



Strategies of Improving CsPbX₃ Perovskite Quantum Dots Optical Performance

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Specialty section:

This article was submitted to
Semiconducting Materials and
Devices,
a section of the journal
Frontiers in Materials

Received: 30 December 2021

Accepted: 10 February 2022

Published: 01 March 2022

Citation:

Wu Y, Jia R, Xu J, Song L, Liu Y,
Zhang Y, Ullah S and Dai J (2022)
Strategies of Improving CsPbX₃
Perovskite Quantum Dots
Optical Performance.
Front. Mater. 9:845977.
doi: 10.3389/fmats.2022.845977

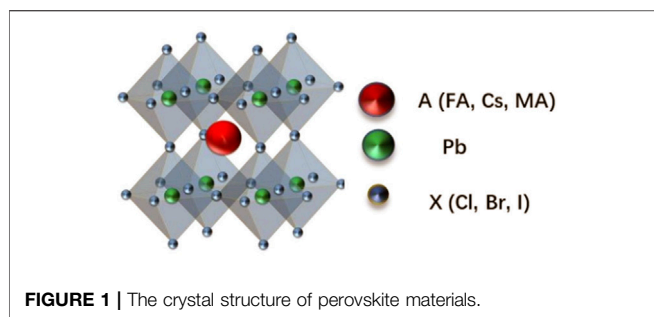
All-inorganic perovskite quantum dots (QDs) (CsPbX₃, X = Cl, Br, I) become promising candidate materials for the new generation of light-emitting diodes for their narrow emission spectrum, high photoluminescence quantum yield, and adjustable emission wavelength. However, the perovskite QDs materials still face instability against moisture, high-temperature, and UV-light. Many strategies have been reported to improve the photoluminescence (PL) performance of QDs while increasing their stability. These strategies can be divided into three main categories: doping engineering, surface ligand modification, coating strategies. This paper reviews the recent research progress of surface ligands, inorganic and polymer coating, and metal ions doping of CsPbX₃ QDs. Partial substitution of Pb²⁺ with non-toxic or low-toxic metal ions can improve the formation energy of the perovskite lattice and reduce its toxicity. The surface polymer modification can use their ligands to bond with the uncoordinated lead and halogen ions on perovskite QDs surface to reduce surface defects, thereby improving the PL intensity and stability. In addition, the organic or inorganic coating materials on perovskite QDs can effectively avoid their contact with the external environment, thereby improving the stability of the perovskite. The optical properties of the modified QDs, including transient absorption spectra, temperature-dependent PL spectra, time-resolved photoluminescence (TRPL) spectra properties, etc. were discussed to explain the physical mechanism. The potential applications of all-inorganic perovskite QDs as down-conversion fluorescent materials in light-emitting diodes are presented. Finally, we provide some possible methods to further improve the PL performance of the all-inorganic perovskite QDs.

Keywords: perovskite, quantum dots, doping, stability, photoluminescence, white light-emitting diodes

INTRODUCTION

Recently, all-inorganic perovskite materials have attracted much attention for their high carrier mobility, high radiation recombination efficiency, high color purity, and tunable bandgap, which are considered promising materials for next-generation light-emitting devices (LED) (Akkerman et al., 2018; Fu et al., 2019; Xu et al., 2020a).

The perovskite materials have the formula of ABX₃, where A generally represents a monovalent organic or metal cation (such as Cs⁺, MA⁺, FA⁺), B often represents a divalent metal cation (typically



Pb^{2+} , Sn^{2+}), and X is a halide anion (typically Cl^- , Br^- , I^-). **Figure 1** shows the regular octahedral perovskite structure. The B site ion is located at the center of the octahedron, and the X site ion is located on the six vertices of the octahedron. The BX_6^- octahedral units are interconnected to form the basic framework of perovskite crystal structure (Abdi-Jalebi et al., 2018). In 2009, perovskite solar cells were reported for the first time, demonstrating that perovskite semiconductor has potential applications in optoelectronic devices. Now power conversion efficiency of the perovskite solar cell has increased to 25.2% in the last years (Kojima et al., 2009; Roy et al., 2020). Since Protesescu et al. (2015) reported all-inorganic metal halide perovskite quantum dots (QDs) in 2015, inorganic perovskite materials have aroused researchers' enthusiasm for their excellent optical properties and low synthesis cost. As a new type of direct bandgap semiconductor material, the all-inorganic metal halide perovskites (CsPbX_3 , X = Cl, Br, I) present some unique advantages as high quantum efficiency, large optical absorption coefficient, narrow emission peak half-width, and tunable luminescence wavelength (Li et al., 2017; Su et al., 2017; Quan et al., 2019). It has broad applications in light-emitting diodes, solar cells, and photodetectors (Wang et al., 2018; Bi et al., 2019a; Huang et al., 2019; Keqiang Chen et al., 2020). Dong et al. (2020) reported that the surface reconstruction of perovskite QDs realized an internal anion bipolar shell and an external composite materials shell with cations and polar solvent molecules. The negatively charged inner layer electrostatically attracts the outer shell, this method not only improved the carrier mobility but also reduced the defect density. In this way, the improved carrier mobility expands the recombination zone, and an active layer that is thinner than the recombination zone width will limit the carrier recombination rate. Stoumpos et al. (2013) used the CsPbBr_3 single-crystal for high-energy radiation detection. Wang et al. (2017) fabricated blue, green, and red VCSELs (vertical cavity surface emitting lasers) by using $\text{CsPb}(\text{Br}/\text{Cl})_3$, CsPbBr_3 , and $\text{CsPb}(\text{I}/\text{Br})_3$ as active materials, which exhibited low threshold, directional output, and good stability. Yi-Xin Chen et al. (2020) also found that the CsPbBr_3 halide perovskite photocatalyst significantly affected the CO_2 reduction performance, achieving a higher reaction rate and long-term stability. Liu et al. (2021) used strained perovskite QDs as nucleation centers to make the film crystallization more uniform and stable. This method reduced gradient crystallization and suppressed halide segregation, leading to the efficient transport of charge carriers, the red

CsPbI_3 QDs films based LED showed external quantum efficiency (EQE) of 18% and remained half of the initial luminance even after 2,400 h working. Fang et al. (2021) achieved a high-performance perovskite green QLED through modulating the charge injection balance with the incorporation of a bilayered electron transport structure, while improving efficiency and operating life, a champion external quantum efficiency (EQE) of 21.63%, representing one of the most efficient perovskite QLEDs so far. All these reports indicate that the all-inorganic perovskite semiconducting material is ideal for optoelectronic device application.

Despite the excellent properties of the perovskite materials, the high sensitivity of CsPbX_3 QDs to the external environment leads to their poor stability, which restricts the commercial application of perovskite (Niu et al., 2015). Hence, it still needs investigation to improve the stability of perovskite QDs. The main strategies for improving the stability of all-inorganic perovskite QDs include doping engineering, surface ligand modification engineering, and surface coating strategies. Ion-doping aims to replace some elements at the A and B sites with equivalent ions (Zou et al., 2017). The A-site doping is helpful to increase the tolerance factor of perovskite material, which thereby improves the stability. The B-site doping method mainly uses the ions with smaller ion radius to substitute Pb^{2+} , which causes a change in the length of the B-X bond, thereby improving its phase stability and also decreasing the amount of toxic Pb^{2+} ions. Surface ligand modification aims to introduce ligands that bind firmly to the uncoordinated lead and halide ions on the QDs surfaces (Noel et al., 2014; Bodnarchuk et al., 2018; Krieg et al., 2018), passivating dangling bonds and defect sites, thus reducing non-radiative channels and enhancing the optical performance. The surface coating method mainly uses transparent wide-bandgap materials to encapsulate and protect the perovskite QDs from the external environment (Liu et al., 2018; Pan et al., 2018; Yajing Chang et al., 2018; Zhang et al., 2018), which dramatically reduces the degradation of QDs, thereby effectively improving their water and oxygen resistances. Meanwhile, it also avoids the reduction of quantum efficiency caused by aggregation and ion exchange effects. After modification, the stability of perovskite QDs is prominently improved, and the photoluminescence quantum yield (PLQY) is also enhanced.

This review focuses on the stability and fluorescence enhancement strategies of all-inorganic CsPbX_3 QDs, primarily describing the aspects of doping engineering, surface ligand modification, and surface coating strategies. In the final section, we summarize the recent research advances and make an outlook about the future development of the perovskite materials.

SYNTHETIC METHODS

For CsPbX_3 (X = Cl, Br, I) QDs, the most commonly used methods are the hot-injection method, room temperature anti-solvent method, and ion exchange method. The hot injection method can synthesize high-performance perovskite

nanomaterials. Protesescu et al. (2015) injected the pre-prepared cesium oleate (Cs-oleate) precursor into dissolved oleic acid (OA), oleylamine (OAm), and octadecene (ODE) under high temperature and nitrogen flow conditions in the PbX_2 solution, and then, the temperature of the reaction was rapidly cooled to room temperature, and the reaction solution was centrifuged to obtain the original perovskite solution. The hot-injection method introduces OA and OAm ligands, which provides the possibility for the subsequent study of ligand modification. In addition, this method facilitates the introduction of ions into the perovskite lattice. Since perovskite QDs materials are ionic crystals, ion migration can take place in the solution. By adding different halogen elements to the perovskite QDs solution prepared by thermal injection and other methods, perovskite QDs with different photoluminescence wavelength ranges can be prepared. Nedelcu et al. (2015) achieved the preparation of perovskite QDs in the entire visible light region by partial or full anion exchange at room temperature. However, mixing different halogens will lead to the phase separation of QDs and reduce photostability.

The room-temperature anti-solvent method mainly uses the principle that the solubility of materials in different solutions is quite different. At room temperature, PbX_2 and CsX are used as material sources and they are dissolved into dimethylformamide (DMF), and then injected into the toluene solution, the solvent is in a highly supersaturated, and a large number of perovskite crystals are precipitated (Pan et al., 2016). This process still requires OA or OAm as a surface ligand to passivate surface defects and enhance the stability of QDs materials. Since the whole experimental process is carried out at room temperature, the preparation method is very simple and low-cost. However, the uniformity of the perovskite QDs obtained by this method is not very good.

DOPING ENGINEERING

The typical formula of all-inorganic perovskite QDs material is ABX_3 . Doping with different elements can adjust the phase transition temperature, optical bandgap, and luminescence performance, reduce the nonradiative recombination rate, and improve the PLQY and LED performance (Zhou et al., 2015; Xu et al., 2019).

The phase structure of the perovskite QDs ABX_3 can change among cubic, tetragonal and orthorhombic phases (Wasylishen et al., 1985) through various doping methods. In the ABX_3 structure, the radii of the A, B, and X-site ions determine the Goldschmidt tolerance factor (t) (Travis et al., 2016):

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

where r_A , r_B , and r_X are the ionic radii for the components A, B, and X atoms. For most three-dimensional perovskite materials, a more stable perovskite phase structure can be formed when the t value is between 0.8 and 1. Other cations can be doped in the perovskite if their radii are similar to those of the A sites and B sites cation elements. The photoluminescence (PL) intensity and

stability of perovskite QDs can be improved effectively by doping a small amount of cations at the A and B sites.

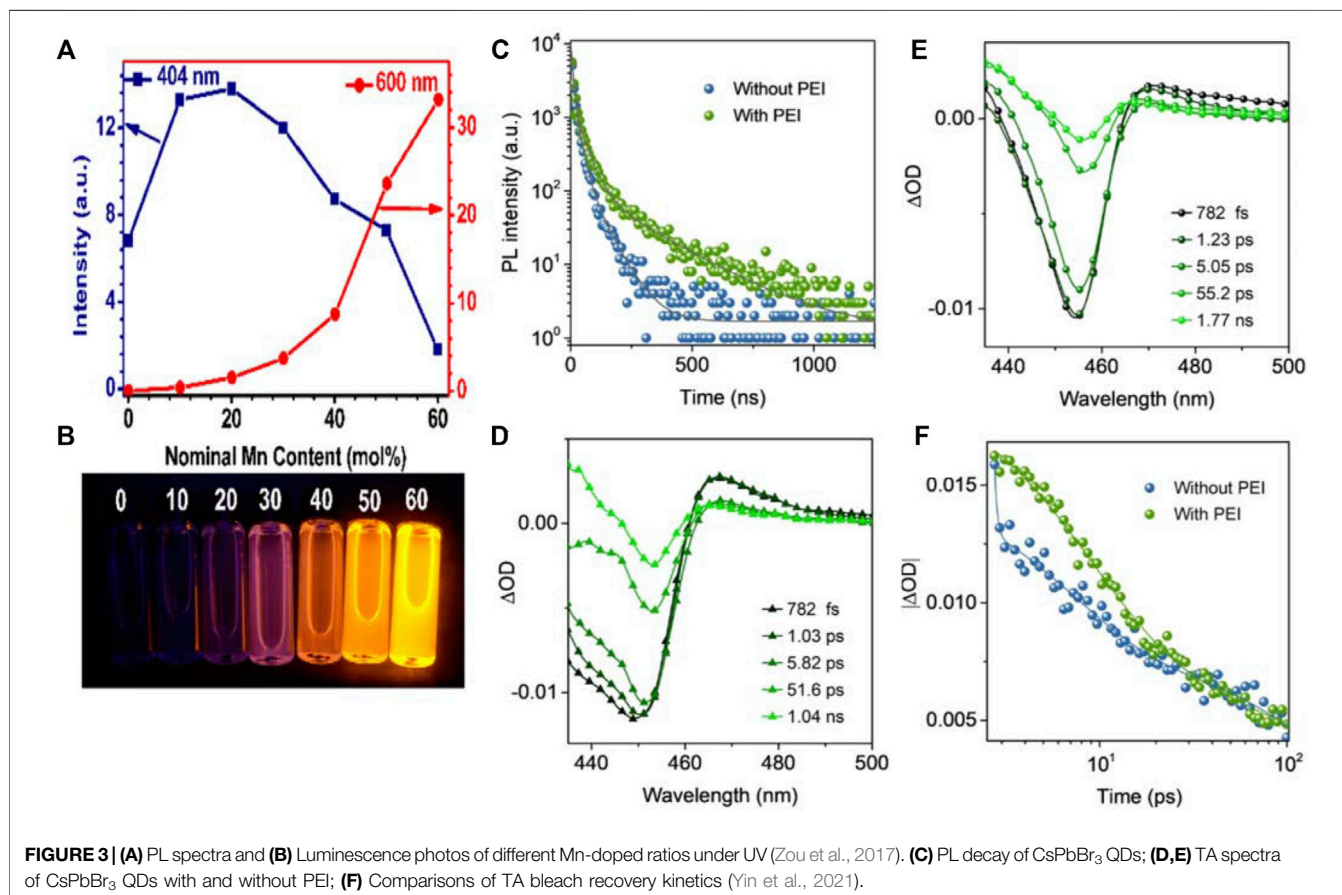
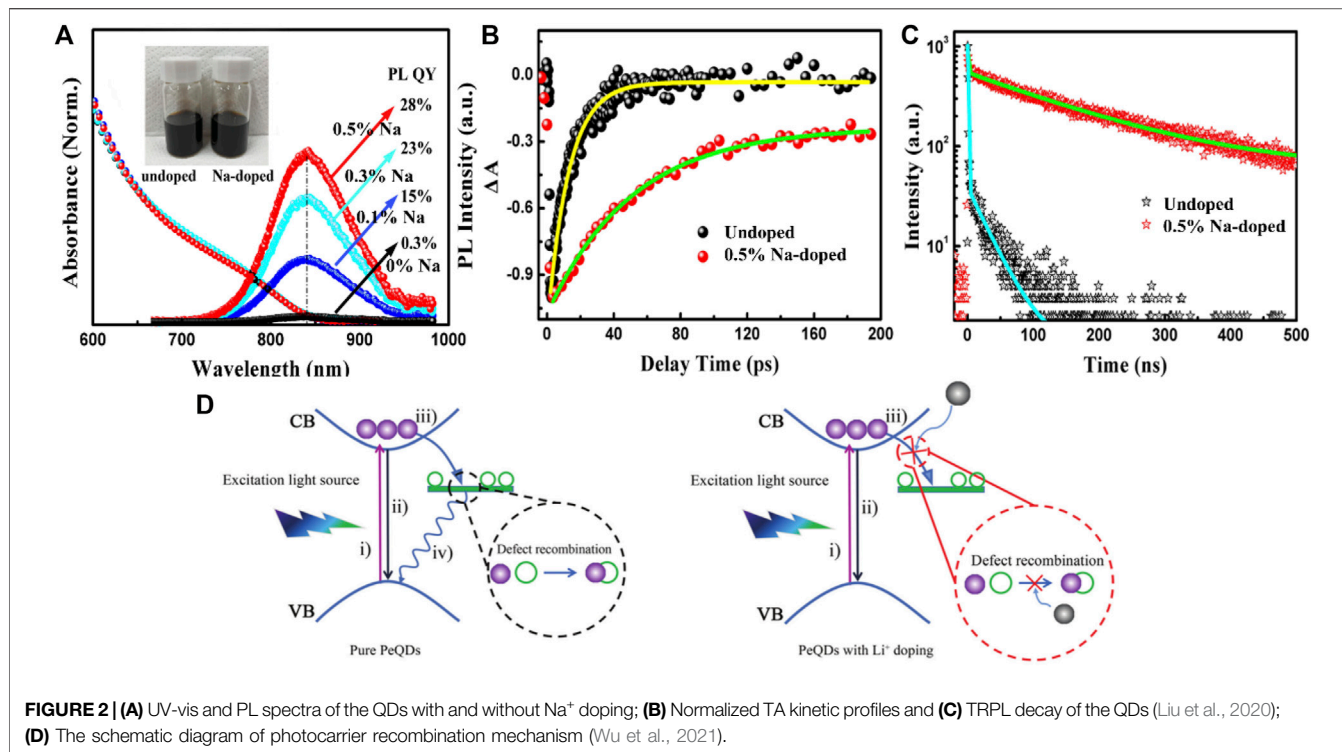
A-Site Doping

Generally, the A-site element of perovskite QDs materials is Cs^+ . Cs^+ ion has similar properties to other alkali metal ions. A strategy for improving the perovskite QDs performance and stability is to replace a small part of Cs^+ in CsPbX_3 with other alkali metal cations.

Liu et al. (2020) doped Na^+ into $\text{CsSn}_x\text{Pb}_{1-x}\text{I}_3$ QDs. The Na^+ doping can effectively inhibit the formation of I^- vacancy defects. The result of XPS demonstrated that the change of binding energy caused by Na^+ doping is noticeable for Cs^+ and I^- . With the incorporation of Na^+ , the chemical bond between Sn^{2+} and I^- ions is enhanced, the diffusion and dissociation of Sn^{2+} and I^- ions are reduced, and the formation of harmful Sn^{4+} and I^- vacancy defects is reduced. **Figure 2A** shows the PL spectra of the perovskite QDs without and with Na doping, Na^+ doping causes the band-edge recombination of perovskite QDs to be significantly enhanced, and the increase of Na concentration leads to stronger near-infrared PL emission. When the Na content is 0.5%, the PLQY can reach 28%. As shown in **Figures 2B,C**, the transient absorption (TA) spectrum and time-resolved photoluminescence (TRPL) spectrum show that the PL lifetime of Na-doped perovskite QDs is significantly longer. Wu et al. (2021) prepared Li^+ -doped CsPbBr_3 and CsPbI_3 QDs and explored their effects on the nonradiative and radiative recombination processes. Doping with the proper concentration of Li^+ could passivate halide vacancies and defects to reduce the nonradiative recombination and improve the phase stability caused by halide migration. Todorović et al. (2019) synthesized stable blue perovskite QDs by incorporating Rb^+ into the A-site of CsPbBr_3 nanocrystals. The Rb^+ can lead to tilting of $[\text{PbX}_6]^{4-}$ octahedral structure, reduce the overall overlap of orbitals and widen the bandgap of CsPbBr_3 , so that QDs exhibit high PLQY (>60%) and tunable stable PL performance. A possible photocarrier recombination process model is shown in **Figure 2D**. The free electrons from Li^+ can passivate the traps, so the trapping of the excited electrons is suppressed, leading to enhanced radiative recombination.

B-Site Doping

For CsPbX_3 , B-site doping is a widely accepted effective method, enhancing the QDs' stability and inducing some novel optical properties (Ming Liu et al., 2017; Swarnkar et al., 2018; Yang et al., 2018). Sn^{2+} , Zn^{2+} , Mn^{2+} and lanthanide ions (e.g., Ce^{3+} , Tb^{3+} , Eu^{3+}) have been reported as B-site doping elements in the CsPbX_3 QDs. Among these B-site doping elements, the Mn-doped perovskite attracts more attention for its effective bright yellow-orange emission for the white light emission device. Zou et al. (2017) developed a thermal injection Mn^{2+} doping strategy to improve the stability and PL intensity. After 120-days exposure of $\text{CsPbBr}_3:\text{Mn}$ QDs to the air, 60% of the initial fluorescence intensity can be maintained. Zou et al. (2017) synthesized $\text{CsPbCl}_3:\text{Mn}$ QDs with controllable size and shape by adjusting the ratio between Mn and Pb via a one-step



ultrasonic approach. As shown in **Figures 3A,B**, With the increase of Mn^{2+} doping concentration, the intensity of Mn^{2+} ions broadband emission band at 600 nm increases gradually, which is obviously different from the exciton emission behavior of $\text{CsPbCl}_3:\text{Mn}$ QDs (404 nm). The intensity of exciton emission peak from $\text{CsPbCl}_3:\text{Mn}$ QDs increases firstly and then decreases. This change produces an overall color output change from blue to orange. Due to surface defects' passivation, the quantum yield can be up to 78% (Parobek et al., 2016) theoretically explained the reason why Mn-doped can improve perovskite PL performance. Under the excitation of CsPbX_3 band-edge exciton recombination emission, the d-d transition of Mn^{2+} ions generated strong luminescence originating from the strong exchange coupling between the host charge carriers and the d electrons in the doped Mn^{2+} ions.

Song's group found that B-site Zn^{2+} doping in the CsPbCl_3 QDs can increase the PLQY to 120% (Li et al., 2020). The EQE of prepared $\text{CsPbCl}_3:\text{Zn}$ QLED devices can be doubled. Deng et al. (2020) fabricated $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ QDs with the PLQY of 91% at room temperature due to the improvement of QDs lattices. The PL intensity increased obviously in $\text{CsPb}_{0.9}\text{Sn}_{0.1}\text{Br}_3$ QDs, and with the increase of Sn-doped, the average PL lifetimes decreased rapidly. Bi et al. (2019b) doped Cu^{2+} into the perovskite lattices to enhance the intrinsic blue exciton emission of $\text{CsPb}_{1-x}\text{Cu}_x(\text{Cl}/\text{Br})_3$ QDs, the smaller Cu^{2+} ions caused lattice shrinkage and thus can eliminate the halide vacancy, which led to increased lattice formation energy and improved short-range order of doping, so that the stability of QDs were improved. A certain proportion of Cu-doped could significantly improve PLQYs, which is associated with the improvement of short-range order and the decrease of lattice vacancies. Through *in-situ* lanthanide cations doping, Shi et al. (2019) synthesized $\text{CsPbI}_3:\text{Yb}^{3+}$ where the surface defects and lattice trap states can be reduced. The CsPbCl_3 QDs with La^{3+} and F^- co-doping were reported with a high PLQY (36.5%) (Zhai et al., 2019), which showed the PL intensity is much higher than undoped pure CsPbCl_3 QDs. Partial cationic doping can effectively improve the PL stability of CsPbX_3 QDs, which is also a hotspot of current research.

Advantages and Disadvantages of Ion Doping

Doping engineering introduces impurity atoms into targeted lattices for efficient modulation of semiconductor optoelectronic properties. The A-site atom has a great influence on the structure and stability of QDs. By changing the size of the A-site doping elements, chemical pressure can be applied to the perovskite octahedral framework structure, and this chemical pressure will cause the octahedral structure to tilt, the central cation shift, etc., and induces some novel optoelectronic properties (Lin et al., 2016). Considering the valence state distribution of the perovskite lattice, the A-site doping ions mostly use monovalent cations, because alkali metals (Li^+ , Na^+ , K^+ , Rb^+) have strong oxidation resistance, they are regarded as the ideal A-site doping ions. Doping some ions with smaller radii may cause lattice shrinkage, thereby reducing the perovskite QDs formation energy and

greatly improving the stability and optical intensity. The B-site has a large contribution to the conduction band of QDs (Li et al., 2016), which mainly affects the optoelectronic properties of the material. The doping strategy of the B-site can reduce the lead content to a certain extent, which is very important for QDs. Commonly used doping ions are Eu^{3+} , Bi^{3+} , Zn^{2+} , Fe^{2+} , Sn^{2+} , Mn^{2+} , and so on. B-site doping is of great significance for reducing the lead content of lead-halide perovskite QDs, providing new energy levels, and reducing surface defects, and has become one of the important feasible schemes for the preparation of efficient and stable perovskite devices.

However, the ion doping method has a relatively limited improvement in the stability of QDs, and the distribution of doped elements into the perovskite structure is difficult to precisely adjust. Excessive or too few doping elements will cause the degradation of optical performance. How to precisely control the quantitative doping of elements is a problem to be solved.

SURFACE LIGAND MODIFICATION

Perovskite QDs' fluorescence is generated by exciton recombination. However, the intrinsic large surface-volume ratio of the perovskite QDs leads to many atomic dangling bonds and substantial defects on their surface. These defects will trap the electrons from the conduction band, causing nonradiative recombination and decreasing the PLQY. During the synthesis reaction of QDs, some ligands can be introduced to bond with the uncoordinated lead and halogen ions on the QDs surfaces to reduce surface defects, thereby improving the PL intensity and stability. Hence, the ligand modification of QDs is also widespread for improving the photoelectric performance of perovskite QDs.

OA and OAm Ligands

In 2015, Kovalenko's group used a pair of oleic acid (OA) and oleylamine (OAm) ligands to form the coordination bond between Pb^{2+} and carboxylate, as well as the hydrogen bond between halogen and protonated amine to modify the QDs surfaces and enhance their stability (Protesescu et al., 2015). Since then, the OA and OAm ligands have been widely used to synthesize CsPbX_3 QDs. However, OA and OAm are prone to protons exchange and detachments during purification and storage, causing aggregation and destabilization of QDs. Besides, excessive OAm also disaggregates the CsPbX_3 QDs into PbX_2 , thereby quenching their fluorescence (Zeke Liu et al., 2017; Yangning Zhang et al., 2019). To achieve better passivation, short-chain ligands were found to bind more firmly to the QDs surfaces during the synthesis reaction to achieve better passivation. Common ligand alternatives can be classified into Lewis acids, Lewis bases, and multidentate ligands depending on covalent bonds.

Lewis Base Ligands

The Lewis base can provide a pair of non-bonding electrons to bond with Pb^{2+} , thereby eliminating the defects on the CsPbX_3

QD surfaces. Using tri-*n*-octyl phosphine oxide (TOPO) as ligands, Wu et al. (2017) synthesized CsPbBr₃-TOPO QDs with adjustable size, whose fluorescence intensity decreased by only 5% after a 2-h treatment with a polar solvent, suggesting that the incorporation of TOPO ligands could remarkably improve the stability of perovskite QDs. After treatment with polar solvent ethanol, the PL intensity of CsPbX₃ was significantly reduced, in contrast, the PL intensity of CsPbX₃-TOPO was basically unchanged after treatment with ethanol at different times. Tan et al. (2018) obtained stable CsPbBr₃-OPA QDs, exploiting the strong interaction between *n*-octyl phosphonic acid (OPA) and Pb²⁺, which not only maintained a considerably high PLQY (>90%), but also achieved high-quality dispersion in the solvent after multiple purifications, and its LEDs devices present an EQE of 6.5%.

Lewis Acids Ligands

The Lewis acids can bond with the uncoordinated halides on QDs surfaces, thereby decreasing the surface defect state of CsPbX₃ QDs. Yang et al. (2019) used Dodecyl benzene sulfonic acid (DBSA) to eliminate halogen vacancy defects on the QDs surfaces. In contrast, the QDs prepared with either OAm or OA exhibited a severe decrease in the PLQY with increased washing time in ethanol. In addition, the TRPL lifetime under various washing times is almost the same for the CsPbX₃ QDs with DBSA ligands, indicating a strong interaction between sulfonate groups and lead ions. Feng Liu et al. (2017) used Tri-*n*-octyl phosphine (TOP) ligands to obtain CsPbI₃-TOP QDs, whose quantum efficiency is approximately 100% and still can be 85% after 1 month. The chemical stability of CsPbI₃ QDs has been tremendously enhanced.

Multidentate Ligands

Multidentate ligands have at least two coordinating atoms in a ligand, with a stronger binding force with CsPbX₃ QDs. Pan et al. (2017) passivated CsPbI₃ QDs using 2, 2'-iminodibenzoic acid (IDA), a short-chain bidentate ligand that bound tightly to the PbI₂-rich surfaces through dicarboxylic groups, thereby reducing surface defects while injecting additional electrons into QDs. Compared to the conventional long-chain OAm and OA ligands, they featured stronger conductivity and carrier transport capacity. Additionally, the CsPbI₃-IDA QDs retained 90% of the initial luminescence peak after 15 days, exhibiting tremendously improved stability than the QDs without IDA treatment. Yin et al. (2021) used polyethyleneimine (PEI), a multidentate ligand rich in amine-based polymers on the branches, to stabilize and enhance the blue light emission of CsPbBr₃ nanosheets. PEI effectively prevented the aggregation of CsPbBr₃ nanosheets and reduced the vacancy defect density of bromide ions through the interaction between the electrons in its alkylamine group and the PbBr₆ octahedrons. CsPbBr₃ nanosheets show short-term transient absorption on the low energy side (Figure 3D), which is not as strong as the CsPbBr₃ with PEI (Figure 3E), and the bleach minimum of CsPbBr₃ nanosheets lies to a higher energy than the CsPbBr₃ with PEI. In addition, the bleaching recovery kinetics and TRPL spectra of CsPbBr₃ nanosheets with PEI are much slower

(Figures 3C–F), which indicates the elimination speed of excitons is much slower for the CsPbBr₃ with PEI ligands.

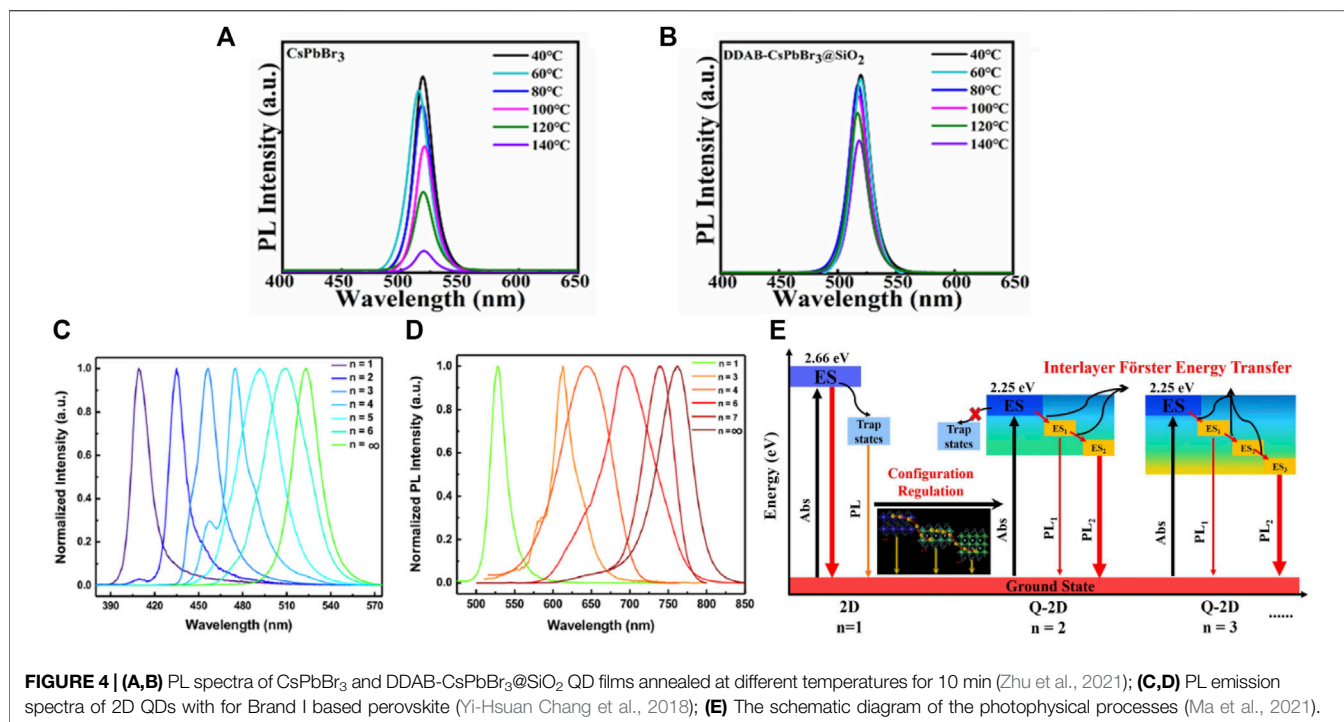
Ligand Exchange Strategies

Except for the above three types of surface ligand modifications, researchers have proposed ligand exchange strategies to improve the stability of CsPbX₃ QDs. Zhu et al. (2021) were exchanged the OAm and OA ligands with the Dodecyl dimethyl ammonium bromide (DDAB) to synthesize CsPbBr₃ QDs. The shorter-chain ligand DDAB replaced the OA and OAm and then anchored onto the surfaces of CsPbX₃ QDs. DDAB had a stronger binding force with the QD surfaces than the long-chain ligands as a short-chain ligand. Owing to the DDAB large branched structure and a strong affinity with X site elements (Br⁻) in the perovskite QDs, DDA⁺ cations could effectively passivate the surface defect state of CsPbX₃ QDs, resulting in narrow FWHM and high PLQY. As shown in Figures 4A,B, the thermal stability of DDAB-CsPbX₃ QDs was significantly improved, which was attributed to the synergistic effect between the large steric hindrance of DDAB and the SiO₂ core-shell protection. Bin-Bin Zhang et al. (2019) used thionyl halides (SOCl₂, SOBr₂) as the passivator of CsPbCl₃ instead of OAm and OA ligands. The thionyl halides take a well-controlled mild reaction with the carboxyl and amine groups on the QDs surfaces, which could easily achieve ligand exchange. After modification, a blue LED with an FWHM of only 14.6 nm was obtained, whose EQE was 1.35%.

Two-Dimensional Perovskite Ligands

In addition, two-dimensional (2D) Ruddlesden-Popper perovskite materials can be formed by inserting different kinds of large organic cations into the A sites of three-dimensional perovskite ABX₃. The general chemical formula of this layered perovskite structure is L₂(APbX₃)_{n-1}PbX₄, where L is the large organic cation (phenylethylamine (PEA⁺), butylammonium (BA⁺)) that acts as a barrier spacer between different layers, and *n* represents the layer number of [BX₆]⁴⁻ octahedron sandwiched between the organic spacer layers. In the synthesis process, the *n* value is generally controlled by adjusting the L-site and A-site cations ratio. Compared with three-dimensional perovskite, due to the strong dielectric and quantum confinement effects, quasi-2D perovskite materials have excellent optical properties, including large exciton binding energy and better stability against light and moisture. The corresponding colloidal perovskite nanocrystals show great potential for LEDs and other optoelectronic applications.

By introducing large cation BA⁺, Yi-Hsuan Chang et al. (2018) synthesized quasi-2D (BA)₂(MA)_{n-1}Pb_nX_{3n+1} QDs using ligand-assisted reprecipitation method and obtained a PL quantum yield as high as 48.6% by adjusting the *n* value (Figures 4C,D). The introduction of BA⁺ improves the optical stability of QDs, thereby reducing non-radiative recombination decay originating from electron-phonon coupling and increasing PL lifetime, promoting the application of durable solution-processed perovskite materials in the photoelectric field. Ma et al. (2021) introduced PEA⁺ cations to regulate the dimension of perovskite and obtained *n* = 1–3 quasi-2D perovskite (PEA)₂Cs_{n-1}Pb_nBr_{3n+1} nanocrystals with different



thicknesses. The results of the transient absorption spectrum show that most of the free excitons in quasi-2D perovskite nanocrystals can be transferred from the highly-excited state to the lowest excited state through interlayer Förster energy transfer, and then the occurrence of radiative recombination results in the redshift. As shown in **Figure 4E**, for Quasi-2D QDs, most free excitons can be transferred from the excited state (ES) to the lowest ES at higher-dimensionality perovskites by interlayer Förster energy transfer (ES → ES₁ → ES₂ → ES₃), and then realize radiative recombination, which could cause the electronic spectral redshift during the energy transfer process. In addition, the $n = 2-3$ nanocrystal solution has excellent UV light stability and great environmental stability. With the decrease of n value, the grain size decreases continuously, and the effect of quantum confinement effect becomes more significant, which increases the bandgap and makes the PL spectrum and absorption spectrum blueshift. Deng et al. (2019) synthesized ultrathin single-crystalline (PEA)₂PbBr₄ nanoplates by completely replacing A cation with PEA⁺ cation. The nanoplate-based films synthesized by an electric-field-deposition method exhibit PL emission at 410 nm with a narrow FWHM of 10.6 nm and high stability in high humidity (60%) environment. Temperature-dependent PL spectroscopy showed that (PEA)₂PbBr₄ nanoplates exhibited ultrahigh exciton binding energy (398.7 meV), which significantly reduced the probability of non-radiative recombination. Finally, the deep-blue LED devices were prepared based on (PEA)₂PbBr₄ nanoplates, which have bright luminescence and high stability under continuous operation. It can be used as an excitation light source for the construction of white light LEDs,

showing great application potential in the fields of optical communication and display lighting.

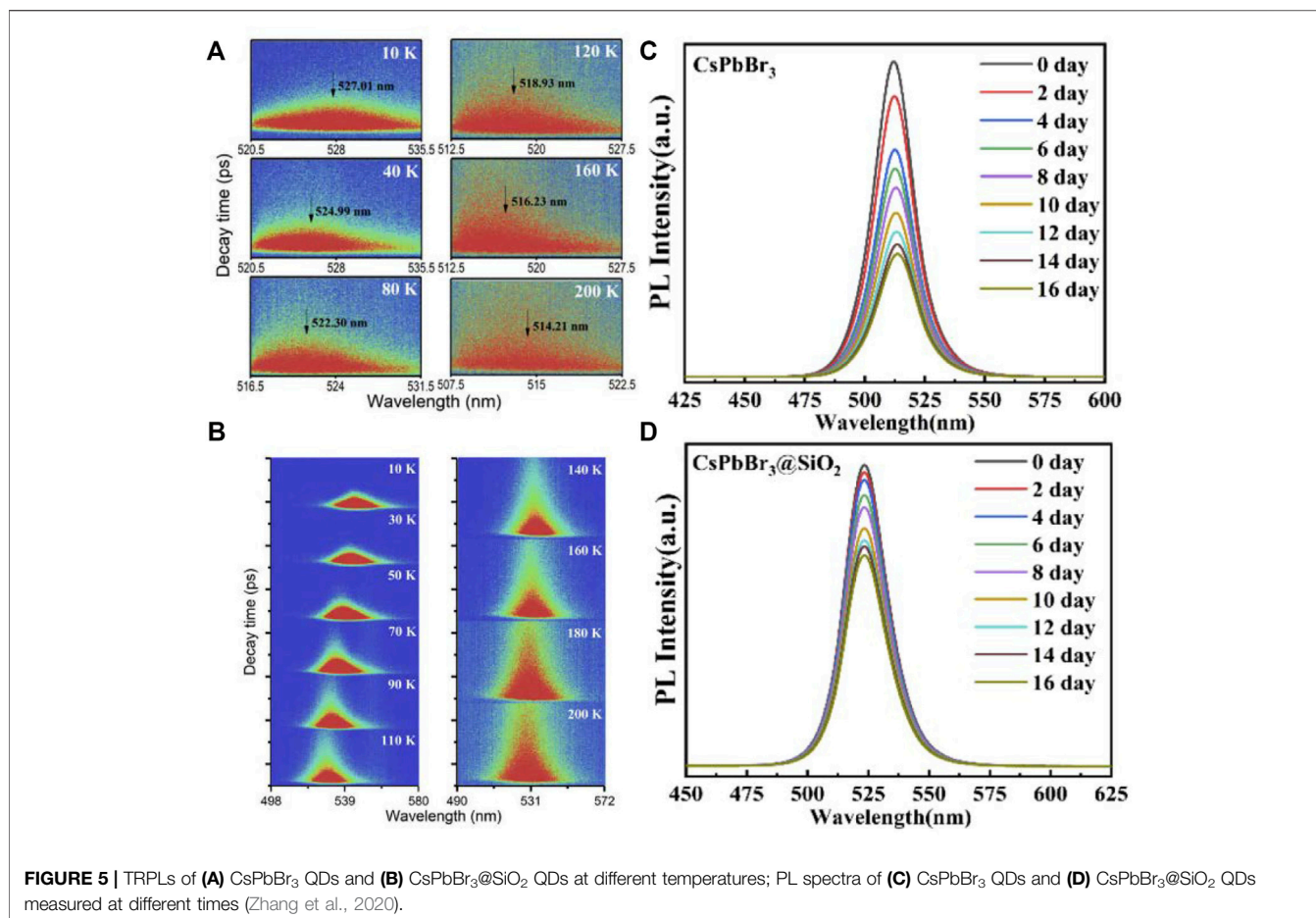
The surface ligand modifications for improving the stability of perovskite QDs mainly inhibit the shedding of their surface ligands, so that their non-radiative transitions and surface defects could be reduced. More importantly, short-chain ligands would not excessively impact the electrical conductivity of QDs, thus allowing more comprehensive application of the perovskite QDs in optoelectronic devices.

SURFACE COATING

Although the all-inorganic lead halide perovskite QDs exhibited unique advantages in the luminescence field, their poor stability and easy dissolution in polar solvents are unavoidable shortcomings. So, the surface coating strategy for improving their stability is widely investigated. Surface coating of CsPbX₃ QDs with appropriate materials can avoid direct contact with moisture, light, and oxygen and reduce the Pb diffusion to the environment. The coating materials can be inorganic or polymer materials (Loiudice et al., 2017; Zhang et al., 2017; Park et al., 2018; Bhattacharyya et al., 2019; Gao et al., 2021).

Inorganic Material Coating

Silica is a nontoxic, transparent optical material and can protect the perovskite QDs from the external environment without changing their original luminous properties. Tang's group encapsulated the CsPbBr₃ QDs with silica and effectively increased the humidity and thermal stability (Tang et al., 2019). Researchers found that the silicon shells could

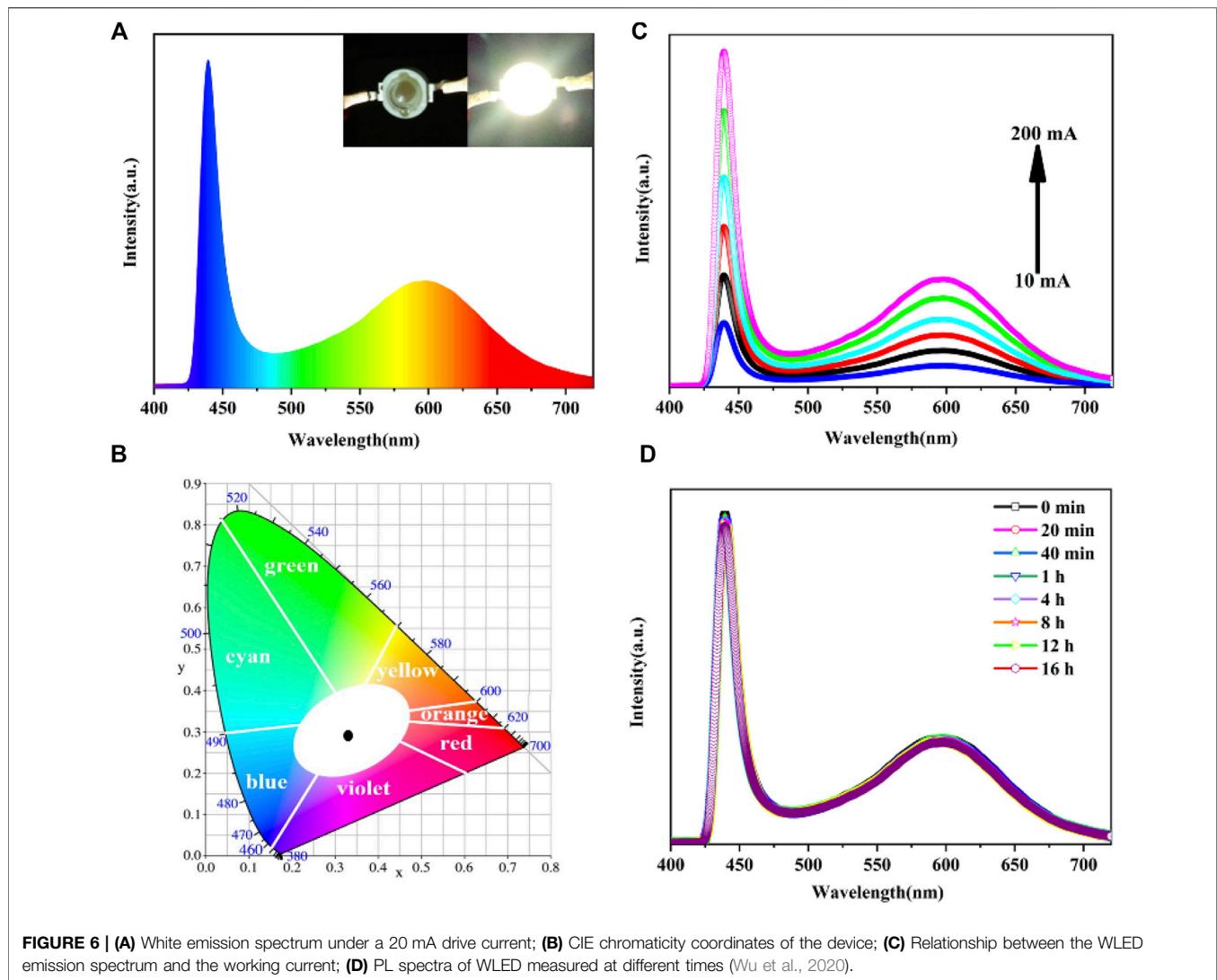


terminate the anion exchange when the silica-coated perovskite QDs with different halide elements (Sun et al., 2016).

Currently, tetraethyl orthosilicate (TEOS) is the most common silicon source. Gao et al. (2021) prepared CsPbBr₃@SiO₂ QDs using TEOS as the silicon source and hydrophobic TOPO as the inhibitor, whose PLQY reached 87% compared to the pristine QDs, thereby prominently improving the stability. However, coating with the TEOS silicon source required a harsh alkaline environment, and the QDs were prone to quenching. Hence, the particle powder silicon sources were tried. Wang et al. (2016) utilized mesoporous silica as the silicon source and fabricated mesoporous perovskite QDs nanocomposites. In the presence of water vapor, (3-aminopropyl) triethoxysilane (APTES) can be hydrolyzed into SiO₂, which can also be used as a silicon source. Cao et al. (2020) prepared QDs@SiO₂ composite using APTES as the silicon source instead of TEOS, which can maintain about 95% initial PL intensity after 30 days of storage in the air or 96 h of exposure to ultraviolet light. Additionally, tetramethoxysilane (TMOS) is also an excellent precursor alternative. Further, He et al. (2018) reported SiO₂/Al₂O₃-coated perovskite QDs to realize highly-luminescent and ultra-stable Mn-doped CsPbCl₃ QDs, where nonpolar hexane solvent was used to prevent the polymer solvent effect. Compared to uncoated CsPbCl₃ QDs, SiO₂/Al₂O₃-coated samples exhibited

stronger photostability under blue light radiation. This was attributed to the effective protection of dense SiO₂ and Al₂O₃ layers, which prevent erosion by oxygen and moisture.

Zhang et al. (2020) comparatively analyzed the optical properties between CsPbBr₃@SiO₂ and CsPbBr₃ QDs, found that the exciton binding energy of CsPbBr₃ QDs after silica coating is higher than that of uncoated CsPbBr₃ QDs. As shown in **Figures 5A,B**, although the optical band gaps of both QDs were continuously broadened from 10 to 300 K, the fitting results of the temperature-dependent spectra indicate that the electron-phonon coupling in the CsPbBr₃@SiO₂ QDs is smaller. The encapsulation layer outside the QDs has a great influence on the strength of the electron-phonon coupling effect on the dielectric constant. SiO₂ is an insulator, which can insulate the influence of the substrate and solution on the QDs, resulting in the reduction of the electron-phonon coupling effect of CsPbBr₃@SiO₂ QDs. According to the temperature-dependent TRPL results (**Figures 5C,D**), the PL lifetime increased with rising temperature, showing a longer PL lifetime than CsPbBr₃ QDs when the temperature increased from 110 K to room temperature. The less phonon effect and longer photoluminescence lifetime of the CsPbBr₃@SiO₂ QDs indicate the silica-coated perovskite materials are more suitable for the down-conversion luminescent materials. During the 16 days PL



test, the results show that CsPbBr₃@SiO₂ QDs exhibited better stability than CsPbBr₃ QDs in the air environment.

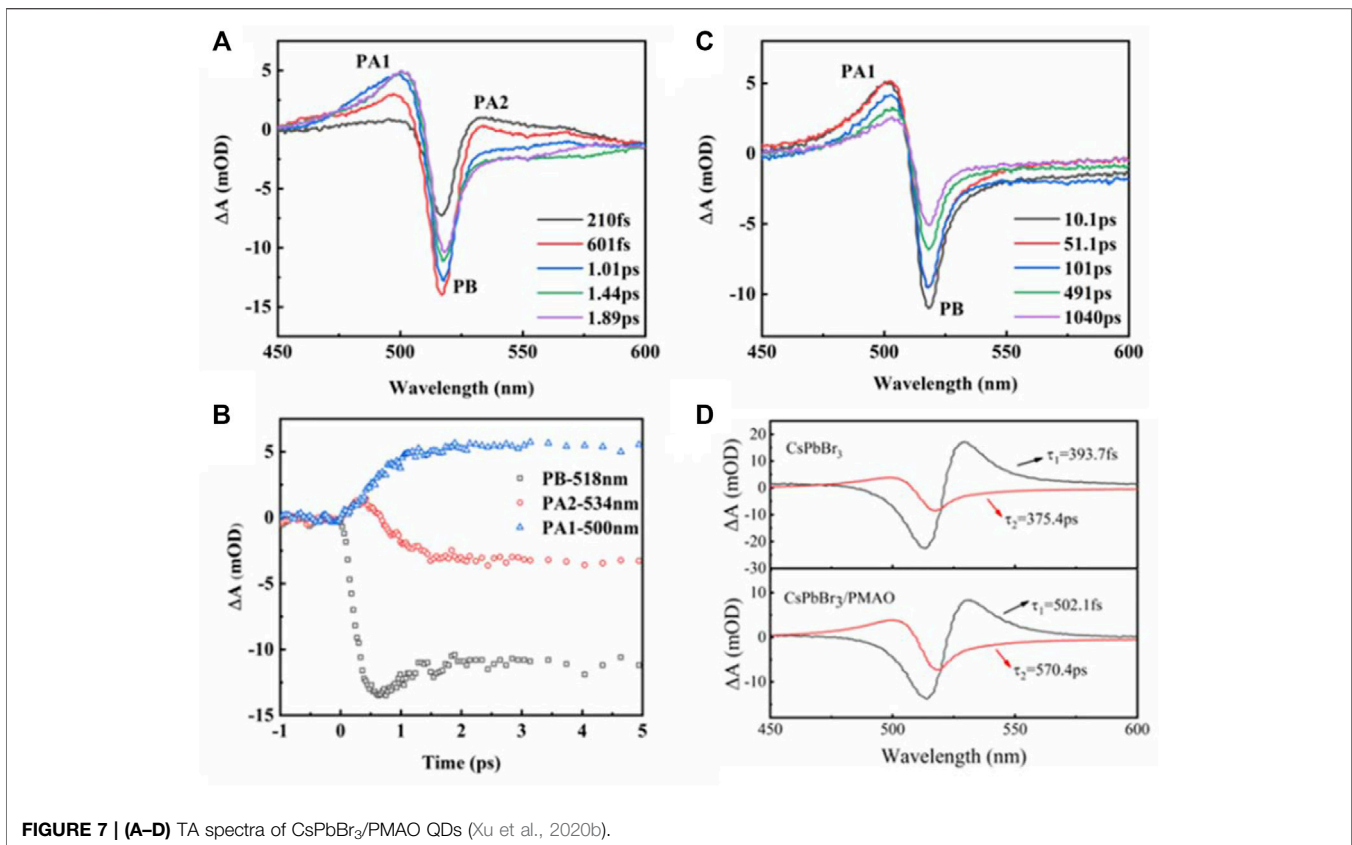
Wu et al. (2020) synthesized SiO₂-coated CsPbX₃ QDs doped with Mn²⁺ at room temperature, which had high PLQYs. The orange-yellow PL of the CsPb_{0.7}Mn_{0.3}Br_{0.75}Cl_{2.25}@SiO₂ QDs exhibited strong thermal and moisture stabilities, and their PLQY was also relatively high. As shown in **Figures 6A,B**, by coating the orange-yellow QDs on the UV LED chip (365 nm), a high-quality WLED device was fabricated. The luminous intensity did not change evidently after 16 h of continuous operation.

Metal oxides with dense structure and outstanding stability, such as TiO₂ and Al₂O₃, are also reported to protect the CsPbX₃ QDs. Loiudice et al. deposited alumina by ALD to coat CsPbBr₃ QDs (Loiudice et al., 2017). The composite had uniform morphology and composition, with an Al₂O₃ coating thickness of about 10 nm. It retained over 50% of PL intensity after exposure to air or heating up to 200°C. Zhi-Jun Li et al. (2018) synthesized CsPbBr₃@TiO₂ composite by calcination at

300°C with TiO₂ precursor. Compared to the pristine CsPbBr₃ QDs, the UV spectrum absorbance of CsPbBr₃@TiO₂ increased slightly, which was attributed to the UV activity of the core/shell TiO₂ surface layer. After encapsulating the TiO₂ shell, the PL intensity of CsPbBr₃@TiO₂ decreased, indicating that a new nonradiative path was formed in the core/shell NCs, probably caused by the transfer of electrons from the conduction band of CsPbBr₃ to the TiO₂. The formed TiO₂ shell layer kept the perovskite QDs undegraded in water for at least 3 months.

Polymers Coating

Polymers have the advantages of high flexibility, easy processing, and low photo-absorption coefficient. Polymers can wrap CsPbX₃ QDs via their dense polymer chains. By strengthening the binding between the polymer ligand and QDs, the surrounding medium can be an effective block, thus improving the water and oxygen resistances of the perovskite QDs. Meanwhile, fluorescence quenching, toxic Pb²⁺ contamination, and QDs aggregation



can be avoided. The thermal and moisture stabilities of QDs are significantly improved after polymer coating.

Zhang et al. (2017) developed a method for coating CsPbX₃ QDs with synthetic polyvinylpyrrolidone (PVP). The PVP formed a protective layer on the CsPbBr₃ surface, which also acted as an interface layer to embed QDs into polystyrene microspheres. By the protection and modification effects of PVP polymers, the quantum efficiency was increased to 27%. Raja et al. explored the combination of hydrophobic bulk polymer and CsPbBr₃ to enhance the light and water stabilities, and the high fluorescence intensity can be maintained even after several months of storage (Raja et al., 2016). The metal-organic framework (MOF) was constituted by an inorganic metal center and an organic connecting substrate through coordination bonds, which enabled effective encapsulation of all-inorganic perovskite QDs. Li et al. (2019) wrapped CsPbX₃ QDs with MOF material. Owing to the highly uniform microporous structure of MOF, the QDs could be prevented from contacting the external environment. Yang Li et al. (2018) employed the one-step method to prepare CsPbBr₃/ethylene vinyl acetate (EVA) composite films. The EVA coated CsPbBr₃ exhibited long-term stable luminescence performance in air and water, whose fluorescence intensity remained unchanged after keeping in the air for 192 and 240 h in the water, the prepared CsPbBr₃ PQDs/EVA films had sufficient flexibility to be repeatedly bent 1,000 times without causing changes of PL intensity.

When the polymer structure contains polyamino, carboxyl, hydroxyl, and other groups to form a multidentate polymer, the stability of perovskite QDs can be improved due to the strong binding between the ligand and the perovskite QDs. Meyns et al. (2016) introduced poly (PMA) to coat perovskite QDs and improve its stability, where the diamine polymerization can further enhance the combination of OA and OAm ligands with the perovskite QD surfaces, thereby effectively improving the QD stability. Xu et al. (2020b) used poly maleic anhydride-alt-1-octadecene (PMAO) to coat the CsPbX₃ QDs. The PMAO could act as a protective layer by combining its anhydride group with the surface ligands of the perovskite QDs. The TRPL results revealed a prolonged PL lifetime of CsPbX₃/PMAO. According to the transient absorption spectroscopy results displayed in **Figures 7A–D**, the PMAO could slow down the intra-band hot exciton relaxation and the exciton recombination of CsPbX₃ QDs. After PMAO coating, the PLQYs of green CsPbBr₃ QDs and red CsPbBr_{0.6}I_{2.4} QDs increased. WLED device was fabricated by integrating the green CsPbBr₃/PMAO QDs and the red CsPbBr_{0.6}I_{2.4}/PMAO QDs on a blue GaN chip, whose stability was greatly improved as compared to that pristine perovskite QDs.

The polymer materials coated CsPbX₃ QDs present the advantages of simple preparation, good compatibility, and anion exchange blockage. However, most polymers have high oxygen diffusion coefficients which result in low stability and PLQY of perovskite QDs. The charge transport

performance of the polymers is relatively poor. These polymer-encapsulated CsPbX₃ QDs still face many problems to be solved urgently.

CONCLUSION

All-inorganic perovskite QDs, as a novel material, exhibit wide color tunability, narrowband PL emission, and high quantum yield. All of these properties make halide perovskite QDs an ideal candidate for light-emitting and display devices. Tremendous work has been done to improve the luminescence intensity and thermal stability of CsPbX₃ QDs by strategies such as doping engineering, surface passivation, and surface coating. Nonetheless, there are still some aspects of metal halide perovskite materials that need to be further studied:

- 1) Although doping perovskite materials can improve their optical properties to a certain extent, excessive or too little doping will hinder the optical strength and stability of QDs. For metal ion-doped perovskites, especially non-divalent metal ions, the actual amount of doping into the lattice is hard to be controlled due to the mismatch with the valence state of Pb²⁺. In addition, the effects of dopants on the crystal and electronic structures of CsPbX₃ QDs also require more detailed studies.
- 2) Ion migration occurs at defect sites in perovskites. Ion migration is one of the main reasons for the spectral instability and short worktime in perovskite QDs-based LED devices. Strategies such as the incorporation of passivation in perovskite films and interfacial layers to reduce defects may suppress ion migration in perovskite films.
- 3) Although doping and coating strategies can improve the air stability of perovskite materials, stability is still an inevitable problem due to the inherent structural properties of perovskite materials. Perovskite QDs with either doping or

surface passivation may be a feasible way to further improve their stability.

- 4) Another major problem for lead halide perovskite QDs-based LEDs is the toxicity of lead. At present, researchers mainly use non-toxic cations to partially replace Pb²⁺ or use suitable packing materials to encapsulate QDs and suppress lead leakage. Materials with hydroxyl, carboxyl, amino, and sulfonic acid groups are expected to act as surface passivation materials, which have good complexing ability to Pb²⁺ and can prevent the diffusion of heavy metal ions to the environment.

In summary, inorganic perovskite materials demonstrate great potential in luminescent devices. With the progress of the research, more new semiconductor perovskite materials were found, and more effective methods will be designed to increase the stability and performance of the perovskite materials. With the tremendous efforts in the perovskite optoelectronic device research, we believe the perovskite can be the ideal candidate for the next-generation semiconductor material.

AUTHOR CONTRIBUTIONS

YW, RJ, and JX have equally contributed to the paper writing. LS, YL, YZ, SU helped collected the references and revised the manuscript. JD provided project motivation, guidance and corrected the manuscript. All authors contributed to the article and approved the submitted version.

FUNDING

This work was supported by the National Science Foundation of China (11874185).

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