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Research Highlight

Ultra-small perovskites: breakthrough of blue LEDs

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Light-emitting diodes (LEDs) are popular for lighting and displays due to their energy efficiency and long lifespan. With the development of high-efficiency LEDs, new technologies such as the Internet of Things have emerged. However, scientists are still working to improve the color purity and expand the color gamut of LEDs to meet the demands of a wide range of applications. As a result, the pursuit of high-quality LED technology continues to drive innovation [1]. During last few years, perovskite-based light-emitting diodes (PeLEDs) are the attractive candidate for commercial LEDs devices, such as solid-state lights and high-definition displays, by virtue of their high photoluminescence quantum yields (PLQYs), narrow emission linewidths (<100 meV), and tunable emission wavelengths covering the whole visible spectrum [2]. Specifically, high external quantum efficiencies (EQEs) exceeding 20% have been achieved for green, red, and near-infrared PeLEDs, which are comparable to the values achieved by organic LEDs [3,4]. Blue-emitting PeLEDs devices have historically been performed, which either suffered from wide emission linewidths and/or low quantum efficiencies; as a result, PeLEDs are still not widely used in practical applications [5]. Therefore, the development of blue PeLEDs with high EQEs could pave the way to the improvements in solid-state lighting and colorful displays, and further advance the scientific research.

Perovskite quantum dots (QDs) are made by synthesizing perovskite materials into nanocrystals. Their size usually ranges from 2 to 20 nm, which leads to the emergence of quantum confinement effects, resulting in unique optical and electronic properties. One of the advantages of perovskite QDs is their ability to emit bright and tunable light across the visible spectrum, which makes them useful in display applications. Due to their size-dependent optoelectronic properties, perovskite QDs are particularly useful in the synthesis of multi-color light-emitting materials. In a work published in *Nature*, Yuan and Chen's group from Nankai University and Sargent's group from University of Toronto [6] demonstrated a new synthesis protocol for the synthesis of ultra-small $CsPbBr_3$ QDs with sizes of 3–5 nm (whereas the Bohr exciton diameter of $CsPbBr_3$ is 7 nm) [4,7]. In previous attempts, it has been challenging to synthesize and assemble these sub-5-nm QDs via the traditional colloidal synthesis followed by ligand exchange [8]. In many cases, the ligand exchange and purification procedure induces Ostwald ripening which widens and redshifts the emission wavelengths of the QDs [7,9]. In 2020, it was demonstrated the use of chelating agents to control the size distribution of $CsPbBr_3$ quantum well (QW), which were able to synthesize blue LEDs with CIE coordinates of (0.12, 0.14) and an EQE of 6.3% [10]. However, the EQE of blue $CsPbBr_3$ PeLEDs remains much lower than those of green and red counterparts that can achieve to 20% [11].

In this recent study, Yuan and co-workers [6] combined the perovskite synthesis and film fabrication into one step and implemented synthesis-on-substrate (SoS) of device-compatible QD films via ligand engineering. To prepare the perovskite films, they first mixed $PbBr_2$ and CsBr with different ligands in dimethyl sulfoxide (DMSO) to create a precursor solution. Then, they used a single-step spin-coating process to deposit the perovskite films onto the desired substrate (Fig. 1a). Interestingly, the structural characterization of the films with the MBA^+ (α-methyl-benzyl-ammonium) ligands confirmed bulk $CsPbBr_3$—rather than layered structure observed in phenylethyl ammonium (PEA^+) system. They further observed that employing halide-substituted α-methyl-4-bromide-benzylammonium (Br-MBA^+) ligand deliveried quantum confinement of $CsPbBr_3$ QDs, and the emission of the QDs film shifted to higher energies as the increased of Br-MBA^+ concentration (Fig. 1b). They achieved a maximum film bandgap of 2.68 eV, well above the $CsPbBr_3$ bandgap of 2.37 eV [12]. The QDs films also demonstrated continuous-tunable PL wavelength with steps as fine as approximately 2 nm.

They also used density functional theory (DFT) calculations to exposit the binding energy and the confinement difference in different ligand adsorption models. They have considered the cases of the single and multiple ligand adsorption. The halide-substituted X-MBA^+ (X = F, Cl, Br, I) ligands exhibited higher binding energy compared to the MBA^+, indicating more robust binding ability. They further defined the adsorption barrier (ΔE_b) as the binding energy difference between single- and multiple-adsorption modes. They found that Cl, Br, and I-substituted MBA^+ ligands displayed lower ΔE_b for full adsorption compared with F-MBA^+ ligands, thus facilitating multiple-adsorption and devoting small-size QDs formation. As an example, the Br-MBA^+ based QD films showed an emission peak at 463 nm, reaching the maximum band gap.

The synthesized perovskite QDs were used to fabricate pure blue PeLEDs with a wavelength of 480 nm or less and a CIE

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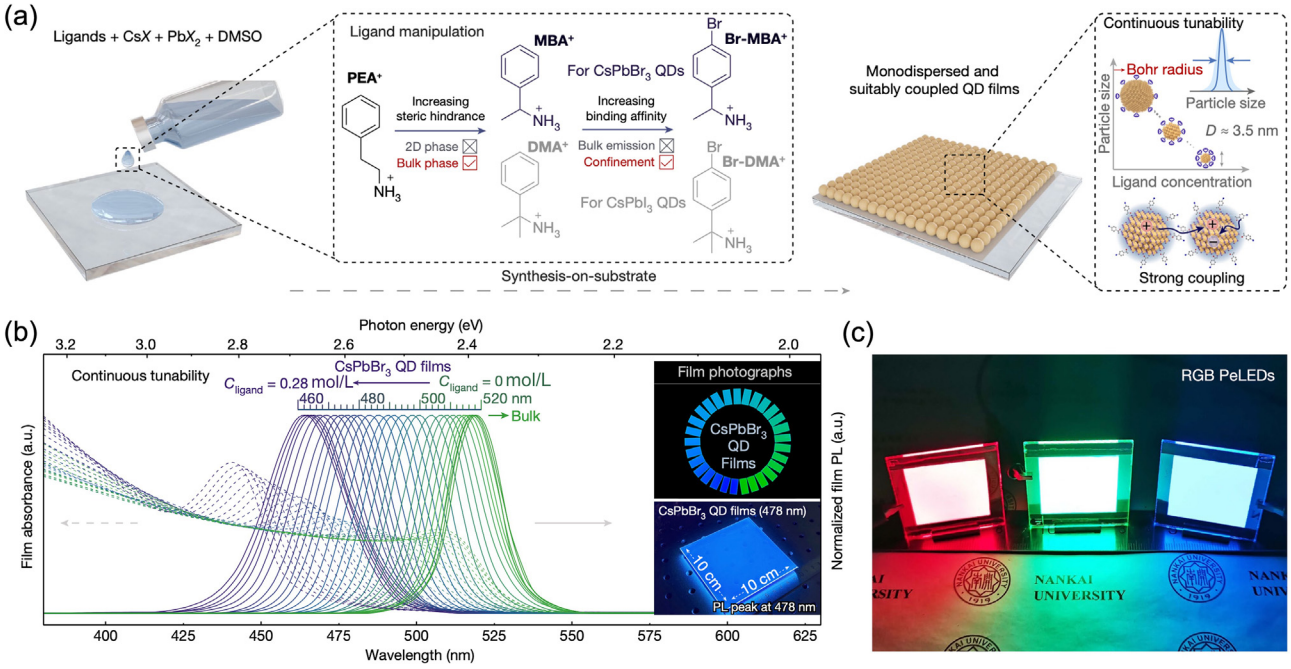

Fig. 1. (a) Illustration of the approach for preparing the perovskite films. *D*, diameter. (b) The photoluminescence (PL) and absorption spectra of $CsPbBr_3$ QDs films were measured with varying concentrations of ligands, C_{ligand}, from 0 to 0.28 mol/L. Inset photographs of the QDs films were taken under excitation. (c) A photograph was taken of red–green–blue (RGB) perovskite LEDs with different QDs films. Reproduced with permission from Ref. [6], Copyright © 2022, Springer Nature.

1931 color space *y*-coordinate value of 0.13 or less. Across all sets of the fabricated LEDs, they were able to demonstrate a maximum EQE of 17.9%. The electroluminescence (EL) peak was observed at 478 nm with a full-width half-maximum (FWHM) of approximately 23 nm, which corresponds to the CIE color-space coordinate of (0.11, 0.13). They also fabricated deep-blue, green, and red PeLEDs with corresponding wavelengths of 465, 515, and 679 nm, respectively. These PeLEDs demonstrated high EQEs of 10.3%, 21.6%, and 20.8%, respectively. Additionally, they constructed devices composed of red, green, blue-emitting PeLEDs as representatives of commercial devices with active areas of (3×3) cm^2 (Fig. 1c); for these devices, the authors claimed that they were able to achieve good uniformity in film thickness, roughness, and optical properties—suggesting the ability to scale these devices for commercial applications.

Overall, Yuan and co-workers reported a solid-state synthesis of films (which they termed as SoS) based on suitably coupled, monodispersed, ultra-small perovskite QDs. This new approach endowed high color-purity films and high-efficient LED devices. They reported fabricating blue PeLEDs with the external quantum efficiencies of 17.9% at 480 nm and 10.3% at 465 nm. The results stand for the highest values among state-of-the-art perovskite-based blue LEDs. Furthermore, the proposed synthesis strategy could guide the development of more efficient, spectrally stable, blue LEDs. Researchers could consider using this direct SoS approach to tune the EQEs of other ultra-small perovskite QDs systems. Moreover, challenges may remain to be addressed in future works. At first, the stability of perovskite materials needs to be tested to determine their device lifetime and sensitivity to high temperatures, as well as ambient humidity and oxygen [13]. Additionally, to meet the regulations in the European Union regarding the use of lead in consumer devices, the content of lead in PeLEDs needs to be reduced, which is currently under investigation [14]. Overall, further research and development are necessary to optimize the performance and stability of perovskite QD-based devices for practical applications.

Conflict of interest

The authors declare that they have no conflict of interest.

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