Inorganic-ligand exchanging time effect in PbS quantum dot solar cell
Byung-Sung Kim, John Hong, Bo Hou, Yuljae Cho, Jung Inn Sohn, SeungNam Cha, and Jong Min Kim

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Colloidal quantum dots (CQDs) are promising candidates for next-generation photovoltaics owing to their unique properties such as high absorption coefficient, tunable band gap, and multiple exciton generation effect. The solution-process also has provided high feasibility of realizing flexible and large scale photovoltaic devices with cost-effective fabrication. Despite these favorable characteristics, poor charge transport and imperfect surface status of CQDs hinder high photovoltaic performance compared to the theoretical conversion efficiency. During the synthetic process, CQDs are capped by long and bulky organic ligands which enable to control the size of CQDs by preventing over-size aggregation and enhancing chemical stability. However, the insulating properties of long hydrocarbon ligands limited photoexcited carrier transport, eventually resulting in low power conversion efficiency (PCE). Control of the ligand exchange process which efficiently substitutes the surface from long ligands to short molecules is necessary for CQD-based device applications. The ligand exchange effect of lead sulfide (PbS) nanocrystal films. With optimal processing time, volume shrinkage induced by residual oleic acid of the PbS colloidal quantum dot (CQD) was minimized and a crack-free film was obtained with improved flatness. Furthermore, sufficient surface passivation significantly increased the packing density by replacing from long oleic acid to a short iodide molecule. It thus improves exciton dissociation via enhanced charge carrier transport in PbS CQD films, resulting in the improved power conversion efficiency from 3.39% to 6.62%. We also found that excess iodine ions on the PbS surface rather hinder high photovoltaic performance of the CQD solar cell.© 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).
with the XPS energy spectra, the atomic ratios of lead and iodine on the surface of PbS CQD films can be evaluated with respect to the ligand exchange time. Note that the short ligand exchanging time ($T_L < 30$ s) does not provide enough surface passivation and considerable oleic acids still remain on the PbS surface. With an increasing of $T_L$, the oleic acids were almost eliminated and surface iodine concentration is quantitatively increased. (Figs. 1(c) and 1(d)).

A degree of surface passivation could affect the morphological property of the PbS CQD film. Micro- and nano-scale cracks have been frequently observed in ligand-exchanged CQD devices due to the considerable volume shrink of the films when long oleic acids were substituted by short organic and/or inorganic ligands.\textsuperscript{15–17} Furthermore, the crack formation results in severe problems such as highly inducing short circuit or leakage current in CQD-based device applications.\textsuperscript{18} Therefore, careful control of the ligand exchange process is essential for producing crack-free CQD films. The morphological changes of the PbS CQD film were shown with the different ligand exchanging times of $T_L$ (Fig. 2, Figs. S1 and S2 in supplementary material). A very rough surface with the numerous cracks was obtained at the $T_L$ of 15 s while longer ligand exchanging time leads to a crack-free surface with the improved film flatness. This result implies that the presence of the residual oleic acids observed at insufficient ligand exchanging time induces the large physical strain with the coexistent short iodide ligands in PbS CQD films. It thus leads to the non-uniform volume shrink and accelerating crack formation during the solvent evaporation.

A highly densely packed CQD film is a critical factor to determine the photovoltaic performance since the charge carrier transport is enhanced with minimizing the CQD interparticle distance.\textsuperscript{10,11} Figure 3 shows that the packing densities of the CQD film could be effectively tuned by adjusting the ligand exchanging time. Compared to OA-capped PbS CQDs, the packing densities were gradually increased with proceeding ligand exchange from OA to iodide molecules. (Figs. 3(a)–3(c)) Longer treatment makes the neighboring QDs closer, resulting in partially connection between each other. Furthermore, exciton absorption peaks were certainly

![FIG. 1. A schematic illustrating the ligand exchange process on PbS CQD films. (b) FTIR spectra and (c) binding energy of I 3d and Pb 4f in TBAI-PbS CQD films with an increasing ligand exchanging time of $T_L$. They show successful exchange of iodine on the CQD surface. (d) Variation of the atomic ratio of lead to iodine as a function of the corresponding $T_L$. The squares and solid lines of black, orange, blue, and red are $T_L = 15, 30, 60,$ and 90 s, respectively. The dotted lines in Fig. 1(b) are pristine PbS CQD film capping with oleic acid.](#)

![FIG. 2. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of surface morphologies of TBAI-PbS films with increasing $T_L$: ((a) and (e)) 15 s, ((b) and (f)) 30 s, ((c) and (g)) 60 s, and ((d) and (h)) 90 s. These samples are prepared by spin coating the 3 layers of PbS onto the glass substrates. It was shown that the root mean square (RMS) roughness of PbS CQD films was gradually decreased, dependent on $T_L$.](#)
To investigate the relationship between photovoltaic performance of the PbS film with the different packing densities, we obtained photocurrent density and voltage (\(J–V\)) curves of the PbS CQD films with the different ligand exchanging times of \(T_L\) under AM 1.5G illumination (100 mW cm\(^{-2}\)). (Fig. 4(a)) The devices were prepared by 10 cycles spin coating of TBAI-PbS CQD films on ZnO/ITO substrates (Fig. S3 in supplementary material) and the photovoltaic performance of the devices is summarized in Figs. 4(c) and 4(d) (also see Fig. S4 in supplementary material). Incomplete passivation on the PbS surface caused by short ligand exchanging time of \(T_L\) hinders efficient charge transport in the film (Fig. 4(b)), resulting in relatively low short-circuit current (\(J_{sc}\)) and PCE with high series resistance (\(R_s\)). The device with a short \(T_L\) of 15 s gives a low PCE of 3.39% with a \(J_{sc}\) of 13.75 mA/cm\(^2\). Moreover, in Fig. S5, \(J_{sc}\) from the external quantum efficiency (EQE) measurement also shows the same trend which correlates with the \(J_{sc}\) enhancement of the \(J–V\) measurement by the different ligand exchanging times. With an increase of the ligand exchanging time, the packing densities of PbS QDs as well as surface coverage of the iodide molecule were significantly increased. (Figs. 1 and 3) It thus facilities exciton dissociation via enhanced charge transfer in PbS films, leading to substantial improvement of 77.58% and 74.98% in PCE, and \(J_{sc}\) at \(T_L\) of 60 s, respectively (Fig. 4(c) and Table S1 in supplementary material). The values of \(R_s\) were also decreased from 10.14 \(\Omega\) to 3.51 \(\Omega\), dependent on the \(T_L\). Interestingly, we found that the photovoltaic performance was declined after longer \(T_L\) of 90 s in spite of the high surface coverage of iodide ligands on the PbS CQDs. It can be assumed that excess iodide molecules which are not bound to Pb cations may act as the insulating barrier between PbS CQDs. These results clearly indicate that the controlling ligand exchange on the PbS CQD film should be highly required to manipulate the photovoltaic performance.
We have demonstrated time-dependent inorganic ligand exchanging effect in PbS CQD films. Controlled surface passivation increases the packing density with a crack-free PbS surface by minimizing residual oleic acid. It also enables to facilitate charge transport and significantly improve PbS solar cell efficiency from 3.39% to 6.62%. Ligand exchange over a longer $T_L$ of a critical value further decreases interparticle spacing but rather slightly deteriorates the photovoltaic performance by excess iodide molecules acting as a charge transport barrier on the PbS surface. These results distinctively prove that appropriate ligand passivation is highly required for high performance of the CQD solar cell.

See supplementary material for detailed growth procedures, supporting characterization, and analysis of nanomaterials.

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