The role of cetyltrimethylammonium bromide in efficiency of organic-quantum dot hybrid solar cell

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ABSTRACT

We investigated the effects of cetyltrimethylammonium bromide (CTAB) in organic-quantum dot hybrid solar cell. Hybrid active layer was composed of poly (3-hexylthiophene) (P3HT) and PbS colloidal quantum dot (CQD). By employing hybrid active layer, which absorbed the light in wide range, expected power conversion efficiency of hybrid solar cell will be increased. However, PbS CQD has relatively low performance compared with P3HT. We used CTAB as inorganic ligand of PbS CQD surface. As a result, we observed short circuit current density of hybrid solar cell and open circuit voltage were increased.

Keywords: PbS colloidal quantum dot, hybrid solar cell, inorganic passivation, cetyltrimethylammonium bromide

1 INTRODUCTION

Near-infrared (NIR) emitting colloidal quantum dot (CQD) has great attentions due to quantum confinement which rearranges density of states near the band edges. It can be used in wide range of photovoltaics [1], photodetector [2], biological applicaions [3], and etc. In NIR emitting CQD, one of the most suitable materials for those applications is PbS CQD, because bulk PbS has a large Bohr radius (20 nm) and band gap is 0.41 eV at 300 K [4]. When particle size is reduced (~5.2 nm), the band gap of PbS CQD becomes 1.1 eV [4]. Especially, PbS CQD has a highly efficient multiple exciton generation. Many researchers expect that PbS CQD solar cell has higher efficiency than Si based solar cell through this phenomenon. Therefore, these properties can give us the ideal concept of highly efficient and transparent photovoltaics. However, the main limitation of applications using CQD is an inefficient charge carrier transport caused by organic ligands. The organic ligands affect size and shape of CQD. Also, they prevent densely packed arrays in PbS CQD films due to their long chain. These directly influences electrical and optical properties. Thus, the choice of ligand is important. For this reason, many researchers have been trying to finding optimized material as a ligand of CQD. The research trends were focused on reducing length of ligand [5]. However, researches on inorganic passivation have recently been reported [6], because of its excellent electrical properties.

Here, we introduce device architecture that allows to improve the absorption of solar light. Our bilayer-type hybrid solar cell has two active layers: poly (3-hexylthiophene) (P3HT) and PbS CQD. Also, we conducted a solution-phase ligand exchange from organic material to inorganic material.The cetyltrimethylammonium bromide (CTAB) methanol which is cationic ligand was used for a ligand exchaing from Br atom to oleic acid (OA) attached on CQD surface in our experiment. This procedure clearly showed a power conversion efficiency enhancement in our hybrid solar cell due to improved conductivity.

2 EXPERIMENTAL SECTIOIN

2.1 Materials

Lead chloride ($PbCl_2$, 98%), elemental sulfur, zinc acetate ($Zn(Ac)_2{\cdot}2H_2O$), oleylamine (OLA, technical grade 70%), OA (technical grade 90%), 2-methoxyethanol (2ME), CTAB (99%), chlorobenzene, and toluene were obtained from Sigma-Aldrich. Ethanol and methanol were purchased from Duksan chemical. P3HT and (6.6) phenyl-C_{61}-butyric acid methyl ester (PCBM) were purchased from Rieke Metals. All chemicals were used as received with no further purification.

2.2 Synthesis and ligand exchange

Our synthesis was based on the Cademartiri synthesis [7]. We made slurry of excess $PbCl_2$ in OLA (1:2 molar ratio) at 100 °C under N_2 flow. The temperature was increased to 120 °C for 30 min. At the same time, sulfur dissolved in OLA (0.1:0.2 molar ratio) at 80° C for 30 min. We injected sulfur-OLA solution into $PbCl_2$-OLA solution. The growth temperature was 100 °C for 30 min. We extracted the solution, and quenched by pouring the product in cold toluene. For ligand exchange OLA to OA, we added OA into the PbS CQD dispersed in toluene (20:3 volume ratio) at room temperature. The solution was dispersed by ultrasonication. Our solution was conducted with following washing steps. The solution was centrifuged for precipitating excess $PbCl_2$ precursor. Ethanol was added to supernatant for precipitate of quantum dot. The solution was centrifuged. The supernatant was discarded, and the precipitate was redispersed in toluene and repeating previous washing steps. The prepared PbS CQD has OA

ligand and then CTAB methanol solution was used for exchanging OA to Br atom in PbS CQD films through layer-by-layer spin-coating. The chemical structures of all the ligands used in this experiment are showed in Figure 1.

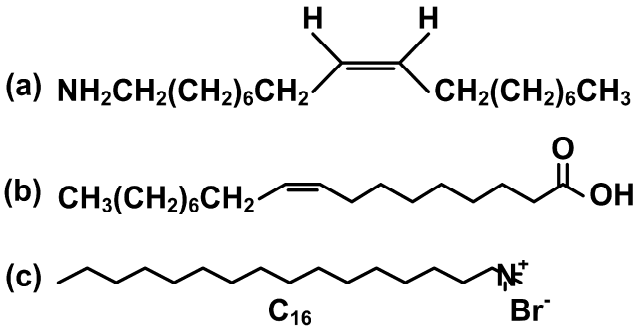

Figure 1: Chemical structures of (a) OLA, (b) OA, and (c) CTAB.

2.3 Device fabrication

We prepared two types of hybrid solar cell for confirming effects of CTAB: CTAB treated cell which has PbS CQD films with Br atomic ligand, and OA treated cell which has PbS CQD films with oleate ligand. CTAB treated PbS CQD films were fabricated in an air ambient using layer-by-layer spin-coating. Three-step of spin-coating procedure was considered one cycle: 1) 50 mg/ml PbS CQD solution was spin coated; 2) 0.5 ml CTAB methanol solution was dropped onto PbS CQD films; 3) the films were washed by methanol. We conducted experiment at room temperature, in air, and without annealing during ligand exchange. We repeated this cycle for 7 times. OA treated PbS CQD films, on the other hands, were made by spin coating PbS CQD solution 7 times without other steps. Both CTAB treated cell and OA treated cell are the same structure. Solution-processed ZnO thin films were spin coated onto ITO substrate and annealed at 500 °C for 4 hours. Then, our two types of PbS CQD films were deposited without annealing. P3HT and PCBM were spin coated onto PbS CQD films in argon-filled glove box and annealed at 120 °C for 10 min. 3 nm of MoO_3 and 100 nm of Au were deposited onto active layer using thermal evaporation.

3 RESULTS AND DISCUSSION

3.1 Synthesis and characterization of PbS QD

It is necessary to determine the size and shape of PbS CQD in order to understant their properties such as bandgap size, extinction coefficient, and etc. The actual CQD size determination was performed using high-resolution transmission electron microscopy (HRTEM). We analyzed about 300 particles for each specimen. From the analysis, their average size was 6.39 nm, and standard deviation was 0.68 nm. It means our PbS CQD system has low polydispersity. Figure 2 shows the polydispersity and spherical shape.

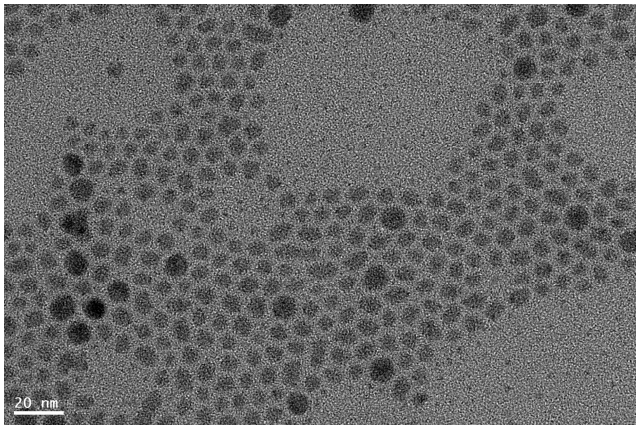

Figure 2: HRTEM image of PbS CQD.

X-ray diffraction (XRD) of PbS CQD, shown in Figure 3, indicated the cubic rock-salt (Fm3m) structure of PbS. Also, we confirmed particle size of PbS CQD was 6.44 nm through Scherrer analysis on the (111) peak [8]. It matched with the size from HRTEM image.

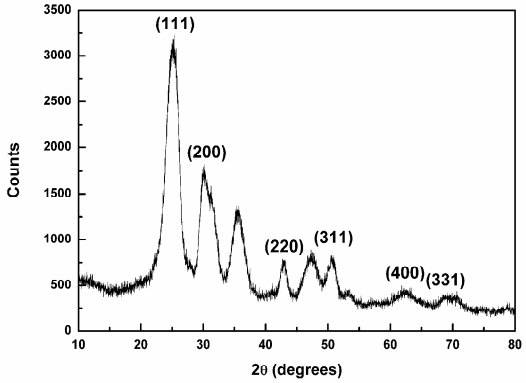

Figure 3: XRD spectra of PbS CQD.

3.2 Ligand identification

In this research, we conducted a ligand exchange from OLA to Br atom. OLA detached from PbS CQD surface during first stage of the ligand exchange. To confirm first ligand exchange, we measured Fourier transform-infrared (FT-IR). In order to obtain the FT-IR spectra, we used ZnSe attenuated total reflectance cell and deuterated triglycine sulfate detector. The resolution was 4 cm^{-1} and 128 scans were taken. As seen in figure 4, the ligand exchange was successful. The peak at 3400 cm^{-1} due to the ν(N-H) stretching mode was absent from spectrum after ligand exchange [9]. It means there isn't the NH_2 group which represents OLA. However, this is indirectly measurement method. So we have to confirm whether OA is free ligand

or not. In order to understand the bonding of OA to particles, we observed the COOH group. The ν(C=O) mode at 1709 cm^{-1} and the ν(O-H) stretch of the dimerized acid at 2670 cm^{-1} are reduced. According to the result, we assert that OA in PbS CQDs solids is not free ligand and bonded with Pb atoms on quantum dot surface. From this result, we can conclude that our PbS CQD with OA has better conductivity compared to PbS CQD with OLA. But PbS CQD still has a large ligand compared to itselves: the length of OA is about 3 nm and the size of PbS CQD is 6 nm. Therefore, we exchanged ligand from OA to Br atom for the efficient charge carrier path. X-ray photoelectron spectroscopy (XPS) analysis was used for confirming states of Br atom in PbS CQD films. Figure 5 shows there is only one chemical state of Br attached Pb atom, because Br $3d^{5/2}$ at 68.5 eV is that of the bulk $PbBr_2$ [10].

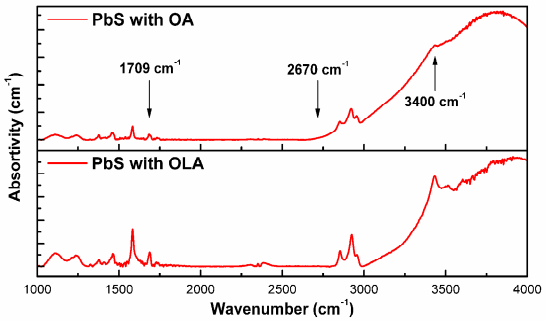

Figure 4: FTIR spectra of PbS CQD capped with OA and OLA.

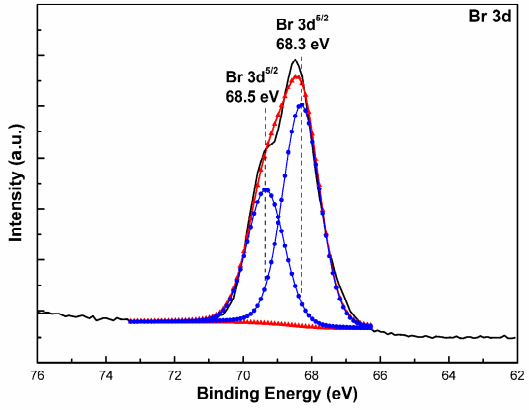

Figure 5: XPS spectra of CTAB treated PbS CQD films.

3.3 Device performance

To evaluate the role of CTAB in solar cell, we fabricated two samples using PbS CQD with OA and Br atomic ligands. Figure 6 shows the current density-voltage characteristics of our best cell under 100 mW/cm^2 Air Mass 1.5 Global irradiation. We employed an active area of 2 mm^2. The best device in CTAB treated cell exhibited an open circuit voltage, V_{OC} = 0.529 V, short circuit current density, J_{SC} = 6.54 mA/cm^2, fill factor, FF = 37.7 %, and power conversion efficiency, PCE = 1.30 %. On the other hands, the maximum PCE of OA treated cell was 0.41 %. The decrease in solar cell efficiency could be due to organic ligand. They act as barrier in charge carrier transport. Also, the voids in PbS CQD films from OA which have relatively large volome can be trap sites in charge carrier transport. Therefore, the high quality PbS CQD films in CTAB treated cell make it possible to increase efficiency in hybrid solar cell.

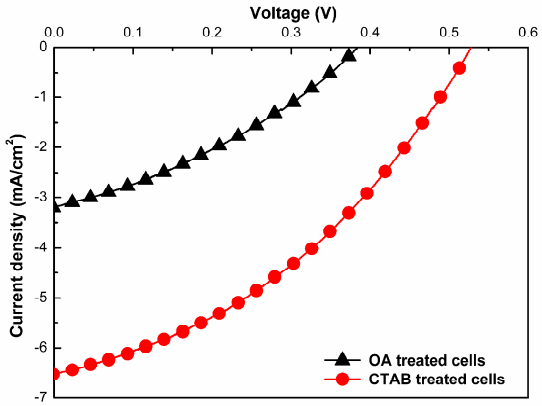

Figure 6: J-V characteristics of OA and CTAB treated cell.

4 SUMMARY

The role of CTAB in improved efficiency of organic-quantum dot hybrid solar cell was inverstigated by comparing oleate ligand with Br atomic ligand. The efficiency of CTAB treated cell was improved through increased both J_{SC} and V_{OC}. As a result, we found the Br atomic ligand had enabled charge carriers to transport quickly between PbS CQDs.

ACKNOWLEDGMENT

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