Review Article

Recent Advances and Opportunities of Lead-Free Perovskite Nanocrystal for Optoelectronic Application

Fei Zhang, Zhuangzhuang Ma, Zhifeng Shi, Xu Chen, Di Wu, Xinjian Li, and Chongxin Shan

Key Laboratory of Materials Physics of Ministry of Education, School of Physics and Microelectronics, Zhengzhou University, Zhengzhou 450052, China

Correspondence should be addressed to Zhifeng Shi; shizf@zzu.edu.cn and Chongxin Shan; cxshan@zzu.edu.cn

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Metal halide perovskite nanocrystals (NCs), as a new class of light-emitting and light-harvesting materials, have recently attracted intensive attention for an impressive variety of optoelectronic applications. However, the lead toxicity and poor stability of such materials severely restrict their practical applications and future commercialization. Lead-free perovskite NCs and their derivatives, designed by the reasonable chemical substitution of Pb with other nontoxic elements, are recently booming as an attractive alternative to lead-based counterparts. In this review, we firstly present a comprehensive overview of currently explored lead-free perovskite NCs with an emphasis on their design routes, morphologies, optoelectronic properties, and environmental stability issues. Then, we discuss the preliminary achievements of lead-free perovskite NCs in versatile optoelectronic applications, such as light-emitting devices, solar cells, photodetectors, and photocatalysis. We finish this review with a critical outlook into the currently existing challenges and possible development opportunities of this rapidly evolving field.

1. Introduction

In recent years, lead-halide perovskites with a chemical formula of APbX₃ (where A = CH₃NH₃⁺ (MA), HC(NH₂)₂⁺ (FA), or Cs⁺; X = Cl⁻, Br⁻, or I⁻) have attracted extensive attention increasingly for their excellent optoelectronic characteristics, including high photoluminescence quantum yield (PLQY), precise tunable bandgap, superior charge transport capability, high light absorption coefficient, and low-cost solution processability [1–7]. Since the first attempt to use organic-inorganic lead-halide perovskites (MAPbX₃) as light sensitizers in photovoltaic solar cells in 2009, the power conversion efficiency (PCE) of photovoltaic devices using these materials has exceeded 24% [8–19]. The great success of the lead-halide perovskites in photovoltaic solar cells has triggered various researches on other optoelectronic applications, including light-emitting devices (LEDs), lasers, X-ray imaging, photodetectors, and photocatalysis [20–45].

Along with the rapid development of bulk perovskites synthesized by the solution method, the research into colloidal perovskite nanocrystals (NCs) has also emerged very recently. Nanosized perovskite NCs exhibit unique electrical and optical properties compared to the bulk phase because of their strong quantum confinement, tunable size, and reduced dimensionality [46, 47]. The various micro-nanomorphologies of perovskite NCs, including quantum dots (QDs), quantum rods (QRs), nanocubes, nanowires (NWs), and nanoplatelets (NPLs), have also expanded their applications in optoelectronic devices [48–52]. In addition, the photoluminescence (PL) performances of perovskite NCs are also superior: they exhibit high PLQY up to 90% without any posttreatment, wide color gamut covering up to 140% of the National Television System Committee (NTSC) color standard, and narrow PL linewidths that can be easily tuned over the entire visible spectral region by adjusting the halide composition or NC size [53–58]. The above excellent properties make lead-halide perovskite NCs particularly suitable for next-generation lighting and display technologies [59–61]. To
date, the perovskite NC-based LEDs have reached admirable external quantum efficiency (EQE) surpassing 20% [62], which represents a substantial step toward their commercial applications.

Despite the abundant advances and extraordinary potentials of lead-halide perovskite NCs, two serious challenges attributed from the Pb toxicity and poor stability may become bottlenecks for practical commercial deployment. This is because the heavy metal Pb is easily soluble in water and can affect the human body and the environment [63–68]. Currently, the European Union regulates the use of heavy and toxic materials (including Pb) in electronic devices and the U.S. EPA has set the maximum content of Pb in air and water to be 0.15 μg·L⁻¹ and 15 μg·L⁻¹, respectively, and the use of lead-based technology is expected to decline in the future [69, 70]. Additionally, the commercial application of perovskite NC-based optoelectronic devices is impeded by their poor stability against environment oxygen/moisture [65–67], heat [64], and ultraviolet (UV) light [65, 68]. Therefore, searching suitable lead-free perovskite NCs with low or no toxicity, excellent optoelectronic performance, and high environmental stability is the most straightforward strategy. Thanks to the rich structure and elements of the perovskite family, various lead-free halide perovskite NCs have been developed and characterized in recent years. So far, Sn(II), Sn(IV), Sb(III), Bi(III), Pd(IV), Cu(I), In(III), Ag(I), Na(I), Eu(II), and Yb (II) have been used to replace Pb, and some of the resulting lead-free perovskite NCs show decent optoelectronic performance comparable to that of the Pb-based counterparts. These encouraging results on the exploration of lead-free perovskite NCs show promising indication of major breakthrough in the fabrication of new optoelectronic devices. However, a comprehensive overview of lead-free perovskite NCs, with emphasis on their fundamental performances, limitations, and advanced optoelectronic applications, is not yet thoroughly reported.

In this review, we provide a summary of the recent progress in lead-free halide perovskite NCs, focusing mainly on their design routes, morphologies, optoelectronic properties, and environmental stability issues. Following this, we discuss the preliminary applications of lead-free perovskite NCs in versatile optoelectronic devices, such as LEDs, solar cells, photodetectors, and photocatalysis. Finally, we propose current existing challenges, possible solutions, and future development directions, with the goal of stimulating further research interest and potential applications.

2. Design Route of Lead-Free Halide Perovskite NCs

When selecting elements for which lead may be substituted, basic chemical design rules can narrow the search. In order to form a structurally stable metal halide perovskite, ionic radius and formal charge neutrality need to be considered. It is proposed for the first time that Pb in lead-halide perovskite is replaced by divalent Sn and Ge cations because they both satisfy the prerequisites for coordination and charge balance [71, 72]. In addition, Sn²⁺ has an ion radius comparable to Pb²⁺ (1.35 Å for Sn²⁺ and 1.49 Å for Pb²⁺), thereby avoiding significant lattice vibration caused by substitution [73]. The selected metal ion that has outer electronic configurations similar to that of Pb is another factor that needs to be considered. The low-toxic elements Bi³⁺ and Sb³⁺ containing the lone pair ns¹ were first selected [74, 75]. This process was accompanied by the formation of metal vacancies, which changed the crystal structure, especially the connectivity of the metal halide octahedron, and a cation-deficient structure is formed in order to balance the excess charge. The A₂B₂X₆ (□ is a vacancy) structures are formed by trivalent cations (Bi³⁺ and Sb³⁺), which occupy 2/3 of the B position in the crystal structure [76]. Similarly, the A₂B₃X₉ structures are formed by tetravalent cations (Sn⁴⁺), in which the B site occupies 1/2 of the crystal structure. In order to replace the toxic lead and still retain the three-dimensional (3D) perovskite connectivity and the favorable photovoltaic performance, tentatively the unit cell is doubled and a pair of Pb²⁺ ions is replaced with one Bi(Ⅰ) cation and one B(Ⅲ) cation. The resulting perovskite is characterized by a A₂B(BI)(Ⅲ)X₉ stoichiometric. For the tolerance factor, only the average of the ion radii at the B(Ⅰ) and B(Ⅲ) positions should be used. The theoretical conditions for a stable structure are 0.44 < μ < 0.90 and 0.81 < t < 1.11 (μ: octahedral factor, t: tolerance factor) [77]. The recent studies based on the machine-learning and first-principles density functional theory (DFT) calculations show that the double perovskites have a stable crystal structure, which is consistent with the experimental information. However, cubic unit cells can limit the interaction of their outermost orbits by confining adjacent cations to only B(Ⅰ) cations or B(Ⅲ) cations, which results in the local narrow conduction band and wide bandgap [78, 79]. The direct bandgap nature of lead-free perovskite candidates is also an important pursuit, which ensures a fast radiation process of photon-induced or electrical-injected carriers [80]. Recently, copper-based ternary halides with direct bandgap have been extensively studied and have shown great potential for applications in the field of optoelectronics. Figure 1 summarizes all possible alternatives and presents the crystal structure and advantages of each group of materials, thus providing a clear overview of the consequences of lead alternatives. At present, lead-free metal halide perovskite materials still need in-depth exploration, and the theoretical and experimental work of material design should be strengthened.

3. Lead-Free Halide Perovskite NCs: Morphologies, Optoelectronic Properties, and Environmental Stability

3.1. Sn(II)-Based Halide Perovskite NCs. The group-14 element Sn(II) is the most obvious substitute for Pb because of the similar ionic radius (Pb: 1.49 Å, Sn: 1.35 Å) and the similar ns² electronic configuration to Pb²⁺, which makes it possible to form a perovskite with a formula A3SnX₇ similar to the lead-based counterparts [81, 82]. For Sn²⁺-based halide perovskite NCs, the colloidal synthesis and optical properties
were first reported by Jellicoe et al. in 2016 [83]. The CsSnX₃ (X = Cl, Br, and I) perovskite NCs were synthesized by the hot injection (HI) method with the assistance of the coordinating solvent trioctylphosphine. The typical transmission electron microscopy (TEM) image of CsSnI₃ NCs exhibited a perfect cubic morphology with compact size distribution of ~10 nm (Figure 2(a), A and B). By controlling the ratio of halogen ions, the bandgap of CsSnX₃ can be adjusted from 2.8 eV to 1.3 eV, thus spanning the visible light to the near-infrared region (Figure 2(a), C). Moreover, the optical bandgap of CsSnBr₃ NCs can be tuned from 630 to 680 nm by varying the size of NCs. Nevertheless, the highest PLQY measured in these Sn-based NCs is only 0.14%, which is attributed to the creation of nonradiative defect states as evidenced by the transient PL results. In addition, the formation energy of defects in Sn-based perovskites is relatively low (~250 meV), which provides a considerable driving force for the formation of defect densities up to 10¹⁹ cm⁻³ [84]. Some of these defects tend to create trap states in the forbidden band, leading to the nonradiative recombination and deteriorating the PL performance [85].

Colloidal NPLs are regarded as a promising class of semiconductor nanomaterials, showing bright luminescence as well as tunable and spectrally narrow absorption and emission [86]. Sn-based perovskite NPLs with the formula of L₂[ABX₃]n₋₁BX₄ were first synthesized by Weidman and colleagues using a nonsolvent crystallization method [86]. In this case, L is chosen to represent the ligand species, which not only endows the stability of NPL colloids but also limits the 1D growth of NPLs [87]. The cation (A) species have a small effect on the NPL absorption and emission energy yet can have a large effect on the stability. In addition, such a decrease in the inter-NPL distance can drive the evolution from discrete electronic behavior to high-carrier migration through band-like electron transport, which can significantly extend the lifetimes of photogenerated carriers and improve the emission efficiency. Chen et al. recently reported organic–inorganic Sn-based perovskite NPLs with PEA₂SnX₄ (PEA = C₆H₅(CH₂)₂NH₃, X = Br, I) composition, which has a strongly coupled layered structure [88]. The typical PEA₂SnI₄ showed an efficient red emission at 640 nm with a narrow full-width at half-maximum (FWHM) of 36 nm and a relatively high PLQY of 6.40 ± 0.14%. By controlling the composition of bromine and iodine in the precursors, the emission wavelength of the products was successfully adjusted from 640 nm (PEA₂SnI₄) to 550 nm (PEA₂SnBr₄), and the corresponding PLQY and FWHM were 0.16–6.40% and 36–80 nm, respectively. The all-inorganic CsSnI₃ NPLs were also synthesized by Wong and colleagues, featuring the use of capping ligand in the catalyst-free colloid synthesis process [89]. These CsSnI₃ NPLs exhibited thicknesses of less than 4 nm and showed strong quantum confinement with PL emission at 1.59 eV compared to 1.3 eV in the bulk. Theoretical calculations show that the formation energy of Sn vacancy (VSn) defect is the lowest, which would induce the hallow acceptor levels in CsSnI₃. Therefore, the synthesis of CsSnI₃ under Sn-rich conditions can significantly reduce defect density and improve stability, which matches insights gained experimentally [90–92].

Semiconductor QRs are visible at the transition between 0D QDs and 1D NWs. QR volumes are obviously larger than those of QDs, and therefore, they have significantly larger per-particle absorbance cross-sections [93, 94]. This is expected to increase the optical density of electrodes covered
by up to a single layer of nanoparticles and therefore improve light harvesting. Chen et al. firstly reported the synthesis of CsSnX$_3$ ($X = \text{Cl, Br, and I}$) perovskite QRs with tunable emission wavelength ranging from 625 to 709 nm through halide mixing and substitution [94]. Figures 2(b)–2(f) display the typical morphology of CsSnI$_3$ QRs with a length of several tens of nanometers and a diameter of ~5 nm, indicating the high quality of the resulted samples. The CsSnI$_3$ QRs also demonstrated higher stability against heat, light, and environment moisture/oxygen than MAPbI$_3$ counterparts, which suggests that the CsSnI$_3$ QRs are a reliable absorber layer for photovoltaic applications [94]. Lately, Wang et al. performed a modified HI approach to synthesize CsSnBr$_3$ nanocages with a cubic hollow nanostructure [93]. As seen in Figure 2(g), the CsSnBr$_3$ nanocages showed a broad absorption band located at around 655 nm and a corresponding emission peak at 685 nm with a FWHM of 56 nm. The morphology and optical properties of CsSnBr$_3$ nanocages were controlled by using different coordinating acids and varying the reaction temperature. They also observed the hollow nanocages are more stable than solid nanocubes (Figure 2(h)). Using large-volume and strong electron-withdrawing perfluorooctanoic acid as a surface capping agent can further stabilize the Sn(II) ions on the surface of the hollow nanocube [95–97]. It is worth mentioning that hollow nanostructures are important for applications in drug delivery, energy storage, catalysis, and molecular separation.

3.2. Sn(IV)-Based Halide Perovskite NCs. Since Sn(II) is easily oxidized to Sn(IV), it has been extensively studied to replace Sn$^{2+}$ with air-stabilized Sn$^{4+}$ to produce a relatively stable Sn-based halide perovskite [98–102]. As shown in
Figures 3(a)–3(f), the colloidal Cs$_2$SnI$_6$ NCs with different morphologies (QDs, NRs, NWs, nanobelts, and NPLs) were synthesized by altering the reaction time and ligands [95]. It is worth noting that the sole use of oleic acid (OA) in the synthesis process would not lead to the formation of Cs$_2$SnI$_6$ NCs and the use of oleylamine (OAm) alone would produce bulk Cs$_2$SnI$_6$ crystals. In addition, the typical Cs$_2$SnI$_6$ nanobelts exhibited an orange-colored emission at 620 nm with a FWHM of 49 nm, showing a significant blue shift compared to the bulk due to quantum confinement effect. However, the measured PLQY of as-synthesized Cs$_2$SnI$_6$ NCs is very low (up to 0.48%).
which may be attributed to the dominant defects of iodine vacancies and interstitial Sn [103]. Following this work, Dolzhnikov et al. reported the Cs$_5$Sn$_3$ NCs with no organic capping ligands via a modified HI method [104]. In this synthesis procedure, the diameter of the resulting NCs increases from 12 ± 2.8 nm to 38 ± 4.1 nm with increasing the reaction temperature. They also observed that the bandgap, energies of the first excitonic peak, ground-state bleach peak, and PL peak depend linearly on the inverse square of NC diameter, consistent with quantum-confined excitons with an effective mass of (0.12 ± 0.02) $m_0$, where $m_0$ is the mass of an electron, a factor of 4.6 smaller than that in the bulk material.

Impurity doping has been demonstrated as an effective strategy to improve the photophysical properties and even to introduce new functions to the host materials [105, 106]. To enhance the PL performance of Sn-based perovskites, a strategy of doping Bi into Cs$_5$SnCl$_3$ was employed by Tan and coworkers, and the resulting Cs$_5$SnCl$_3$:Bi$^{3+}$ exhibited an efficient blue emission with a high PLQY of 78.9% [107]. The combination of material characterization and first-principles calculations revealed that Bi$^{3+}$ is incorporated into the Cs$_5$SnCl$_3$ matrix at the Sn site and would preferably form Bi$_{Sn} + V_{Cl}$ luminescent center which is responsible for strong PL emission. In addition, Jing et al. demonstrated the Sh$^{3+}$-doped Cs$_5$SnCl$_3$ NCs via a HI approach, showing a double emission centered at 438 and 615 nm with an improved PLQY of 8.25% (Figure 3(g)) [105]. Upon high-energy photexcitation at 322 nm (3.85 eV), the 438 nm emission band (singlet self-excited exciton) is attributed to the $^{1}P_{1} - 1S_0$ transition, while the lower energy 615 nm emission band (triplet self-excited exciton) is ascribed to the $^{3}P_{n} - 1S_0$ transition ($n = 0, 1, 2$). TEM images showed that the shape and size of Sh$^{3+}$-doped Cs$_5$SnCl$_3$ NCs were almost unchanged under high-energy electron beam irradiation for 20 s, indicating the structural stability of Sh$^{3+}$-doped Cs$_5$SnCl$_3$ NCs. Additionally, Lin et al. reported a bright Mn$^{2+}$ red emission in the preferred blue-emissive Cs$_5$SnCl$_3$ host when Mn ions were gradually doped into the Cs$_5$SnCl$_3$ matrix [106]. The PL mechanism is ascribed to the energy transfer from the Cs$_5$SnCl$_3$ host to the Mn$^{2+}$ activators with d-d orbital transition. Moreover, the as-synthesized Mn$^{2+}$-doped Cs$_5$SnCl$_3$ NCs presented enhanced stability against environmental moisture/oxygen and UV light. These results obtained indicate that doping strategy is an effective approach to improve the emission efficiency and stability of lead-free perovskite nanomaterials, showing promising potentials for their optoelectronic applications.

3.3. Ge(II)-Based Halide Perovskite NCs. Another potential candidate for the substitution of Pb in the perovskite structure is the group-14 element Ge(II) [107–120]. The divalent cation Ge is in the same oxidation state as Pb but exhibits lower electronegativity and stronger covalent properties than Pb. Moreover, the bandgap of Ge-based perovskites is theoretically lower than that of Pb-based perovskites, making them advantageous for photovoltaic applications [108–114]. Experimentally, the colloidal CsGeI$_3$ NCs were first reported by Wu et al. by employing the modified HI method. The CsGeI$_3$ NCs exhibited a cube-shaped morphology with an average edge length of 45 nm, as shown in Figure 4(a) [115]. Furthermore, high-resolution TEM and corresponding fast Fourier transformation (FFT) analysis revealed the single-crystalline nature of the CsGeI$_3$ NCs (Figures 4(b) and 4(c)). The optical measurements show that the CsGeI$_3$ NCs have a narrow PL emission peak at 804 nm with a PLQY of 3.7%. However, under continuous high-energy electron beam irradiation, the CsGeI$_3$ NCs suffered serious morphology deterioration and structure variation caused by the oxidation of I$^{-}$ anions and reduction of Ge$^{2+}$ cations simultaneously [116]. In addition to the cube-shaped morphology, Chen also reported a series of CsGeX$_3$ (X = Cl, Br, and I) NCs with rod-shaped morphology (Figures 4(d)–4(h)) [121]. The CsGeX$_3$ QDs showed typical sharp absorption onsets, similar to those of the bulk dispersion. When varying the halogen composition from chlorine to iodine, the absorption and emission band of CsGeX$_3$ were found to be red-shifted from 565 to 655 nm and 607 to 696 nm, respectively (Figure 4(i)). At present, Ge-based halide perovskites have rarely been investigated experimentally, which is presumably due to the chemical instability upon oxidation of the divalent Ge$^{2+}$ cation. Due to the reduced inert electron pair effect, this oxidation stability issue is even more prominent in Ge-based perovskites than in Sn-based ones.

3.4. Bi(III)-Based Halide Perovskite NCs. Bismuth (Bi) is one of the group-15 metal and has the ns$^2$ valence electronic configuration similar to Pb (ns$^2$ lone pair) [122–127]. The ionic radius of Bi$^{3+}$ (103 pm) is comparable with that of Pb$^{2+}$ (119 pm), and therefore, many attempts on replacing Pb$^{2+}$ by Bi$^{3+}$ to realize lead-free perovskites for optoelectronic applications were conducted [128–131]. In 2016, Kim et al. firstly reported the colloidal synthesis of MA$_3$Bi$_2$X$_9$ (X = Cl, Br, and I) perovskite QDs by a facile ligand-assisted recrystallization (LARP) approach [123]. The as-synthesized MA$_3$Bi$_2$Br$_9$ QDs with an average diameter of 3.05 nm exhibited a bright blue emission at 423 nm and a PLQY of 12% (Figures 5(a) and 5(b)). Besides, the PL emission peaks of MA$_3$Bi$_2$Br$_9$ QDs could be easily tuned from 360 to 540 nm by varying the anion composition. Although the MA$_3$Bi$_2$Br$_9$ QDs displayed high stability in ethanol, the moisture stability was not satisfactory [123], and their photostability under UV light irradiation was observed to be similar to the Pb-based perovskites and CdSe QDs. However, the PLQY of such QDs is still relatively low, inferior to Pb-based perovskite counterparts, which is mainly due to the residual surface defects caused by dangling bonds on the QD surface [131]. To improve the PL performance, Cl$^{-}$ anions were employed as the passivating ligands to suppress the surface defect and enhance the radiative recombination of the MA$_3$Bi$_2$Br$_9$ QDs [132]. The resulting Cl$^{-}$-passivated MA$_3$Bi$_2$Br$_9$ QDs achieved a substantially improved PLQY of 54.1% (Figures 5(c)–5(f)). Moreover, Cl$^{-}$-passivated MA$_3$Bi$_2$Br$_9$ QDs also demonstrated better storage stability and photostability than the pristine MA$_3$Bi$_2$Br$_9$ QDs. In addition, Shen et al. synthesized FA$_3$Bi$_2$Br$_9$ (FA = NH$_2$HCNH$_2$) perovskite QDs with an
The average diameter of ~4.9 nm by a convenient room temperature (RT) solution process [133]. The PLQY of FA$_3$Bi$_2$Br$_9$ QDs synthesized using this method reached 52% with excellent air stability (up to 30 days), showing clearly the application prospect of this material in optoelectronic devices. Here, it is proposed that the high PLQY of FA$_3$Bi$_2$Br$_9$ QDs can be attributed to the following three points mainly, high exciton binding energy (strong quantum confinement effect), direct bandgap nature (favorable radiative recombination process), and low defect density (Br-rich component and ligand-passivation effect) [133, 134]. This modified synthesis method with appropriate ligands and Br-rich surface is quite useful for synthesizing highly efficient Bi$^{3+}$-based perovskite QDs.

All-inorganic Cs$_3$Bi$_2$X$_9$ (X = Cl, Br, and I) perovskite NCs have more promise regarding the stability compared to hybrid organ-inorganic perovskites because of the volatile nature of methylammonium or formamidine [134–137]. Zhang et al. reported for the first time the synthesis and tuning of optical properties of all-inorganic Cs$_3$Bi$_2$X$_9$ NCs by a HI method [126]. Surprisingly, the obtained Cs$_3$Bi$_2$I$_9$ NCs exhibited a dual-spectral PL feature with comparable intensity at RT, which is different from the emission behavior of CsPbX$_3$ NCs. Temperature-dependent PL and DFT calculations revealed that the occurrence of the exciton recombination process involves both indirect and direct transitions simultaneously [126]. Despite the success of Cs$_3$Bi$_2$X$_9$ NCs synthesis, the optical performances, especially PLQY, seem to be inferior than that of Pb-based counterparts [138]. Some recent studies in this field have shown that Cs$_3$Bi$_2$X$_9$ NCs with high PLQY can be produced through careful manipulation of surface ligands and solvents [139]. For example, Yang and coworkers synthesized Cs$_3$Bi$_2$X$_9$ NCs through a ligand-free facile reaction at RT and the resulting Cs$_3$Bi$_2$Br$_9$ NCs exhibited a low PLQY (~0.2%) because of the ultrafast trapping process [131]. At almost the same time, Leng et al. obtained a brightly luminescent Cs$_3$Bi$_2$Br$_9$ QD with a PLQY of 19.4% by optimizing the amount of ligand, reaction temperature and time, and precursor concentration during the synthesis [140]. With UV lamp irradiation (325 nm), the
NC colloidal solution exhibited a strong blue emission and the absence of aggregation phenomenon (Figure 5(g)). Recently, Ma et al. proposed an effective strategy of employing water-induced Cs$_3$Bi$_2$Br$_9$/BiOBr nanocomposites to improve the PLQY of Cs$_3$Bi$_2$Br$_9$ QDs [141]. After adding a small amount of water into Cs$_3$Bi$_2$Br$_9$ QD solutions, these QDs will spontaneously hydrolyze to form Cs$_3$Bi$_2$Br$_9$/BiOBr nanocomposites, in which multiple Cs$_3$Bi$_2$Br$_9$ QDs were encapsulated into one BiOBr matrix (Figure 5(h)). Due to the self-passivation effect of the BiOBr matrix, the treated Cs$_3$Bi$_2$Br$_9$ QDs exhibited suppressed residual surface defects and exhibited a bright blue emission at 410 nm with an improved PLQY of 46.4% (Figure 5(i)). The PL spectral shape and position of the water-treated Cs$_3$Bi$_2$Br$_9$ QDs showed almost no obvious changes, but the FWHM was significantly reduced by 42.9 meV compared with the untreated
QDs [141]. Furthermore, the treated Cs$_3$Bi$_2$Br$_9$ QDs possessed increased exciton binding energy and PL lifetime. These findings clearly showed that the BiOBr matrix can effectively reduce the number of surface trap states and enhance the radiative recombination. This might provide a prosperous way in developing lead-free perovskite QDs with superior optical properties for future optoelectronic applications. In addition, previous studies have demonstrated that the doping of metal ions into perovskite NC through substituting Pb$^{2+}$ sites can effectively improve its optical performance and expand its emission wavelength [142–145]. Considering that Bi$^{3+}$ ions have a similar ion radius and the same valence as lanthanide ions, the incorporation of lanthanide ions into Bi$^{3+}$-based perovskite QDs has therefore been proposed as a promising strategy to improve their optical performances [143]. For example, Ding et al. fabricated Eu$^{3+}$-doped Cs$_3$Bi$_2$Br$_9$ QDs employing a modified LARP approach and achieved a substantial increase of PLQY from 18% to 42.4% [142]. They consider that the Eu$^{3+}$-doping reduces the defect states of Cs$_3$Bi$_2$Br$_9$ QDs, and also, the energy transfer efficiency from QD host to Eu$^{3+}$ ions is high. Importantly, compared with the bare QDs, the Cs$_3$Bi$_2$Br$_9$:Eu$^{3+}$ QDs demonstrated largely enhanced water stability. After storing the sample in water for 24 h, the relative PL intensity of Cs$_3$Bi$_2$Br$_9$:Eu$^{3+}$ QDs was only decreased by 0.3%, while that for pristine Cs$_3$Bi$_2$Br$_9$ QDs exceed 55%.

The combination of Cs$^+$, Bi$^{3+}$, and halide anions (Cl$^-$, Br$^-$, and I$^-$) can produce a variety of different crystalline substances with different compositions or structures, including Cs$_8$BiX$_{16}$ Yang et al. synthesized the 0D Cs$_3$BiX$_6$ (X = Cl, Br, I) perovskite NCs with a uniform cubic shape by the HI method [136]. But the emission performance obtained is not satisfactory, and no emission was detected at RT. At 80 K, the PL spectrum of Cs$_3$BiCl$_6$ NCs was characterized by a large Stokes shift (59 nm, 0.56 eV) and a broad emission profile (FWHM: 60 nm, 0.47 eV), indicating that the self-trapped exciton-induced emission mechanism was responsible for the cause of the phenomenon. It is worth noting that the Cs$_3$BiX$_6$ NCs remain stable when heated to 200°C without crystal structure degradation.

3.5. Sb(III)-Based Halide Perovskite NCs. Antimony-(Sb-) based halide perovskites are a potential alternative to lead-based counterparts for optoelectronic applications to address the chemical stability and toxicity issues. Analogous to Bi$^{3+}$-based perovskites, the trivalent Sb$^{3+}$ is iso-electronic with divalent Pb$^{2+}$ cations and possesses similar electronegativity [146–152]. Additionally, the similarity of the electronic configuration of A$_3$Sb$_2$X$_9$ (A = MA$^+$, Cs$^+$, or Rb$^+$) to the lead-halide perovskites suggests the important advantages of such materials [153–157]. For Sb-containing perovskites, the chemical formula A$_3$Sb$_2$I$_9$ is known to exhibit 0D and 2D crystal structures [148]. The preferred formation of 0D and 2D structures depends on the sample preparation technique and the ligand selection. For example, Pal et al. synthesized colloidal 2D structured Cs$_3$Sb$_2$I$_9$ and Rb$_5$Sb$_2$I$_9$ NCs by using the HI method [158]. The as-synthesized Cs$_3$Sb$_2$I$_9$ NCs showed different morphology of NPLs (180°C) and NRs (230°C) by simply varying the reaction temperature (Figure 6(a)). The NPLs possessed the average length of ~27 nm, breadth of ~14 nm, and thickness of ~1.5 nm, and the NRs had the average length of ~655 nm and diameter of ~46 nm (Figures 6(b)–6(e)). In this synthesis, ODE, OnA, and OAm were used together with SbI$_3$ to prepare the antimony precursors for the reaction and it is desired to passivate surface defects by these ligands [158]. The NCs obtained show sharp band-edge emission, but the low PL lifetime of the NPLs and NRs obtained by experiments clearly reveals the possible role of defect density factor over the ligands. Subsequently, uniform colloidal Cs$_3$Sb$_2$Cl$_9$ perovskite NWs with lengths up to several microns and nanorods with the same ~20 nm diameter were obtained by Pradhan et al. by tuning the precursors and ligands in the reaction [152]. Here, the use of hexadecylamine as surfactant yields monodispersed NRs, while the use of hexadecylammonium chloride salt can promote more elongated 1D growth to produce NWs. Moreover, the aspect ratio and size of the synthesized NRs can be adjusted by simply changing the amount of SbCl$_3$, while the PLQY value obtained in this work is only 4% [159]. Therefore, more work needs to be performed to further improve their optical properties through suppressing the defect states, such as using appropriate surface ligands and posttreatment processes.

Through modified LARP synthesis strategy, Zhang et al. reported and synthesized Cs$_3$Sb$_2$X$_9$ (X = Cl, Br, and I) QDs, which have a quasispherical shape with an average diameter of ~3.07 nm and relatively small size distributions (Figure 6(f)) [160]. The emission peak of Cs$_3$Sb$_2$Br$_9$ QDs exhibited a blue shift of ~120 nm compared to that of the single crystal, indicating a strong quantum confinement effect (Figure 6(g)). By further controlling the crystallization kinetics of QDs, they found that the PLQY of Cs$_3$Sb$_2$Br$_9$ QDs was in the range of 20–46%, which manifested that the inhibition of nonradiative recombination occurred. The relatively high PLQY of such QDs was related to the large exciton binding energy and Br-rich surface configuration [161–163]. They proposed that such a Br-rich surface can form a quantum-well band structure (Figure 6(h)), which contributes to efficient radiative recombination by increasing the exciton binding energy [163]. Besides, tunable emission wavelength from 370 to 560 nm was realized by the anion exchange reaction. However, this anion exchange technique is usually difficult to completely obtain pure halogen perovskites, which may result from the thermodynamically unstable crystallization during the exchange process. Recently, Ma et al. adopted a strategy of directly controlling halide components to achieve full-composition adjustment without phase separation [164]. The obtained Cs$_3$Sb$_2$X$_9$ QD solutions with different halide compositions showed a regular color change from violet to red (385–640 nm). Such a good spectral tunability facilitates their applications in multicolor lighting and display technologies. Moreover, these QDs demonstrated outstanding photostability against UV light irradiation compared to conventional CsPbX$_3$ QDs. When the Cs$_3$Sb$_2$Br$_9$ QD solutions were exposed to UV light continuous irradiation for 73 h, the PL intensity was only decreased by ~17.5%, while the conventional CsPbBr$_3$ QDs decreased to 9% of the initial value even with a much shorter irradiation time of 12 h.
The significantly different photostability of Cs$_3$Sb$_2$Br$_9$ and CsPbBr$_3$ is closely connected with their distinct structural dimensions [164]. It is well known that Cs$_3$Sb$_2$I$_9$ is characterized by a 2D layer structure, while that for CsPbBr$_3$ is a 3D cubic structure [165, 166]. Compared with the cubic CsPbBr$_3$, the shortening of Sb–Br bond length

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(Figure 6(i)). The significantly different photostability of Cs$_3$Sb$_2$Br$_9$ and CsPbBr$_3$ is closely connected with their distinct structural dimensions [164]. It is well known that Cs$_3$Sb$_2$Br$_9$ is characterized by a 2D layer structure, while that for CsPbBr$_3$ is a 3D cubic structure [165, 166]. Compared with the cubic CsPbBr$_3$, the shortening of Sb–Br bond length
and reduction of distortion angle in the SbBr$_6$ octahedron would decrease the total energy of the system, thus increasing the intrinsic structural stability of Cs$_3$Sb$_2$Br$_9$ [73]. Moreover, the decomposition energy of trigonal Cs$_3$Sb$_2$Br$_9$ is much higher than that of cubic CsPbBr$_3$ according to DFT calculation, which also indicated that the former is more stable than the latter (Figure 6(j)). Besides, native defect migration in perovskites (i.e., Br vacancy, $V_{Br}^+$) was considered to be one of the factors leading to poor stability [167]. From the theoretical results shown in Figure 6(k), one can see that the diffusion barriers of $V_{Br}^+$ in trigonal Cs$_3$Sb$_2$Br$_9$ were much higher than those in cubic CsPbBr$_3$ in the diffusion paths along the ab plane and c axis. Clearly, the difficulty in diffusion of the dominant defects also increases the stability of Cs$_3$Sb$_2$Br$_9$. These observations confirmed experimentally and theoretically that such Sb$^{3+}$-based perovskites have higher stability than the Pb-based counterparts, emphasizing that they are suitable candidates for optoelectronic applications even under harsh conditions.

3.6. Double Perovskite NCs. To maintain the advantages of 3D corner-sharing perovskite structure and replace Pb with low toxic elements, halide double perovskite with a formula of A$_2$B$^+$B$^+$X$_6$ is regarded as a promising approach for optoelectronic applications [168–194]. The halide double perovskites can offer huge opportunities in terms of combinatorial chemistry because of the rich selectivity of B$^+$ and B$^+$ ions. Since 2016, many different types of halide double perovskites have been explored, including Cs$_2$AgBiX$_6$ (X = Br, Cl) [168–187], Cs$_2$AgSbBr$_6$ [188–190], Cs$_2$AgInCl$_6$, (MA)$_2$AgBiBr$_6$ [191, 192], (MA)$_2$KBiCl$_6$ [193], and (MA)$_2$TlBiBr$_6$ [194]. Among them, the colloid synthesis and characterization of Cs$_2$AgBiX$_6$ (X = Cl, Br) double perovskite NCs were first reported by Creutz et al. in 2018 [179]. The as-synthesized Cs$_2$AgBiX$_6$ NCs exhibited a cube-shaped morphology with edge lengths of ~8 nm and relatively narrow size distributions. The phase pure NC formation is highly sensitive to the precursor’s stoichiometry ratio, surface ligand ratio, reaction time, and temperature. In addition to the synthesis of Cs$_2$AgBiCl$_6$ and Cs$_2$AgBiBr$_6$ NCs, they also prepared a new Cs$_2$AgBiI$_6$ material by using trimethylsilyl iodide for postsynthetic anion exchange under an inert atmosphere. Almost at the same time, Zhou et al. demonstrated the synthesis of Cs$_2$AgBiBr$_6$ double NCs with cubic shape and high crystallinity via a modified HI approach (Figures 7(a) and 7(b)) [195]. Bekenstein et al. recognized that the sharp peak in the absorption spectrum of Cs$_2$AgBiBr$_6$ NCs was ascribed to a direct bismuth s-p transition and not to a quantum-confined excitonic transition [168, 196]. The resulting Cs$_2$AgBiBr$_6$ NCs showed impressive stability against light, moisture, and temperature. Typically, the NCs can maintain their structural stability up to 3 weeks in low polarity solutions, and phase uniformity against 55% relative humidity for 90 days, UV light soaking for 500 h or 100°C heating for 300 h. Stoichiometric analysis shows that this material degradation is related to the Ag coalescence and diffusion, as well as the formation of Cs$_3$Bi$_2$Br$_9$ and Cs$_3$Bi$_2$Br$_9$. This is mainly because the excess OAm ligand on the surface and surroundings of the NC can act as a reducing agent for converting Ag$^+$ into Ag particles, and its size will gradually increase as the reaction time increases.

Later, Yang et al. developed a ligand-free approach to synthesize Cs$_2$AgBiX$_6$ (X = Cl, Br, and I) NCs with an average diameter of 5 nm [197]. The typical Cs$_2$AgBiBr$_6$ NCs exhibited a low absorption tail up to 700 nm due to the presence of surface defects [198, 199], indicating a transition involving a subbandgap state (Figure 7(c)). These undesirable surface traps can be suppressed effectively by adding additional ligands (OA), resulting in a 100-fold increase in the PL intensity (Figure 7(d)). However, the highest PLQY is only 6.7% even if the synthesis conditions are optimized, which is mainly due to the indirect bandgap natures that cause the Cs$_2$AgBiX$_6$ NCs to easily form internal defects during the growth process, such as Bi vacancies and AgBi antisites [187]. To overcome this vexation, the same group designed an effective strategy of doping In into Cs$_2$AgBiCl$_6$ to achieve the transition from indirect bandgap to direct bandgap (Figure 7(e)) [200]. The Cs$_2$AgIn$_{0.9}$Bi$_0.1$Cl$_6$ NCs with direct bandgap exhibited 3 times greater absorption cross-section, lower subbandgap trap states, and 5 times PLQY compared to those observed for indirect bandgap NCs (Cs$_2$AgBiCl$_6$). Moreover, a bright dual-color emission located at 410 and 570 nm, respectively, was observed in the direct bandgap NCs. Theoretical calculations and optical analysis show that the dual-color emission originates from the direct band-to-band transition (violet) and forbidden transition (orange), respectively. Inspired by the success of developing Ag-Bi-based double perovskite NCs, Yang et al. explored the possibility of developing Ag-Sb-based double perovskite NCs [201]. The Cs$_2$AgSbBr$_6$ NCs synthesized by the HI method showed a typically cube-shaped morphology with edge lengths of ~14.3 nm. Further, they synthesized a series of Ag-Sb/Bi double perovskite Cs$_2$AgSb$_{1-y}$Bi$_y$X$_6$ (X: Br, Cl; 0 ≤ y ≤ 1) NCs with cubic phase (Figure 7(f)), which exhibited enhanced stability in colloidal solution compared to the Ag-Bi or Ag-Sb NCs due to that, the ionic size matches better after Sb incorporating into Ag-Bi double perovskite [202, 203].

Among the possible double perovskite materials, Cs$_2$AgInCl$_6$ with direct bandgap has been recently proposed as candidates for optoelectronic applications because of their high absorption coefficients, enhanced PLQY, and rapid carrier recombination rates [204–207]. The colloidal synthesis of double perovskite Cs$_2$AgInCl$_6$ NCs with a control size distribution was first reported by Locardi et al. in 2018 [208]. Figure 8(a) illustrates the typical 3D crystal structure of as-synthesized Cs$_2$AgInCl$_6$ NCs, and a low PLQY of ~1.6% was achieved. After the Mn$^{2+}$ ion doping, the emission performance of NCs was substantially improved due to the $^{4}T_{1g}→{^6}A_{1g}$ transition of Mn$^{2+}$ [209–212], and a strong orange emission centered at 620 nm emerges. With an optimized Mn$^{2+}$-doping ratio of 1.5%, the PLQY of Cs$_2$AgInCl$_6$Mn NCs was eventually promoted to ~16% (Figure 8(b)). After that, Liu et al. optimized the colloidal synthesis of undoped and Bi-doped Cs$_2$AgInCl$_6$ NCs by a facile HI process [213]. The undoped Cs$_2$AgInCl$_6$ NCs showed a blue emission at 470 nm, and the Bi-doped Cs$_2$AgInCl$_6$ NCs exhibited a broad
orange emission at 580 nm with the PLQY of 11.4%. Theoretical calculations and transient PL results suggested that the weak emission of the undoped NCs with the short-lifetime process may originate from the transition involving different defect states or surface-related states. In contrast, the broad-band emission of Bi-doped NCs with long-lifetime is derived from the self-trapped excitons (STEs) stemming from the Jahn-Teller distortion of [AgCl₆]³⁻ octahedron in the excited state. These results indicated that altering the electronic structure of double perovskites by doping suitable metal ions will be one of the potential methods for future improvements of the optical properties.

In addition, lanthanide (rare earth) ion doping is also considered as a promising strategy to tailor the electrical and optical properties of Cs₂AgInCl₆ perovskites [214, 215]. For instance, Liu et al. successfully incorporated Tb³⁺ (rare earth) ions into double perovskite Cs₂AgInCl₆ NCs, and the crystal structure and uniform cubic morphology remained unchanged [214]. Moreover, Bi³⁺ ions doping in NCs further adjusted the emission of Tb³⁺ ions and variation of Tb³⁺ ion doping concentration, which resulted in a broadband emission of Cs₂AgIn₀.7₉Bi₁.₂₁Cl₆ NCs derived from STEs, with the emission located at 490, 550, and 620 nm, corresponding to the intrinsic transition of Tb³⁺ ions ⁵D₄-⁷F₆, ⁵D₄-⁷F₅, and ⁵D₄-⁷F₄, respectively. Surprisingly, the STE emission in highly Tb³⁺-doped Cs₂AgInCl₆:Bi system almost disappeared and only the strong and sharp lines from Tb³⁺ ion emission existed, indicating that a high doping

**Figure 7:** (a) Schematic illustration of the solution phase synthesis of Cs₂AgBiBr₆ NCs. (b) Crystal structure of cubic Cs₂AgBiBr₆ NCs. (c) Steady-state absorption spectra of ligand-free and OA-capped Cs₂AgBiBr₆ NCs. (d) PL spectra of ligand-free and 1% OA-capped NCs. Inset: photographs of the colloidal ligand-free Cs₂AgBiBr₆ NCs. (e) PLQY value of Cs₂AgInₓBi₁₋ₓCl₆ (x = 0, 0.25, 0.5, 0.75, and 0.9) NCs capped with 8% OA. Inset: corresponding photographs under UV light of 365 nm. (f) TEM images of Cs₂AgSb₁₋ₓBiₓBr₆ (x = 0, 0.25, 0.5, 0.75, 1) NCs. (a, b) Reproduced with permission from Ref. [195], copyright 2018 Small. (c, d) Reproduced with permission from Ref. [197], copyright 2018 Angewandte Chemie International Edition. (e) Reproduced with permission from Ref. [200], copyright 2018 Journal of the American Chemical Society. (f) Reproduced with permission from Ref. [201], copyright 2019 Angewandte Chemie International Edition.
concentration promoted the energy transfer from STEs to Tb$^{3+}$ ions (Figure 8(c)). The transient PL measurement further confirmed the existence of efficient energy transfer channels (Figure 8(d)). Based on the results discussed above, a possible PL mechanism for Bi-doped Cs$_2$Ag(In$_{1-x}$Tb$_x$)Cl$_6$ NCs is proposed and illustrated in Figure 8(e). Upon photoexcitation, the electrons are excited from the ground states into the excited states of Cs$_2$AgInCl$_6$:Bi host and then shift to the self-trapped state through the nonradiative relaxation, generating broadband orange emission due to the STE recombination. Meanwhile, partial energy is transferred to Tb$^{3+}$ ion, and electrons at a higher level of Tb$^{3+}$ are relaxed to the lowest excited level $5D_4$, causing the Tb$^{3+}$ ions ($5D_4$-$7F_6$-3) characteristic emission. Therefore, the emission colors of Bi-doped Cs$_2$Ag(In$_{1-x}$Tb$_x$)Cl$_6$ NCs could be continuously adjusted from green to orange.

Monovalent B$^+$ ions can also be replaced by Na$^+$ metal ions to form Na-In-based double perovskite NCs. The lead-free direct bandgap Cs$_2$NaInCl$_6$ NC was synthesized by a variable temperature one-pot HI method [216], which exhibited a poor PL performance because of the presence of dark STEs in perovskites. The dark STEs can be converted into bright STEs by doping with Ag$^+$ to produce a bright yellow emission, with the highest PLQY of 31.1%. In addition, the Ag-doped Cs$_2$NaInCl$_6$ NCs exhibit higher air stability compared to the undoped NCs, attributed to the improvement of short-range order of the Ag-doped NCs caused by the reduction of volume defects [217, 218]. The Cs$_2$AgInCl$_6$ NCs can break the wavefunction symmetry of the STEs by partial replacement of Ag$^+$ ions with Na$^+$ ions and consequently allow radiative recombination. Assisted with Bi$^{3+}$ ion doping, the PLQY of Cs$_2$Ag$_{0.17}$Na$_{0.83}$In$_{0.88}$Bi$_{0.12}$Cl$_6$ NCs is further promoted to 64% [219]. This is because the Bi$^{3+}$ introduction can break the parity forbidden transition of Cs$_2$AgInCl$_6$ by manipulating the crystal symmetry [200]. From all of the above discussions, it can be concluded that the diversification
of a double perovskite structure will stimulate future attempts to design and manufacture novel lead-free perovskite NCs for optoelectronic applications.

Recently, a novel double perovskite with the chemical formula of Cs$_2$M(II)(M(III))X$_4$ (M(II): Cu$^{2+}$, Mn$^{2+}$, Cd$^{2+}$, etc.; M(III): Sb$^{3+}$, Bi$^{3+}$, etc.) was also explored [220–227]. Such a layered perovskite structure consists of a layer of [M(II)]$X_4$$^{2-}$ octahedral sandwiched between two adjacent vacant layers [M(III)]$X_3$$^{3-}$ octahedron. Single-layer Cs$_2$CuSb$_2$Cl$_12$ NCs were prepared by the ultrasonic peeling technique [226]. Exfoliating Cs$_2$CuSb$_2$Cl$_12$ microcrystal into NCs will cause indirect to direct bandgap transition and reduced electron effective mass, thereby providing a fast and stable photoelectrochemical response. Recently, Cai et al. used a HI method to completely decouple the cation and anion precursors to synthesize colloidal Cs$_4$CuSb$_2$Cl$_12$-layered double perovskite NCs [228]. The resulting NC showed a layered double perovskite structure with regular vacancies and a direct bandgap of 1.79 eV. In addition, a series of Cs$_3$Cu$_2$Ag$_{2−x}$Sb$_2$Cl$_12$ (0 ≤ x ≤ 1) NCs were synthesized by adjusting the stoichiometry ratio of Cu$^{2+}$ and Ag$^{+}$ precursors. With the increase of Cu$^{2+}$ content (x ≥ 0.5), the crystal structure of Cs$_3$Cu$_2$Ag$_{2−x}$Sb$_2$Cl$_12$ transitioned from cubic double perovskite to monoclinic-layered double perovskite and changed from indirect bandgap to direct bandgap. The direct correlation between crystal phase and electronic bandgap structure reveals an effective means to control the optical properties of the material by adjusting the composition, thereby adjusting the crystal structure of NCs.

3.7. Cu(II)-Based Halide Perovskite NCs. Copper (Cu), a first-row transition metal, is of particular interest for the incorporation into the perovskite structure as replacement for Pb in virtue of their nontoxicity, low cost, and earth abundance [229–234]. The Cu$^{2+}$-based halide perovskites crystallize in $A_2$CuX$_4$ (A = MA$^+$, Cs$^+$, X = CI, Br$^-$, and I$^-$) structure. The first report on the synthesis of Cs$_2$CuX$_4$ QDs was proposed by Yang et al. by an improved LARP technique at RT [230]. In their work, the chloride and bromide perovskite QDs could be crystallized in an orthorhombic crystal structure, while the pure iodine QDs cannot be obtained due to the instability of copper diiodide (Figure 9(b)). The obtained Cs$_2$CuCl$_4$, Cs$_2$CuBr$_4$, and Cs$_2$Cu(Br/Cl)$_4$ QDs exhibited strong emission at 385, 410, and 504 nm, respectively (Figure 9(a)). The halide-induced spectral tunability is attributed to the direct modulation of the band structure, because the halide orbitals have the greatest contribution to the frontier orbital in the halide perovskites [235, 236]. Moreover, the resulting Cs$_2$CuX$_4$ QDs all showed a quasispherical shape with uniform size distribution, and the average diameters of them were almost the same (Figures 9(c)–9(e)). Importantly, the PLQY of Cs$_2$CuCl$_4$ QDs is as high as 51.8%, which is quite promising for application in the field of lighting and display [230]. These Cu-based QDs also exhibited excellent air stability, in which the PL intensity decreased only to 92% of the initial value after storing in air ambient for 30 days.

In addition to the LARP technique, the high-temperature HI method was also proposed by Booker et al. to prepare the Cu-based halide NCs [231]. By changing the ratio of OA and OAm, a series of Cs$_2$CuCl$_4$ NCs with different morphologies (QDs, NPLs, NRs, and NWs) and sizes (6–300 nm) were obtained (Figures 9(f)–9(k)). Differently, the nanomaterials are QDs with a variety of particle sizes (2:1, 4:1, and 1:4), NRs with an average length of 1.2 µm (1:2), NPLs with a 200 nm radius (2:2), and NWs with a length over 2 µm but only 50 nm wide (4:4). This is because different coordination solvents can significantly affect the NC morphology via either oriented attachment or inhibition or promotion of different growth facets [231]. All these nanomaterials exhibited quite broad emission spectra with an emission peak at 525 nm, possibly because of the copper defects inside the NCs. It can be anticipated that such ternary copper halide NCs represent a new class of nontoxic, solution-processable semiconductor building blocks for optoelectronic applications.

3.8. Cu(I)-Based Halide Perovskite NCs. Another possible ternary copper halide compound with monovalent Cu$^+$ has recently also attracted great research interest due to their promising optoelectronic performances [237–245]. Han et al. first reported the colloidal synthesis of low-dimensional cesium copper halide NCs (including 0D Cs$_2$Cu$_2$I$_3$ and 1D Cs$_2$Cu$_2$I$_3$) and demonstrated that the reaction temperature is crucial for the final products, as illustrated schematically in Figure 10(a) [246]. At a high reaction temperature of ~110°C, the final products can be synthesized as 1D Cs$_2$Cu$_2$I$_3$ NRs. Such 1D crystal structure is characterized by edge-shared [CuI$_3$]$^{3-}$ ribbons surrounded by Cs$^+$ ions. In contrast, 0D Cs$_2$Cu$_2$I$_3$ NCs were obtained at low reaction temperature (~70°C). The typical Cs$_2$Cu$_2$I$_3$ crystal structure exhibited two types of Cu$^+$ sites, namely, tetrahedral site and trigonal site [244]. Both of them form [CuI$_3$]$^{3-}$, and each [CuI$_3$]$^{3-}$ is separated by surrounding Cs$^+$ ions, forming a characteristic 0D structure at the molecular level. The 0D Cs$_2$Cu$_2$I$_3$ NCs showed a strong blue emission peaked at 441 nm with a PLQY up to 67%, while 1D Cs$_2$Cu$_2$I$_3$ NRs exhibited a weak yellow emission centered at 553 nm with a PLQY of 5%. Besides, both samples are characterized by large Stokes shifts (Cs$_3$Cu$_2$I$_5$, ~144 nm; Cs$_2$Cu$_2$I$_3$, ~229 nm) and wide linewidths (Cs$_2$Cu$_2$I$_3$, ~60 nm; Cs$_2$Cu$_2$I$_3$, ~100 nm). Such large Stokes shift and the broadband feature mean that the emission does not originate from the band-edge-related recombination but may be caused by the STEs [246]. Through using femtosecond transient absorption spectroscopy measurement, a broad excited state absorption plateau across the region of 400–700 nm was probed, which confirmed the formation of STEs. Furthermore, an ultrafast rise time of ~100 fs was obtained in the photoinduced absorption band, indicating that the STEs formed rapidly. Following this work, Luo et al. systematically investigated the colloidal syntheses and optical properties of 0D copper halide materials with isostructural series (such as Cs$_3$Cu$_2$X$_5$, X = Cl, Br, and I) [247]. In this preparation, Cs$_3$Cu$_2$I$_5$ NCs were synthesized by a hot plate method, while Cs$_3$Cu$_2$Br$_5$ and Cs$_3$Cu$_2$Cl$_5$ NCs were obtained by the standard Schelenk technique because they are easily oxidized in ambient conditions. Moreover, both Cs$_3$Cu$_2$I$_5$ and Cs$_3$Cu$_2$Br$_5$ NCs exhibited a rod-like morphology with the average size of
~20 \times 10 \text{ nm} \) (Figures 10(b)–10(e)), and Cs$_3$Cu$_2$Cl$_5$ NCs displayed a cube-like shape with the average edge length of 13 nm (Figures 10(f) and 10(g)) [247]. An interesting phenomenon is that the PL peaks of Cs$_3$Cu$_2$X$_5$ NCs showed a red shift via successive substitution of X halogen ions from I$^-$ to Br$^-$, and Cl$^-$ (Figure 10(h)), which is very different from...
the typical CsPbX₃ NCs. For the STE emission, the PL peak energy is given by \( E_b - E_e - E_s - E_l \), where \( E_b \) is the bandgap energy, \( E_e \) is the exciton binding energy, \( E_s \) is the self-trapping energy, and \( E_l \) is the lattice deformation energy [248–250]. The final emission energy is determined by all these factors, which is a quite complicated process. Therefore, these CsₓCu₂X₅ NCs showed a gradually red shift with lighter halides, indicating that their emission energy decreases along this line [251–254].

Through the reverse HI method, Shi et al. achieved an obvious enhancement in the PLQY of Cs₃Cu₂I₅ NCs up to ~87%. Such a high PLQY value may be attributed to the improved crystallinity of NCs and a large exciton binding energy (138.4 meV), which allows for an efficient radiative recombination of exciton at RT [255]. Similar to other previous reports, the PL spectra of such NCs are characterized by a large Stokes shift and a large FWHM. Through fitting the temperature-dependent FWHM, a relatively large Huang-Rhys factor of 42.97 was derived, which indicates the presence of strong electron-phonon coupling in Cs₃Cu₂I₅ and facilitates the formation of STEs. Furthermore, by conducting theoretical calculations of Cs₃Cu₂I₅, their electronic structure and optical properties were deeply understood. Figure 10(i) illustrates the specific STE-related excitation
and recombination processes of Cs$_3$Cu$_2$I$_5$. Due to the strong photoacoustic coupling, the free electrons upon relaxation will fall into the lower energy self-trapped excited states through ultrafast excited-state structural reorganization [256–259]. Subsequently, the recombination between trapped electrons and holes generates a broadband emission with a large Stokes shift.

Excitingly, these emerging copper halide materials possess excellent stability. Experimentally, the PL intensity of Cs$_3$Cu$_2$I$_5$ NCs almost can recover to the initial level after four temperature cycles (20–100–20°C) with a duration time of 18 h, and the spectral shape and peak position were almost unchanged [255]. In addition, the Cs$_3$Cu$_2$I$_5$ NCs, without any encapsulation and protection, also demonstrated remarkable stability against oxygen and water degradation after a 35-day storage in air ambient. Theoretical results from first-principles molecular dynamics simulations further showed that Cs$_3$Cu$_2$I$_5$ materials have a positive enthalpy of 39.1 meV/atom and a small potential energy fluctuation, manifesting its good thermodynamic stability (Figure 10(i)). This study also extended the theoretical investigation into the defect properties of Cs$_3$Cu$_2$I$_5$. It is worth noting that the formation energy of Cu vacancy ($V_{Cu}$) can be calculated as the lowest at two growth conditions (Cu-poor and Cu-rich). Unlike the conventional perovskites with halide vacancy as the natural defects [206], in 0D Cs$_3$Cu$_2$I$_5$, the strong spatial localization of dominant defect $V_{Cu}$ in the [Cu$_3$I$_5$]$^{3-}$ cluster enhances its diffusion barrier, leading to robust material stability. It is reasonably believed that these copper halide materials with excellent stability could serve as an ideal candidate for fabricating high-performance optoelectronic applications compatible with practical applications.

3.9. Rare Earth-Based Halide Perovskite NCs. Rare earth (RE) elements are called "the vitamins of modern industry" and are widely used as dopants or components to adjust the specific physical and chemical properties of different materials [260, 261]. The variable valence states and electronic structures of RE ions give them flexible redox properties and have unique luminescence and electromagnetic characteristics [262]. Therefore, RE elements have been widely incorporated into perovskite nanostructures to improve their performance and broaden their applications [263, 264]. Both RE-doped and RE-based perovskite NC materials exhibit satisfactory optical, magnetic, electronic, and catalytic properties. These unique properties originate from the effectively shielded electrons in the 4f subshell by the externals in the outer 5s and 5p subshells [265, 266]. Recently, an Eu$^{2+}$-doped CsBr NC with an average particle size of 51.5 nm was synthesized by a facile HI method [267]. The resulting CsBr:Eu$^{2+}$ NCs exhibited an emission band at 440 nm with a FWHM of 31 nm. The emission band occurring near 440 nm is attributed to the 4f$^5$5d$^1$ to 4f$^6$ transition in the Eu$^{2+}$ ion [268, 269]. Moreover, the excitation spectrum of CsBr:Eu$^{2+}$ NCs showed two absorption peaks at 272 and 345 nm, similar to those observed in bulk crystals [269]. The peak observed at 272 nm is ascribed to the 4f$^6$→4f$^5$5d$^1$ ($t_{2g}$) transitions, while the peak at 345 nm is attributed to the 4f$^6$→4f$^5$5d$^1$ (e$_g$) transition [269, 270]. At an optimized reaction time of 20 min, high-quality blue-emissive NCs were achieved with a high PLQY of 32.8%.

Lately, Huang et al. synthesized the perovskite-structured CsEuCl$_3$ NCs with a uniform size of about 15 nm using the solution-phase method (Figures 11(a)–11(e)) [271]. The CsEuCl$_3$ NCs exhibited a sharp emission peak at 435 nm with a narrow FWHM of 19 nm. In addition, a strong excitonic absorption at ~350 nm was observed, corresponding to an optical bandgap of 3.09 eV. The CsEuCl$_3$ NCs can be stable for several months in toluene solution under an inert atmosphere, but they will quickly decompose in moisture/oxygen environment conditions due to the orbital transition of the Eu$^{3+}$ (Figure 11(f)). In addition, Moon et al. reported the colloidal synthesis and optical characterization of RE-based CsYbI$_3$ perovskite NCs with a high crystallinity and a highly uniform size distribution [272]. During the NC growth process, Yb was introduced into the B site of the cubic AB$_3$ perovskite lattice. The as-synthesized NCs exhibited a strong excitation-wavelength-independent emission at 671 nm with a small Stokes shift of 7 nm and a narrow FWHM of 47 nm (Figure 11(g)). Furthermore, the exciton binding energy of CsYbI$_3$ NCs was derived to be ~33 meV (Figures 11(h) and 11(i)), which is higher than the RT thermal ionization energy (~26 meV) but significantly lower than those of previously reported lead-free perovskite NCs [273, 274]. The PL emission behavior of CsYbI$_3$ NCs is mainly due to the exciton-like transition. The NCs also achieved a high PLQY of 58%. These results indicated that CsYbI$_3$ NCs could offer plentiful opportunities in optoelectronic applications, such as LEDs, photovoltaic solar cells, photodetectors, and energy conversion and storage devices.

Table 1 summarizes the morphologies, optical properties, and stabilities of the reported lead-free perovskite NCs. Although the synthesis of lead-free perovskite NCs with various morphologies has progressed significantly, their optoelectronic properties have not yet been fully explored. Moreover, the optical properties of most lead-free perovskite NCs are far lower than lead-based counterparts, especially their PLQY hardly exceeds 80%, which is not conducive to their application in light-emitting applications. Both experimental and theoretical studies on the photophysical processes in the materials should be performed to elucidate the nature of defects in lead-free halide perovskite NCs.

4. Lead-Free Halide Perovskite NCs for Optoelectronic Applications

4.1. Optically Pumped White Light-Emitting Devices. Highly luminescent metal-halide perovskite NCs with tunable emission are a promising light emitter for solid-state lighting and display applications [267, 275]. Optically pumped WLEDs that combined UV or blue chips with downconverting phosphors are regarded as a novel solid-state lighting technology to replace currently used incandescent and fluorescent lamps [267]. For optically pumped WLEDs, ideal down-converting phosphors are considered to be key and technologically important components of white light generation [275]. Encouragingly, the lead-free perovskite NC system shows many fascinating characteristics of highly luminescent,
broadband emission, and large Stokes shift, which makes them a promising candidate for WLED applications. For example, Tan et al. used the highly stable and efficient blue-emitting Cs₂SnCl₆:2.75% Bi perovskite to fabricate WLEDs by integrating with the commercial yellow-emitting phosphors (Ba₂Sr₂SiO₄:Eu²⁺ and GaAlSiN₃:Eu²⁺) and a 365 nm LED chip [107]. The fabricated WLEDs exhibited a warm-white light with a Commission Internationale de l’Eclairage (CIE) color coordinate of (0.36, 0.37) and a correlated color temperature (CCT) of 4486 K. Leng and coworkers demonstrated a WLED based on lead-free blue-emitting Cs₃Bi₂Br₉ QDs combined with the yellow-emitting Y₃Al₅O₁₂ (YAG), exhibiting decent white light with a CIE of (0.29, 0.30) and a CCT of 8477.1 K [140]. The fabricated WLEDs also showed satisfactory stability, with the device maintaining 78% of the initial PL intensity after 365 nm UV illumination for 16 h and remaining 68% even at heated at 60°C for 15 h. Similarly, Ma et al. used Cs₃Bi₂Br₉/BiOBr nanocomposite powders with improved PL performance along with commercial phosphors (Ba₅Sr₃SiO₁₀:Eu²⁺) to demonstrate a WLED with color coordinates of (0.312, 0.334) (Figures 2(a) and 2(b)). Moreover, the device exhibited excellent operation stability, and almost
Table 1: Chemical formula, morphology, optical properties, stability, and synthesis methods of currently explored lead-free halide perovskite NCs.

| Formula       | Morphology (size) | Abs. peak (nm) | Em. peak (nm) | PLQY (%) | FWHM (nm) | Stability                  | Method                  | Ref.          |
|---------------|-------------------|----------------|---------------|----------|-----------|----------------------------|-------------------------|---------------|
| CsSnCl₃ NC    | ~420              | 490 ≤0.14      | ~180          |          |           | Up to 2 weeks in air       | HI [83]                |               |
| CsSnBr₃ NC    | ~610 ~660         | ~140 ~200      |               |          |           | Up to 2 weeks in air       | HI [83]                |               |
| CsSnI₃ NC (12 nm) | ~750 ~945       | ≤0.14 ~245     |               |          |           | Up to 2 weeks in air       | HI [83]                |               |
| PEA₂SnI₄ NPL (1.5 × 1.5 µm) | ~620 640 | 6.4 36 | PL intensity: 75% (illumination for 120 h) | Nonsolvent crystallization | [88] |
| PEA₂SnBr₄ NPL (3 × 3 µm) | ~450 550 | 0.1 80 | - | Nonsolvent crystallization | [88] |
| CsSnI₃ NPL (0.7 µm) | ~760 780 | - ~80 | - | - | LARP [89] |
| CsSnCl₃ QR    | 588 625 ≤32      | 2 months in inert atmosphere | |          |           | - | LARP [94]                |               |
| CsSnBr₃ QR    | 630 660 ≤32      | 2 months in inert atmosphere | |          |           | - | LARP [94]                |               |
| CsSnI₃ QR (30 × 5 nm) | 668 709 | - ≤32 | - | - | LARP [94] |
| CsSnBr₃ Nanocage (~0.1 µm) | 655 685 | 2.1 56 | 95% decomposition (illumination for 1 day) | HI [93] |
| Cs₂SnI₆ Nanobelt (~1 µm) | ~600 620 | 0.11 49 | 1 week in ambient environment | HI [95] |
| Cs₂SnI₆ NPL (~0.5 µm) | 722 742 | 28 70 | - | - | HI [102] |
| Cs₂SnCl₆ NC (14.25 nm) | 317 438 | 4.37 | 20 s in electron beam irradiation | HI [105] |
| CsGeCl₃ QR (5 nm) | 565 607 | - ~25 | - | - | LARP [121] |
| CsGeBr₃ QR (5 nm) | 610 650 | - ~25 | - | - | LARP [121] |
| CsGeI₃ QR (5 nm) | 655 696 | - ~25 | 45% decomposition (48 h, in ambient) | LARP [121] |
| CsGeI₃ NC (45 nm) | 660 804 | 3.7 ~50 | Few hours in ambient environment | HI [115] |
| Cs₃Bi₂Cl₉ QD (5 nm) | 320 393 | 26.4 60 | - | - | LARP [140] |
| Cs₃Bi₂Br₉ QD (5 nm) | 350 410 | 19.4 48 | PL intensity: 72% (illumination for 16 h) | LARP [140] |
| Cs₃Bi₂I₉ QD (5 nm) | 510 597 | 0.018 66 | - | - | LARP [140] |
| Cs₃Bi₂Br₆ NC (14.2 nm) | 406 440 | 6.03 ~100 | - | - | HI [139] |
| Cs₃Bi₂Cl₆ NC (14.2 nm) | 340 - | - | - | - | HI [303] |
| Cs₃Bi₂I₆ NC (15.5 nm) | 480 - | - | - | - | HI [303] |
| Cs₃Bi₂Cl₉ NPL (20 × 3 nm) | 360 - | - | - | - | HI [303] |
| Cs₃Bi₂Br₉ NPL (25 × 3 nm) | 430 - | - | - | - | HI [303] |
| Rb₃Bi₄Cl₁₆ QD (1.85 nm) | 365 437 | 28.43 93 | 20% reduction (illumination for 12 h) | LARP [138] |
| FA₃Bi₂Cl₉ QD | 360 400 | ~65 | - | - | LARP [132] |
| FA₃Bi₂Br₉ QD (4.9 nm) | 404 435 | 52 65 | PL intensity: 75% (1 month in inert atmosphere) | LARP [132] |
| FA₃Bi₂I₉ QD | 460 526 | ~70 | - | - | LARP [132] |
| MA₃Bi₂Cl₉ QD | 340 360 | 15 50 | - | - | LARP [122] |
| MA₃Bi₂Br₉ QD (3.1 nm) | 390 423 | 12 62 | PL intensity: 89% (illumination for 12 h) | LARP [122] |
| MA₃Bi₂I₉ QD | 400 540 | 0.03 91 | - | - | LARP [122] |
| Cs₃Sb₂Cl₉ QD (5.2 nm) | 300 385 | 19.5 61 | - | - | LARP [164] |
| Cs₃Sb₂Br₉ QD (5.4 nm) | 360 409 | 51.2 55 | PL intensity: 50% (illumination for 108 h) | LARP [164] |
| Cs₃Sb₂I₉ QD (5.8 nm) | 550 640 | 26 73 | - | - | LARP [164] |
| Cs₃Sb₂I₉ NPL (27 × 14 nm) | 540 574 | 32 | Decompose at 400°C | HI [158] |
| Cs₃Sb₂I₉ NR (655 × 46 nm) | 560 600 | 30 | 3 months in inert atmosphere | HI [158] |
no emission decay was observed after 10h running time, which is much better than the reference device with blue-emitting CsPbCl_{1.5}Br_{1.5} QDs as the phosphors [141]. RE-based CsBr:Eu\textsuperscript{2+} NCs also were used as down converters to fabricate WLEDs combined with the YAG phosphors and 365 nm GaN LED chips (Figure 12(c)) [267]. A CIE color coordinate (0.321, 0.336) of the device could be obtained under a forward current of 50 mA (Figure 12(d)), and little shift was observed under different forward bias currents, indicating good color stability of the output light of the WLED.

However, the above devices still rely on commercial phosphors containing RE elements, and their potential supply risks and price increases are obstacles for future large-scale commercialization. To address this issue, a highly promising strategy is to achieve a single-component white-light emitter that can be pumped by UV chips. In this respect, lead-free double perovskite Cs\textsubscript{2}AgInCl\textsubscript{6} with a broadband white emission is a good choice. For example, Hu et al. used Cs\textsubscript{2}Ag\textsubscript{1-}\textsubscript{x}Na\textsubscript{x}In\textsubscript{1-}\textsubscript{y}Bi\textsubscript{y}Cl\textsubscript{6} (x = 0 – 1, y = 0.03 – 0.16) NCs to achieve an efficient single-component white light under UV light excitation [219]. Also, they demonstrated that the double perovskite NCs possess a tunable color temperature. Through the incorporation of Na\textsuperscript{+} and Bi\textsuperscript{3+}, the NCs displayed a bright near-white light emission with tunable CCT ranging from 9759.7 to 5813.4 K and CIE coordinates ranging from (0.246, 0.362) to (0.321, 0.445) (Figure 12(e)). Similarly, Yella et al. observed that Bi\textsuperscript{3+}-alloyed Cs\textsubscript{2}AgInCl\textsubscript{6} double perovskite NCs exhibited tunable white emission with the CIE coordinates from orange to blue under UV light excitation, by simply increasing the Bi dopant content [276]. In addition to the single-component white-light emitters, two-component broadband emission combinations can also realize high-quality white light with a good color-rendering due to their extended visible light spectrum range. Recently, Vashishtha et al. demonstrated a bright white light emission with a good color-rendering by mixing two broadband emissive copper halides [251]. Moreover, a tunable emission color from blue-white to yellow-white with the CIE coordinate ranging from (0.145, 0.055) to (0.418, 0.541) was achieved by mixing Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} NPLs and CsCu\textsubscript{2}I\textsubscript{3} NRs in different proportions. Since Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{5} and CsCu\textsubscript{2}I\textsubscript{3} are pure iodide phases, the mixed halide migration observed in perovskites can be avoided, and therefore, pure white emission was obtained by appropriate mixing of both phases. These studies above showed that the lead-free perovskite NCs are potentially attractive candidates for the preparation of environmentally friendly and stable WLEDs, making practical applications of them a real possibility.

### Table 1: Continued.

| Formula       | Morphology (size) | Abs. peak (nm) | Em. peak (nm) | PLQY (%) | FWHM (nm) | Stability                  | Method       | Ref.   |
|---------------|-------------------|----------------|---------------|----------|-----------|----------------------------|--------------|--------|
| Rb\textsubscript{3}Sb\textsubscript{2}I\textsubscript{9} NC (7.5 nm) | 500 | 550 | 30 | Decompose at 400°C | HI | [158] |
| Cs\textsubscript{2}AgBiBr\textsubscript{6} NC (9.5 nm) | 500 | 625 | - | ~140 | No decomposition (illumination for 500 h) | HI | [195] |
| Cs\textsubscript{2}AgBiCl\textsubscript{6} NC (8.2 nm) | 366 | 738 | - | - | - | HI | [179] |
| Cs\textsubscript{2}AgBiBr\textsubscript{6} NC (8.2 nm) | 432 | 629 | - | - | - | HI | [179] |
| Cs\textsubscript{2}AgInCl\textsubscript{6} NC (10 nm) | 310 | 600 | 0.6 | ~200 | - | HI | [203] |
| Cs\textsubscript{2}AgSbCl\textsubscript{6} NC (10 nm) | 360 | - | - | - | - | HI | [203] |
| Cs\textsubscript{2}AgSbBr\textsubscript{6} NC (14.3 nm) | 360 | - | - | - | - | HI | [205] |
| Cs\textsubscript{2}NaInCl\textsubscript{6} NC (12.5 nm) | 269 | - | - | - | Decomposition (1 month in inert atmosphere) | HI | [208] |
| Cs\textsubscript{4}Cu\textsubscript{2}Sb\textsubscript{2}Cl\textsubscript{12} NC (12.5 nm) | 523 | - | - | - | 2 months in the air | HI | [228] |
| Cs\textsubscript{3}CuCl\textsubscript{4} NC (8.2 nm) | 330 | 388 | 51.82 | 68 | PL intensity: 92% (in inert atmosphere) | LARP | [230] |
| Cs\textsubscript{2}CuBr\textsubscript{4} QD (3.7 nm) | 360 | 393 | 37.5 | 74 | PL intensity: 92% (in inert atmosphere) | LARP | [230] |
| Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{3} NC (20 x 30 nm) | 284 | 445 | 73.7 | 80 | PLQY stable for 30 days in air | HI | [241] |
| Cs\textsubscript{3}Cu\textsubscript{2}I\textsubscript{3} NC (20 nm) | 285 | 441 | 67 | 82 | Decompose at 600°C | HI | [246] |
| Cs\textsubscript{2}Cu\textsubscript{2}I\textsubscript{3} NR (1 \( \mu \)m) | 310 | 553 | 5 | 90 | PL intensity: 58% (in air for 16 days) | HI | [247] |
| Cs\textsubscript{3}Cu\textsubscript{2}Br\textsubscript{3} NC (21 nm) | 269 | 461 | 16.9 | 90 | PL intensity: 58% (in air for 16 days) | HI | [247] |
| Cs\textsubscript{3}Cu\textsubscript{2}Cl\textsubscript{3} NC (13 nm) | 259 | 527 | 48.7 | 130 | Slow decrease under irradiation for 1 h | HI | [247] |
| Cs\textsubscript{2}Cu\textsubscript{2}I\textsubscript{3} NC (2.86 nm) | 360 | 575 | 11 | 111 | - | LARP | [254] |
| CsBr:Eu NC (51.5 nm) | 350 | 440 | 32.8 | 31 | PLQY stable for 60 days at RT | HI | [267] |
| CsYb\textsubscript{2}I\textsubscript{5} NC (20 nm) | 664 | 671 | 0.58 | 47 | PL intensity: 58% (in air for 16 days) | HI | [272] |
| Cs\textsubscript{3}Cu\textsubscript{2}Cl\textsubscript{5} NC (13 nm) | 259 | 527 | 48.7 | 130 | Slow decrease under irradiation for 1 h | HI | [247] |
| Cs\textsubscript{3}Cu\textsubscript{2}Br\textsubscript{5} NC (21 nm) | 269 | 461 | 16.9 | 90 | PL intensity: 58% (in air for 16 days) | HI | [247] |
4.2. Electrically Pumped Light-Emitting Devices. Along with the success of lead-free perovskites in optically pumped WLEDs, their application in electrically pumped LEDs has recently attracted considerable attention. The excellent luminescent properties and high environmental stability of lead-free perovskite NCs endow them with great potential in LEDs. A classic device structure of the perovskite LED consists of a p-type hole transport layer (HTL), a perovskite active emission layer (EML), and an n-type electron transport layer (ETL). Under the driving voltage, electrons and holes are, respectively, injected into ETL and HTL and recombined at the intermediate perovskite layer to emit photons [162]. In the past three years, the research and exploration of lead-free perovskite LEDs have been in full swing. For example, Zhang et al. proposed an orange-emissive lead-free LED by using \((\text{C}_{18}\text{H}_{35}\text{NH}_{3})_{2}\text{SnBr}_{4}\)-layered perovskite as the active layer [277], and the corresponding inverted device structure is ITO/ZnO/PEI/(\(\text{C}_{18}\text{H}_{35}\text{NH}_{3})_{2}\text{SnBr}_{4}\)/TCTA/MoO3/Au, as illustrated in Figure 13(a), where the ZnO/PEI bilayer was used as the ETL, the TCTA layer was served as the HTL, and the MoO3/Au bilayer was used as the anode. Light emission occurs when injected electrons and holes meet in the \((\text{C}_{18}\text{H}_{35}\text{NH}_{3})_{2}\text{SnBr}_{4}\) active layer. The \((\text{C}_{18}\text{H}_{35}\text{NH}_{3})_{2}\text{SnBr}_{4}\)-based LEDs exhibited a broad electroluminescence (EL) band located at 625 nm with a FWHM of 162 nm, and a maximum luminance of 350 cd/m2 and an EQE of 0.1% were achieved (Figures 13(b) and 13(c)). Another observation is that the FWHM of the EL peak is much wider than that of the PL, which may be ascribed to the thermally activated nature of STEs. Considering that the organic chains in such Sn-based perovskite are easily decomposed in high-temperature environments, all-inorganic halide perovskites are more promising in terms of stability. As mentioned earlier, all-inorganic Sb-based perovskite QDs have both excellent stability and good luminescence performance, so they are suitable for use as an active layer in LEDs [152, 160, 164]. More recently, an electrically pumped violet LED based on lead-free CsSbBr9 QDs with an inverted architecture of ITO/ZnO/(PEI)/QDs/TCTA/MoO3/Al was demonstrated by Ma and coworkers (Figures 13(d) and 13(e)) [164]. The device shows a violet emission located at 408 nm, which is the shortest wavelength of perovskite LEDs as far as we know. Moreover, a maximum luminance of \(\sim 29.6\) cd/m2 and an EQE of \(\sim 0.206\)% were achieved at a driven voltage of 7.0 V (Figure 13(f)). Unlike the above-discussed Sn-based perovskite LEDs, the CsSbBr9 QD-based LEDs exhibited excellent working stability in a continuous current mode [278]. After 6 h continuous running, the emission intensity and current density of the studied LED remain almost unchanged, which can be attributed to the non-diffusion behavior of halide vacancy defect in the CsSbBr9 layer that suppresses the accumulation of charge carriers at the interface under an electric field.
Blue-emitting perovskite LEDs currently remain a challenging issue compared with the efficient red and green counterparts [209, 230]. This is because the blue emission usually relies on the mixed-halide strategy, which always suffers from ineluctable phase separation, especially under electrical potential [163]. In addition, most previously reported perovskite LEDs were made from the lead-based perovskites, and the lead toxicity and environmental instability have cast a gloomy shadow over their practical applications [237–240].

Ternary copper halides have recently been strongly studied in electrically pumped LEDs due to their nontoxicity, low cost, and high luminescence efficiency [241–245]. Recently, the blue-emitting Cs₃Cu₂I₅ NCs were successfully used as the light emitter for electrically pumped LED fabrication (Figures 13(g)–13(i)) [255]. The device exhibited a deep-blue EL emission centered at ~445 nm with the color coordinates of (0.16, 0.07), meeting the crucial blue NTSC standard. In addition, a maximum EQE of ~1.12% and a luminance of ~263.2 cd/m² were realized, comparable with the best-performing blue LEDs based on lead-halide perovskites. More importantly, the deep-blue LED demonstrated remarkable operating stability, producing a record long half-lifetime of ~108 h, which is much better than other halide perovskite LEDs [163]. Two main reasons were summarized by analyzing the experimental and theoretical results and listed as follows: (1) Thanks to the remarked stability of Cs₃Cu₂I₅ NCs against heat and environmental oxygen/moisture, the EL performance degradation caused by Joule heat during long-term operation was alleviated. (2) The EL degradation of conventional Pb-based perovskite LEDs over working time...
is usually due to the formation of a mass of halide vacancy defects and the accumulation of undesirable charges at the interface caused by ion migration. Fortunately, the strong spatial localization of dominant defect ($V_{\text{Cu}}$) in orthorhombic Cs$_3$Cu$_2$I$_5$ would increase its diffusion barrier, leading to the stable existence of NCs in the electric field.

Although wow-toxicity perovskite LEDs have been developed rapidly in recent years, the device performances in terms of EQE, luminance, and turn-on voltage were far inferior for commercial applications. On the one hand, owing to the relatively large bandgap of some lead-free perovskite emitters, the selection of suitable carrier transport layers appears to be particularly important, and the well-designed device configuration is required to ensure efficient charge injection. On the other hand, the PLQY of most lead-free perovskite NCs hardly exceed 80%, which is very unfavorable for the preparation of high-performance devices. More attempts should be focused on increasing the PLQY by defect passivation with different ligands, metal ion doping, and controlling the spatial distribution of the composite. Through the above efforts coupled with the promising properties of lead-free perovskite NCs, we have reasons to believe that the environmental-friendly high-performance LEDs are not far from being realized.

4.3. Photovoltaic Solar Cells. In addition, perovskite materials have a huge potential in the field of solar cells due to their large absorption coefficients, long diffusion lengths of charge carriers, high defect tolerance, and low exciton binding energies [279]. Lead-free perovskite NCs always have tunable bandgap, light-response ranges, scalable materials, and cost-effectiveness; therefore, they are regarded as good light harvesters to replace organic dyes in mesoscopic solar cells. Recently, lead-free CH$_3$NH$_3$SnBr$_{3-x}$I$_x$ (MASnBr$_{3-x}$I$_x$, $x = 0, 1, 2, 3$) QDs as a light-harvesting material for mesoscopic photovoltaic solar cells were proposed by Chen in 2018.
(Figure 14(a)) [121]. By adjusting the Br/I ratio, the bandgap of QDs is adjusted from 2.3 to 1.5 eV to expand the absorption range from visible to the near-infrared region. The PCE characterization in Figure 14(b) showed that the photorelectron response range of MASnBr$_3$-$_x$I$_y$ NCs sensitized solar cells extends from 300 to 800 nm. MASnBr$_3$I QD and TiO$_2$ have the best matching energy level. N719 dye, which is closely combined with TiO$_2$ and NCs, is used to make it covalently adsorbed on the surface of NCs and TiO$_2$. As shown in Figure 14(c), the MASnBr$_3$I QDs and N719-cosensitized solar cell achieve an efficiency of 8.79%. The lead-free all-inorganic CsSnI$_3$ QDs are expected to increase the optical density of the active layer due to their low cost, nontoxic compounds, and inorganic hybrids possessing better chemical effect and photostability, thereby improving the light collection [280]. In addition, the surface area of the quantum rod is larger than that of the bulk, which can allow a larger contact area and hence improve the conversion efficiency. Therefore, a high photovoltaic performance with a PCE close to 13% was obtained for the CsSnI$_3$ device, and the PCE value of the solar cell was the lowest, i.e., Cl (Figure 14(d)). The EQE plotted in Figure 14(e) confirms the increased current density value of these devices, where the combined current density values of devices derived from lead-free perovskites CsGeI$_3$, CsGeBr$_3$, and CsGeCl$_3$ were determined to be 11.08, 10.22, and 9.15%, respectively. The EQE values of the highest performing devices were observed to exceed 66% (for CsGeCl$_3$), 68% (for CsGeBr$_3$), and 79% (for CsGeI$_3$) (Figure 14(f)).

4.4. Photodetectors. Except for the optoelectronic applications as mentioned above, perovskite photodetectors that directly convert optical signals into the electrical signal have also attracted extensive attention in recent years [39–45, 238]. Due to the large absorption coefficients, high carrier mobility coupled with low-toxicity and good environmental stability, lead-free perovskite NCs are therefore suitable for photodetector applications. In 2018, Ghosh et al. fabricated high-performance photodetectors based on the Cs$_2$SnI$_6$ nanomaterials with different morphologies, through a simple spin-casting approach on the patterned ITO substrate [103]. Under white light irradiation, the devices constructed by Cs$_2$SnI$_6$ NRs exhibited higher photocurrent gain values than other morphologies. This is because that the 1D NRs provide improved carrier migration and are found to be advantageous compared to the other Cs$_2$SnI$_6$ morphologies. Similarly, a photodetector based on highly uniform 1D Cs$_5$Sb$_2$Cl$_9$ NWs with lengths of several microns was fabricated (Figure 15(a)) [152]. As shown in Figure 15(b), a significant increase in the current was observed upon light illumination. Moreover, a highly sensitive photodetection response with a stable photocurrent signal was observed over repetitive on/off illumination cycles. The rise time and decay time of the photodetectors were measured to be ~0.13 and ~0.23 s, respectively, at a bias voltage of 0.9 V (Figure 15(c)). This stable and repeatable photoswitching property indicates that Cs$_5$Sb$_2$Cl$_9$ NWs are potential photovoltaic materials for optoelectronic applications. Lead-free perovskite nanomaterials with 1D morphology could be also used as the photoactive materials for polarization-sensitive photodetection, resulting in linear polarization sensitivity. For instance, Li et al. demonstrated a polarization-sensitive UV photodetector based on solution-processed 1D CsCuI$_3$ NWs (Figure 15(d)) [239]. Ternary copper halide CsCuI$_3$ has an obvious anisotropy crystal structure and could easily grow into a 1D linear morphology, which is conducive to achieving a high photocurrent anisotropy ratio [240]. Under linearly polarized light excitation, the photocurrent of the device is a strong function of the angle between the polarization of the incident light and the orientation of the NW, as well as the bias voltage (Figure 15(e)). The photocurrent achieves the maximum when the polarization of the light is parallel to the wire (0°), reaches its minimum when it is perpendicular to the wire (90°), and completely recovers to the initial value at 180° polarization. By further extracting the evolution of photocurrent at a bias voltage of 1.0 V as a function of the polarization angle in polar coordinates (Figure 15(f)), a high photocurrent anisotropy ratio of ~3.16 was obtained, which is the maximum value among the perovskite-based polarized photodetectors as far as we know [192]. Lead-free rare-earth-based perovskite NCs have also been used as a photoactive layer for photodetector applications due to their outstanding optical and electrical properties. For example, Lee et al. reported an organic-inorganic hybrid photodetector using graphene and CsYbI$_3$ NCs as the channel materials (Figure 15(g)) [272]. The credible energy level diagram illustrated in Figure 15(h) indicates that under illumination, the photogenerated charge carriers in the NCs can be effectively transferred to the graphene channel before the exciton recombination. Further, the PL decay time of the CsYbI$_3$ NCs/graphene film is substantially reduced compared to the pristine CsYbI$_3$ NC film, which suggests that the photogenerated excitons are well dissociated at CsYbI$_3$ NC/graphene interfaces, with the charge carriers being rapidly and efficiently transferred to the graphene layer [155]. Such fast charge transfer could be elucidated by the intermolecular chemical interactions, such as the van der Waals interaction and π–π interaction, between graphene and the NCs. Therefore, CsYbI$_3$ NC/graphene-based photodetector exhibited an excellent photoresponsivity of 2.4 × 10$^3$ A/W and a high EQE of 5.8 × 10$^3$ at the microwatt level of incident light power (Figure 15(i)). These results indicate that the CsYbI$_3$ NC/graphene hybrid system can be utilized as an effective photoactive channel to enhance the detection performance for visible light illumination.

4.5. Photocatalytic. The composition engineering of halide perovskites can make the tunability of the bandgap over a wide range, so that the photons can be collected effectively, which is essential for improving the photocatalytic efficiency in sunlight. The electronic energy band structure (conduction band edge and valence band edge position) of halide perovskite materials is also expected to achieve effective photocatalytic applications. In recent years, photocatalytic hydrogen evolution from halide perovskites, photocatalytic reduction of CO$_2$, and photocatalytic organic synthesis have
been reported for lead-halide perovskites [281–285]. However, due to the instability of perovskites in the aqueous solution, a hydrogen evolution reaction must be performed in the supersaturated MAPbI3 solution to inhibit the decomposition of perovskites [281, 286]. In this regard, lead-free perovskite NCs are suitable candidates for photocatalysis due to their excellent stability.

Bi-based materials (such as bismuth oxyhalide) have been widely used in the photocatalytic and electrocatalytic reduction of CO2 [287–289]. It was observed that the incorporation of defects into the material increased the adsorption of CO2 and the trapping of excited electrons, resulting in the enhancement of photocatalytic activity [290, 291]. Besides, the crystal structure of the catalyst is another factor that can improve its photocatalytic activity. According to this standard, the Bi-based defect halide perovskite (A3M2X9) forming a 0D monoclinic crystal is an excellent candidate for photocatalytic reduction of CO2 [292]. Generally, Bi-based perovskites are expected to accept defect-tolerant electronic structures in which the conduction and valence bands are formed by antibonding orbits [293]. Similar to the effect of lead-halide perovskite, Bi-based perovskite is expected to stabilize the electrons excited by Bi3+ and the holes formed by Bi4+, just like AgX and PbX2 crystals (X represents halide) [294]. Rb3Bi2I9, Cs3Bi2I9, and MA3Bi2I9 NCs were used to photoreduce CO2 to CO and CH4 at a gas-solid interface.

Figure 15: (a) Schematic representation of the photodetector structure based on Cs3Sb2Cl9 NWs. (b) Current versus voltage characteristics of the Cs3Sb2Cl9 NWs under dark and light irradiation conditions. The inset displays an optical image of the device. (c) Rise and decay time of a single on/off cycle. (d) Schematic illustration of the polarization-sensitive photodetection. (e) Anisotropic response in photocurrent under 325 nm light excitation described via a 2D colormap. (f) Polarization dependence of the photocurrent for CsCu2I3 NWs. (g) Schematic illustration of the perovskite NC-graphene hybrid photodetector. (h) Energy level diagram of the proposed device under illumination. (i) Photoresponsivity and EQE as a function of the illumination power. (a–c) Reproduced with permission from Ref. [152], copyright 2018 Chemistry of Materials. (d–f) Reproduced with permission from Ref. [239], copyright 2020 Materials Horizons. (g–i) Reproduced with permission from Ref. [272], copyright 2019 Advanced Materials.
The photocatalytic activity of Bi-based photocatalysts showed a trend of Cs$_3$Bi$_2$I$_9$ > Rb$_3$Bi$_2$I$_9$ > MA$_3$Bi$_2$I$_9$ > TiO$_2$. Therefore, a conclusion can be made that the cation (site A) and crystal structure are important factors that affect the catalytic activity. In Rb$_3$Bi$_2$I$_9$ and Cs$_3$Bi$_2$I$_9$, the holes are effectively stabilized by Bi$^{4+}$ and oxygen ions, but for MA$_3$Bi$_2$I$_9$, the holes are stabilized by Bi$^{4+}$, CH$_2$NH$_3$$^+$ radical cations, and oxygen anions. Therefore, for MA-based NCs, the efficiency of hole transfer to water (the oxidation channel) is low. This effect makes MA$_3$Bi$_2$I$_9$ worse than the other two NC catalysts, consistent with the results shown in Figures 16(a)–16(c). By contrast, the Cs$_3$Bi$_2$I$_9$ NC has the largest photocatalytic activity due to its excellent charge generation and transfer ability in the presence of CO$_2$ and H$_2$O. Rb$_3$Bi$_2$I$_9$ adopts a crystal structure of distorted-defect variant perovskite type (A$_3$M$_2$X$_9$), for which every third M layer of the perovskites in facet [001] is depleted [293]. Since bismuth constitutes the active site of the catalyst, so the depletion of bismuth in Rb$_3$Bi$_2$I$_9$ reduces the photocatalytic activity relative to Cs$_3$Bi$_2$I$_9$.

In addition, Cs$_2$AgBiBr$_6$ double perovskites have also been demonstrated in photocatalysis applications because of their high optical absorption coefficient and good stability [286]. After a continuous irradiation by simulated solar light (AM 1.5 G, 150 mW cm$^{-2}$) for 6 h, Cs$_2$AgBiBr$_6$ NCs could afford the evolution of CO(R(CO)) and CH$_4$(R(CH$_4$)) with 5.5 and 0.65 $\mu$mol g$^{-1}$, respectively. At the same time, electron consumption reached 16.2 $\mu$mol g$^{-1}$, and since no side reaction of H$_2$O occurred, the selectivity to CO$_2$ reduction reached 100% (Figure 16(d)) [195]. In Figure 16(e), the tentative mechanism of photocatalytic reduction of CO$_2$ on Cs$_2$AgBiBr$_6$ NCs is proposed, in which Cs$_2$AgBiBr$_6$ NCs have a suitable conduction band to drive CO$_2$ reduction. In addition, the total electron consumption of the bulk Cs$_2$AgBiBr$_6$ under AM 1.5 G light for 6 h was 5.6 $\mu$mol g$^{-1}$ (18.75 times lower than that of Cs$_2$AgBiBr$_6$ NCs (105 $\mu$mol g$^{-1}$)), indicating that the nanostructured particles are more effective for enhancing photocatalytic performance.

5. Summary and Future Perspectives

Up to now, driven by the toxicity of Pb, the research work on the development of suitable lead-free perovskite NC substitutes has made great progress. A series of low-toxic or nontoxic metal cations, such as Sn(II), Sn(IV), Ge(II), Pd(II), Bi(III), Sb(III), Cu(I), Cu(II), Eu(II), Yb(II), Na(I), In(III), and Ag(I), have been exploited as Pb substitutes to produce lead-free perovskite NCs. In this review, we summarized the recent developments of lead-free perovskite NCs, including the material exploration, crystal structures, stability, optoelectronic properties, and their applications. Considering that the device performances obtained are still behind those attained from the lead-halide perovskites, this subject deserves further research and more efforts should be made. In the following, we list the currently existing challenges and possible development opportunities of lead-free perovskite NCs in the field of optoelectronics.

Material synthesis is the foundation of device applications. Compared with the conventional lead-halide perovskite NCs, the synthesis route of lead-free perovskite NCs is narrower and is limited to the HI and LARP method. Seeking novel or modified methods for preparing lead-free perovskite NCs should be a priority for all working in this field. Moreover, one of the fundamental issues is the controllable synthesis of high-quality lead-free perovskite NCs with definite structures from sizes, morphologies, compositions, defect types and positions, and crystallinities. Currently, there is still a lack of in-depth understanding on how to control the nucleation, growth, and shape evolution of lead-free perovskite NCs involved in the synthesis process. In this regard, we can draw inspiration from the successful synthesis of lead-halide perovskite NCs and cadmium-based QDs, that is, through ligands, precursors, solvents, and temperature profile tunings to control the rapid nucleation and growth stages to yield high-performance lead-free perovskite NCs.

In terms of stability, many research groups have experimentally demonstrated that lead-free NCs have improved stability compared with the conventional lead-halide counterparts. On the one hand, most lead-free perovskites have a low-dimensionality crystal structure, which may give rise to strong covalent bonds and stable crystal structure due to the low electronic dimensionality. On the other hand, a lot of theoretical work has demonstrated that the decomposition energy and diffusion barrier of intrinsic defect (i.e., halogen vacancy) in lead-free perovskites are significantly higher than those in lead-halide counterparts, indicating that lead-free perovskites have improved thermodynamic and chemical stability. Despite this, they are still far away from commercial requirements. This is partially because of the ionic nature of perovskite materials with low formation energy and soft crystal lattices, which makes them easy to decompose in ambient and harsh conditions. In addition, a combination of superior resistance to UV light, heat, oxygen, moisture, and chemicals is still a big challenge. Further stabilizing lead-free perovskite NCs and preventing their decomposition are required. Except for the experimental characterization of the degradation evolution of NCs, more attention should be paid to the theoretical cognition of the origin of instability and possible degradation pathways, which is beneficial to obtain high-stability lead-free perovskite NCs.

Due to the safety of lead-free perovskite NCs, they are expected to be used in optoelectronic applications such as LEDs, solar cells, photodetectors, and photocatalysis. As the light-emitting materials, lead-free perovskite NCs are still unsatisfactory in terms of optical performance. Particularly, majority of lead-free perovskite NCs can hardly exceed 80% PLQY, which impedes the realization of high-performance LEDs. Also, the nature of nonradiative recombination processes and defects in lead-free perovskite NCs are not clearly understood, and a more comprehensive and in-depth analysis is required. Another peculiar phenomenon is that most lead-free perovskite NCs exhibit STE-related emission with a broad emission spectrum and a large Stokes shift. However, the current understanding of STEs is still preliminary [296–299], and it is urgent to further elucidate the decay pathways of STE emission, the process of lattice distortion,
Figure 16: (a) Schematic diagram of the synthesis of bismuth-based perovskite NCs and their application in solid-gas photocatalytic reduction of CO₂. (b) Each hour of reaction, the yield of methane produced by the catalyst (detected by GC-FID). (c) Comparison of the production of methane and CO in the photochemical reaction for 10 h (detected by GC-MS). (d) Comparison of photocatalytic CO₂ reduction performance of prepared Cs₂AgBiBr₆ NCs and washed NCs. (e) Schematic diagram of CO₂ photoreduction on the surface of Cs₂AgBiBr₆ NCs. (a–c) Reproduced with permission from Ref. [295], copyright 2019 Journal of the American Chemical Society. (d, e) Reproduced with permission from Ref. [195], copyright 2018 Small.
and other related mechanisms through combining experimental and theoretical investigation. Moreover, some lead-free perovskite emitters based on Cu(I), Cu(II), In(III), and Ag(I) substitutes are always characterized by large bandgaps. Thus, in terms of electrically pumped LEDs, it is difficult to design well-matched device configuration to ensure barrier-free charge injection, which certainly will lead to a poor device performance. Therefore, future work should first be on to modify the electronic band structure of such materials, for example, exploring possible element doping or alloying and halide ion substitution in lead-free perovskite NCs assisted by computation-supported combinatorial chemistry. Besides, selecting suitable carrier transport layers or proper interface modification or introduction of carrier blocking layers in the electrically pumped device structure is required.

As a potential light-harvesting material, their preliminary applications in photovoltaic solar cell are encouraging, with potential for low-cost and large-scale manufacturing from abundant materials. Although various strategies and efforts have been attempted, the current PCE obtained based on lead-free perovskite NCs is still far behind the conventional lead-halide counterparts. The main reasons were the fast carrier recombination process that happened in a very short time, low carrier mobility, and short carrier diffusion length in NC film, resulting in a limited device performance. Therefore, future research should focus on NC surface passivation to reduce the surface traps and realize the long carrier lifetimes for their application in efficient photovoltaic solar cells [300–302]. Moreover, the difficulties of simultaneously balancing the multiple competing processes in multilayer heterostructures, including light absorption, charge generation, separation, and transfer, are also the cause of poor device performances. Better understanding on the carrier dynamics at these interfaces and using of suitable electron and hole extracting layers can be effective in improving the performance of lead-free perovskite NC-based solar cells. These possible development directions are also applicable to the photodetectors and photocatalysis applications. With the above efforts paired with the promising properties of lead-free perovskite NCs, we firmly believe that these NCs have bright prospects in optoelectronic fields and future commercial deployment will not be too far.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

Authors’ Contributions

Fei Zhang and Zhuangzhuang Ma contributed equally to this work.

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