then annealed at 200 °C for 20 min under nitrogen to transform the CP

into BP. The thickness of the composite layer was ca. 100 nm. Subsequently, a chloroform dispersion of BA-capped QDs was spin-cast onto the composite layer. The thickness of the QD buffer layer was ca. 100 nm. To make the separation distance between QDs shorter, the buffer layer was treated with a 60 mg/mL acetonitrile solution of ethylenediamine (EDA) for 30 min under nitrogen to crosslink the QDs. Fig. 1(c) shows the TEM image of the EDA-linked PbSe QDs. The mean surface-to-surface interparticle distance between QDs was ca. 0.5 nm. Note that the samples for the TEM observations were prepared separately. After the treatment, the device was dried in vacuum. Finally, Al was deposited on the buffer layer. The effective area of the devices was 0.04 cm<sup>2</sup>. In Fig. 2, the device structure and the energy band diagram of the constituent materials are shown. The energy level of the HOMO of BP and the 1S<sub>h</sub> level of the QDs were measured using a photoelectron spectrometer (Riken Keiki, AC-2). The energy level of the LUMO of BP and the 1S<sub>e</sub> level of the QDs were estimated from the Q band peaks and the first exciton absorption, respectively.

### 3. Results and discussion

The current density ( $J$ ) vs voltage ( $V$ ) characteristics of the devices in darkness and under illumination were measured at room temperature under nitrogen with a Keithley 2612 source meter. To confirm the results were reproducible, the  $J$ - $V$  characteristics for two different samples, fabricated under the same conditions, were measured. Fig. 3(a) shows the  $J$ - $V$  curve for the device without EDA treatment, i.e., the buffer layer consists of BA-capped QDs (ITO/PEDOT/BP:QD/BA-capped QD/Al), under 100 mW·cm<sup>-2</sup> illumination at 800 nm. The short-circuit current density ( $J_{SC}$ ) was 13.1–15.1 μA·cm<sup>-2</sup>, the open-circuit voltage ( $V_{OC}$ ) was 0.57–0.59 V, the fill factor (FF) was 0.22, and the energy conversion efficiency ( $\eta$ ) was 1.6–2.0×10<sup>-3</sup> %. Fig. 3(b) shows the  $J$ - $V$  curve for the device with EDA treatment (ITO/PEDOT/BP:QD/EDA-linked QD/Al). For this EDA-treated device,  $J_{SC} = 22.5$ – $25.8$  μA·cm<sup>-2</sup>,  $V_{OC} = 0.63$ – $0.65$  V, FF = 0.21–0.22, and  $\eta = 3.1$ – $3.5$ ×10<sup>-3</sup> %. Hence the energy conversion efficiency for the EDA-treated device was approximately 2 times more than the untreated device.

It has been reported that the conductivity of QD films can be increased by replacing the surface ligands of the QDs with shorter, bifunctional ligands such as diamines and dithiols. Guyot-Sionnest *et al.* reported that the conductivity of a CdSe QD film was improved by replacing the TOP/TOPO capping molecules with a 1,4-phenylenediamine linker [8]. On the other hand, the conductance of a PbSe nanocrystalline solid increased by ca. 10 orders of magnitude after treatment with a hydrazine linker [9,10]. It has also been reported that an ethanedithiol treatment significantly increased the carrier mobility in field-effect transistors consisting of PbS [11] and PbSe [12] QD films. As mentioned above,  $J_{SC}$  of the EDA-treated device is 170% higher than that of the untreated device. On the other hand,  $V_{OC}$  of the EDA-treated device is only 110% higher than that of the untreated device. These results indicate that the EDA-treatment of the buffer layer increases the quantum efficiency, while it does not influence significantly the built-in potential. Hence, the improvement in  $J_{SC}$  observed in the EDA-treated device is likely due to an increase in the conductivity of the buffer layer from the decrease in the probability of carrier recombination and/or trapping. Alternatively, the change in  $J_{SC}$  could be due to an improvement of the contact between the buffer layer and the Al electrode (or between the composite layer and the buffer layer), or be due to an improvement of the homogeneity of the active region.

In conclusion, the EDA treatment of PbSe QD buffer layer improves the energy conversion efficiency of the polymer-free QDSCs fabricated using PbSe QDs and BP. This is because the EDA-treatment decreases the surface-to-surface interparticle distance and improves  $J_{SC}$  of the device. Although the detail mechanism of the improvement in  $J_{SC}$  is not clear at this moment, the following reasons would be plausible: 1) an increase in the conductivity of the buffer layer, 2) an improvement of the contact between the layers and/or 3) an improvement of the homogeneity of the active region.

## **Acknowledgement**

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## Figure captions

**Fig. 1.** TEM images of PbSe QDs capped with (a) oleic acid (OA), (b) butylamine (BA), and (c) treated with ethylenediamine (EDA). (d) Absorption spectra of PbSe QDs dispersed in tetrachloroethylene and BP deposited on a glass substrate.

**Fig. 2.** (a) Schematic illustration of the device (ITO/PEDOT/BP:QD/QD/Al) and (b) energy band diagram of the constituent materials.

**Fig. 3.** Current density ( $J$ ) vs voltage ( $V$ ) curves measured under  $100 \text{ mW}\cdot\text{cm}^{-2}$  illumination at 800 nm for (a) the untreated (ITO/PEDOT/BP:QD/BA-capped QD/Al) and (b) EDA-treated (ITO/PEDOT/BP:QD/EDA-linked QD/Al) devices. To confirm the reproducibility, the  $J$ - $V$  curves were measured from two different samples fabricated under the same conditions.

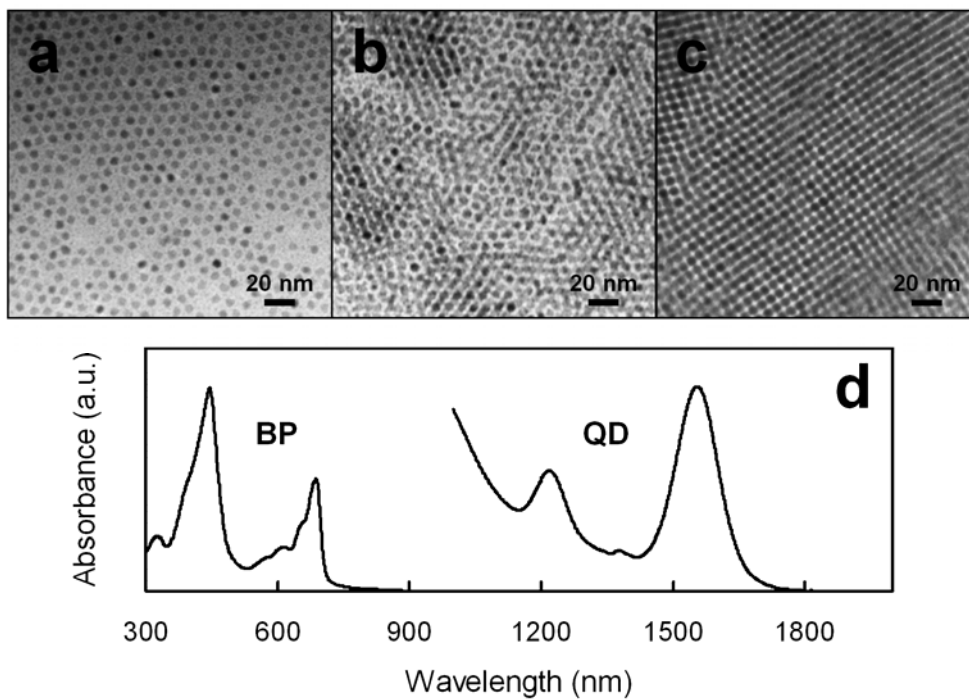


Fig. 1

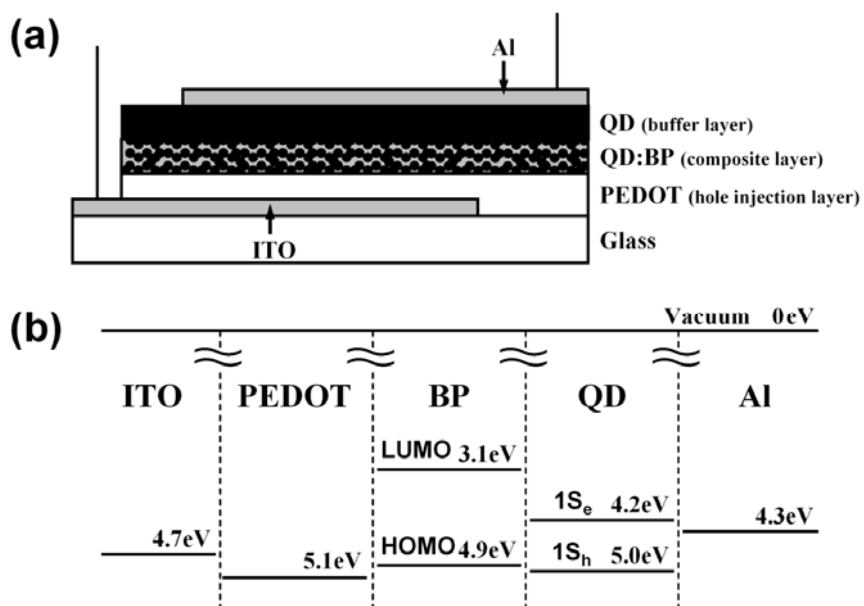


Fig. 2

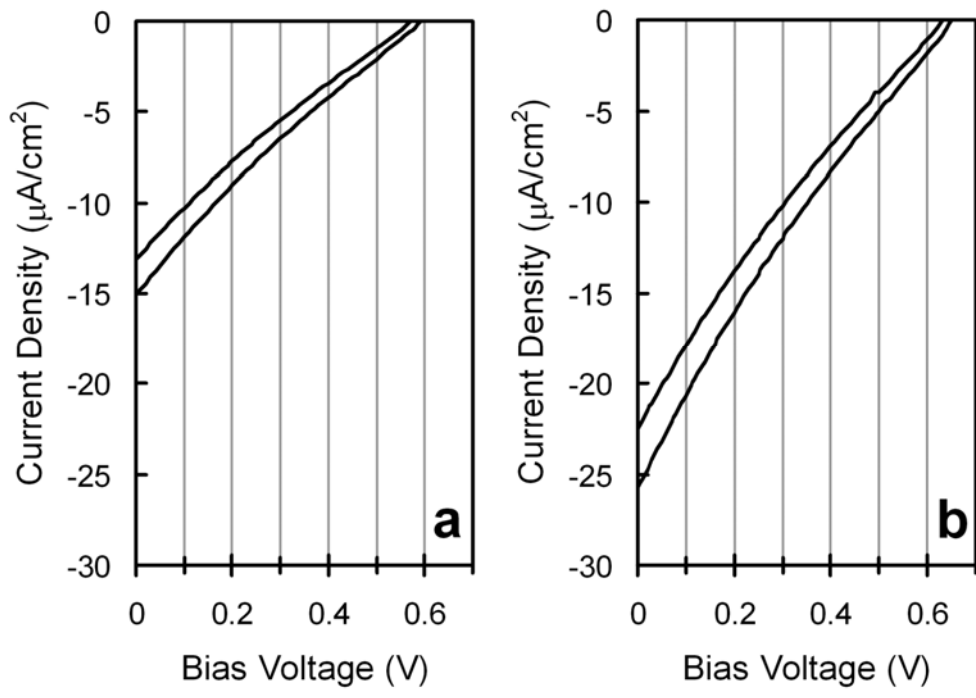


Fig. 3