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Author(s)	Kikuchi, Einosuke; Kitada, Seiki; Ohno, Akira; Aramaki, Shinji; Maenosono, Shinya
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Description	

## Solution-processed polymer-free photovoltaic devices consisting of PbSe colloidal quantum dots and tetrabenzoporphyrins

Einosuke Kikuchi,<sup>1</sup> Seiki Kitada,<sup>1</sup> Akira Ohno,<sup>2</sup> Shinji Aramaki,<sup>2</sup> and Shinya Maenosono<sup>1,a)</sup>

<sup>1</sup>Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

<sup>2</sup>Mitsubishi Chemical Group Science and Technology Research Center, Inc., 1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502, Japan

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Polymer-free photovoltaic devices were fabricated via a solution process using PbSe colloidal quantum dots and an organic semiconductor, tetrabenzoporphyrin, that can be derived from a soluble precursor. Flat heterojunction (FHJ) and bulk heterojunction (BHJ) devices were fabricated and the current-voltage characteristics of the devices were measured. Consequently, we observed photovoltaic conversion for both devices and found the energy conversion efficiency of the BHJ device ( $1.8 \times 10^{-3}\%$ ) is 40 times that of the FHJ device under  $100 \text{ mW cm}^{-2}$  illumination at 800 nm. © 2008 American Institute of Physics. [DOI: 10.1063/1.2920166]

Organic photovoltaic cells (OPVCs) are expected to be next-generation solar energy conversion devices because they have the potential to be flexible and low cost. Many device structures have been proposed, such as Schottky junction,<sup>1,2</sup> flat (bilayer) heterojunction<sup>3,4</sup> (FHJ), and bulk heterojunction<sup>5-9</sup> (BHJ) structures. Above all, the BHJ devices are thought to be promising for increasing the energy conversion efficiency ( $\eta$ ) of OPVCs. So far, BHJ devices have been fabricated by blending fullerene derivatives<sup>5,6</sup> or CdSe colloidal quantum dots<sup>7,8</sup> (QDs) into conjugated polymers, or by utilizing the phase separation of donor and acceptor conjugated polymers.<sup>9</sup> However,  $\eta$  and durability remain insufficient for practical use.

Conjugated polymers can be dissolved in various solvents and, thus, are useful in fabricating BHJ devices via solution processes. However, the conjugated polymers have low carrier drift mobility ( $\mu$ ) and they are usually easily degraded. On the other hand, low-molecular-weight organic semiconductors (low- $M_w$  OSs), e.g., pentacene, rubrene, and porphyrin, generally have higher  $\mu$  ( $>10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and higher durability compared with polymeric semiconductors because of their high crystallinity. However, these low- $M_w$  OSs are usually insoluble and not suited for solution processes with a few exceptions. One example is tetrabenzoporphyrin (BP), which is derived from a precursor with four bicyclo structures (CP) by elimination of four ethylene molecules.<sup>10-12</sup>

Fullerene derivatives, such as [6,6]-phenyl  $C_{61}$ -butyric acid methyl ester, and wide-gap semiconductor (e.g., CdSe and InP) QDs have very little absorption at infrared (IR) wavelengths. Type IV-VI semiconductors, such as PbS, PbSe and PbTe, are known as narrow-gap semiconductors and, thus, IV-VI QDs are expected to be good candidates as acceptor materials in BHJ solar cells to improve the coverage of the solar spectrum. In addition, the PbSe QD solar cell (QDSC) is thought to attain maximum  $\eta$  up to 60% due to carrier multiplication.<sup>13</sup> Based on these expectations, several groups have proposed QDSCs consisting of PbSe QDs and conjugated polymers.<sup>14-16</sup>

In this letter, we demonstrate the idea that the high  $\mu$  of BP ( $\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) leads to a high  $\eta$  due to a decrease in carrier recombination probability in the fabrication of polymer-free QDSCs using PbSe QDs and BP via a solution process. FHJ and BHJ structures were fabricated and the current-voltage characteristics of the devices measured. Consequently, we observed photovoltaic conversion for both devices and found that  $\eta$  of the BHJ device is 40 times higher than that of the FHJ device under  $100 \text{ mW cm}^{-2}$  illumination at 800 nm.

PbSe QDs were synthesized by a known colloidal chemical method<sup>17</sup> with some modifications. Briefly, 4.0 mmol of lead(II) oxide, 10.0 mmol of oleic acid, and 12.3 g of 1-octadecene were placed in a three-necked flask and the temperature was raised to 180 °C under Ar. 25.24 g of trioctyl phosphine (TOP) solution with Se (5 wt %) and diphenylphosphine (DPP) (0.6 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. The absorption spectrum of PbSe QDs is shown in Fig. 1(a). The first exciton absorption peak was found at 1302 nm. The inset in Fig. 1(a) shows a transmission electron microscopy (TEM) image of as-synthesized PbSe QDs. The mean diameter and standard deviation of the size distribution were 4.7 nm and 8%, respectively. Figure 1(b) shows an x-ray diffraction (XRD) pattern of PbSe QDs indicating that the crystal structure of QDs was the rock-salt phase. Energy-dispersive x-ray analysis confirmed the average composition of QDs was  $\text{Pb}_{49}\text{Se}_{51}$ . The CP material used in this study was synthesized according to the previously reported method.<sup>10,11</sup> The absorption spectrum of BP is also shown in Fig. 1(a). The Soret and  $Q$  bands were found at 446 and 687 nm, respectively. Indium tin oxide (ITO) coated glasses were used as the bottom anodes. The ITO anodes were sequentially washed 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 buffer 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  $\text{N}_2$ .

<sup>a)</sup>Electronic mail: shinya@jaist.ac.jp.

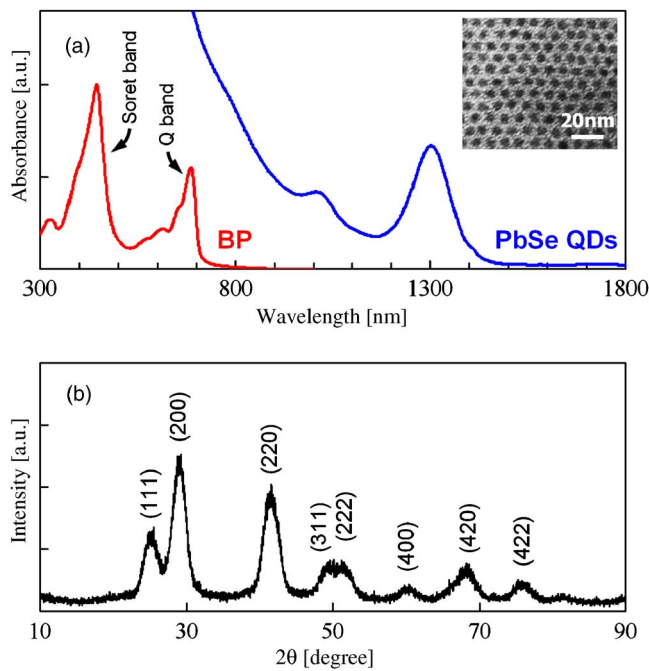


FIG. 1. (Color online) (a) Absorption spectra of PbSe QDs dispersed in tetrachloroethylene (blue line) and BP deposited on a glass substrate (red line). The inset shows a TEM image of PbSe QDs. (b) XRD pattern of PbSe QDs obtained in the reflection geometry at room temperature with Cu  $K\alpha$  radiation.

The FHJ structure (BP/QD) [Fig. 2(a)] was fabricated as follows. First, a chloroform solution of CP was spin coated on the PEDOT:PSS layer. It was then annealed at 200 °C for 20 min under  $N_2$  to transform CP to BP (50 nm thick). Secondly, a chloroform dispersion of PbSe QDs was spin cast onto the BP film (50 nm thick). Finally, an Al cathode (100 nm thick) was fabricated on the QD layer via vacuum deposition. The BHJ structure (BP:QD) [Fig. 2(b)] was fabricated as follows. A chloroform solution of CP and QDs (40:60, vol:vol) was spin coated on the PEDOT:PSS layer. It was then annealed at 200 °C for 20 min under  $N_2$ . Note that the first exciton absorption peak of QDs was slightly blue-shifted during the annealing possibly due to the surface ox-

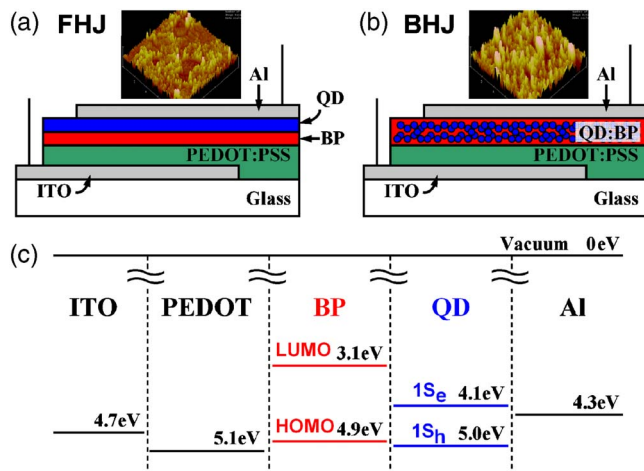


FIG. 2. (Color online) Schematic illustrations of (a) the FHJ device (ITO/PEDOT:PSS/BP/QD/Al) and (b) the BHJ device (ITO/PEDOT:PSS/QD:BP/Al). The insets in (a) and (b) show surface morphologies ( $10 \times 10 \mu\text{m}^2$ ) of pure BP and BP:QD composite layers, respectively, taken by AFM. (c) Energy band diagram of the constituent materials.

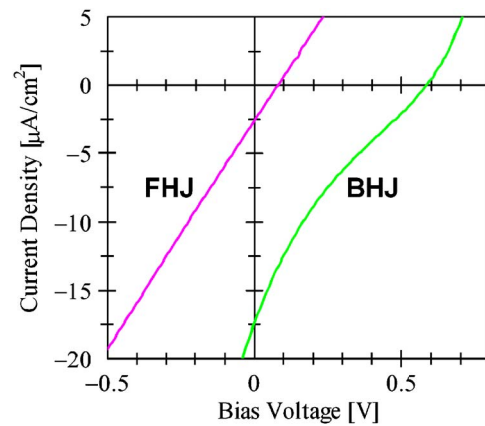


FIG. 3. (Color online) Current density ( $J$ ) vs voltage ( $V$ ) curves measured under  $100 \text{ mW cm}^{-2}$  illumination at 800 nm for the FHJ and BHJ devices.

ation. The thickness of the composite layer was  $\sim 50$  nm. Al was then deposited on the composite layer. The effective area of the devices was  $0.04 \text{ cm}^2$ . In Fig. 2(c), the energy band diagram of the constituent materials is shown. The highest occupied molecular orbital (HOMO) level of BP and the  $1S_h$  level of the QDs were measured using a photoelectron spectrometer (Riken Keiki, AC-2). The lowest unoccupied molecular orbital (LUMO) level of BP and the  $1S_e$  level of the QDs were estimated from peaks of the  $Q$  band and the first exciton absorption, respectively. The insets in Figs. 2(a) and 2(b) show the atomic force microscopy (AFM) images of the surfaces of pure BP and BP:QD composite layers, respectively. The surface of the pure BP film was slightly rough reflecting the existence of grains ( $R_a=7$  nm). Thus, the QD and BP layers are considered able to partly interpenetrate each other in the FHJ device. The surface roughness of the composite layer ( $R_a=11$  nm) significantly increased in comparison with that of the pure BP film. An increase in the surface roughness of the composite layer was rather reproducible. These results suggest phase separation between BP and QDs took place in the composite layer during annealing in the BHJ device because the chemical affinity between the porphyrin ring and fatty acid is known to be not so high.

The current density ( $J$ ) versus voltage ( $V$ ) characteristics of the devices in darkness and under illumination were measured at room temperature under  $N_2$  with a Keithley 2612 source meter. Figure 3 shows the  $J$ - $V$  curves for the FHJ and BHJ devices under  $100 \text{ mW cm}^{-2}$  illumination at 800 nm. Note that the device fabricated without QDs did not show any photovoltaic response under illumination. In the case of the FHJ device, the short-circuit current density ( $J_{SC}$ ), open-circuit voltage ( $V_{OC}$ ), fill factor (FF), and  $\eta$  are  $2.9 \mu\text{A cm}^{-2}$ , 0.08 V, 0.22, and  $5 \times 10^{-3}\%$ , respectively. In the case of the BHJ device,  $J_{SC}$ ,  $V_{OC}$ , FF, and  $\eta$  are  $17.4 \mu\text{A cm}^{-2}$ , 0.58 V, 0.18, and  $1.8 \times 10^{-3}\%$ , respectively. The value of  $\eta$  for the BHJ device is approximately 40 times that for the FHJ device. Under AM1.5G illumination with an intensity of  $100 \text{ mW cm}^{-2}$ , no significant change in the  $J$ - $V$  curve for the BHJ device was observed, suggesting that carriers generated in BP hardly contribute to photovoltaic current, while QDs generate carriers that absorb light of wavelengths shorter than 1300 nm.

The value of  $\eta$  for our BHJ device is two orders of magnitude smaller than that for the QDSC using a blend of PbSe QDs and poly(3-hexylthiophene) (P3HT) ( $\eta=0.14\%$

under AM1.5G illumination with an intensity of  $100 \text{ mW cm}^{-2}$ ) (Ref. 14) because  $J_{\text{SC}}$  for our device was somewhat lower than that for the PbSe QDs/P3HT device ( $J_{\text{SC}}=1.08 \text{ mA cm}^{-2}$ ). However,  $\eta$  for our BHJ device is an order of magnitude larger than that for the PbSe QDs/P3HT device doped with pentacene ( $\eta=1.8 \times 10^{-4}\%$  under AM1.5G illumination with an intensity of  $60 \text{ mW cm}^{-2}$ ).<sup>16</sup> This indicates that polymer-free PbSe QDs/BP devices have potential as an alternative type of QDSC. There are several conceivable explanations for the low photovoltaic performance of the PbSe QDs/BP BHJ device. (1) The small band offset between the HOMO level of BP and  $1S_h$  level of PbSe QDs hinders hole injection from QDs to BP. (2) There is poor electrical contact between QDs and BP (or between QDs) due to the existence of ligand molecules on QD surfaces and/or low affinity between QDs and BP. (3) There is low crystallinity and hence low  $\mu$  of the BP matrix due to an inhibition of crystallization by QDs. (4) The device has a low rectifying property probably due to the direct contact between BP and Al cathode caused by the roughened surface of the active layer.

In conclusion, the polymer-free QDSCs, which can operate with IR light, were fabricated using PbSe QDs and BP via a solution process. We observed photovoltaic conversion for the devices in the IR region and the energy conversion efficiency was found to be  $1.8 \times 10^{-3}\%$  under  $100 \text{ mW cm}^{-2}$  illumination at 800 nm in the case of the BHJ device, which is a much higher efficiency than that of the FHJ device. However, optimally balancing the crystallization of BP and BP-QD interfacial compatibility is a problem remaining to be solved.

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