Ionic Conduction in Ultrathin Ligand-Free Lead Sulfide Colloidal Quantum Dots

Byoung-Nam PARK*

Department of Materials Science and Engineering, Hongik University, 72-1, Sangsu-dong, Mapo-gu, Seoul 121-791, Korea

* Corresponding author: metalpbn@hongik.ac.kr

ABSTRACT
We fabricated an ultrathin ligand-free lead sulfide (PbS) colloidal quantum dot (CQD) field effect transistor (FET) and probed interfacial charge transport properties sensitized by the combination of gate electric field and ultrathin CQD layer thickness at low temperature. Large gate-modulated current hysteresis of the (NH₄)₂S-treated PbS CQD FET was significantly reduced at lower temperature. Interfacial charge transport after oleic acid ligand removal of PbS CQDs close to the gate dielectric is investigated through analysis of temperature dependent mobility and threshold voltage, hypothesizing that gate field screening by ionic conduction and thermally-activated electronic transport determine the interfacial charge transport properties.

© The Author(s) 2020. Published by ECSJ. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium provided the original work is properly cited. [DOI: 10.5796/electrochemistry.20-00026]. Uploading “PDF file created by publishers” to institutional repositories or public websites is not permitted by the copyright license agreement.

Keywords : Ionic Conduction, PbS, Ligand Treatment, Interfacial Charge Transport

1. Introduction
Colloidal quantum dots (CQDs) have attracted much interest due to their simple colloidal processing, exhibiting optoelectronic tunability resulting from size dependent quantum confinement effect.¹² CQDs have successfully been integrated into energy, display and sensing electronic devices. When CQDs were, however, incorporated into the electronic devices, low efficient phonon-assisted tunneling between neighboring CQDs has limited charge transport, degrading device efficiency due to a substantial tunneling barrier of long organic CQD capping ligands.³

To overcome the barrier, CQD capping ligands have been replaced by shorter ligands including alkylthiols, alkyl amines and mercaptocarboxylic acids, exhibiting far higher mobility in CQD transport, degrading device efficiency due to a substantial tunneling barrier of long organic CQD capping ligands.³

2. Experimental
2.1 Fabrication of field effect transistor and formation of ultrathin PbS CQD film
Bottom-contact FETs were fabricated by patterning metal contacts on the 200 nm SiO₂ substrate using a conventional photolithography process. Highly-doped Si substrate is used as a gate electrode. PbS CQDs (~3 nm) were synthesized by the hot injection method as described in our previous study.⁶ PbS films were prepared through drag-coating using a glass blade as shown in Fig. S1(a) and the morphology is investigated using atomic force microscopy (AFM) in Fig. S1(b). For ligand removal using (NH₄)₂S, an ultrathin drag-coated PbS film is dipped into an (NH₄)₂S methanol solution (0.1 M) for 30 s followed by rinsing in methanol, eliminating (NH₄)₂S residues. As a control sample, an ethanedithiol (EDT)-treated PbS CQD FET was used through ligand exchange process in which a PbS CQD FET device was dipped into an EDT acetonitrile solution for 20 s. Low temperature measurements were carried out in the temperature range between 77 and 293 K in a cryostat chamber. Optical absorption and x-ray diffraction (XRD) measurements were carried out for characterization of synthesized PbS CQDs.

2.2 Calculation of field effect transistor parameters: mobility and threshold voltage
The drain current, \( I_D \), in an FET electrical probe is determined by the FET mobility of holes (\( \mu \)) and the 2D carrier concentration, \( n = C(V_G - V_T)/q \), represented by the product of the capacitance (\( C \)) per unit area of the interface and the gate voltage (\( V_G \)) and the threshold voltage (\( V_T \)), as shown in the below equation:⁸

\[
I_D = \frac{Z}{L} \mu C(V_G - V_T) V_D
\]

where \( L \) and \( Z \) represent the channel width and length, respectively. The FET mobility and threshold voltage in the (NH₄)₂S-treated PbS CQD FETs were calculated from the plot of the gate voltage vs. drain current (\( I_D \)). Threshold voltage is defined as a required gate voltage to create mobile carriers in the channel. It is extracted from the gate voltage at which the drain current is zero, satisfying the relation in the above equation. Importantly, the above relation is
satisfied above the threshold voltage in the linear regime of transistor operation ($V_D \leq V_T$). In the subthreshold region below the threshold voltage, FET is not turned on. Mobile carriers are available after carriers fill the deep traps. In the subthreshold region below threshold voltage, carriers are preferentially occupied in the deep traps, showing non-linear $I_D - V_G$ characteristic curves.

3. Results and Discussion

Ligand removal process using (NH₄)₂S and Pb-OA ligand complexes and a bottom contact (NH₄)₂S-treated PbS CQD FET structure are illustrated in Fig. 1(a). As described in the chemical reaction, Pb(OA)₂ + (NH₄)₂S → PbS + 2(NH₄)OA, metal-surface-tant surface is replaced by sulfd-rich layer. The size of PbS CQDs was estimated from optical absorption in Fig. S1(c) and it is consistent with the XRD data in which the size of crystalline PbS CQDs (~3 nm) was estimated from Debye-Scherrer equation in Fig. S1(d). It is important to note that after ligand removal process quantum confinement effect was retained as described in our previous report. From the AFM height measurement in Fig. S1(b), the thickness of a drag-coated PbS CQD film is close to 3.48 nm, which is close to the size of the PbS CQD.

After (NH₄)₂S treatment, p-channel FET characteristics were observed with a far higher conductivity in comparison with those in a pristine and EDT-treated PbS CQD FETs which show a negligible magnitude of current below pico-ampere, as seen in Fig. 1(b). It is important to emphasize that a large threshold voltage difference depending on the gate scan direction was observed, exhibiting a large current hysteresis at room temperature.

Charge transport properties of (NH₄)₂S-treated PbS CQDs were investigated at low temperature in Fig. 2(a). Determination of the FET mobility and threshold voltage was detailed in the supporting information. Temperature dependent mobility and threshold voltage were plotted in Figs. 2(b) and 2(c). At a low temperature below 150 K, mobility increased with temperature while the mobility decreased with temperature increasing above 200 K. Importantly, the threshold voltage difference between the forward and reverse scans decreased as the temperature decreases, reaching ~14 V at 77 K.

In elucidating the temperature dependent mobility and threshold voltage, electronic trapping in the localized states should be considered. At a very low temperature region below 150 K, current is more significant at higher temperature which is interpreted that thermally activated carrier hopping process dominates through carrier trap and release model, as typically observed in polaronic hopping process in disordered materials. In the framework, decrease in the threshold voltage at a lower temperature is equivalent to the fact that the number of carriers in the deep traps increase to turn on the FET while the number of carriers in the shallow traps decrease. Indeed, decrease in the threshold voltage was observed at a lower temperature in the forward scan. At a higher temperature above
150 K, however, increase in the total number of carriers in the shallow traps is not consistent with the reduced mobility, clarifying that the electronic carrier trapping and release model can not solely explain the behavior.

Here, we hypothesize that gate electric field screening by ion conduction contributes to the temperature dependent charge transport behavior. Hydroxyl and hydrogen species have been observed in the disordered materials systems. Particularly, OH⁻ and O₂ in the PbS CQD surface have been known to activate the following reactions during charge injection:13–15

\[
\begin{align*}
O_2 + 2H_2O + 4e^- & \rightarrow 4OH^- \\
O_2 + 4H^+ + 4e^- & \rightarrow 2H_2O
\end{align*}
\]

In other words, during device operation, surface hydroxyl and hydrogen ions can be formed as results of chemical reactions and/or exposure to air, contributing to the ionic conduction. Moreover, organic species such as solvent (methanol) molecules could be another possible origin of the ionic conduction through solvent coordination.16 It is important to note that, removal of passivated molecules through (NH₄)₂S treatment can facilitate ion formation via a variety of chemical reactions at the bare PbS CQD surface.

Significant reduction in the current hysteresis at a lower temperature region, reflecting decrease in the threshold voltage difference between the forward and reverse gate scans, is thought to arise from deactivation of ionic conduction in the (NH₄)₂S-treated PbS CQD film at the interface. As the ionic conductivity decreases with increasing temperature, causing a dramatic decrease in current hysteresis. It has, indeed, been reported that screening effect by accumulated ions at the interface weakens gate voltage dependent current modulation, causing a large current hysteresis.16 It is important to emphasize that significant current hysteresis occurred with suppression of mobility enhancement with temperature increasing, indicating that accumulation of ions at the gate dielectric/PbS CQD interface increases energetic disorder due to increased electrostatic coulombic interaction between electronic carriers and the immobilized ions, reducing the FET mobility. The use of an ultrathin PbS CQD film allows us to focus on the surface treatment effect on the interfacial charge transport because ligand removal carried out by diffusion of (NH₄)₂S solution into the PbS CQD film is highly favorable in such a thin film, which was confirmed through comparison of FTIR data in which the C-H stretching peaks (2800–3000 cm⁻¹) were almost disappeared after (NH₄)₂S treatment (Data not shown).16

After (NH₄)₂S treatment, bare PbS CQDs are easily merged, forming an metal-sulfide bond. The bare PbS CQDs have a far greater density of surface traps than that of the ligand-modified PbS CQDs treated with 1,2-ethanedithiol (EDT) and mercaptocarboxylic acids (MPA), as reported in previous studies.16–18 Surface passivation through ligand modification using EDT mitigates the effect of organic species-induced ionic conduction on charge transport. Xu et al. report that, after (NH₄)₂S treatment, dramatic exciton quenching was observed, leading to non-radiative recombination.18 Zhang et al. also show that, after treatment, photoluminescence intensity decreased with a reduced life time.16 For those reasons, additional surface passivation after ligand removal process has been carried out to alleviate carrier trapping in the bare surface-induced defect sites.19–21 In other words, the highly reactive bare surfaces are vulnerable to the formation of ion species with solvent and other impurity molecules while ligand-modified film is still passivated, mitigating formation of ionic species. It is also important to emphasize that the effect of interfacial ionic conduction on charge transport is more prominent in the ultrathin film with bare CQD surface because the ligand removal reaction through diffusion of (NH₄)₂S solution into the ultrathin film is more complete than that in the thick film. To elucidate the origin of the interfacial charge transport behavior, further experiments in more controlled environments are required.

4. Conclusions

In conclusion, we fabricated, for the first time, an ultrathin (NH₄)₂S-treated PbS CQD FETs and probed interfacial charge carrier transport, eliminating the effect of the bulk current. We found that electronic trapping and gate field screening by ionic conduction at the PbS/gate dielectric interface competes depending on the temperature region, determining the interfacial charge transport. As temperature increases gate field screening by thermally activated ionic conduction becomes dominant over polaronic hopping. Formation of ultrathin surface-treated CQD layer becomes crucial as a functional layer for device optimization and our work presented herein provides insight into understanding interfacial charge transport and transfer sensitized by carrier confinement through gate electric field and CQD size scale thickness.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-00026.

Acknowledgments

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2015R1A6A1A03031833, NRF-2019R1F1A1060042 and NRF-2020R1A2C1007258). This work was also supported by the 2020 Hongik Faculty Research Support Fund.

References

1. Y. Shirasaki, G. J. Supran, M. G. Bawendi, and V. Bulović, Nat. Photonics, 7(1), 13 (2013).
2. X. Li, Y.-B. Zhao, F. Fan, L. Levinia, M. Liu, R. Quintero-Bermudez, X. Gong, L. N. Quan, J. Fan, and Z. Yang, Nat. Photonics, 12(3), 159 (2018).
3. R. Wang, Y. Shang, P. Kanjaniaboo, W. Zhou, Z. Ning, and E. H. Sargent, Energy Environ. Sci., 9(4), 1130 (2016).
4. P. R. Brown, D. Kim, R. R. Lunt, N. Zhao, M. G. Bawendi, J. C. Grossman, and V. Bulovic, ACS Nano, 8(6), 5863 (2014).
5. D. V. Talapin, J.-S. Lee, M. V. Kovalenko, and E. V. Shevchenko, Chem. Rev., 110(3), 389 (2009).
6. C. Dun, W. Huang, H. Huang, J. Xu, N. Zhou, Y. Zheng, H. Tsai, W. Nie, D. R. Onken, and Y. Li, J. Phys. Chem. C, 118(51), 30302 (2014).
7. Y. Kim, H. Ko, and B. Park, J. Phys. D, 51(14), 145306 (2018).
8. L. Torsi, M. Magliulo, K. Manoli, and G. Palazzo, Chem. Soc. Rev., 42(22), 8612 (2013).
9. B. Park, Thin Solid Films, 550, 696 (2014).
10. P. Stallings, Adv. Mater., 23(30), 3356 (2011).
11. N. Tessler, Y. Prezant, N. Rappaport, and Y. Roichman, Adv. Mater., 21(7), 2741 (2009).
12. V. Podorojov, E. Menard, A. Borissov, V. Kiyukhin, J. Rogers, and M. Gershenson, Phys. Rev. Lett., 93(8), 086602 (2004).
13. Y. Zhang, Q. Chen, A. P. Alivisatos, and M. Salmeron, Nano Lett., 15(7), 4657 (2015).
14. Y. Zhang, D. Zherebetskyy, N. D. Bronstein, S. Banj, L. Lichtenstein, D. Scheppevisser, L.-W. Wang, A. P. Alivisatos, and M. Salmeron, Nano Lett., 15, 3249 (2015).
15. D. Zherebetskyy, M. Scheele, Y. Zhang, N. Bronstein, C. Thompson, D. Britt, M. Salmeron, P. Alivisatos, and L.-W. Wang, Science, 344, 1380 (2014).
16. Y. Zhang, H. B. Hu, L. Sun, R. Hovden, F. W. Wise, D. A. Muller, and R. D. Robinson, Nano Lett., 11(12), 5535 (2011).
17. X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno, and C. Soci, Nat. Commun., 6, 7383 (2015).
18. F. Xu, L. F. Gerlein, X. Ma, C. R. Haughn, M. F. Doty, and S. G. Cloutier, Materials, 8(4), 1858 (2015).
19. H. Zhang, J. Yang, J.-R. Chen, J. R. Engstrom, T. Hanrath, and F. W. Wise, J. Phys. Chem. Lett., 7(4), 642 (2016).
20. A. F. Palmstrom, P. K. Santra, and S. F. Bent, Nanoscale, 7(29), 12266 (2015).
21. Z. Ning, O. Voznyy, J. Pan, S. Hoogland, V. Adinolfi, J. Xu, M. Li, A. R. Kimani, J.-P. Sun, and J. Minor, Nat. Mater., 13(8), 822 (2014).