Journal of Semiconductors
(2022) 43, 090201
doi: 10.1088/1674-4926/43/9/090201
JOS

RESEARCH HIGHLIGHTS

Perovskite nanocrystals for light-emitting diodes

Xinyi Mei[1], Lixiu Zhang[2], Xiaoliang Zhang[1, †], and Liming Ding[2, †]

[1]School of Materials Science and Engineering, Beihang University, Beijing 100191, China

[2]Center for Excellence in Nanoscience (CAS), Key Laboratory of Nanosystem and Hierarchical Fabrication (CAS), National Center for Nanoscience and Technology, Beijing 100190, China

Citation: X Y Mei, L X Zhang, X L Zhang, and L M Ding, Perovskite nanocrystals for light-emitting diodes[J]. *J. Semicond.*, 2022, 43(9), 090201. https://doi.org/10.1088/1674-4926/43/9/090201

With superior photoluminescence quantum yields (PLQYs), tunable bandgap, high color purity and solution processibility[1, 2], metal halide perovskite nanocrystals (PNCs) with a general formula of ABX_3 (A = $CH_3NH_3^+$ (MA^+), $CH(NH_2)_2^+$ (FA^+) and Cs^+, B = Pb^{2+}, Sn^{2+} and Mn^{2+}, X = Cl^-, Br^- and I^-) emerge as promising luminescent materials in light-emitting diodes (LEDs) and solid-state lighting[2–4]. Since electroluminescence (EL) of PNCs was first observed in $CsPbBr_3$ PNC-based LEDs with an external quantum efficiency (EQE) of 0.07% in 2015[5], the efficiencies for different LEDs have been significantly boosted. The red and green LEDs demonstrated an EQE of >23% and the highest EQE for blue LEDs reached 13.8%[6–8], comparable to conventional LEDs based on organic emitters or metal chalcogenide (II–VI) quantum dots (QDs)[9, 10].

Compared to traditional emitters, the ionic bonding and relatively low formation energy of perovskite lattice enabled the facile formation of PNCs through liquid-phase synthesis[11, 12] (e.g. hot-injection (Fig. 1(a))[1], ligand-assisted reprecipitation[13] and ultrasonic-assisted synthesis[14]). Thanks to the great efforts in regulating the types and ratios of precursors, modifying the reaction temperature and adjusting the solvents and anti-solvents, near-unity PLQYs have been demonstrated for as-synthesized PNCs[15–17]. However, the luminescence properties for fresh PNCs would always be impaired during the subsequent purification, assembly process and storage in ambient conditions. The highly dynamic binding between the capping ligands and PNC surface induced the surface ligand desorption and subsequent generation of surface defects[18, 19]. In particular, the facilely formed halide ion (X^-) vacancies and uncoordinated Pb^{2+} ions on PNC surface would yield carrier trapping centers and also provide sites for the invasion of external water and oxygen[20, 21], seriously deteriorating the performance of PNCs[22–25]. Chiba *et al.* utilized ammonium iodine salts, oleylammonium iodide (OAM-I) and aniline hydroiodide (An-HI), for post-treatment of $CsPbBr_3$ PNCs to fill in the surface Br^- vacancies and redshift their PL emission (Fig. 1(a)), leading to pure red PNC-LEDs with an EQE of 21.3%[26]. Similarly, didodecyldimethylammonium fluoride (DDAF) endowed $CsPbBr_3$ PNCs with well-passivated surface and improved resistance to thermal quenching of PL[27]. As a result, the LEDs presented an EQE of 19.3% with a low efficiency roll-off and enhanced thermal stability. Dong *et al.* proposed an ordinal surface-passivating strategy involving short-chain isopropylammonium bromide (IPABr) and NaBr to coat $CsPbBr_3$ PNCs with a relatively stable bipolar shell, while also enhancing inter-dot charge coupling due to adequate removal of insulating OA and OAm ligands[28]. This strategy yielded blue and green $CsPbBr_3$ PNC-LEDs with EQEs of 12.3% and 22%, respectively, as well as improved operational stability. Zheng *et al.* used n-dodecylammonium thiocyanate (DAT) to eliminate the surface defects of mix-halide PNCs without affecting their PL spectra, yielding pure blue PNC-LEDs with an EQE of 6.3% and stabilized EL spectra[29].

Lewis bases containing carbonyl (C=O), carboxylate ($-COO^-$), phosphate (P=O) or sulfonate ($-SO_3^-$) groups can also passivate uncoordinated surface Pb^{2+} and suppress nonradiative recombination in PNCs[30–33]. Zeng *et al.* employed phosphine oxide molecules to passivate both top and bottom surfaces of $CsPbBr_3$ PNC film to suppress trap-assisted nonradiative recombination (Fig. 1(b)). The LEDs gave an EQE of 18.7% and a prolonged half-life of 15.8 h[31]. Zhao *et al.* used 2-naphthalenesulfonic acid (NSA) to passivate the uncoordinated surface Pb^{2+} in $FAPbBr_3$ PNCs, and the green LEDs offered a luminance of 67115 cd/m^2 and an EQE of 19.2%[32]. The removal of redundant Pb^{2+} from PNC surface is an effective strategy to keep the high efficiency. Hassan *et al.* reported that ethylenediaminetetraacetic acid (EDTA) and the reduced L-glutathione could eliminate excess surface Pb^{2+} in $MAPb(Br/I)_3$ PNCs due to their strong interaction with Pb^{2+} (Fig. 1(c))[34]. The PNCs with flattened surfaces presented boosted PLQY and suppressed phase separation, yielding an EQE of >20% for the LEDs with a stable EL peak at 620 nm. Bi *et al.* utilized hydrogen bromide (HBr) to facilitate the desorption of OA ligands and induce the removal of imperfect $[PbBr_6]^{4-}$ octahedra from $CsPbBr_3$ PNC surface. By using didodecylamine (DDDAM) and phenethylamine (PEA) passivating ligands, the damaged PNC surface was recovered with reduced trap density, yielding a pure-blue LED with enhanced stability and a luminance of 3850 cd/m^2[35].

In addition to surface engineering, composition adjustment of PNCs is also a feasible strategy. Kim *et al.* introduced guanidinium cations (GA^+) to occupy A sites in $FAPbBr_3$ PNCs (Fig. 2(a)), which can well passivate surface-exposed Pb^{2+} due to extra amino groups and the well distributed positive charges on GA^+[9]. Because of high PLQY (93.3%) and structural stability of GA^+-doped $FAPbBr_3$ PNCs, the LEDs offered an EQE of 23.4% (Fig. 2(b)) and a current efficiency of 108 cd/A. By contrast, doping cations on B-site modulates the energy band of PNCs (e.g. Mn^{2+}, Cu^{2+}, Sn^{2+} and Sr^{2+})[36–39]. Shen *et al.* converted $CsPbI_3$ PNC from n-type semiconductor to nearly

---

Correspondence to: X L Zhang, xiaoliang.zhang@buaa.edu.cn; L M Ding, ding@nanoctr.cn

Received 12 JUNE 2022.

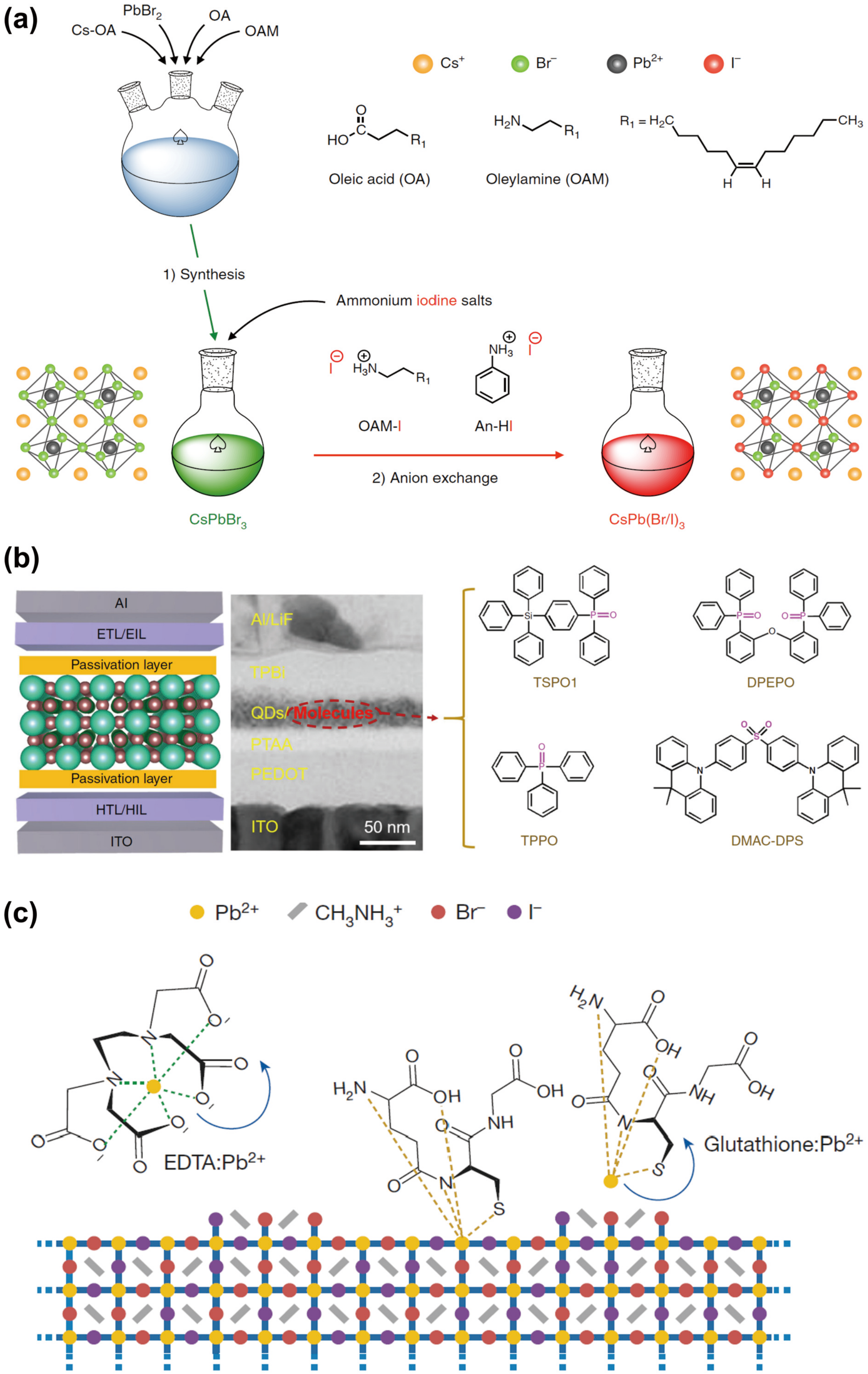


Fig. 1. (Color online) (a) Surface-treating and anion-exchange process of $CsPbBr_3$ PNCs by using OAm-I or An-HI. Reproduced with permission[26], Copyright 2018, Nature Publishing Group. (b) Schematic for PNC-LED with bilateral passivation and the corresponding sectional TEM image. Reproduced with permission[31], Copyright 2020, Nature Publishing Group. (c) Treating PNCs with glutathione and EDTA to remove excess surface Pb^{2+}. Reproduced with permission[34], Copyright 2021, Nature Publishing Group.

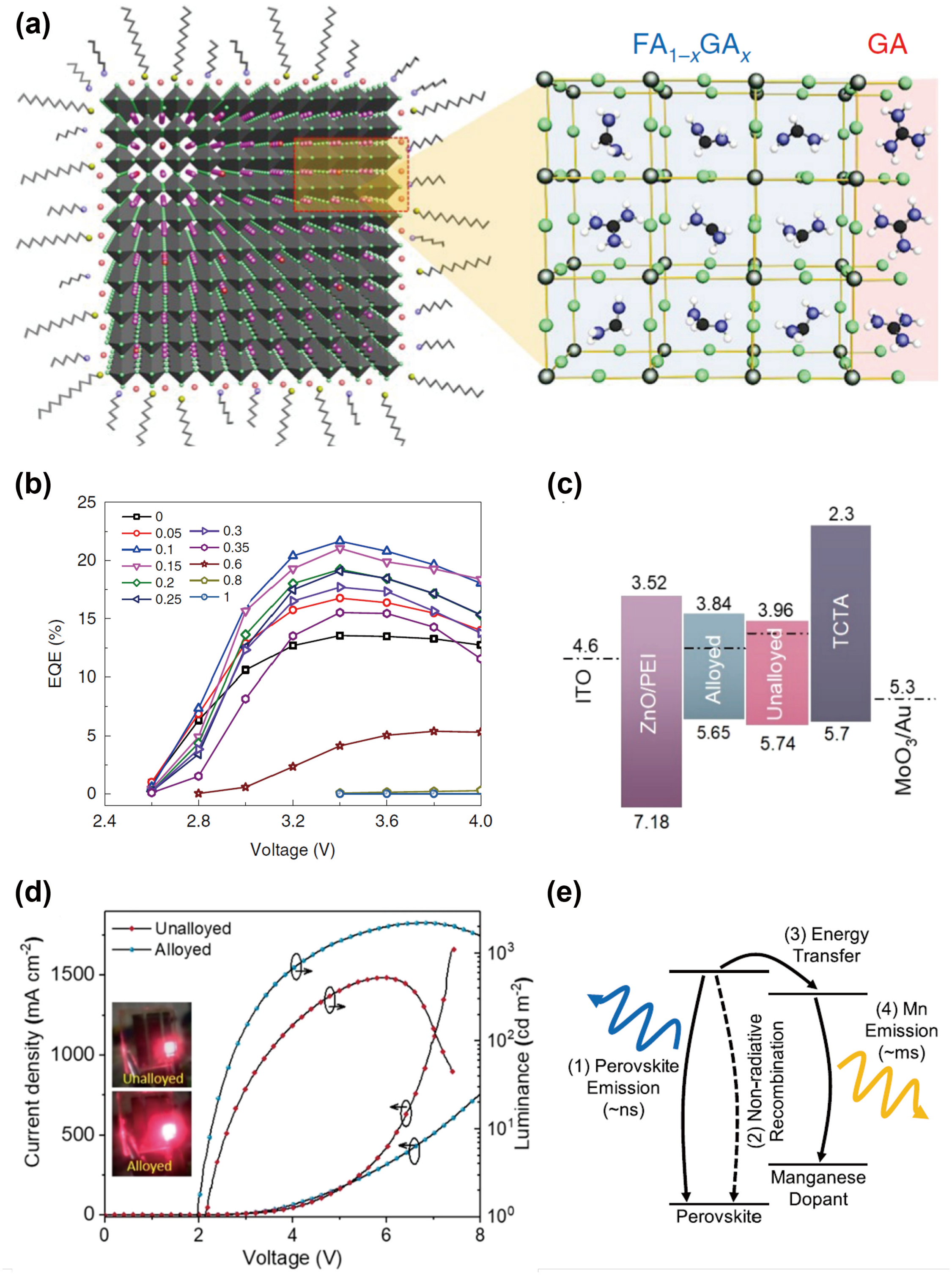


Fig. 2. (Color online) (a) Schematic for GA$^+$-doped FAPbBr$_3$ PNCs. (b) EQE–*V* curves for LEDs based on GA$^+$-doped FAPbBr$_3$ PNCs with different GA$^+$ doping content. (a, b) Reproduced with permission[9], Copyright 2021, Nature Publishing Group. (c) Energy level diagram showing the change in the energy band of Zn^{2+}-doped CsPbI$_3$ PNCs. (d) *J–V–L* curves for LEDs based on CsPbI$_3$ and Zn^{2+}-doped CsPbI$_3$ PNCs. Insets show the working LEDs. (c, d) Reproduced with permission[40], Copyright 2019, American Chemical Society. (e) Energy transfer in Mn^{2+}-doped nanocrystal. Reproduced with permission[36], Copyright 2018, Elsevier.

ambipolar semiconductor *via* doping Zn^{2+} (Fig. 2(c)), leading to more balanced carrier transport within LEDs[40]. The resulting red LEDs achieved brighter EL emission with a luminance of 2202 cd/m^2 and an EQE of 15.1% (Fig. 2(d)). Besides, doping Mn^{2+} into perovskite lattice induced a second emission peak at ~600 nm, which resulted from the energy transfer from perovskite to Mn^{2+} (Fig. 2(e)). Doping Sr^{2+} in CsPbI$_3$ PNCs caused new trap states near the conduction band edge but simultaneously generating an excitonic state at a lower energy level, which prevented the trap-assisted non-radiative recombination, yielding a PLQY of ~95%[39]. Such PNCs showed enhanced stability, due to the increased formation energy of cubic CsPbI$_3$ after being doped with Sr^{2+}. Based on Sr^{2+}-doped CsPbI$_3$ PNCs, Chen *et al.* realized efficient and stable red LEDs with an EQE of 17.1%[41].

Several issues impede the application of PNC-LEDs. (1) Poor stability. More conductive capping matrix can facilitate charge injection into PNC emitters, e.g. 3D perovskite and metal of frame (MOF)[42, 43]. Besides, balanced charge transport favors to combat the efficiency roll-off and enhance device stability[44]. (2) Lead toxicity. Lead-free PNCs always present inferior luminescent properties, e.g. relatively low PLQY and wide emission spectra[45]. More studies on bandgap structure, surface properties and carrier dynamics of lead-free PNCs are needed. In addition, effective encapsulation of lead-halide PNCs may also be a solution.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51872014), the Recruitment Program for Global Experts, the Fundamental Research Funds for the Central Universities and the "111" project (B17002). L. Ding thanks the open research fund of Songshan Lake Materials Laboratory (2021SLABFK02), the National Key Research and Development Program of China (2017YFA0206600) and the National Natural Science Foundation of China (51922032, 21961160720).

References

[1] Protesescu L, Yakunin S, Bodnarchuk M I, et al. Nanocrystals of cesium lead halide perovskites ($CsPbX_3$, X = Cl, Br, and I): Novel optoelectronic materials showing bright emission with wide color gamut. Nano Lett, 2015, 15, 3692

[2] Xiang H, Zuo C, Zeng H, et al. White light-emitting diodes from perovskites. J Semicond, 2021, 42, 030202

[3] Mei X, Jia D, Chen J, et al. Approaching high-performance light-emitting devices upon perovskite quantum dots: Advances and prospects. Nano Today, 2022, 43, 101449

[4] Zhang L, Pan X, Liu L, et al. Star perovskite materials. J Semicond, 2022, 43, 030203

[5] Song J, Li J, Li X, et al. Quantum dot light-emitting diodes based on inorganic perovskite cesium lead halides ($CsPbX_3$). Adv Mater, 2015, 27, 7162

[6] Liu Y, Li Z, Xu J, et al. Wide-bandgap perovskite quantum dots in perovskite matrix for sky-blue light-emitting diodes. J Am Chem Soc, 2022, 144, 4009

[7] Wang Y K, Singh K, Li J Y, et al. In situ inorganic ligand replenishment enables bandgap stability in mixed-halide perovskite quantum dot solids. Adv Mater, 2022, e2200854

[8] Zhang M, Zuo C, Tian J, et al. Blue perovskite LEDs. J Semicond, 2021, 42, 070201

[9] Kim Y H, Kim S, Kakekhani A, et al. Comprehensive defect suppression in perovskite nanocrystals for high-efficiency light-emitting diodes. Nat Photonics, 2021, 15, 148

[10] Shen H, Gao Q, Zhang Y, et al. Visible quantum dot light-emitting diodes with simultaneous high brightness and efficiency. Nat Photonics, 2019, 13, 192

[11] Yang Z, Ding L. Ligand passivation yields long-life perovskite light-emitting diodes. Sci Bull, 2020, 65, 1691

[12] Li Y, Ding L. Single-crystal perovskite devices. Sci Bull, 2021, 66, 214

[13] Li X, Wu Y, Zhang S, et al. $CsPbX_3$ quantum dots for lighting and displays: Room-temperature synthesis, photoluminescence superiorities, underlying origins and white light-emitting diodes. Adv Funct Mater, 2016, 26, 2435

[14] Tong Y, Bladt E, Ayguler M F, et al. Highly luminescent cesium lead halide perovskite nanocrystals with tunable composition and thickness by ultrasonication. Angew Chem Int Ed, 2016, 55, 13887

[15] Dutta A, Behera R K, Pal P, et al. Near-unity photoluminescence quantum efficiency for all $CsPbX_3$ (X = Cl, Br, and I) perovskite nanocrystals: A generic synthesis approach. Angew Chem Int Ed, 2019, 58, 5552

[16] Hassan Y, Ashton O J, Park J H, et al. Facile synthesis of stable and highly luminescent methylammonium lead halide nanocrystals for efficient light emitting devices. J Am Chem Soc, 2019, 141, 1269

[17] Zhang X, Han D, Chen X, et al. Effects of solvent coordination on perovskite crystallization. Acta Phys Chim Sin, 2020, 37, 2008055

[18] De Roo J, Ibanez M, Geiregat P, et al. Highly dynamic ligand binding and light absorption coefficient of cesium lead bromide perovskite nanocrystals. ACS Nano, 2016, 10, 2071

[19] Jia D, Chen J, Qiu J, et al. Tailoring solvent-mediated ligand exchange for $CsPbI_3$ perovskite quantum dot solar cells with efficiency exceeding 16.5%. Joule, 2022, in press

[20] Jia D, Chen J, Mei X, et al. Surface matrix curing of inorganic $CsPbI_3$ perovskite quantum dots for solar cells with efficiency over 16%. Energy Environ Sci, 2021, 14, 4599

[21] Zhou Q, Qiu J, Wang Y, et al. Multifunctional chemical bridge and defect passivation for highly efficient inverted perovskite solar cells. ACS Energy Lett, 2021, 6, 1596

[22] Chen J, Jia D, Johansson E M J, et al. Emerging perovskite quantum dot solar cells: feasible approaches to boost performance. Energy Environ Sci, 2021, 14, 224

[23] Zheng C, Liu A, Bi C, et al. SCN-doped $CsPbI_3$ for improving stability and photodetection performance of colloidal quantum dots. Acta Phys Chim Sin, 2021, 37, 2007084

[24] Yang Z, Qin C, Ning Z, et al. Low-dimensionality perovskites yield high electroluminescence. Sci Bull, 2020, 65, 1057

[25] Zhang D, Qin C, Ding L. Domain controlling and defect passivation for efficient quasi-2D perovskite LEDs. J Semicond, 2022, 43, 050201

[26] Chiba T, Hayashi Y, Ebe H, et al. Anion-exchange red perovskite quantum dots with ammonium iodine salts for highly efficient light-emitting devices. Nat Photonics, 2018, 12, 681

[27] Liu M, Wan Q, Wang H, et al. Suppression of temperature quenching in perovskite nanocrystals for efficient and thermally stable light-emitting diodes. Nat Photonics, 2021, 15, 379

[28] Dong Y, Wang Y K, Yuan F, et al. Bipolar-shell resurfacing for blue LEDs based on strongly confined perovskite quantum dots. Nat Nanotechnol, 2020, 15, 668

[29] Zheng X, Yuan S, Liu J, et al. Chlorine vacancy passivation in mixed halide perovskite quantum dots by organic pseudohalides enables efficient Rec. 2020 blue light-emitting diodes. ACS Energy Lett, 2020, 5, 793

[30] Chen J, Jia D, Qiu J, et al. Multidentate passivation crosslinking perovskite quantum dots for efficient solar cells. Nano Energy, 2022, 96, 107140

[31] Xu L, Li J, Cai B, et al. A bilateral interfacial passivation strategy promoting efficiency and stability of perovskite quantum dot light-emitting diodes. Nat Commun, 2020, 11, 3902

[32] Zhao H, Chen H, Bai S, et al. High-brightness perovskite light-emitting diodes based on $FAPbBr_3$ nanocrystals with rationally designed aromatic ligands. ACS Energy Lett, 2021, 6, 2395

[33] Jia D, Chen J, Yu M, et al. Dual passivation of $CsPbI_3$ perovskite nanocrystals with amino acid ligands for efficient quantum dot solar cells. Small, 2020, 16, 2001772

[34] Hassan Y, Park J H, Crawford M L, et al. Ligand-engineered bandgap stability in mixed-halide perovskite LEDs. Nature, 2021, 591, 72

[35] Bi C, Yao Z, Sun X, et al. Perovskite quantum dots with ultralow trap density by acid etching-driven ligand exchange for high lu-

minance and stable pure-blue light-emitting diodes. Adv Mater, 2021, 33, 2006722

[36] Hou S, Gangishetty M K, Quan Q, et al. Efficient blue and white perovskite light-emitting diodes via manganese doping. Joule, 2018, 2, 2421

[37] Zhang J, Zhang L, Cai P, et al. Enhancing stability of red perovskite nanocrystals through copper substitution for efficient light-emitting diodes. Nano Energy, 2019, 62, 434

[38] Wang H C, Wang W, Tang A C, et al. High-performance $CsPb_{1-x}Sn_xBr_3$ perovskite quantum dots for light-emitting diodes. Angew Chem Int Ed, 2017, 56, 13650

[39] Yao J S, Ge J, Wang K H, et al. Few-nanometer-sized alpha-$CsPbI_3$ quantum dots enabled by strontium substitution and iodide passivation for efficient red-light emitting diodes. J Am Chem Soc, 2019, 141, 2069

[40] Shen X, Zhang Y, Kershaw S V, et al. Zn-alloyed $CsPbI_3$ nanocrystals for highly efficient perovskite light-emitting devices. Nano Lett, 2019, 19, 1552

[41] Chen C, Xuan T, Bai W, et al. Highly stable $CsPbI_3$: Sr^{2+} nanocrystals with near-unity quantum yield enabling perovskite light-emitting diodes with an external quantum efficiency of 17.1%. Nano Energy, 2021, 85, 106033

[42] Liu Y, Dong Y, Zhu T, et al. Bright and Stable light-emitting diodes based on perovskite quantum dots in perovskite matrix. J Am Chem Soc, 2021, 143, 15606

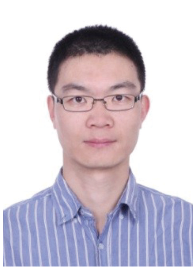
[43] Tsai H, Shrestha S, Vilá R A, et al. Bright and stable light-emitting diodes made with perovskite nanocrystals stabilized in metal–organic frameworks. Nat Photonics, 2021, 15, 843

[44] Wang C, Zhang C, Li R, et al. Charge accumulation behavior in quantum dot light-emitting diodes. Acta Phys Chim Sin, 2022, 38, 2104030

[45] Fan Q, Biesold-McGee G V, Ma J, et al. Lead-free halide perovskite nanocrystals: Crystal structures, synthesis, stabilities, and optical properties. Angew Chem Int Ed, 2020, 59, 1030

Xinyi Mei got her BS from Central South University in 2019. She is now pursuing her PhD degree in Materials Physics and Chemistry at Beihang University under the supervision of Prof. Xiaoliang Zhang. Her research focuses on low-dimensional optoelectronic materials, such as quantum dots, and their application in light-emitting devices.

Lixiu Zhang got her BS from Soochow University in 2019. Now she is a PhD student at University of Chinese Academy of Sciences under the supervision of Prof. Liming Ding. Her research focuses on perovskite solar cells.



Xiaoliang Zhang is a professor at Beihang University. He received his PhD in Materials Physics and Chemistry from Beihang University in 2013. Then, he joined Uppsala University as a postdoc and subsequently was promoted as a Senior Researcher there. He joined Beihang University as a full professor in 2018. His research focuses on semiconducting quantum dots and their application in optoelectronic devices.

Liming Ding got his PhD from University of Science and Technology of China (was a joint student at Changchun Institute of Applied Chemistry, CAS). He started his research on OSCs and PLEDs in Olle Inganäs Lab in 1998. Later on, he worked at National Center for Polymer Research, Wright-Patterson Air Force Base and Argonne National Lab (USA). He joined Konarka as a Senior Scientist in 2008. In 2010, he joined National Center for Nanoscience and Technology as a full professor. His research focuses on innovative materials and devices. He is RSC Fellow, the nominator for Xplorer Prize, and the Associate Editor for Journal of Semiconductors.