Monodispersed perovskite quantum wells for efficient LEDs

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The ability to fabricate monodisperse reduced-dimensional perovskite (RDP) films would enable researchers to further understand and apply RDP films in various optoelectronic applications. Nature recently published a study by Ma et al. where monodisperse RDP was fabricated using a bifunctional molecular additive. The monodisperse-RDP-based LED achieved an external quantum efficiency of 25.6% with an exceptional half-life at an initial luminance of 7,200 cd m⁻².

Reduced-dimensional (two-dimensional [2D] and quasi-2D) metal halide perovskites have emerged as promising materials for stable and highly efficient light-emitting diodes (LEDs). This crystal system is generally formulated as $\text{La}_{n-1}\text{M}_n\text{X}_{3n+1}$, where L is a large-size organic spacer cation such as phenylethylammonium (PEA), naphthylmethylammonium (NMA), or butylammonium (BA); A is a small cation, such as Cs, methylammonium (MA), or formamidinium (FA); M represents a divalent metal cation such as Pb or Sn; X is a halide anion (Cl, Br, or I); and n stands for the number of $\text{MX}_3$ sheets, which form a “quantum well” (QW) sandwiched between the organic barriers.1 Generally, the resultant excitons are trapped within the inorganic slabs of quasi-2D perovskites, which exhibit a QW structure. However, the dielectric constant mismatch between the inorganic well and the surrounding organic ligands results in dielectric confinement. Consequently, the dielectric confinement in quasi-2D perovskite further reinforces exciton binding energy ($E_b$).2 In addition, the organic insulating layers spatially restrict charges, thus reducing exciton dissociation and increasing radiative recombination in perovskite films. However, quasi-2D perovskite materials exhibit a low emission efficiency owing to the presence of a mixture of phases with different n values. Therefore, it is essential to carefully control the composition/phases of quasi-2D perovskites to achieve efficient emission. Furthermore, compared to their three-dimensional (3D) counterparts, solution-processed quasi-2D perovskite thin films exhibit smaller crystals. This results in a higher concentration of defects and traps on the film surface and grain boundaries, which function as non-radiative recombination sites, thus reducing the emission efficiency.3

Lewis bases with a lone pair, such as phosphine oxide (p = O), carbonyl (C = O), carboxyl (–COOH), and amine (–NH₂), are frequently used to minimize the density of lead defects. Furthermore, ammonium-containing Lewis acids can establish strong hydrogen bonds with halide ions, thus enabling the passivation of the halide anions of the $\text{PbX}_3$octahedral.4 Phosphine oxide compounds are well-known additives for increasing the photoluminescence quantum yield (PLQY) of perovskite nanocrystals.5 The dipolar p = O bond and basic oxygen center of...
these compounds facilitate the interaction between oxygen atom and Pb$^{2+}$ ion, which eliminates the defect density and enhances the perovskite grain size, whereas the hydrophobic octyl alkanes or benzene rings on phosphine oxide protect the geometry of perovskite under moisture. Furthermore, benzene rings with a π-conjugation structure in triphenylphosphine oxide (TPPO) enhance the charge transport properties of perovskites. Yang et al. fabricated TOPO-treated quasi-2D perovskites with an external quantum efficiency (EQE) of 14.36%. Several additives, such as methanesulfonate, L-Norvaline, and γ-aminobutyric acid, have been used to fabricate high-performance LEDs. However, the operating half-life of these LEDs at 1,000 cd m$^{-2}$ is lower than those of inorganic quantum dots and organic LEDs.

Recently, Ma et al. fabricated monodispersed QWs of PEA$_2$Cs$_{1.6}$MA$_{0.4}$Pb$_3$Br$_{10}$ using tris(4-fluorophenyl)phosphine oxide (TFPPO), and the LED fabricated using these QWs exhibited high stability and an EQE of 25.6%. The QWs were fabricated using a typical control process, wherein all the precursor salts were dissolved in a highly polar solvent (dimethyl sulfoxide) and spin-casted, after which an antisolvent (chloroform) was added. This endowed the QWs with polydispersity owing to the fast diffusion of PEA organic cations. Four unique bleach peaks, corresponding to $n = 1$, $n = 3$, $n = 5$, and $n = 5+$ QWs, were observed in the transient absorption (TA) spectra of the control reduced-dimensional perovskites (RDPs). However, the addition of TFPPO dramatically improved the monodispersity of QWs and improved their PLQY (Figure 1B). Furthermore, the TA spectrum of the TFPPO-treated RDPs exhibited a narrower peak at 495 nm, which was dominated by the peak corresponding to $n = 5+$ QWs, and exhibited longer radiative lifetimes than the control RDPs. In addition, the TFPPO-treated RDPs exhibited enhanced photostability than the control RDPs.

Ma et al. fabricated RDPs with two different additives to further understand the roles of fluorine atoms and p = O moiety: tris(4-fluorophenyl)phosphine (TFPP), which contains fluorine but no p = O, and triphenylphosphine (TPP), which contains neither fluorine nor p = O. The TFPP-treated RDPs exhibited narrower TA and photoluminescence spectra than the TPP-treated RDPs, indicating that fluorine enhanced...
the monodispersity of QW. In addition, the TFPPO-treated RDPs exhibited a higher PLQY than the TPP-treated RDPs, indicating that the p = O moiety significantly reduced defect densities by passivating the perovskite grain boundaries. The diffusion and surface passivation mechanisms were explored using $^{31}$P nuclear magnetic resonance, X-ray photoelectron spectroscopy, and Fourier-transform infrared spectroscopy. Furthermore, theoretical calculations were consistent with the increased binding energy in the TFPPO-treated RDPs. TFPPO simultaneously offered two advantages: first, TFPPO enabled the formation process of H...F bonds between the strongly electronegative fluorine atoms and the NH$_3^+$ of the organic cations; and second, it enabled the binding of oxygen with the unsaturated Pb$_2^+$ sites. Thus, it acted as a diffusion controller during the film fabrication and removed the trap states, thus increasing the PLQY.

The formation of low n-QWs in the TFPPO-treated RDPs was confirmed using Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements. The TFPPO-treated RDP film exhibited enhanced isotropic orientation of perovskite layers than the TPP-treated film. The diffraction peaks at $q_{c,c}$ 0.5 Å$^{-1}$ and $q_{c,c}$ 0.8 Å$^{-1}$ that were observed in the GIWAXS spectrum of the RDPs without any additive were absent in the GIWAXS spectra of the TPP-treated and TFPPO-treated RDPs. This demonstrates the suppression of the low-n QWs. These results indicate that the TFPPO-treated film can be used to fabricate highly efficient perovskite LEDs. The authors reported that the TFPPO-treated RDP-based LEDs exhibited an EQE of 25.6% with an initial luminance of 7,200 cd m$^{-2}$, whereas the control and TPP-treated LEDs exhibited EQEs of just 10.7 and 17.6%, respectively. In addition, the TFPPO-treated LEDs exhibited an operating stability with a half-life of 115 min, which is higher than those of previously reported LEDs.

The findings of this study will provide a means for an innovative research direction on the fabrication of monodisperse perovskite films with a PLQY of ~100%. Accordingly, the authors utilized fluorinated phosphine oxide as a bifunctional molecular additive, which not only controlled the diffusion of organic cations but also reduced the trap states, thus enhancing the PLQY. However, the underlying mechanism involved in the formation process of the intermediate phase of perovskite remains unknown. In addition, the effect of other low-polar antisolvents is unknown. Furthermore, the role of two types of A-site cations, such as Cs$^+$ and MA$^+$, is still unclear. Moreover, it is essential to understand the effect of the replacement of MA$^+$ with FA$^+$ (formamidinium) or GA$^+$ (guanidinium) on the EQEs. Kim et al. reported FA$^+$ and GA$^+$-based green-LED with an EQE of 23.4%, which may be further increased by the addition of bipolar additives. In addition, it is essential to investigate the practical application of lead-free RDP-based LEDs. Furthermore, future studies should investigate the further application of bulkier cations and other bifunctional molecular additives for a larger range of RDP perovskites. These enhancements will enable the easy fabrication of various monodisperse RDP films with definite n values for various optoelectronic applications.

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DECLARATION OF INTERESTS

The authors declare no competing interests.