Strategies of Improving CsPbX₃ Perovskite Quantum Dots Optical Performance

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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 represents a divalent metal cation (typically Pb²⁺), X represents a halide ion (Cl⁻, Br⁻, I⁻).
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 Protescu 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 CsPb(Br/Cl)$_3$, CsPbBr$_3$, and CsPb(I/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 PbX2 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, PbX2 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 ABX3. Doping with different elements can adjust the phase transition temperature, optical bandgap, and luminescence performance, reduce the nonradiative recombinations rate, and improve the PLQY and LED performance (Zhou et al., 2015; Xu et al., 2019).

The phase structure of the perovskite QDs ABX3 can change among cubic, tetragonal and orthorhombic phases (Wasylishen et al., 1985) through various doping methods. In the ABX3 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 CsPbX3 with other alkali metal cations.

Liu et al. (2020) doped Na+ into CsSnxPb1-xI3 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 Sn2+ and I− ions is enhanced, the diffusion and dissociation of Sn2+ and I− ions are reduced, and the formation of harmful Sn4+ 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 CsPbBr3 and CsPbI3 QDs and explored their effects on the nonradiative and radiative recombinations 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 CsPbBr3 nanocrystals. The Rb+ can lead to tilting of [PbX6]4− octahedral structure, reduce the overall overlap of orbits and widen the bandgap of CsPbBr3, 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 CsPbX3, 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). Sn2+, Zn2+, Mn2+ and lanthanide ions (e.g., Ce3+, Tb3+, Eu3+) have been reported as B-site doping elements in the CsPbX3 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 Mn2+ doping strategy to improve the stability and PL intensity. After 120-days exposure of CsPbBr3:Mn QDs to the air, 60% of the initial fluorescence intensity can be maintained. Zou et al. (2017) synthesized CsPbCl3:Mn QDs with controllable size and shape by adjusting the ratio between Mn and Pb via a one-step
FIGURE 2 | (A) UV-vis and PL spectra of the QDs with and without Na⁺ doping; (B) Normalized TA kinetic profiles and (C) TRPL decay of the QDs (Liu et al., 2020); (D) The schematic diagram of photocarrier recombination mechanism (Wu et al., 2021).

FIGURE 3 | (A) PL spectra and (B) Luminescence photos of different Mn-doped ratios under UV (Zou et al., 2017). (C) PL decay of CsPbBr₃ QDs; (D,E) TA spectra of CsPbBr₃ QDs with and without PEI; (F) Comparisons of TA bleach recovery kinetics (Yin et al., 2021).
ultrasonically. As shown in Figures 3A, B, 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 CsPbCl$_3$:Mn QDs (404 nm). The intensity of exciton emission peak from CsPbCl$_3$: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 CsPbCl$_3$:Zn QLED devices can be doubled. Deng et al. (2020) fabricated CsPb$_{1-x}$Sn$_x$Br$_3$ QDs with the PLQY of 91% at room temperature due to the improvement of QDs lattices. The PL intensity increased obviously in CsPb$_{0.9}$Sn$_{0.1}$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 CsPb$_{1-x}$Cu$_x$ (Cl/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 CsPbI$_3$:Yb$^{3+}$ where the surface defects and lattice trap states can be reduced. The CsPbI$_3$ 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 CsPbI$_3$ 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 (Promescu 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 LED 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’-iminobenzoinoic 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) 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 \( (\text{BA}^+)_n \text{APbX}_3 \), 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 \( [\text{BX}_6]^{n-1}\text{PbX}_4 \) octahedrons 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 PbX3n+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)PbX3n+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)\(_2\)PbBr\(_4\) 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)\(_2\)PbBr\(_4\) 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)\(_2\)PbBr\(_4\) 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 CsPbX\(_3\) 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 CsPbBr\(_3\) 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 CsPb0.7Mn0.3Br0.75Cl0.25@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. Loidudice et al. deposited alumina by ALD to coat CsPbBr3 QDs (Loidudice 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 CsPbBr₀.₆I₂.₄ QDs increased. WLED device was fabricated by integrating the green CsPbBr₃/PMAO QDs and the red CsPbBr₀.₆I₂.₄/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 improve 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.

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Swarnak A., Mir, W. J., and Nag, A. (2018). Can B-Site Doping or Alloying Improve Thermal- and Phase-Stability of All-Inorganic CsPbX3 (X = Cl, Br, I) Perovskites? ACS Energ. Lett. 3 (2), 266–289. doi:10.1021/acsenergylett.7b01197

Tan, Y., Zou, Y., Wu, L., Huang, Q., Yang, D., Chen, M., et al. (2018). Highly Luminescent and Stable Perovskite Nanocrystals with Octylphosphonic Acid as a Ligand for Efficient Light-Emitting Diodes. ACS Appl. Mater. Inter. 10 (4), 3784–3792. doi:10.1021/acsami.7b17166

Tang, X., Chen, W., Liu, Z., Du, J., Yao, Z., Huang, Y., et al. (2019). Ultrathin Core-Shell Structured SiO2 Coated Mn 2+–Doped Perovskite Quantum Dots for Bright White Light-Emitting Diodes. Small 15 (19), 1900484. doi:10.1002/smll.201900484

Todorovic, P., Ma, D., Chen, B., Quintero-Bermudez, R., Saidaminov, M. I., Dong, Y., et al. (2019). Spectrally Tunable and Stable Electroluminescence Enabled by Rubidium Doping of CsPbBr6 Nanocrystals. Adv. Opt. Mater. 7 (24), 1901440. doi:10.1002/adom.201901440

Travis, W., Glover, E. N. K., Bronstein, H., Scarlran, D. O., and Palgrave, R. G. (2016). On the Application of the Tolerance Factor to Inorganic and Hybrid Halide Perovskites: a Revised System. Chem. Sci. 7 (4), 4548–4556. doi:10.1039/CS504854A

Wang, H.-C., Lin, S.-Y., Tang, A.-C., Singh, B. P., Tong, H.-C., Chen, C.-Y., et al. (2016). Mesoporous Silica Particles Integrated with All-Inorganic CsPbBr3 Perovskite Quantum-Dot Nanocomposites (MP-QPDs) with High Stability and Wide Color Gamut Used for Backlight Display. Angew. Chem. Int. Ed. 55 (7), 7924–7929. doi:10.1002/anie.201603698

Wang, Y., Li, X., Nalla, V., Zeng, H., and Sun, H. (2017). Solution-Processed Low Threshold Vertical Cavity Surface Emitting Lasers from All-Inorganic Perovskite Nanocrystals. Adv. Funct. Mater. 27 (13), 1605088. doi:10.1002/adfm.201605088

Wang, H.-C., Bao, Z., Tsai, H.-Y., Tang, A.-C., and Liu, R.-S. (2018). Perovskite Quantum Dots and Their Application in Light-Emitting Diodes. Small 14 (1), 1702433. doi:10.1002/smll.201702433

Wasylfisen, R. E., Knop, O., and Macdonald, J. B. (1985). Cation Rotation in Methylammonium lead Halides. Solid State. Commun. 56 (7), 581–582. doi:10.1016/0038-1098(85)90597-9

Wu, L., Zhong, Q., Yang, D., Chen, M., Hu, H., Pan, Q., et al. (2017). Improving the Stability and Size tunability of CsPbBr3 Nanocrystals. Nanoscale 9 (33), 13051–13059. doi:10.1039/C7NR07022A

Yin, W., Li, M., Dong, W., Luo, Z., Li, Y., Qian, J., et al. (2021). Multidentate Ligand Polyethyleneimine Enables Bright Color-Saturated Blue Light-Emitting Diodes Based on CsPbBr3 Nanoplatelets. ACS Energ. Lett. 6 (2), 477–484. doi:10.1021/acsenergylett.0c00265

Xu, J., Zhu, L., Chen, J., Riaz, S., Sun, L., Wang, Y., et al. (2020). Transient Optical Properties of CsPbBr3@SiO2 Quantum Dots and its Application as a Phosphor Material in Light-Emitting Devices. Opt. Mater. Express 10 (4), 1007. doi:10.1364/om.389847

Yang, D., Li, X., Zhou, W., Zhang, S., Meng, C., Wu, Y., et al. (2019). CsPbBr3 Quantum Dots 2.0: Benzaldehyde Acid Equivalent Ligand Awakens Complete Purification. Adv. Mater. 31 (30), 1900767. doi:10.1002/adma.201900767

Yin, W., Li, M., Dong, W., Luo, Z., Li, Y., Qian, J., et al. (2021). Multidentate Ligand Polyethyleneimine Enables Bright Color-Saturated Blue Light-Emitting Diodes Based on CsPbBr3 Nanoplatelets. ACS Energ. Lett. 6 (2), 477–484. doi:10.1021/acsenergylett.0c00265

Chang, Y.-H., Lin, J.-C., Chen, Y.-C., Kuo, T.-R., and Wang, D.-Y. (2018). Facile Synthesis of Two-Dimensional Ruddlesden-Popper Perovskite Quantum Dots with fine-tunable Optical Properties. Nanoscale Res. Lett. 13 (1), 1–7. doi:10.1186/s11671-018-2664-5

Yu, S., Li, M., Dong, W., Luo, Z., Li, Y., Qian, J., et al. (2021). Multidentate Ligand Polyethyleneimine Enables Bright Color-Saturated Blue Light-Emitting Diodes Based on CsPbBr3 Nanoplatelets. ACS Energ. Lett. 6 (2), 477–484. doi:10.1021/acsenergylett.0c00265

Chen, Y.-X., Xu, Y.-F., Wang, X.-D., Chen, H.-Y., and Kuang, D.-B. (2020). Solvent Selection and Pt Decoration towards Enhanced Photocatalytic CO2 Reduction over CsPbBr3 Perovskite Single Crystals. Sustain. Energ. Fuels 4 (5), 2249–2255. doi:10.1039/c9cf0118d

Zhang, H., Wang, X., Liao, Q., Xu, Z., Li, H., Zhang, L., et al. (2017). Embedding Perovskite Nanocrystals into a Polymeric Matrix for Tunable Luminescence Probes in Cell Imaging. Adv. Funct. Mater. 27 (7), 1604382. doi:10.1002/adfm.201604382

Zhang, F., Shi, Z.-F., Ma, Z.-Z., Li, Y., Li, S., Wu, D., et al. (2018). Silica Coating Enhances the Stability of Inorganic Perovskite Nanocrystals for Efficient and Stable Down-Conversion in white Light-Emitting Devices. Nanoscale 10 (43), 20131–20139. doi:10.1039/C8NR07022A

Zhang, C., Zhang, H., Wang, R., You, D., Wang, W., Xu, C., et al. (2020). Exciton Photoluminescence of CsPbBr3@SiO2 Quantum Dots and its Application as a Phosphor Material in Light-Emitting Devices. Opt. Mater. Express 10 (4), 1007. doi:10.1364/om.389847

Zhu, L., Hofman, E., Li, L., Davis, A. H., Tung, C. H., Wu, L. Z., et al. (2018). Photoelectrochemically Active and Environmentally Stable CsPbBr3/TiO2 Core/Shell Nanocrystals. Adv. Funct. Mater. 28 (1), 1740288. doi:10.1002/adfm.201704288

Zhou, B., Shi, B., Jin, D., and Liu, X. (2015). Controlling Upconversion Nanocrystals for Emerging Applications. Nat. Nanotech. 10 (11), 924–936. doi:10.1038/nnano.2015.251

Zhu, L., Wu, C., Riaz, S., and Dai, J. (2021). Stable Silica Coated DDAR-CsPbX3 Quantum Dots and Their Application for white Light-Emitting Diodes. J. Lumin. 233, 117884. doi:10.1016/j.jlumin.2021.117884

Zou, S., Liu, Y., Li, J., Liu, C., Feng, R., Jiang, F., et al. (2017). Stabilizing Cesium Lead Halide Perovskite Lattice through Mn(II) Substitution for Air- Stable Light-Emitting Diodes. J. Am. Chem. Soc. 139 (33), 11443–11450. doi:10.1021/jacs.7b04000

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