Anion Exchange Perovskite Quantum-Dots for Highly Efficient Light-Emitting-Devices

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ABSTRACT

Perovskites quantum dots have attracted much attention for used in display andlighting applications, owing to their narrow band emission with high photoluminescence quantum yields, color tunability, and solution processability. Here, we demonstrate ligand-exchange and anion-exchange perovskite quantum dots using ammonium salts for use in highly efficient light-emitting devices.

1 INTRODUCTION

All inorganic cesium lead halide perovskite with $CsPbX_3$ (X = Cl^-, Br^-, or I^-) have demonstrated a novel classified colloidal quantum dots (QDs).[1)] Perovskite QDs have been attracted for application in display and lighting due to their high color purity with narrow full-width at half-maximum (FWHM), photoluminescence quantum yields (PLQYs) of up to 90%, tunable emission wavelength in full visible range by halide anion composition (X site = Cl^- for blue emission, Br^- for green emission, or I^- for red emission) or size of QDs, and low cost solution processing (Fig1). Perovskite QDs can be covered the next generation of standard for display, B.T. 2020 color gamut.

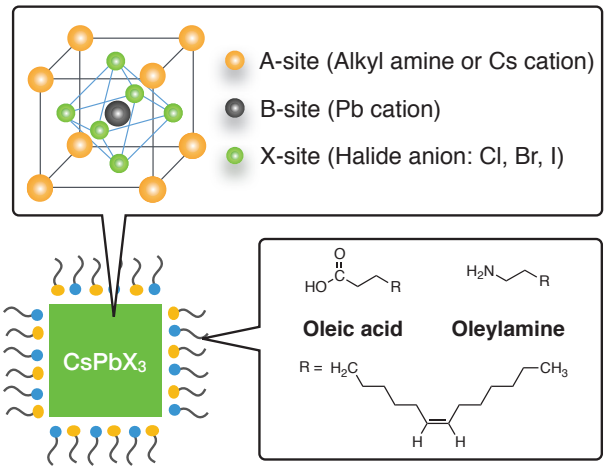

Fig. 1. Perovskite QDs and surface ligand

Perovskite QDs are consisted almost entirely of inorganic elements, the energy levels of perovskite QDs are similar to the organic light-emitting materials, which lead to fabrication of device with similar structure of organic light-emitting devices (OLEDs). The external quantum efficiency (EQE) of LEDs based on $CsPbX_3$ QDs have rapidly increased from 0.1% to over 20% by using surface ligand engineering, surface treatment, energy level alignment, and chemical composition engineering for past only few years.[2-5)] *Here, we demonstrate ligand-exchange and anion-exchange perovskite QDs using ammonium salts for use in highly efficient light-emitting devices.*

2 Ligand exchange for perovskite QDs

Protesescu et al. reported that the development of novel hot-injection synthesis method for colloidal all inorganic $CsPbX_3$ QDs using lead halides (PbX_2, where X is Cl, Br, or I) and cesium-oleate precursors.[1)] These perovskite QDs are ionic nanocrystal materials with cubic crystal shape and phase at room temperature, which result in a relative lower reaction temperature (below 200 ˚C), fast reaction time (only few seconds),

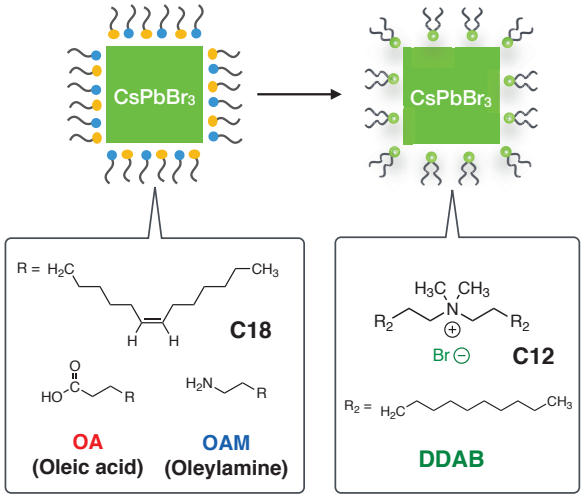

Fig. 2. Ligand exchange for perovskite QDs

and narrow size distributions. Another synthesis method of perovskite QDs, room temperature ligand-assisted reprecipitation (LARP) method[6] and microwave assisted synthesis[7] have also been reported.

Perovskite QDs have a size dependency of optical properties, which exhibits tunable emission wavelength by size of QDs that smaller size lead to wide energy gap and blue shift due to the quantum size effect, whereas larger size of QDs exhibit a narrow gap and red shift of emission. In order to impart dispersibility in non-polar organic solvents (toluene or octane), long alkyl oleic acid (OA) and oleylamine (OAM) were generally used as surface ligands on perovskite QDs. However, these long alkyl ligands are generally electrical insulating that inhibits a charge injection or transport in the perovskite QD-LEDs. To overcome this issue, we demonstrated the ligand exchange for perovskite QDs via simple post-treatment.[2, 3] Di-dodecyl dimethyl ammonium bromide (DDAB) consists of relative shorter alkyl chain (C12) with Br^- anion that lead to facilitate both charge injection or transport and effective surface passivation in perovskite QDs[8] (Fig.2) Small amount of OA was added into purified $CsPbBr_3$ QDs dispersion to desorb OAM from QD surface, subsequently DDAB solution in toluene was quickly injected into mixture dispersion under stirring. The average particles size of $CsPbBr_3$-DDAB QDs was 9 nm, which was identical sized to the pristine QDs (without ligand exchange). Ligand exchange $CsPbBr_3$-DDAB film exhibited a higher PLQY of 42% (FWHM of 19nm) than those of pristine $CsPbBr_3$ with OA and OAM (15%) due to better surface passivation, although peak emission wavelength and size of particle is almost identical during ligand exchange process. The perovskite QD-LED based on $CsPbBr_3$-DDAB exhibited a narrow EL spectra with a FWHM of 17 nm and a very low turn-on voltage of 2.6 V.

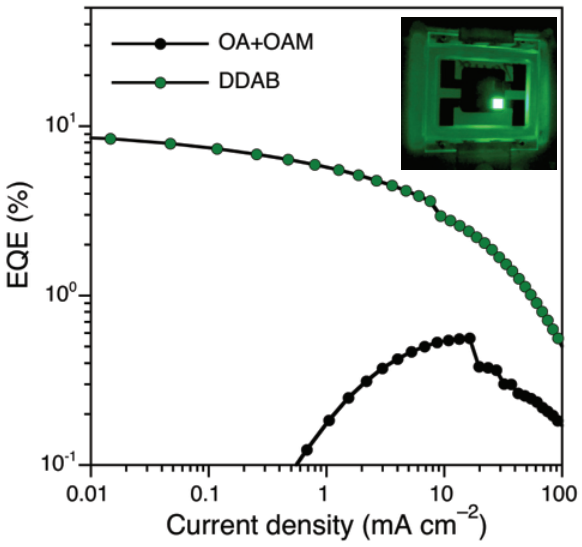

Fig. 3. Ligand exchange for perovskite QDs

The maximum power efficiency and EQE of LED with $CsPbBr_3$-DDAB QD reached 31.7 lm/W and the EQE was 8.7% (Fig.3). Control of the interfacial perovskite QDs through ligand removal and energy level alignment in the device structure are promising methods for obtaining high PLQYs in film state and high device efficiency.

3 Anion exchange for perovskite QDs

The combination of two different halide anions, mix-halide anion perovskite QDs such as $CsPb(Cl/Br)_3$ and $CsPb(Br/I)_3$ can be complemented blue emission (ca. 430–490 nm) and red emission (ca. 550–650 nm) region in visible range by adjustment of mix-halide anion ratio (Fig.4).[1] The mix-halide perovskite QDs are commonly synthesized by three routes, direst synthesis, blend in QDs, and anion exchange reaction using halide salts (Fig.5). For the direct synthesis method, two type of lead halide salts such as $PbCl_2$:$PbBr_2$ or $PbBr_2$:PbI_2 are used in hot-injection synthesis method, which can be easily tuned an optical bandgap and emission wavelength by changing ratio of lead halide salts. On the other hand, post-treatment of synthesized perovskite QDs are also utilized for the form of mix-halide composition due to their high ionic conductive properties. The anion exchange method of perovskite QDs that the replacement halide anion from Br^- anion to Cl^- or I^- anion in perovskite QDs at room temperature demonstrated by Akkerman et al. using various halide salt precursors (ammonium-halides or metal-halide salts) or blended with perovskite QDs dispersion with different halide composition ($CsPbCl_3$:$CsPbBr_3$ or $CsPbBr_3$:$CsPbI_3$).[9] The anion exchange perovskite QDs showed a narrow emission with high color purity in full visible range, in a manner similar to directly synthesized perovskite QDs.

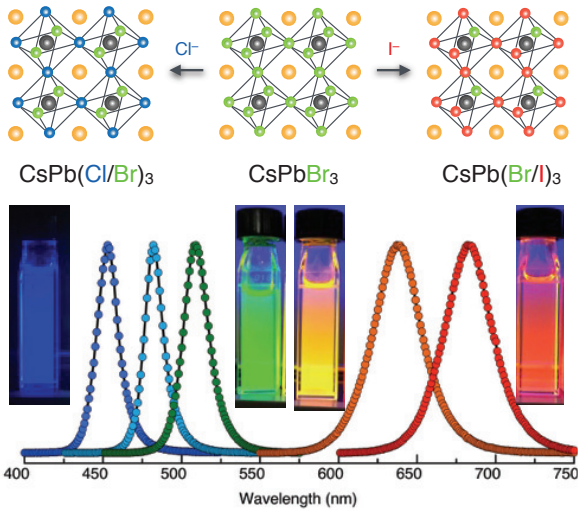

Fig. 4.Mix-halide perovskite QDs

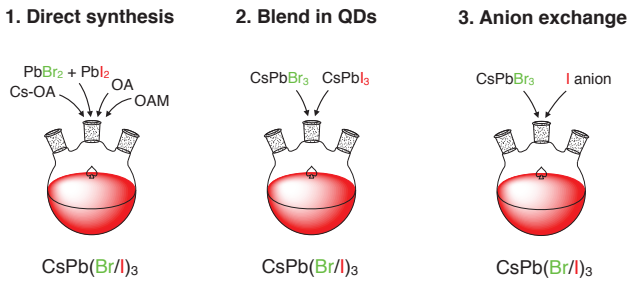

Fig. 5. Synthesis for mix-halide perovskite QDs

We demonstrate anion-exchange red perovskite QDs $CsPb(Br/I)_3$ from pristine $CsPbBr_3$ using ammonium-iodine salts, long alkyl-based oleylammonium iodide (OAM-I) and aryl-based aniline hydoroiodide (An-HI), for use in highly efficient LEDs.[5] The anion-exchange $CsPb(Br/I)_3$ films exhibit a strong red-shift in their of photoluminescence (PL) spectrum from the green emission at 508 nm in the case of the pristine QDs to one in the deep-red region at 649 nm owing to the replacement of Br^- anions by I^- anions in the perovskite QDs. LEDs formed using the anion-exchange $CsPb(Br/I)_3$ based on OAM-I show an remarkable high EQE of more than 20% as well as high color purity, with the Commission Internationale de l'Eclairage (CIE) at (0.72, 0.28), which completely cover BT.2020 color gamut. Similarly, the LEDs formed using the QDs based on An-HI show a peak EQE of 14.1% and CIE coordinates of (0.71, 0.28). Further, they exhibit longer operational stability as compared to that of LEDs formed using the OAM-I-based $CsPb(Br/I)_3$. Therefore, anion exchange perovskite QDs using an ammonium salts is effective approach for highly efficient LEDs.

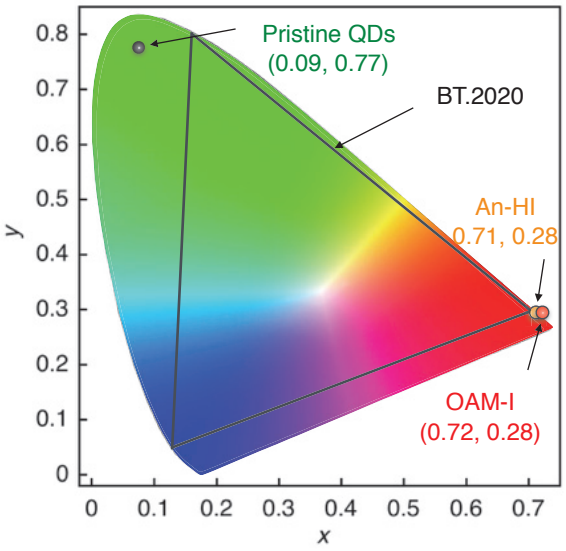

Fig. 6. CIE color coordinate of perovskite QD LEDs.

4 CONCLUSIONS

Perovskite QDs based LEDs with high color purity emission spectra in the full visible range have been demonstrated as a good candidate for next-generation light-emitting materials in lighting and display applications. In this paper, we discussed the current approaches to achieve highly efficient perovskite QD-LEDs, hot-injection synthesis method, ligand exchange approaches for surface passivation, and anion exchange for perovskite QD. These post-treatment approaches are promising ways to obtain high quality perovskite QD and high efficiency perovskite QD-LEDs.

REFERENCES

[1] L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, M. V. Kovalenko, Nano Lett., 15, 3692-3696 (2015).

[2] J. Song, J. Li, X. Li, L. Xu, Y. Dong, H. Zeng, Adv. Mater., 27, 7162-7167 (2015).

[3] T. Chiba, K. Hoshi, Y. J. Pu, Y. Takeda, Y. Hayashi, S. Ohisa, S. Kawata, J. Kido, ACS Appl. Mater. Interfaces, 9, 18054-18060 (2017).

[4] K. Hoshi, T. Chiba, J. Sato, Y. Hayashi, Y. Takahashi, H. Ebe, S. Ohisa, J. Kido, ACS Appl. Mater. Interfaces, 10, 24607-24612 (2018).

[5] T. Chiba, Y. Hayashi, H. Ebe, K. Hoshi, J. Sato, S. Sato, Y. J. Pu, S. Ohisa, J. Kido, Nat. Photon., 12, 11, 681-687 (2018).

[6] F. Zhang, H. Z. Zhong, C. Chen, X. G. Wu, X. M. Hu, H. L. Huang, J. B. Han, B. S. Zou and Y. P. Dong, ACS Nano, 9, 4533-4542 (2015).

[7] Z. Long, H. Ren, J. H. Sun, J. Ouyang and N. Na, Chem. Commun., 53, 9914-9917 (2017).

[8] J. Pan, L. N. Quan, Y. Zhao, W. Peng, B. Murali, S. P. Sarmah, M. Yuan, L. Sinatra, N. M. Alyami, J. Liu, E. Yassitepe, Z. Yang, O. Voznyy, R. Comin, M. N. Hedhili, O. F. Mohammed, Z. H. Lu, D. H. Kim, E. H. Sargent, O. M. Bakr, Adv. Mater., 28, 8718-8725 (2016).

[9] Q. A. Akkerman, V. D'Innocenzo, S. Accornero, A. Scarpellini, A. Petrozza, M. Prato, L. Manna, J. Am. Chem. Soc., 137, 32, 10276-10281 (2015)