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Doping and ion substitution in colloidal metal halide perovskite nanocrystals

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The past decade has witnessed tremendous advances in synthesis of metal halide perovskites and their use for a rich variety of optoelectronics applications. Metal halide perovskite has the general formula ABX_3, where A is a monovalent cation (which can be either organic (e.g., $CH_3NH_3^+$ (MA), $CH(NH_2)_2^+$ (FA)) or inorganic (e.g., Cs^+)), B is a divalent metal cation (usually Pb^{2+}), and X is a halogen anion (Cl^-, Br^-, I^-). Particularly, the photoluminescence (PL) properties of metal halide perovskites have garnered much attention due to the recent rapid development of perovskite nanocrystals. The introduction of capping ligands enables the synthesis of colloidal perovskite nanocrystals which offer new insight into dimension-dependent physical properties compared to their bulk counterparts. It is notable that doping and ion substitution represent effective strategies for tailoring the optoelectronic properties (e.g., absorption band gap, PL emission, and quantum yield (QY)) and stabilities of perovskite nanocrystals. The doping and ion substitution processes can be performed during or after the synthesis of colloidal nanocrystals by incorporating new A', B', or X' site ions into the A, B, or X sites of ABX_3 perovskites. Interestingly, both isovalent and heterovalent doping and ion substitution can be conducted on colloidal perovskite nanocrystals. In this review, the general background of perovskite nanocrystals synthesis is first introduced. The effects of A-site, B-site, and X-site ionic doping and substitution on the optoelectronic properties and stabilities of colloidal metal halide perovskite nanocrystals are then detailed. Finally, possible applications and future research directions of doped and ion-substituted colloidal perovskite nanocrystals are also discussed.

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1. Introduction

Metal halide perovskites are materials with the general structure ABX_3, where A is a monovalent cation (which can be either organic (*e.g.*, $CH_3NH_3^+$ (MA), $CH(NH_2)_2^+$ (FA)) or inorganic (*e.g.*, Cs^+)), B is a divalent metal cation (usually Pb^{2+}), and X is a halogen anion (Cl^-, Br^-, I^-). The divalent metal B is surrounded by six halogen atoms forming a BX_6 octahedral structure while the A cation is located in the cubo-octahedral cavity within the corner-shared BX_6 octahedral framework forming a three-dimensional (3D) structure (Fig. 1). In recent years, metal halide perovskites have attracted great research interest due to their cost-effective solution processability and remarkable performance in optoelectronic applications. The utilization of capping ligands such as oleic acid (OA) and oleylamine (OLA) during colloidal synthesis allows for the creation of perovskite nanocrystals. Demonstrated morphologies of perovskite nanocrystals include nanocubes, nanowires, nanoplatelets, nanoparticles, *etc.*[1–4] Perovskite nanocrystals possess a higher surface-area-to-volume ratio than their bulk counterparts.[12] Additionally, nanocrystals may exhibit different optoelectronic responses than their bulk form due to quantum confinement and strong
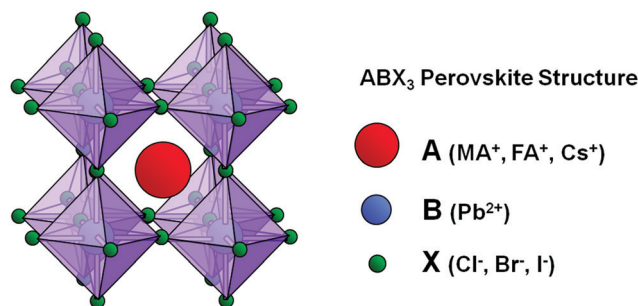
Fig. 1 Schematic of perovskite ABX_3 structure, where the A cation (red ball) can be either an organic cation (*e.g.*, $CH_3NH_3^+$ (MA), $CH(NH_2)_2^+$ (FA), *etc.*) or an inorganic alkali metal (*e.g.*, Cs^+), the B cation (blue ball) is usually Pb^{2+}, and the X anion (green ball) is a halogen ion (*i.e.*, Cl^-, Br^-, I^- or mixture thereof). The A cation is located in the cubo-octahedral cavity within the corner-shared BX_6 octahedral framework, forming a three-dimensional (3D) structure.

anisotropic effects.[5,6] Perovskite nanocrystals have demonstrated a promising future in many optoelectronic applications and have been applied in photovoltaic cells,[7–10] photodetectors,[11–18] lasers,[19–25] light-emitting diodes (LEDs),[26–45] and many other applications.

1.1. Colloidal perovskite nanocrystals

Although all-inorganic and organic–inorganic hybrid perovskites have been synthesized and studied for several decades,[46,47] their optoelectronic potential was first explored only a decade ago. In their seminal work, Kojima *et al.* incorporated $CH_3NH_3PbBr_3$ (MAPbBr$_3$) into a sensitized solar cell and obtained an energy conversion efficiency of $\sim 2.2\%$.[48] Since then, the solar conversion efficiency of perovskite solar cells has improved more than 10 times to $>25\%$ and is comparable to Si-based solar cells.[49] The tremendous photovoltaic efficiency of metal halide perovskites can be attributed to their unique optoelectronic properties: long carrier diffusion lengths,[50,51] high charge carrier mobilities,[52] long-range balanced electron and hole transport,[53] low trap-state density,[54] multiphoton high absorption coefficients,[55–58]

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and direct and tunable band gaps.[5] Colloidal MAPbBr$_3$ nanocrystals were first synthesized in 2014 and have demonstrated excellent photoluminescence (PL) emission properties.[59–61] Perovskite nanocrystals possess many unique advantages over legacy light emitters such as solution processability, bright luminescence (the photoluminescence quantum yield (PLQY) can reach ~100%),[61,62] narrow emission bandwidth (the full width at half maximum (FWHM) can be as low as below 15 nm),[5] and tunable emission spectra over the entire visible region (from roughly 400 nm all the way to around 750 nm).[63] The applications of metal halide perovskite nanocrystals extend beyond those mentioned above into many other uses such as: (1) serving as an intermediate layer to tune band gap alignment in photovoltaic cells,[64,65] (2) filling pinholes and cracks in perovskite film photodetectors through recyclable dissolution–recrystallization (RDR),[66] (3) boosting power conversion efficiency (PCE) of solar cells by down-converting UV to harvestable visible light,[67] (4) tailoring lighting displays to the desired color temperature by down-converting a blue chip LED source,[68–71] (5) probing for 2,4,6-trinitrophenol (TNP, picric acid), tetraoctylammonium halide salts (TOAX), or gaseous HCl by monitoring PL or colorimetric responses,[72–74] (6) serving as X-ray photon detection scintillators by converting X-ray irradiation and radioluminescence into visible wavelengths,[75] (7) generating hydrogen (H$_2$) *via* photocatalytic hydrohalic acid (HX) splitting,[76] (8) reducing carbon dioxide (CO$_2$) *via* photocatalysis with or without the assistance of another carrier transportation material for electron-extraction,[77–83] (9) preventing fraud by serving as fluorescent inks for anti-counterfeit or encryption printing purposes,[84–86] (10) serving as luminescence probes for bioimaging applications,[87–94] and many others.

1.2. Syntheses and morphologies

Colloidal metal halide perovskite nanocrystals can be synthesized using several different methods. The hot injection method, adapted from the method commonly used in the synthesis of traditional II–VI, III–V, and IV–VI semiconductor quantum dots, is the first method introduced to synthesize perovskite nanocrystals which is performed at an elevated temperature.[95] Low temperature (or room temperature) synthesis methods include the ligand-assisted reprecipitation (LARP) method and supersaturated recrystallization (SR) method.[95] Hot-injection, LARP, and SR methods can all be used to synthesize both all-inorganic and organic–inorganic hybrid perovskite nanocrystals.[59–61] Hot-injection method usually involves the use of high-boiling point non-coordinating solvent such as octadecene (ODE), while low temperature synthesis methods usually employ both a polar solvent (with high solubility for ionic perovskite precursors, *e.g.*, *N*,*N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO)) and non-polar solvent (with poor solubility for ionic perovskite precursors, *e.g.*, toluene or hexane).[96] In both high and low temperature methods capping ligands are needed to stabilize the reaction, with the acid–base pair of oleic acid (OA) and oleylamine (OLA) being among the most commonly used. Polymer micelles,[90,97,98] surfactant emulsions,[30] star-like copolymers,[99,100] and microporous metal–organic frameworks (MOFs)[81,101,102] are

examples of some additional capping ligands or templates that have been used for colloidal metal halide perovskite nanocrystal synthesis. Alternative wet-synthesis processes for perovskite nanocrystal synthesis include microwave irradiation,[103–105] ultrasonication,[17,45,106–112] dilution,[113] and solvothermal synthesis.[114]

The nucleation and growth mechanisms of MAPbX$_3$ nanocrystals created using the LARP method have been proposed,[115] and the formation mechanisms of CsPbBr$_3$ nanocrystals have been studied *via* a slowed-down microwave-assisted synthesis.[103] Systematic study of formation mechanisms of mixed halide perovskites has been achieved by a droplet-based microfluidic platform.[116] Gram-scale mass production of CsPbX$_3$ nanocrystals has been achieved by both a microwave irradiation process,[104] and by mixing Cs–oleate and Pb–oleate with tetraoctylammonium halide in toluene at room temperature.[117] In addition to the wet-synthesis processes mentioned above, some dry mechanosynthesis processes such as grinding or milling have been used to synthesize perovskite nanocrystals. After physically mixing precursors by grinding or milling, they can be dissolved in solvent with ligands to form colloidal nanocrystals, or in some cases the mixture of precursors will become bulk crystals in powder form without the addition of solvent or capping ligands. Luminescent MAPbX$_3$,[108,118] MASnBr$_3$,[119] CsPbX$_3$,[120,121] Mn-doped CsPbX$_3$,[122] and Cs(AgBi)$_{x/2}$-Pb$_{1-x}$Br$_3$[123] colloidal nanocrystals or powders have been made using grinding or milling methods.

The diverse dimensionality of perovskites adds an additional degree of freedom for tuning material properties. A multitude of diverse morphologies of metal halide perovskite nanocrystals can be created by fine tuning the synthesis conditions such as: temperature, reaction time, amount or type of the capping ligands, and injection speed of the precursors. Some examples for the various morphologies of the colloidal metal halide perovskite nanocrystals that have been successfully synthesized are 3D nanocubes,[1,2,110,114,124] two-dimensional (2D) nanoplates,[1–4,27,104,110,124–127] 2D nanosheets,[3,128,129] one-dimensional (1D) nanowires,[1,4,104,110,111,114,130–134] 1D nanorods,[1,2,104,135] and zero-dimensional (0D) nanodots.[1–4,96,110,136,137] Hexagonal or irregular shape nanocrystals have also been achieved,[104,138] but it is possible that these hexagonal or irregular shape nanocrystals are a lead-poor phase (*e.g.*, Cs$_4$PbBr$_6$ phase compared to CsPbBr$_3$ phase), because the ratio of acid–base ligand pair will affect the solubility of lead halide salts.[109,139]

1.3. Defect tolerance

Unlike conventional II–VI, III–V, and IV–VI semiconductor quantum dots, lead halide perovskite nanocrystals are defect-tolerant and do not suffer similar quenched emission from surface defect states. The defect tolerance in both CsPbX$_3$ and MAPbX$_3$ nanocrystals can be attributed to the unique electronic band structure configuration of the bonding–antibonding interaction within their conduction bands and valence bands.[140,141] In conventional semiconductors, the valence band (VB) and conduction band (CB) are predominantly composed of bonding (σ) and antibonding (σ^*) orbitals, respectively. In lead halide perovskites, the valence band maximum (VBM) is antibonding (σ^*) in nature and conduction band minimum (CBM) is

stabilized by the spin–orbit splitting of Pb(6p) states (Fig. 2).[142] Schematics of the two limiting cases of semiconductor band structure are in Fig. 2a: (left) conventional defect-intolerant band structure, and (right) ideal hypothetical defect-tolerant band structure. Schematic of lead halide perovskite band structure is shown in Fig. 2b using APbI$_3$ (A = Cs or MA) as an example: (1) the valence band maximum (VBM) is exhibiting antibonding characters originating from the hybridization of Pb(6s) and I(5p) orbitals, which meets the optimal bonding character of defect tolerance as depicted in Fig. 2a, while (2) the conduction band minimum (CBM) is mainly composed of antibonding orbitals contributed from Pb(6p) (rather than Pb(6p)–I(5p) interactions) and does not seem to meet the optimal bonding character of defect-tolerant case. Strong spin–orbit coupling (SOC) effects result in energy level splitting, which leads to a beneficial band broadening that shifts the bottom of the conduction band below the Pb(6p) atomic orbital and increases the chance that defects form as intra-conduction band states.[143] Density functional theory (DFT) calculation has demonstrated that both bulk or surface perovskites show no in-gap defect states between the VBM and CBM,[144] and that removing some of the surface atoms and/or capping molecules (creating dangling bonds) does not introduce localized trap states within the band gap.[145] Defects such as vacancies, interstitial atoms, and surface states will not likely form intra-gap states but rather appear as resonances inside shallow transition levels. Because of this, the surface passivation commonly used in conventional quantum dot synthesis is not strictly required in lead halide perovskites.[143] Because of their defect-tolerant nature, high PLQY lead halide perovskite nanocrystals do not require the same high purity, high temperature, or equipment-intensive vacuum synthesis as conventional semiconductor materials, which make them more easily scalable for mass production.[141] Exploration of other materials with similar defect tolerance electronic band structure is a promising direction, with I–III–VI compound semiconductors and Cu$_3$N being prime examples.[142] It is worth noting that A-site cations do not directly affect the band gap because they form bonding states deep in the VBM and do not hybridize with PbI$_6$ octahedra near VBM or CBM.[146] The A-site cations do, however, indirectly change the band gap because their size determines both

the structural stability and the expansion or contraction of the perovskite lattice, both of which alter band structure.[142]

1.4. Tolerance factor and octahedral factor

Not all combinations of A^{1+}, B^{2+}, and X^{1-} can form the complex ABX$_3$ halide perovskite structure. Tolerance factor (t), a rule proposed by Goldschmidt in the early 1920s, is used to understand and quantify what combination of chemical species can form perovskite structure.[147]

$$t = \frac{(R_A + R_X)}{\sqrt{2}(R_B + R_X)} \quad (1)$$

R_A, R_B and R_X are the ionic radii for the ions in the A, B and X sites of ABX$_3$ perovskites, respectively. A t value close to unity ($t \approx 1$) indicates a perfect fit and thus successful perovskite formation. The tolerance factor (t) can be used to determine whether the A site cations can fit in the cavities within the BX$_6$ octahedral framework. Differing from their oxide perovskite counterparts (A^{2+}B^{4+}O$_3$$^{2-}$), metal halide perovskite (A^{1+}B^{2+}X$_3$$^{1-}$) has a limited choice of cations because: (1) the relatively smaller negative charge of halides (1− vs. 2−) is only able to compensate A-site and B-site cations with lower oxidation states, and (2) the ionic radii of halides are larger than oxides, which requires larger B-site metal ions to maintain octahedral coordination geometry.[148] For lead halide perovskites, the tolerance factor ranges from $0.81 < t < 1.11$.[149] If t lies outside this range, 3D perovskite structure will not be formed and instead polymorphs of corner-sharing BX$_6$ octahedra with a lower dimensional connectivity such as 2D layers, 1D chains, or 0D BX$_6$ octahedral clusters will appear.[150–152] These lower-dimensional lead halide compounds usually possess much larger band gaps and are not suitable for photovoltaic applications.[153] In addition to tolerance factor (t), the octahedral factor (μ) is also used to indicate perovskite stability,

$$\mu = \frac{R_B}{R_X} \quad (2)$$

where μ is defined as the ratio of the ionic radii of the species occupying the B-site to X-site. For lead halide perovskites, the range for the octahedral factor is $0.44 < \mu < 0.90$.[149] Both the
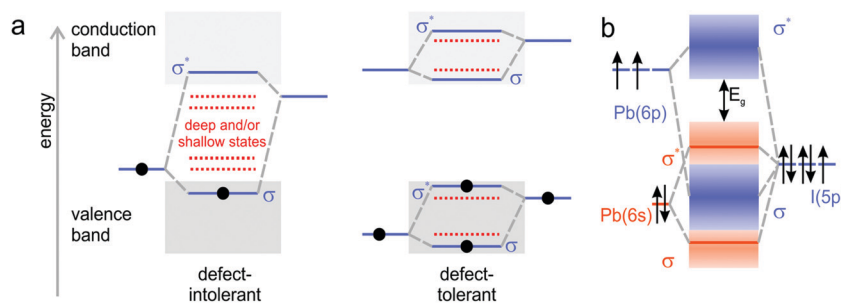
Fig. 2 (a) Schematics of two limiting cases of band structure in semiconductors: (left) conventional defect-intolerant band structure and (right) ideal hypothetical defect-tolerant band structure. Bonding and antibonding orbitals are denoted as σ and σ*, respectively. (b) Schematic of simplified bonding and band structure in APbI$_3$ perovskite. The valence band maximum (VBM) exhibits a desired antibonding character similar to the ideal defect-tolerant case shown in (a). Reprinted with permission from ref. 143, copyright 2016, American Chemistry Society.

tolerance factor and the octahedral factor are necessary but not sufficient conditions for the formation of stable ABX_3 3D perovskites.[154]

Selecting species that fit the criteria listed above for ABX_3 perovskite can be challenging. For the A site, cesium (Cs^+) is the only monovalent metal with a sufficiently large ionic size (R_A of 1.88 Å) to sustain the lead halide perovskite structure, while Li^+, Na^+, K^+, Rb^+ cations all result in a tolerance factor smaller than 0.8.[155,156] Two other monovalent organic molecular cations are known to fit in the 3D PbX_6 framework, and they are methyl-ammonium (MA, $CH_3NH_3^+$) and formamidinium (FA, $CH(NH_2)_2^+$) with ionic radii (R_A) of 2.17 Å and 2.53 Å, respectively.[151,157] It appears that for organic cations, both the size and distribution of the net positive charge are important. This helps explain why MA and FA can stabilize 3D lead halide perovskite structures and other monovalent organic cations with similar size (see effective ionic radii (R_A) in Table 1) cannot.[148] A wider range of divalent metal cations are candidates for the B-site (such as alkaline metals, transition metals, and lanthanides), but the use of many of them leads to limited ability to form 3D perovskite structures or band gaps too large for photovoltaic applications.[157] The most logical candidates to replace Pb^{2+} in the B site are the other group-14 elements, Ge^{2+} and Sn^{2+} (the effective radii (R_B) for Ge^{2+}, Sn^{2+}, and Pb^{2+} are 0.73 Å, 1.15 Å, and 1.19 Å, respectively), because they have a similar electronic configuration to Pb^{2+}. Unfortunately, Sn^{2+} and Ge^{2+} are not stable and oxidize to Sn^{4+} and Ge^{4+} easily.[157,158] For X-site anions, the effective radii of halide anions (R_X) are 1.81 Å, 1.96 Å, and 2.20 Å for chloride (Cl^-), bromide (Br^-), and iodide (I^-), respectively.[151]

1.5. Challenges and overview

Different properties can be achieved by substituting ions in either the A-site, B-site, or X-site. Generally, A-site substitution can improve the overall stability by tuning the tolerance factor. B-site substitution can reduce the toxic Pb content and improve phase stability by altering the B–X bond length. X-site substitution can tune the band gap *via* changing the ratio of mixed-halide ions. It is worth noting that these simplified generalities do not fully capture all the effects that substituting ions in A-, B-, and X-sites can have on the final products. For example, substituting in any site of ABX_3 metal halide perovskites could alter its band gap (Table 2), yet only X-site substitution shows a clear trend in band gap tailoring.

Initial studies suggest that metal halide perovskite nano-crystals carry a promising future in many applications, yet sub-stantial obstacles such as lead toxicity, hysteresis, and long-term stability may prevent them from successful commercialization. Notably, composition engineering has shown to be an effective route to overcoming many of those issues. By doping and sub-stituting different ions into perovskites, their overall performance

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Table 1 The effective ionic radii of organic molecular cations and Shannon ionic radii (*i.e.*, considering the respective coordination) of inorganic cations as well as the effective ionic radii of various anions

A-site cation: ionic radius (R_A)

Ammonium (NH_4^+): 1.46 Å[a]	Guanidinium (($NH_2)_3C^+$): 2.78 Å[a]
Hydroxylammonium (NH_3OH^+): 2.16 Å[a]	Tetramethylammonium (($CH_3)_4N^+$): 2.92 Å[a]
Methylammonium ($CH_3NH_3^+$) 2.17 Å[a]	Thiazolium ($C_3H_4NS^+$): 3.20 Å[a]
Hydrazinium ($NH_3NH_2^+$): 2.17 Å[a]	Tropylium ($C_7H_7^+$): 3.33 Å[a]
Azetidinium (($CH_2)_3NH_2^+$): 2.50 Å[a]	Piperazinium ($C_4H_{12}N_2^{2+}$): 3.22 Å[b]
Formamidinium ($CH(NH_2)_2^+$): 2.53 Å[a]	Dabconium ($C_6H_{14}N_2^{2+}$): 3.39 Å[b]
Imidazolium ($C_3N_2H_5^+$): 2.58 Å[a]	K^+: 1.64 Å[b]
Pyrrolinium ($NC_4H_8^+$): 2.72 Å[a]	Rb^+: 1.72 Å[b]
Dimethylammonium (($CH_3)_2NH_2^+$): 2.72 Å[a]	Cs^+: 1.88 Å[b]
Ethylammonium ($CH_3CH_2NH_3^+$): 2.74 Å[a]	

B-site cation: ionic radius (R_B)

Be^{2+}: 0.45 Å[a]	Pd^{2+}: 0.86 Å[a]	Dy^{2+}: 1.07 Å[c]	Ce^{3+}: 1.01 Å[b]
Mg^{2+}: 0.72 Å[a]	Pt^{2+}: 0.80 Å[a]	Tm^{2+}: 1.03 Å[a]	Pr^{3+}: 0.99 Å[b]
Ca^{2+}: 1.00 Å[a]	Cu^{2+}: 0.73 Å[a]	Yb^{2+}: 1.02 Å[a]	Nd^{3+}: 0.98 Å[b]
Sr^{2+}: 1.18 Å[a]	Ag^{2+}: 0.94 Å[d]	Np^{2+}: 1.10 Å[d]	Sm^{3+}: 0.96 Å[b]
Ba^{2+}: 1.35 Å[a]	Zn^{2+}: 0.74 Å[a]	Tl^+: 1.50 Å[b]	Eu^{3+}: 0.95 Å[b]
Ti^{2+}: 0.86 Å[c]	Cd^{2+}: 0.95 Å[a]	Cu^+: 0.77 Å[d]	Gd^{3+}: 0.94 Å[b]
V^{2+}: 0.79 Å[c]	Hg^{2+}: 1.02 Å[a]	Ag^+: 1.15 Å[d]	Dy^{3+}: 0.91 Å[b]
Cr^{2+}: 0.80 Å[c]	Ge^{2+}: 0.73 Å[a]	Au^+: 1.37 Å[b]	Er^{3+}: 0.89 Å[b]
Mn^{2+}: 0.83 Å[a]	Sn^{2+}: 1.15 Å[a]	Au^{3+}: 0.85 Å[b]	Tm^{3+}: 0.88 Å[b]
Fe^{2+}: 0.78 Å[a]	Pb^{2+}: 1.19 Å[a]	Sb^{3+}: 0.76 Å[b]	Lu^{3+}: 0.86 Å[b]
Co^{2+}: 0.75 Å[a]	Sm^{2+}: 1.22 Å[c]	Bi^{3+}: 1.03 Å[b]	Pu^{3+}: 1.00 Å[b]
Ni^{2+}: 0.69 Å[a]	Eu^{2+}: 1.17 Å[a]	La^{3+}: 1.03 Å[b]	

X-site anion: ionic radius (R_X)

Fluoride (F^-): 1.29 Å[b]	Iodide (I^-): 2.20 Å[b]
Chloride (Cl^-): 1.81 Å[b]	Formate ($HCOO^-$): 1.36 Å[b]
Bromide (Br^-): 1.96 Å[b]	Thiocyanate (SCN^-): 2.17 Å[e]

[a] Effective ionic radius values are obtained from ref. 159. [b] Effective ionic radius values are obtained from ref. 157. [c] Effective ionic radius values are obtained from ref. 160. [d] Effective ionic radius values are obtained from ref. 161. [e] Effective ionic radius values are obtained from ref. 162.

Table 2 Summary of the tolerance factor (t) and band gap (E_g) values of ABX$_3$ metal halide perovskites with A-, B-, or X-site substitution. The t values are calculated based on the effective radii obtained from Table 1

ABX$_3$	Tolerance factor	Band gap (eV)	ABX$_3$	Tolerance factor	Band gap (eV)	ABX$_3$	Tolerance factor	Band gap (eV)
CsPbCl$_3$	$t = 0.87$	$E_g = 2.7^a$	CsSnCl$_3$	$t = 0.88$	$E_g = 2.8^b$	CsGeCl$_3$	$t = 1.03$	$E_g = 3.6^b$
MAPbCl$_3$	$t = 0.94$	$E_g = 2.9^a$	MASnCl$_3$	$t = 0.95$	$E_g = 2.8^c$	MAGeCl$_3$	$t = 1.11$	$E_g = 3.7^b$
FAPbCl$_3$	$t = 1.02$	$E_g = 3.0^a$	FASnCl$_3$	$t = 1.04$		FAGeCl$_3$	$t = 1.21$	
CsPbBr$_3$	$t = 0.86$	$E_g = 2.4^a$	CsSnBr$_3$	$t = 0.87$	$E_g = 1.8^b$	CsGeBr$_3$	$t = 1.01$	$E_g = 2.4^b$
MAPbBr$_3$	$t = 0.93$	$E_g = 2.3^a$	MASnBr$_3$	$t = 0.94$	$E_g = 2.0^c$	MAGeBr$_3$	$t = 1.09$	$E_g = 2.8^b$
FAPbBr$_3$	$t = 1.01$	$E_g = 2.2^a$	FASnBr$_3$	$t = 1.02$		FAGeBr$_3$	$t = 1.18$	
CsPbI$_3$	$t = 0.85$	$E_g = 1.8^a$	CsSnI$_3$	$t = 0.86$	$E_g = 1.3^c$	CsGeI$_3$	$t = 0.98$	$E_g = 1.6^d$
MAPbI$_3$	$t = 0.91$	$E_g = 1.5^a$	MASnI$_3$	$t = 0.92$	$E_g = 1.2^c$	MAGeI$_3$	$t = 1.05$	$E_g = 1.9^d$
FAPbI$_3$	$t = 0.99$	$E_g = 1.4^a$	FASnI$_3$	$t = 1.00$	$E_g = 1.4^c$	FAGeI$_3$	$t = 1.14$	$E_g = 2.2^d$

^{a} Band gap (E_g) values are obtained from ref. 163. ^{b} Band gap (E_g) values are obtained from ref. 157. ^{c} Band gap (E_g) values are obtained from ref. 164. ^{d} Band gap (E_g) values are obtained from ref. 151.

can be markedly improved by optimizing band alignment and emission range,[165] increasing stability, improving film morphology, enhancing charge carrier transport, minimizing hysteresis, and reducing toxic lead content.[146] For example, fully or partially replacing methylammonium (MA, CH$_3$NH$_3$$^+$) with formamidinium (FA, CH(NH$_2$)$_2$$^+$) in MAPbI$_3$ perovskite thin film solar cell devices results in a smaller band gap, longer exciton lifetime, superior thermal stability, and reduced hysteresis.[166–168] Nonetheless, composition engineering has its own limitation as partially substituting MA with FA increases the crystallization temperature of MAPbI$_3$ perovskite, leading to phase separation or unwanted non-perovskite yellow δ-phase.[168,169] A few recent reviews have discussed the importance of composition engineering in metal halide perovskite nanocrystals.[170–174] Yet, an in-depth summary of both theoretical background and experimental guidelines on doping and ion substitution for crafting perovskite nanocrystals with outstanding optoelectronic properties and stabilities is still lacking. In this context, mixed-cation or mixed-anion colloidal metal halide perovskite nanocrystals achieved *via* doping or ion substitution is the primary focus of this review. This review will discuss relevant topics in the following order: general background of perovskite nanocrystals (Chapter 1), recent studies on doping and ion substitution in A-site (Chapter 2), B-site (Chapter 3), and X-site (Chapter 4), and applications (Chapter 5) and outlook (Chapter 6) of mixed-cation/mixed-anion colloidal metal halide perovskite nanocrystals. It is notable that this review will concentrate primarily on ABX$_3$ type 3D perovskites. Other perovskites such as A$_2$B$'$B$''$X$_6$, A$_3$B$_2$X$_9$, or Ruddlesden–Popper type low-dimensional perovskites will only be briefly discussed.[175–183]

2. A-site substitution

At room temperature, MAPbX$_3$ and FAPbX$_3$ usually exhibit cubic structure and CsPbX$_3$ usually has orthorhombic structure. The difference in structure is due to the fact that the Cs$^+$ ion is relatively smaller which leads to octahedral tilting/distortion and thus less symmetry leading to orthorhombic structure.[150] Due to the relatively small A-site cation, all inorganic CsPbX$_3$ perovskite nanocrystals have a relatively small tolerance factor (t) (Table 2). By changing the relatively small Cs$^+$ ion to larger A-site cations, the tolerance factor can be raised closer to 1.

If the substituted A-site cations are too large for the PbX$_6$ octahedral framework, the Ruddlesden–Popper type layered perovskite structures may form.[158,184] For traditional lead halide perovskite, FA is the relatively largest usable A-site cation and can achieve a tolerance factor (t) closer to 1 than MA and Cs cations. Compared to MAPbI$_3$, FAPbI$_3$ has shown superior solar cell performance due to red-shifted absorption (reduced band gap) and better charge transport. First-principles calculations demonstrate that the advantages of FA result from structure-induced enhancement of spin–orbit coupling (SOC).[185] The size of cations is not the only factor that determines crystal structure, as demonstrated by the fact that MAPbI$_3$ is tetragonal and FAPbI$_3$ is trigonal/pseudocubic even though the size of MA ($R_A = 2.17$ Å) and FA ($R_A = 2.53$ Å) are not that different. This difference can be explained by the fact that FA is more likely to form hydrogen bonds than MA, thereby stabilizing the pseudocubic structure.[185] The interaction between organic cations and the inorganic PbX$_6$ octahedra matrix mainly takes place through weak electrostatic interactions, but by careful cation design, it is possible to enhance the stability of perovskite by triggering stronger electronic coupling and electrostatic interactions like hydrogen-bonding, halogen-bonding, and van der Waals interaction.[186]

FAPbX$_3$ colloidal nanocrystals with emission spanning the whole visible range have been successfully synthesized using both hot-injection method[187–189] and room temperature LARP method.[190,191] Both hot-injection and room temperature synthesis methods can obtain FAPbBr$_3$ colloidal nanocrystals with similar optical properties (*i.e.*, emission peak at ∼530 nm, PLQY > 85%, and FWHM < 22 nm), but some mixed-halide FAPbX$_3$ colloidal nanocrystals are not single phase. Phase segregation has been widely observed in mixed-halide perovskite systems including FAPbX$_3$,[188] MAPbX$_3$,[192] and CsPbX$_3$.[193,194] An automated droplet-based microfluidic platform was used to show that phase segregation occurred in FAPb(Cl/Br)$_3$ nanocrystals when Cl:Br ≥ 0.4.[188] Ion migration has been proposed as a cause of the hysteresis phenomena observed in perovskite photovoltaic cells.[195,196] Two different mechanisms of PL intermittency, blinking (binary on–off switching) and flickering (gradual undulation) behaviors, have been identified in single FAPbBr$_3$ nanocrystals.[197] It was found that surface treatment with sodium thiocyanate (NaSCN) enhanced PLQY and completely suppressed flickering, but had no effect on blinking behavior.[197]

## 2.1. FA–MA mixed-cation lead halide perovskite nanocrystals

$FAPbX_3$ can be synthesized *via* cation exchange by replacing MA in $MAPbX_3$ with FA. Post-synthetic cation exchange of $MAPbX_3$ nanocrystals to $FAPbX_3$ nanocrystals was achieved through a solid–liquid–solid cation exchange reaction by adding solid formamidine acetate (FA(Ac)) salts into a toluene solution of $MAPbX_3$ nanocrystals.[198] This cation exchange proceeds slowly due to the minimal solubility of FA(Ac) in toluene. $FAPbX_3$ nanocrystals with emissions spanning from 395 nm to 700 nm can be achieved, depending on the halide ratio of the initial $MAPbX_3$ nanocrystals. Both the absorption and emission spectral features of the perovskite nanocrystals red shifted after cation exchange. The PL peak of the initial $MAPbBr_3$ nanocrystals was 515 nm and gradually shifted to 531 nm for the final $FAPbBr_3$ nanocrystals. This red shift corresponds to an energy shift of $\sim$73 meV, which is comparable to the $\sim$80 meV difference in bulk band gaps of $MAPbBr_3$ (E_g = 2.34 eV) and $FAPbBr_3$ (E_g = 2.26 eV) (Fig. 3B).[198] Interestingly the FWHM of the PL peak decreased from $\sim$26 nm (122 meV, initial $MAPbBr_3$) to $\sim$20 nm (88 meV, final $FAPbBr_3$), suggesting a narrower particle size/shape distribution of the final $FAPbBr_3$ (Fig. 3C). The PLQY slightly decreased from 72% (initial $MAPbBr_3$) to 69% (final $FAPbBr_3$), which could be attributed to an increased number of trap states formed as a result of larger FA^+ cations transporting inside the perovskite crystalline lattices.[198] The evolution of PL lifetime decay during the FA^+ cation exchange reaction were measured and an increase of the overall photo-excited carrier lifetime from 10.2 ns (initial $MAPbBr_3$) to 35.9 ns (final $FAPbBr_3$) was observed (Fig. 3D). Longer lifetimes were suggested to result from the relatively stronger interaction between the inorganic sublattice and FA^+, which originates from FA^+'s ability to form four short hydrogen bonds while MA^+ can only form three.[198,199] The crystal structure of the perovskite nanocrystals was monitored by X-ray diffraction (XRD) and was found to maintain a cubic crystal structure during the cation exchange process. The calculated lattice constant increased from 5.91 Å (initial $MAPbBr_3$) to 6.01 Å

(final $FAPbBr_3$), which corresponds to a unit cell volume expansion of 5.2%, induced by the ionic radius difference between the MA^+ and FA^+ cations (the effective radii of MA^+ and FA^+ cations are 2.17 Å and 2.53 Å, respectively).[198]

Perovskite's instability in polar solvents proves to be a challenge for ion exchange preparation of $FAPbI_3$ perovskite thin film solar cells from $MAPbI_3$ crystals. Usually, the cation-exchange process would involve immersing an as-prepared $MAPbI_3$ substrate in a FA^+-containing alcohol solution, but the polar nature of alcohol would immediately destroy the existing $MAPbI_3$.[200] To overcome this dissolution issue, $FAPbI_3$ thin film solar cell have been synthesized by converting $MAPbI_3$ to $FAPbI_3$ by exposing the $MAPbI_3$ perovskite film to gaseous FA, allowing the process to occur without polar solvents.[200] Although $FAPbI_3$ demonstrates better thermal stability than $MAPbI_3$, some structural instability challenges remain. It was found that the anisotropically strained (111) plane in the $FAPbI_3$ lattice can promote the transformation of black perovskite phase $FAPbI_3$ (α-phase) to yellow non-perovskite polymorph (δ-phase). Alloying smaller size methylammonium bromide (MABr) into $FAPbI_3$ (forming $FAPbI_3$–MABr) balances this lattice strain (which has shown to significantly enhance moisture stability) as well as contracts the overall lattice by increasing Coulombic interactions due to MABr's relatively smaller size (Fig. 4).[201] $FA_xMA_{1-x}PbBr_3$ mixed-cation colloidal nanocrystals have been synthesized using LARP method by mixing different ratios of FABr and MABr precursors together with $PbBr_2$. Their optical properties have exhibited a continuous red-shift with increasing MA doping ratio,[70] a result which contradicts the fact that $FAPbBr_3$ (E_g = 2.26 eV) has a smaller band gap than that of $MAPbBr_3$ (E_g = 2.34 eV).[198] No clear explanation was given for this contradictory finding.

2.2. FA–Cs mixed-cation lead halide perovskite nanocrystals

In addition to $MAPbX_3$ nanocrystals, cation exchange of FA ions has also been implemented on $CsPbX_3$ nanocrystals. $FA_xCs_{1-x}PbI_3$ nanocrystals can be obtained by mixing $CsPbI_3$ nanocrystals with a
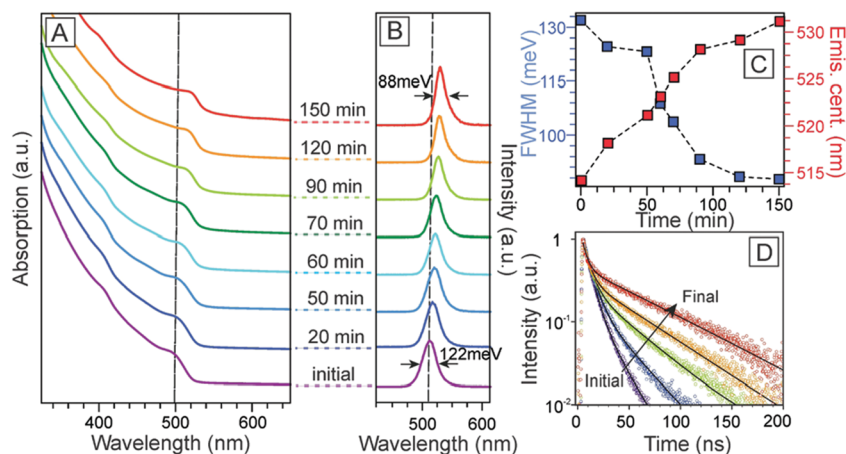
Fig. 3 Evolution of optical properties during FA^+ cation exchange reaction from the initial $MAPbBr_3$ (purple lines) to the final $FAPbBr_3$ (red lines) perovskite nanocrystals: (A) absorption spectra, (B) photoluminescence (PL) spectra, (C) the PL peak position (red square) and the full width at half maximum (FWHM) (blue square) as a function of reaction time, and (D) the evolution of the PL lifetime decay curves. Reprinted with permission from ref. 198, copyright 2017, Royal Society of Chemistry.
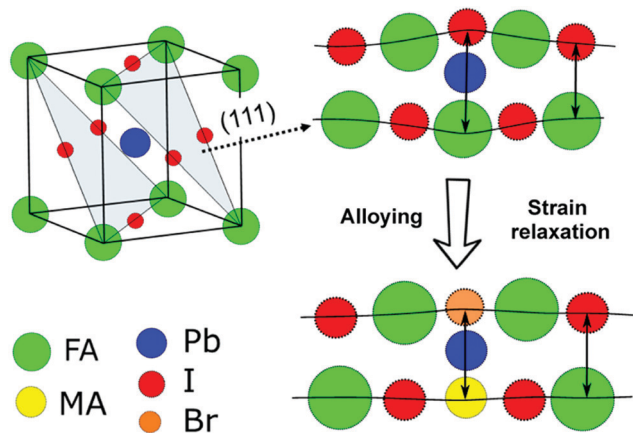
Fig. 4 Schematic representation of strain relaxation of FAPbI$_3$ perovskite after MABr alloying (side view). Reprinted with permission from ref. 201, copyright 2016, American Chemistry Society.

FA–oleate precursor in toluene solution.[202] The FA$_{0.1}$Cs$_{0.9}$PbI$_3$ nanocrystals show a red emission peak at 685 nm with PLQY exceeding 70% and much better stability than their parent CsPbI$_3$ nanocrystals (PL stability improved from several days to a few months under storage at ambient conditions). The enhanced stability was proposed to be attributed to the lattice expansion caused by insertion of the larger FA$^+$ (pure FAPbI$_3$ nanocrystals retain their PL stability of near-IR region emission at ∼780 nm for a few months when stored in ambient conditions as well).[202] The

cation exchange mechanism of Cs$^+$ and FA$^+$ ions is reversible (one can obtain FA$_x$Cs$_{1-x}$PbI$_3$ nanocrystals by mixing FAPbI$_3$ nano-crystals with Cs–oleate precursor as well), though there is an energetic cost of atomic rearrangement since FAPbI$_3$ is a cubic phase and CsPbI$_3$ is a γ-orthorhombic phase.[202] Substituting I with Br is an effective method to tune the band gap of FAPbX$_3$, but crystal will transform from a trigonal to a cubic phase at a critical I/Br ratio.[203] To overcome this issue, Cs has been introduced to stabilize the structure and form FA$_{0.83}$Cs$_{0.17}$Pb(I$_{1-x}$Br$_x$)$_3$ mixed-cation lead mixed-halide perovskite.[203] The introduction of relatively smaller Cs cations in the A-sites of FAPbX$_3$ contracts the lattice, which reduces the cubo-octahedral volume, thereby inducing stronger interaction between the cations and halides, facilitating the formation of highly crystalline perovskite crystals at a low temperature.[42] Colloidal FA$_{1-x}$Cs$_x$PbBr$_3$ mixed-cation perovskite nanocrystals with x = 0–0.6 have been synthesized to study the effect of Cs doping (Fig. 5a).[42] XRD detected standard perovskite phase throughout the entire composition range for x = 0–0.6 (Fig. 5b), though a peak shift from 15.01° to 15.39° was observed, which indicates the shrinking of d-spacing due to incorporation of the smaller Cs cation. Cs doping has also shown to decrease lattice spacing by high-resolution transmission electron microscopy (HR-TEM). Fast Fourier transformation of HR-TEM images allow for the calculation of lattice fringe spacing (Fig. 5c), and the linear relation-ship between d-spacing and Cs content indicates this doping system follows Vegard's law. As Cs doping content increases, the absorption band is blue shifted from 525 nm (x = 0) to 503 nm (x = 0.6),
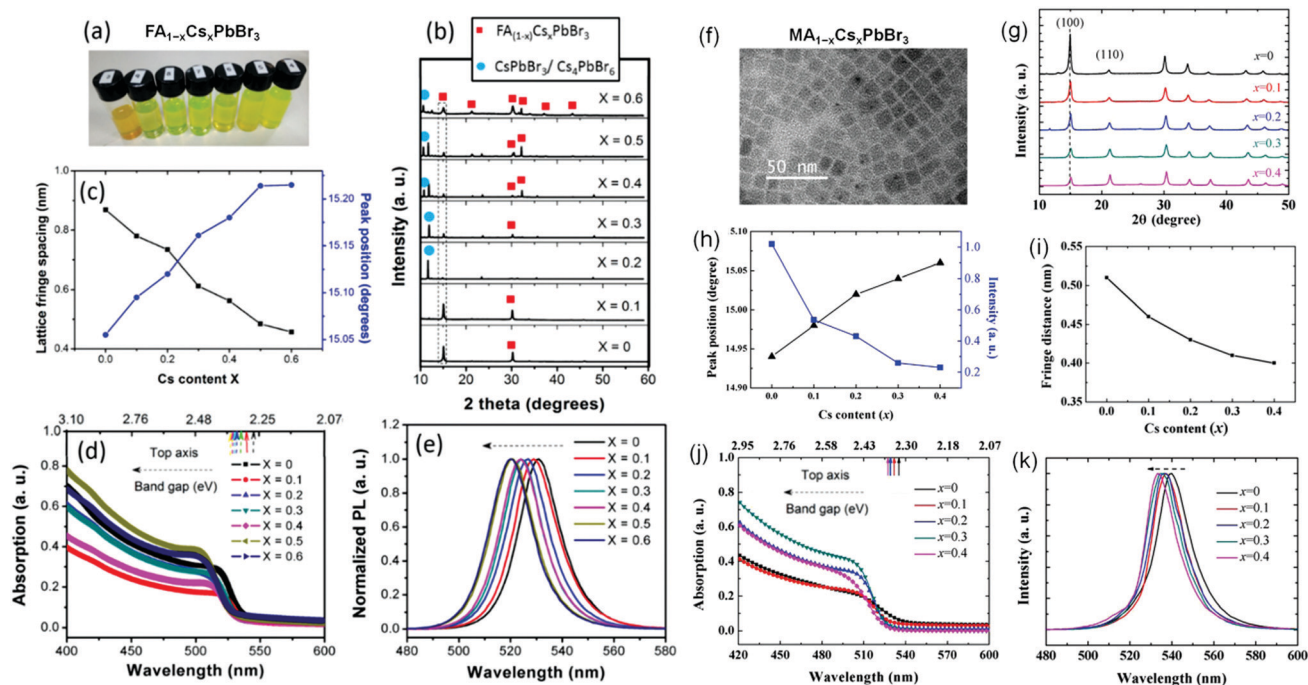

Fig. 5 (a) Photographs of different perovskite nanocrystals in solution. (b) XRD patterns of FA$_{1-x}$Cs$_x$PbBr$_3$ (x = 0–0.6). (c) Lattice fringe and peak position (≈15°) as a function of Cs content, x, in FA$_{1-x}$Cs$_x$PbBr$_3$. (d) Absorption spectra and (e) PL emission spectra of FA$_{1-x}$Cs$_x$PbBr$_3$ (x = 0–0.6). Reprinted with permission from ref. 42, copyright 2017, Wiley-VCH. (f) TEM image of the MA$_{0.7}$Cs$_{0.3}$PbBr$_3$ nanocrystals. (g) The XRD patterns obtained for the MA$_{1-x}$Cs$_x$PbBr$_3$ (x = 0 to 0.4) perovskites. (h) The (100) peak position and (100) peak, as well as (i) the fringe distance with different Cs content, x. (j) The absorption spectra and (k) PL spectra of MA$_{1-x}$Cs$_x$PbBr$_3$ (x = 0 to 0.4) perovskites measured at room temperature. Reprinted with permission from ref. 206, copyright 2017, Royal Society of Chemistry.
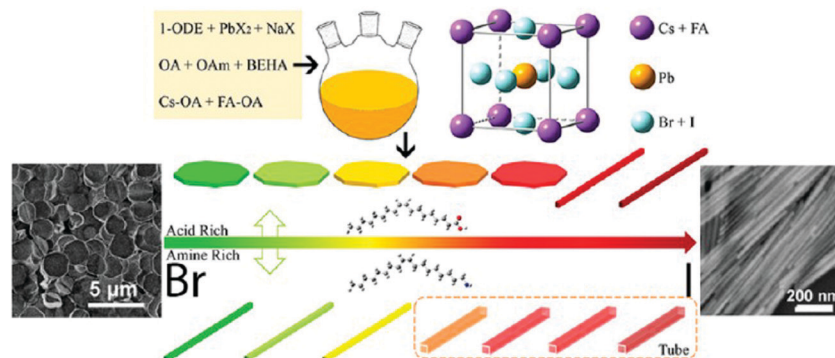
Fig. 6 Schematic illustration for the formation of $FA_{0.33}Cs_{0.67}PbBr_{3-x}I_x$ ($0 \leq x \leq 3$) perovskite nanowires and nanosheets, where OA, OAm, and BEHA in the schematic represent oleic acid, oleylamine, and bis(2-ethylhexyl)-amine, respectively. Reprinted with permission from ref. 204, copyright 2017, American Chemistry Society.

(Fig. 5d bottom axis) corresponding to a band gap shift from 2.27 to 2.33 eV (Fig. 5d top axis). The PL peak is also blue shifted from 531 nm ($x = 0$) to 519 nm ($x = 0.6$), with narrow FWHMs of about 19–23 nm (Fig. 5e).[42] Colloidal $FA_{0.33}Cs_{0.67}PbBr_{3-x}I_x$ ($0 \leq x \leq 3$) mixed-cation lead mixed-halide perovskite nanocrystals with controllable morphologies such as nanowires and nanosheets over a wide range of halide compositions were achieved by tuning the ligand participating in the reaction (Fig. 6).[204] Nanosheets and nanorods can be grown by altering the ratio between oleic acid (OA) and oleylamine (OAm) during the reaction with the existence of bis(2-ethylhexyl)-amine (BEHA).[204] NIR emissive $Cs_xFA_{1-x}Pb(Br_{1-y}I_y)_3$ perovskite nanocrystals has been systematic studied by an automated droplet-based microfluidic platform.[205]

2.3. MA–Cs mixed-cation lead halide perovskite nanocrystals

Colloidal $MA_{1-x}Cs_xPbBr_3$ perovskite nanocrystals were synthesized using the LARP technique. Briefly, MABr, CsBr, $PbBr_2$, oleylamine, and oleic acid were dissolved in DMF and then added dropwise into toluene to form green colloidal nanocrystals. The as-prepared $MA_{1-x}Cs_xPbBr_3$ perovskite nanocrystals are primarily cubic, with sizes varying from 8 nm to 12 nm (Fig. 5f). It was found that the absorption spectra blue-shifted from 515 nm to 505 nm when the Cs doping content increased from 0 to 0.4 (Fig. 5j) and the PL spectra also gradually blue-shifted from 539 nm to 533 nm as Cs doping levels increased (Fig. 5k). The crystallinity of $MA_{1-x}Cs_xPbBr_3$ perovskite was studied by XRD (Fig. 5g). It was found that increasing the Cs doping amount decreased the (100) peak intensity and increased the (110) peak intensity, which indicates that (110) is the preferred crystal growth direction. The (100) peak shifted from 14.91 degree to higher values, which indicates shrinkage of the crystal lattice (Fig. 5h). To further investigate the effect of Cs doping on the crystal structure, the lattice fringe was calculated from the fast Fourier transformation of the HR-TEM analyses (Fig. 5i). Increased Cs doping into $MAPbBr_3$ lead to a reduction of lattice fringe distance due to the relatively smaller ionic radius of Cs atoms, which results in a reduction of the cubo-octahedral volume for the A-site cation. Smaller lattice spacing results in a larger band gap because a smaller lattice constant indicates stronger binding between the

valence electrons and their parent atoms, therefore requiring more energy to promote from the valence band to conduction band.[206] This trend is visible in Fig. 7, where, for every halide choice, nanocrystals with the smallest cation (Cs) emit the shortest wavelength, and nanocrystals with the largest cation (FA) emit the longest wavelength. Note that nanocrystals with MA always emit somewhere between those with Cs and FA, reflecting the fact that its size lies between those two extremes (ionic radii of Cs = 1.88 Å, MA = 2.17 Å, FA = 2.53 Å).[17] This trend helps explain why the energy band gap increased (optical properties blue-shifted) with increasing Cs doping content in the $FA_{1-x}Cs_xPbBr_3$ (Fig. 5d and e)[42] and $MA_{1-x}Cs_xPbBr_3$ (Fig. 5j and k)[206] systems. However, individual cases with results contradictory to this trend were still observed in the literature. For example, colloidal $MA_{1-x}Cs_xPbI_3$ perovskite nanocrystals were synthesized using a novel anhydrous toluene assisted method in Dowtherm A. Peak emission wavelength from the nanocrystals was observed to red
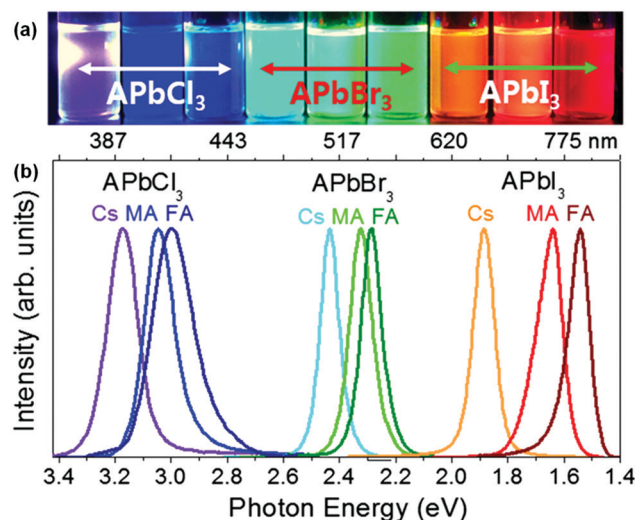

Fig. 7 (a) Digital photographs of composition-tuned ultrasound–assist-synthesized colloidal $APbX_3$ (where A = Cs, MA, or FA, and X = Cl, Br, or I) perovskite nanocrystals under UV-lamp (Hg vapor lamp) irradiation, and (b) their corresponding PL spectra. Reprinted with permission from ref. 17, copyright 2016, Royal Society of Chemistry.

Table 3 Summary of the emission peak wavelength, full width at half maximum (FWHM), photoluminescence quantum yield (PLQY), and synthesis method of colloidal metal halide perovskite nanocrystals with different A-site substitutions

Nanocrystals	Emission peak (nm)	FWHM (nm)	PLQY (%)	Ligands	Synthesis method	Ref.
$CsPbCl_3$	390	~25	—	Oleylamine	Ultrasound synthesis	17
$MAPbCl_3$	407	~25	—	Oleylamine	Ultrasound synthesis	17
$FAPbCl_3$	413	~25	—	Oleylamine	Ultrasound synthesis	17
$CsPbBr_3$	510	~15	—	Oleylamine	Ultrasound synthesis	17
$MAPbBr_3$	532	~15	—	Oleylamine	Ultrasound synthesis	17
$FAPbBr_3$	541	~15	—	Oleylamine	Ultrasound synthesis	17
$CsPbI_3$	660	~15	—	Oleylamine	Ultrasound synthesis	17
$MAPbI_3$	756	~15	—	Oleylamine	Ultrasound synthesis	17
$FAPbI_3$	805	~15	—	Oleylamine	Ultrasound synthesis	17
$MA_{0.9}Cs_{0.1}PbBr_3$	539	~17	—	Oleylamine, oleic acid	LARP	206
$MA_{0.6}Cs_{0.4}PbBr_3$	533	~17	—	Oleylamine, oleic acid	LARP	206
$MA_{0.9}Cs_{0.1}PbI_3$	671	~70	58	Octylamine	Anhydrous toluene assisted method	207
$MA_{0.8}Cs_{0.2}PbI_3$	738	~87	44	Octylamine	Anhydrous toluene assisted method	207
$MA_{0.7}Cs_{0.3}PbI_3$	744	~56	35	Octylamine	Anhydrous toluene assisted method	207
$MA_{0.5}Cs_{0.5}PbI_3$	744	~49	26	Octylamine	Anhydrous toluene assisted method	207
$FA_{0.9}Cs_{0.1}PbBr_3$	~531	~20	~73	Octylamine, oleic acid	LARP	42
$FA_{0.8}Cs_{0.2}PbBr_3$	~529	~20	~65	Octylamine, oleic acid	LARP	42
$FA_{0.7}Cs_{0.3}PbBr_3$	~525	~20	~54	Octylamine, oleic acid	LARP	42
$FA_{0.6}Cs_{0.4}PbBr_3$	~525	~20	~55	Octylamine, oleic acid	LARP	42
$FA_{0.5}Cs_{0.5}PbBr_3$	~520	~20	~47	Octylamine, oleic acid	LARP	42
$FA_{0.4}Cs_{0.6}PbBr_3$	~520	~20	~34	Octylamine, oleic acid	LARP	42
$K^+:CsPbCl_3$	~405	~15	2.08	Octylamine, oleic acid	Reduced temperature recrystallization	208
$K^+:CsPbBr_3$	~500	~30	71.51	Octylamine, oleic acid	Reduced temperature recrystallization	208
$K^+:CsPbI_3$	~675	~20	79.51	Octylamine, oleic acid	Reduced temperature recrystallization	208
$Rb_{0.2}Cs_{0.8}PbCl_3$	~414	~12	~3	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method	210
$Rb_{0.4}Cs_{0.6}PbCl_3$	~400	~13	~2	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method	210
$Rb_{0.6}Cs_{0.4}PbCl_3$	~394	~13	~7	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method	210
$Rb_{0.8}Cs_{0.2}PbCl_3$	—	—	~9	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method	210
$Rb_{0.2}Cs_{0.8}PbBr_3$	~514	~18	~35	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method	210
$Rb_{0.4}Cs_{0.6}PbBr_3$	~512	~22	~59	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method	210
$Rb_{0.6}Cs_{0.4}PbBr_3$	~505	~22	~48	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method	210
$Rb_{0.8}Cs_{0.2}PbBr_3$	~495	~24	~36	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method	210
$Rb_xCs_{1-x}PbBr_3$	460–500	<25	60–90	Oleylamine, oleic acid	Hot injection method	211
Tl_3PbI_5	~530	~115	—	Oleylamine, oleic acid	Hot injection method	212

shift from 671 to 744 nm as the Cs doping increased from $x = 0.1$ to 0.5 (Table 3).[207] The emission shift was attributed to displacement of the valence band edge due to the Cs-driven transition of nanocrystals from tetragonal to orthorhombic phase. Notably, the shift was not believed to result from any electronic effects from the Cs incorporation.[207]

2.4. Other mixed-cation lead halide perovskite nanocrystals

Potassium (K)-doped $CsPbX_3$ nanocrystals have been produced *via* a reduced temperature recrystallization method using Cs_2CO_3, PbX_2 and KX as precursors.[208] Rubidium (Rb)-doped bulk $Rb_xCs_{1-x}PbCl_3$ and $Rb_xCs_{1-x}PbBr_3$ solid solutions have been achieved through grinding and heating,[209] and colloidal $Rb_xCs_{1-x}PbCl_3$ and $Rb_xCs_{1-x}PbBr_3$ nanocrystals have been synthesized using a hot-injection method.[219] Colloidal $Rb_xCs_{1-x}PbBr_3$ nanocrystals showed a green emission with maximum PLQY of ~60% for $Rb_{0.4}Cs_{0.6}PbBr_3$.[210] Interestingly, another study demonstrated that emission could be tuned from 460 to 500 nm with PLQYs greater than 60% simply by varying the reaction temperatures.[211] Thallium (Tl) has also been used to synthesize perovskite nanocrystals. Orthorhombic Tl_3PbX_5 spheroidal nanocrystals and perovskite $TlPbI_3$ nanowires have been synthesized using a hot-injection method and displayed absorption in the UV range (281–440 nm) and had very weak wide emission across the

visible spectrum (450–600 nm).[212] It was suggested that thallium halide (TlBr, TlI) alone has a similar band structure to perovskite, and possesses strong spin–orbit coupling effects and the ability to form photoluminescent colloidal semiconductor nanocrystals.[213]

3. B-site substitution

It was suggested that the formation energy of the B-site is relatively larger than that of the A-site and X-site, which makes partial substitution of the B-site cation more difficult than the other ions in ABX_3 perovskites.[214] The main motivation for B-site substitution is to (1) reduce the toxic lead content, and (2) stabilize the perovskite phase. (1) Lead (Pb), a commonly used B-site species, is a toxic element with restricted use in many countries (including the entire European Union).[215] Identifying a safer, lead-free perovskite with performance equal to that of lead halide perovskite is currently one of the biggest challenges in the field. Isovalent substitution of Pb^{2+} with other divalent cations in the same group of the periodic table (*i.e.* Ge^{2+}, Sn^{2+}), is the most intuitive strategy and has been realized by many research groups.[216–219] Unfortunately, Sn^{2+} is not stable and easily oxidizes to Sn^{4+}. This oxidation problem is even more pronounced for Ge^{2+} owing to its $4s^2$ electrons, which possess even lower binding energy.[157,158] Some also argue that the

stereoactive lone pair on the Ge^{2+} center may result in highly distorted GeI_6 octahedra with three short and three long Ge–I bonds (quasi-3-D hexagonal structure).[160,220] (2) Due to the size difference between Br^- and I^- ions, the tolerance factor for lead iodide perovskite is smaller (less stable) than that of the lead bromide perovskite (Table 2). The longer B–X bond length in the $[PbI_6]^{4-}$ octahedra allows it to rotate and tilt more compared to that of the $[PbBr_6]^{4-}$ octahedra. Partial substitution of Pb^{2+} with a smaller B-site cation can reduce the B–X bond length and stabilize the lead iodide perovskite by reducing the extent of octahedral rotation or distortion, thereby leading to larger tolerance factor (improved phase stability) and larger formation energy (improved thermal stability).[214] Despite improved stability, devices made from perovskite with partial or complete substitution of Pb^{2+} often show less impressive optoelectronic properties than those containing Pb. This degradation of optoelectronic properties is because, as mentioned earlier, the 6s and 6p orbitals of Pb^{2+} determine the valence band maximum (VBM) and conduction band minimum (CBM) of lead halide perovskites and substituting Pb^{2+} with other metal ions potentially introduces new defect states between VBM and CBM, destroying the defect tolerant nature of the lead halide perovskites. As a consequence, care must be taken when choosing B-site cations for doping or alloying to retain the impressive optoelectronic properties of metal halide perovskites.[214,221]

Most effort in finding B-site replacements has focused on alternative isovalent cations that do not oxidize easily, are less toxic, and are smaller than Pb^{2+} ions. The partial replacement of Pb^{2+} with other divalent metal species (*e.g.*, Co^{2+}, Cu^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Sn^{2+}, Sr^{2+}, and Zn^{2+}) for improving the phase stability or band energy alignment in lead iodide perovskite solar cells have been systematically studied.[214,222] Besides isovalent substitution, aliovalent (heterovalent) substitution is also an alternative direction for B-site substitution. One can form a so-called "double perovskite" $(A_2B'B''X_6)$ structure by replacing two B-site divalent Pb ions with two heterovalent ions $(2B \rightarrow B' + B'')$, consisting of one with a higher and one with a lower oxidation state (*i.e.*, one trivalent ion (M^{3+}) and one monovalent ion (M^+) or a quadrivalent ion (M^{4+}) and a vacancy (V^{0+}) forming A_2MX_6 structure). The most intuitive thought would be to substitute Pb^{2+} with Bi^{3+} and Tl^{1+}, two elements directly adjacent to Pb in the periodic table (*i.e.*, with same number of atomic orbitals). The lower binding energy of Bi 6p orbitals is likely to reduce the electronic band gap and the combination of trivalent and monovalent ions would cause fluctuations in electrostatic potential.[158] One advantage of this approach is that one can tune the carrier concentrations of perovskite by controlling the substitution ratio between the trivalent and monovalent ions making it into either n-type (by excess Bi) or p-type (by excess Tl).[158] Because this review mainly focuses on ABX_3 type perovskites, double perovskites or other heterovalent doping perovskites will only be lightly discussed.

3.1. Sn-Based (divalent or quadrivalent substitution) perovskite nanocrystals

Sn is the most obvious substitute for Pb because they are in the same group. By introducing some $SnBr_2$ to partially replace

$PbBr_2$ during hot-injection synthesis, Sn(II)-doped $CsPbBr_3$ $(CsPb_{1-x}Sn_xBr_3)$ nanocrystals have been synthesized.[223] Increasing the Sn content gradually blue-shifted the absorption edges from 520 nm ($x = 0$) to 496 nm ($x = 0.7$) and blue-shifted the PL peak positions with decreased PLQY from 71% ($x = 0$) to 37% ($x = 0.7$) (Fig. 8a and b). The blue-shifted band gaps can possibly be attributed to lattice spacing shrinkage due to the smaller ionic radius of Sn cation (1.45 Å) compared to Pb cation (1.80 Å).[223] According to the empirical Vegard's law,[224] the band gap of a semiconductor is approximately a linear function of its lattice parameter and composition. Another group also demonstrated the substitution of Sn by partially replacing $PbBr_2$ with $SnBr_2$ during hot-injection synthesis, yet by using more oleic acid and oleylamine, they achieved a higher PLQY of 73.4%.[225] In their study they found that reaction time, temperature, and the precursor ratio of Pb : Sn all play an important role in the final product, and that both cubic $CsPbBr_3$ and tetragonal Cs_4PbBr_6 may form, depending on the growth conditions. A blue shift in the optical response was also observed when changing the precursor ratio of Pb : Sn from 1 : 1, 1 : 2.5 to 1 : 5.[225] Similarly, $CsPb_{1-x}Sn_xBr_3$ nanocrystals have been synthesized by LARP method (Fig. 9).[226] PL intensity was observed to drastically improve at $x = 0.1$, indicating that some Sn doping can promote radiative exciton recombination (Fig. 9b). However, PL intensity was found to decrease when $x > 0.1$, suggesting that significant Sn doping generated numerous defect states with oxidation. The lack of a significant shift in the absorption peak positions signifies that the band gaps of doped nanocrystals were similar to that of pristine nanocrystals, which are defined by the Pb(6s)–Br(4p) hybridized orbitals and the Pb(6p) orbitals (Fig. 9c). However, their PL peak positions were seen to also slightly blue-shifted, consistent with the results noted above. The XRD results suggested that the cubic structure of $CsPbBr_3$ nanocrystals was well maintained upon Sn doping (Fig. 9d), but some Cs_2SnBr_6 impurity peaks (assigned by red triangles) were observed as Sn content increased. The morphology of nanocrystals became more irregular as the Sn concentration increased (Fig. 9e–j). Notably, room-temperature synthesis of $CsSnBr_3$ nanocrystals has not yet been reported due to their instability and extremely low PL, thus the highest x value can only be 0.9 instead of 1.[226] $CsPb_{1-x}Sn_xBr_3$ nanocrystals obtained by postsynthetic cation exchange using $SnBr_2$ toluene solution also showed a trend of blue-shifting up to a critical $SnBr_2$ concentration.[227] Doping during hot-injection synthesis is mainly a thermodynamically controlled process, and the room temperature postsynthetic ion exchange reaction is mainly a kinetically controlled process. Due to the rigid nature of the Pb cationic octahedral sublattice, postsynthetic cation exchange of Pb takes much longer than halide exchange.[228,229] It was found to be easier to substitute Pb ions while the halide ions were being substituted simultaneously. Pb to Sn ion exchange of $CsPbBr_3$ nanocrystals was attempted using both SnI_2 and $SnBr_2$, and after 10 min of stirring only the sample containing SnI_2 successfully exchanged ions.[228] This suggested that the anion exchange reaction between the I/Br anions broke the Pb–Br bonding in the octahedral structure and provided a driving force for the cation exchange between Sn/Pb to
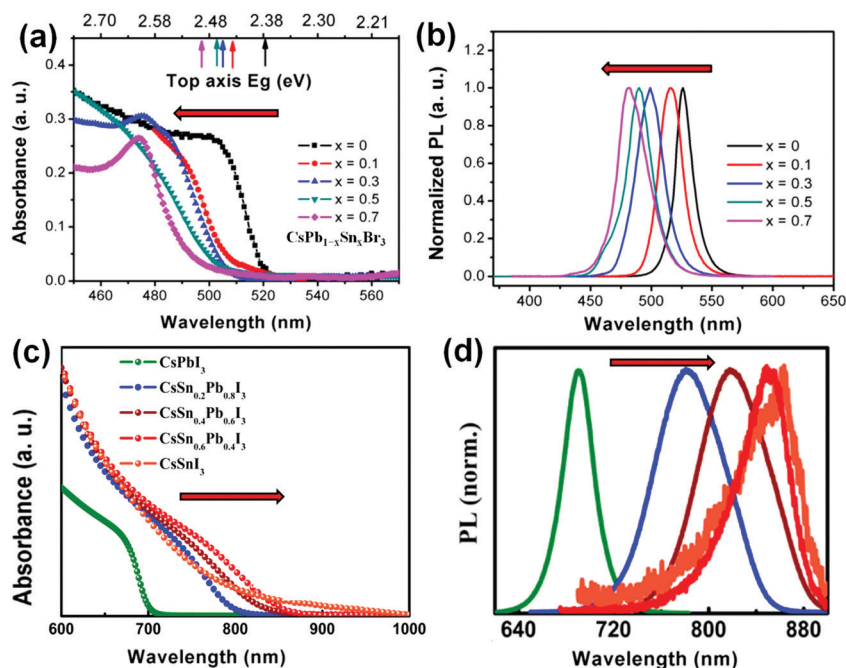
Fig. 8 (a) Absorption spectra and (b) normalized PL spectra of $CsPb_{1-x}Sn_xBr_3$ nanocrystals as a function of Sn content (x = 0–0.7). Reprinted with permission from ref. 223, copyright 2016, Elsevier. (c) Absorption spectra and (d) normalized PL spectra of $CsSn_{1-x}Pb_xI_3$ nanocrystals prepared at 160 °C with various Sn/Pb stoichiometries. Reprinted with permission from ref. 10, copyright 2017, American Chemistry Society. The red arrows indicating the directions of increasing Sn-doping content: (a and b) blue-shifted optical responses were observed in the Sn-doped cesium lead bromide systems, while (c and d) red-shifted optical responses were observed in the Sn-doped cesium lead iodide systems.
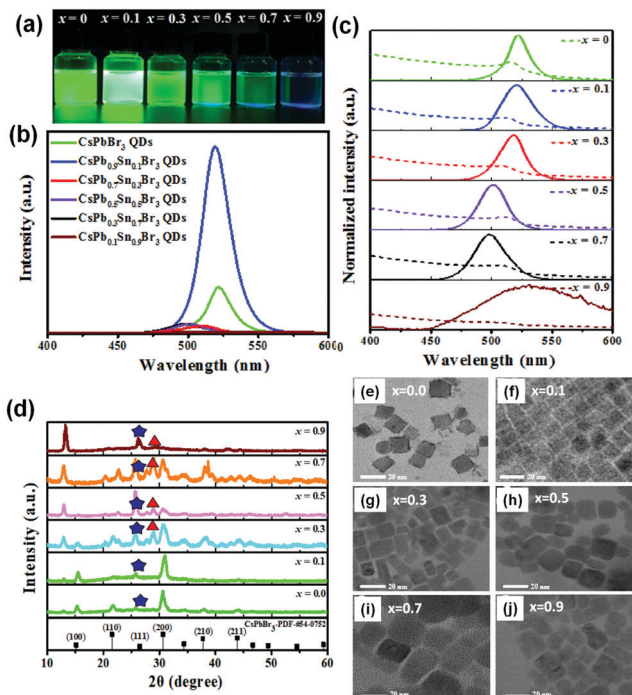

Fig. 9 (a) Photographs of $CsPb_{1-x}Sn_xBr_3$ perovskite nanocrystals hexane solutions under 365 nm UV illumination. (b) PL spectra, (c) normalized steady-state absorption and PL spectra, (d) XRD patterns and (e)–(j) TEM images of $CsPb_{1-x}Sn_xBr_3$ perovskite nanocrystals as a function of Sn content x. Reprinted with permission from ref. 226, copyright 2020, Elsevier.

happen. X-ray photoelectron spectroscopy (XPS) revealed that the Sn-exchanged perovskites displayed a lower binding energy shift of the Pb(4f) spectrum, which demonstrates an increase in the number of Pb–oleate (Pb–OA) (corresponding to lower band energy regions) complexes and a decrease in the number of Pb–Br (corresponding to higher band energy regions) species.[228] This anion-driven cation exchange process in the perovskite systems has also been called halide exchange-driven cation exchange (HEDCE).[229] Interestingly blue-shifted optical responses were observed in most Sn-doped colloidal nanocrystal cases,[223,225–227,230] and red-shifted optical responses were observed in most Sn-doped thin film solar cell cases including: $CsPb_{1-x}Sn_xX_3$[231] and $MAPb_{1-x}Sn_xX_3$[216,219] systems. Some even observed that the band gaps of $MAPb_{1-x}Sn_xX_3$ perovskites did not fall in between their parent perovskites ($MAPbX_3$ and $MASnX_3$) but that they are smaller than both of them.[217] A clear explanation of the contradictory optical responses in colloidal nanocrystal systems and thin film solar cell systems was not yet given in the literature. It is possible, however, that this contradiction is related to the halide content in the perovskite systems, noting that most studied thin film perovskite solar cells contain iodide ions and most studied colloidal nanocrystals perovskites contain bromide ions. In colloidal nanocrystal study related to iodide containing perovskites ($CsSn_{1-x}Pb_xI_3$), red-shifted optical responses were observed (Fig. 8c and d), which is consistent with those trends found in the thin film solar cell systems.[10] Similarly, $MASnI_3$ nanocrystals demonstrate red-shifted optical responses compared to $MAPbI_3$.[232] One possible explanation for the counterintuitive blue-shifted optical properties observed in the $CsPb_{1-x}Sn_xBr_3$ nanocrystal systems is that the absorption and PL properties for bromide

containing perovskite nanocrystals are solely determined by the $PbBr_6$ octahedra and would shift to higher energies with stronger interactions.[227] $SnCl_2$ has been used as a co-precursor to dope $CsPbI_3$ nanocrystals in conventional hot injection method. Sn^{2+} can partially replace Pb^{2+}, causing a slight lattice contraction and thus improving the perovskite stability. Cl^- has been found to passivate the surface defects of $CsPbI_3$ nanocrystals, thereby enhancing the PLQY, prolonging the emission lifetime, and improving the stability. The blue-shifted PL observed in this case is attributed to the lattice contraction due to the introduction of Sn.[233]

$CsSnX_3$ perovskite nanocrystals have been synthesized via hot-injection method with the assistance of trioctylphosphine (TOP) (Fig. 10a–c), but the resulting $CsSnBr_3$ nanocubes have a relatively low PLQY of 0.14%.[234] Interestingly, unlike the above mentioned $CsPb_{1-x}Sn_xBr_3$ nanocrystals which blue-shifted upon doping of Sn, the optical properties of $CsSnX_3$ nanocrystals are red-shifted when compared with $CsPbX_3$, even in the bromide system. The absorption and emission wavelength of $CsSnX_3$ nanocrystals can be tuned from visible to near-infrared (NIR) (roughly from 500 to 900 nm, see Fig. 10b), while the absorption and emission wavelength of $CsPbX_3$ nanocrystals can only be tuned within the visible range (roughly from 400 nm to 700 nm).[234] It was proposed that the band gaps of Sn-containing perovskite nanocrystals are relatively red-shifted (compared with their Pb-based counterparts) because Sn ions have a higher Pauling electronegativity (1.96) than Pb ions (1.87), which leads to a smaller separation between the X(5p) states in the valence band and the Sn(5p) states in the conduction band.[151] Contrary to this trend, Ge-based perovskites (with high electronegativity of 2.01) like $CsGeX_3$ do not have smaller band gaps than $CsSnX_3$. The X(5p) and Ge(4p) do not yield band gaps smaller than their Sn counterparts (Table 2) because the smaller Ge^{2+} cation results in a substantially different quasi-3D hexagonal structure.[151] Similarly,

the reported band gap values for $MAGeX_3$ are larger than that of $MASnX_3$ analogs (Table 2) due to its substantially different quasi-3D hexagonal structure resulting from a second-order Jahn–Teller (SOJT) effect.[151] $CsSnX_3$ perovskite quantum rods with a narrow emission range (from 625 to 709 nm, Fig. 10d–f) have been synthesized using a solvothermal method with the assistance of trioctylphosphine oxide (TOPO) and diethylene-triamine (DETA) in a sealed Teflon-lined autoclave. Three unique crystal structures were obtained (Fig. 10e), each corresponding to a different halide (monoclinic for $CsSnCl_3$, cubic for $CsSnBr_3$, and orthorhombic for $CsSnI_3$).[235] Besides the nanocubes and quantum rods mentioned above, hollow $CsSnBr_3$ perovskite cubic nanocages have been achieved by hot-injection method using stannus 2-ethylhexanoate (a branched n-alkanoates ligand) as the tin(II) source and $MgBr_2$ as the bromine source (Fig. 11).[236] The stability of the $CsSnBr_3$ nanocages can be significantly improved with the surface treatments of perfluorooctanoic acid (PFOA) where PFOA serves as a strong electron-withdrawing group to stabilize Sn^{2+} species.[236]

Because Sn(II) easily oxidizes to Sn(IV) (which causes the instability of $CsSnX_3$), direct synthesis of nanocrystals using Sn(IV), instead of ion exchanging with Sn(II), will lead to more stable Sn-based perovskite. $CsPb_{1-x}Sn_xBr_3$ perovskite nanocrystals with Sn(IV) substitution were achieved by hot-injection method.[230] The PLQY increased from 45% to 83% when the relative amount of Sn increased from $x = 0$ to $x = 0.33$ probably due to the suppression of nonradiative Auger recombination trions (charged excitons). Further incorporation of Sn will lead to a decrease in PLQY, which is likely due to the formation of the Cs_2SnBr_6 phase. It is worth noting, however, that the study was conducted using Sn(II) ($SnBr_2$) instead of Sn(IV), so their statement of Sn(IV) substitution is questionable.[230] Cs_2SnI_6 nanocrystals with morphologies of spherical quantum dots, nanorods, nanowires, nanobelts, and
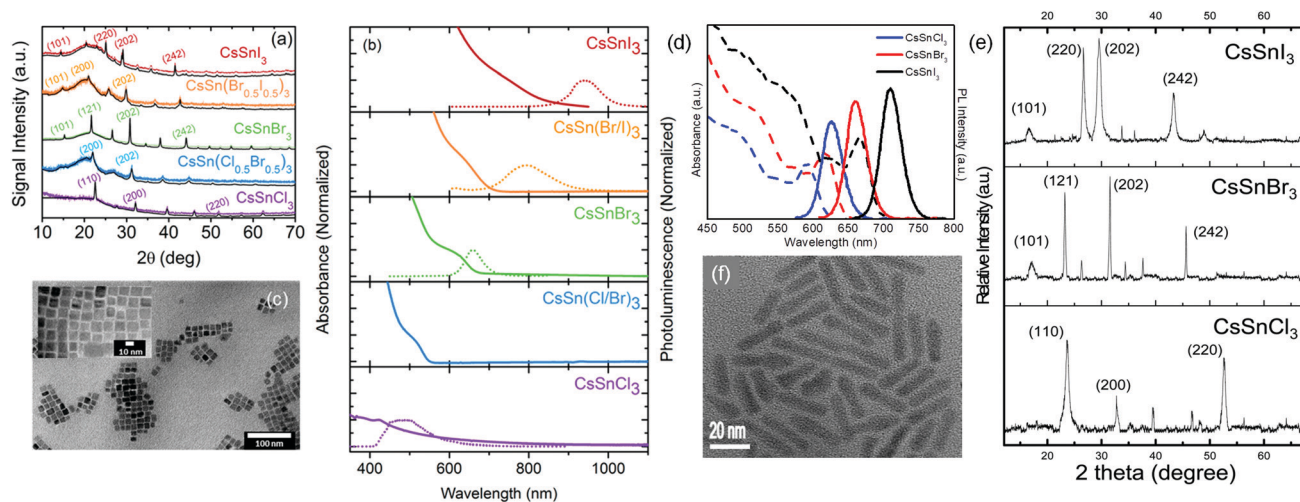
Fig. 10 (a) Powder XRD patterns of $CsSnX_3$ (X = Cl, $Cl_{0.5}Br_{0.5}$, Br, $Br_{0.5}I_{0.5}$, I) perovskite nanocrystals. (b) Absorption and steady-state PL spectra of nanocrystals containing pure and mixed halides (note that due to anion disorder non-emissive mixed halide phase, $CsSn(Cl_{0.5}Br_{0.5})_3$ nanocrystals only showed a very weak emission originating from a small subset of pure $CsSnCl_3$ nanocrystals). (c) TEM images of $CsSnI_3$ nanocrystals. Reprinted with permission from ref. 234, copyright 2016, American Chemistry Society. (d) Absorption and PL spectra for $CsSnX_3$ (X = Cl, Br, and I) perovskite quantum rods. (e) XRD patterns for $CsSnX_3$ (X = Cl, Br, and I) perovskite quantum rods. (f) High-resolution TEM (HRTEM) image of $CsSnI_3$ perovskite quantum rods. Reprinted with permission from ref. 235, copyright 2016, American Chemistry Society.
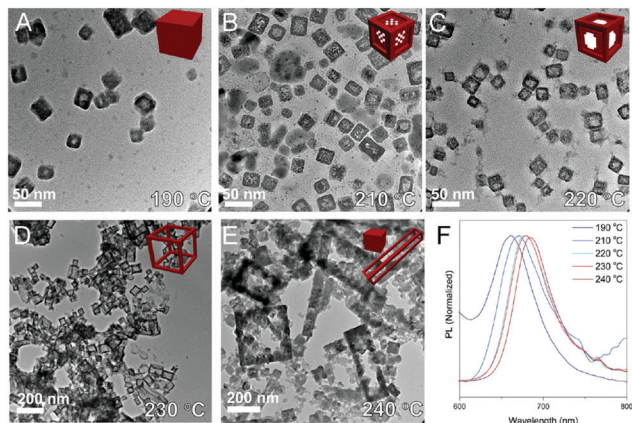
Fig. 11 (A–E) TEM images of CsSnBr$_3$ nanocages synthesized at different reaction temperatures (190, 210, 220, 230, and 240 °C, respectively). (F) Normalized PL emission spectra of the corresponding samples. Reprinted with permission from ref. 236, copyright 2017, American Chemistry Society.

nanoplatelets have been achieved by using a tetravalent tin ion (Sn^{4+}) instead of divalent tin ion (Sn^{2+}) as a Pb^{2+} replacement (Fig. 12).[237] Ligand-free Cs$_2$SnI$_6$ perovskite nanocrystals have

also been achieved and demonstrated colloidal stability for 30 min to 12 hours, depending on the particle size.[238] Cs$_2$SnI$_6$ is a double perovskite structure, which can be visualized by removing half of the B-site cations in ABX$_3$ perovskite. Orange emitting 2D Ruddlesden–Popper type (C$_{18}$H$_{35}$NH$_3$)$_2$SnBr$_4$ ((OAm)$_2$SnBr$_4$) perovskite nanocrystals have also been achieved with high PLQY of 88%.[239] CsSnI$_3$ also shows phase instability similar to that of CsPbI$_3$: under ambient conditions, the black phase easily transforms to yellow phase.[240] It has been demonstrated that alloyed CsSn$_{1-x}$Pb$_x$I$_3$ nanocrystals are stable in ambient air for up to a few months, which is far superior to both of its parent CsSnI$_3$ and CsPbI$_3$ nanocrystals, which are both only air stable for a few minutes.[10] Notably, monovalent, divalent and trivalent cations such as Li$^+$, Na$^+$, K$^+$, Rb$^+$, Mn^{2+}, Zn^{2+}, Cd^{2+}, Sn^{2+}, Sr^{2+}, Ni^{2+}, Cu^{2+}, Mg^{2+}, Bi^{3+}, In^{3+}, Mn^{3+}, and Sb^{3+} have been doped into CsSn$_{1-x}$Pb$_x$I$_3$ nanocrystals to improve their PLQY. Interestingly, only monovalent Na$^+$ doping displayed a significant PLQY enhancement from $\sim$0.3% to $\sim$28%, while Zn^{2+} and Cd^{2+} doping only improved the PLQY from $\sim$0.3% to $\sim$8%. Moreover, Na$^+$ doping can enhance the single-color near-band-edge emission, yet the PL spectra of Zn- and Cd-doped CsSn$_{1-x}$Pb$_x$I$_3$ nanocrystals exhibited a wide
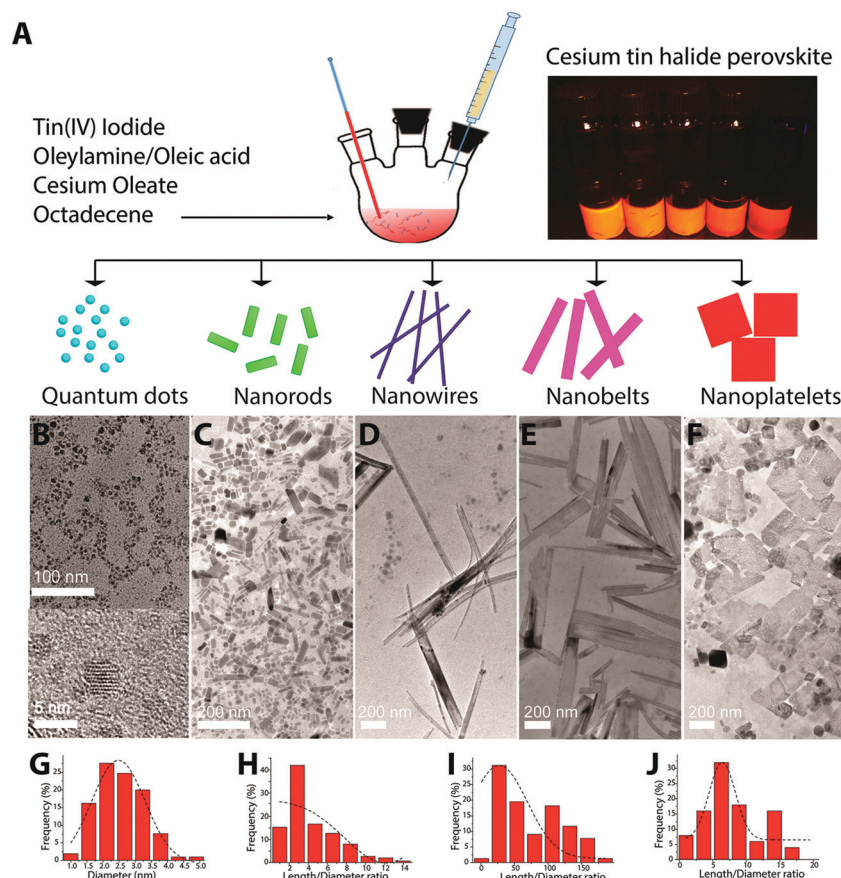
Fig. 12 (A) Schematic of the controlled synthesis procedures of Cs$_2$SnI$_6$ perovskite nanocrystals with different shapes (left panel) and photograph of the as-prepared Cs$_2$SnI$_6$ samples under UV light (top right panel). (B–F) TEM images of Cs$_2$SnI$_6$ nanocrystals with different shapes (the inset of B gives an HRTEM image of Cs$_2$SnI$_6$ spherical quantum dots). (G) particle size distribution histogram corresponding to (B), and (H–J) length–diameter ratio histograms corresponding to (C–E) (G–J give imaginary lines showing the best-fit Gaussian distributions). Reprinted with permission from ref. 237, copyright 2016, American Chemistry Society.

emission plateau extending from 700 to 900 nm. On the basis of these observations, it was suggested that the formation of a stronger chemical interaction between I$^-$ and Sn^{2+} ions upon Na$^+$ doping could potentially assist the stabilization of Sn^{2+} and suppress the formation of I vacancy defects, thereby resulting in PL enhancement.[241] Incorporation of fluorine (*via* addition of SnF$_2$ during fabrication) resulted in significant improvements in both the stability and performance of FASnI$_3$ and CsSnI$_3$ thin film solar cells and CsSnI$_3$ near-infrared lasing. The increased performance can probably be attributed to the suppression of both trap states (Sn vacancies/free carrier density) and Sn^{2+} oxidation, both of which can be explained by the fact that the F$^-$ is a strong electron-withdrawing group that has a stronger interaction with Sn^{2+} than other halides.[242–247] Further study is needed to determine if the increased stability from incorporation of SnF$_2$ extends into CsSnI$_3$, MASnI$_3$, and FASnI$_3$ nanocrystals.[240] CsSn$_{1-x}$Pb$_x$I$_3$ powders with different phases have been prepared *via* self-organizing processes in aqueous solutions followed by annealing under nitrogen or air for different temperatures and times.[248] It is interesting to see that most studies in tin(II)-based perovskite nanocrystals focus on all-inorganic CsSnX$_3$ nanocrystals, although an early work does document solid state synthesis of CH$_3$NH$_3$SnBr$_3$ powders.[119]

It is worth noting that though scientists have intensively studied using Sn^{2+} as a non-toxic substitute for Pb^{2+} in lead halide perovskite systems, one recent study stated that health effects from SnI$_2$ are more harmful than potential lead poisoning induced by PbI$_2$.[249] The synthesis of Sn-based perovskite nanocrystals also usually requires the use of toxic phosphines (TOP or TOPO) as coordinating solvent, which further calls into question whether Sb truly is a safe alternative to Pb.[228,230,234,235]

3.2. Mn-Based (divalent substitution) perovskite nanocrystals

Mn-Doping is another widely studied strategy to replace Pb in perovskite nanocrystals.[250] Due to the rigid nature of the Pb cationic sublattice in lead halide perovskite nanocrystals, halide exchange-driven cation exchange (HEDCE previously mentioned) is required to dope Mn.[229] By adding MnCl$_2$ as a doping agent into previously-synthesized CsPbBr$_3$, Pb cations can be partially exchanged by Mn ions and CsPb$_{1-x}$Mn$_x$(Cl/Br)$_3$ can be obtained. The resulting CsPb$_{1-x}$Mn$_x$(Cl/Br)$_3$ is dual-emitting, with two PL peaks. The HEDCE strategy demonstrates that postsynthetic partial cationic replacement is more likely to occur when the rigid halide octahedron structure is opened due to halide exchange. It was found that only MnCl$_2$ molecules (rather than mixture of Mn and Cl ions) facilitate successful partial cation exchange. The partial cation exchange reaction occurs over an extended time span, and though the final product possesses only two PL peaks, up to three emission peaks appear during the exchange process.[229] Fig. 13a illustrates the temporal evolution of PL spectra of CsPbBr$_3$ nanocrystals after adding the MnCl$_2$ precursor. The original emission peak of CsPbBr$_3$ nanocrystals
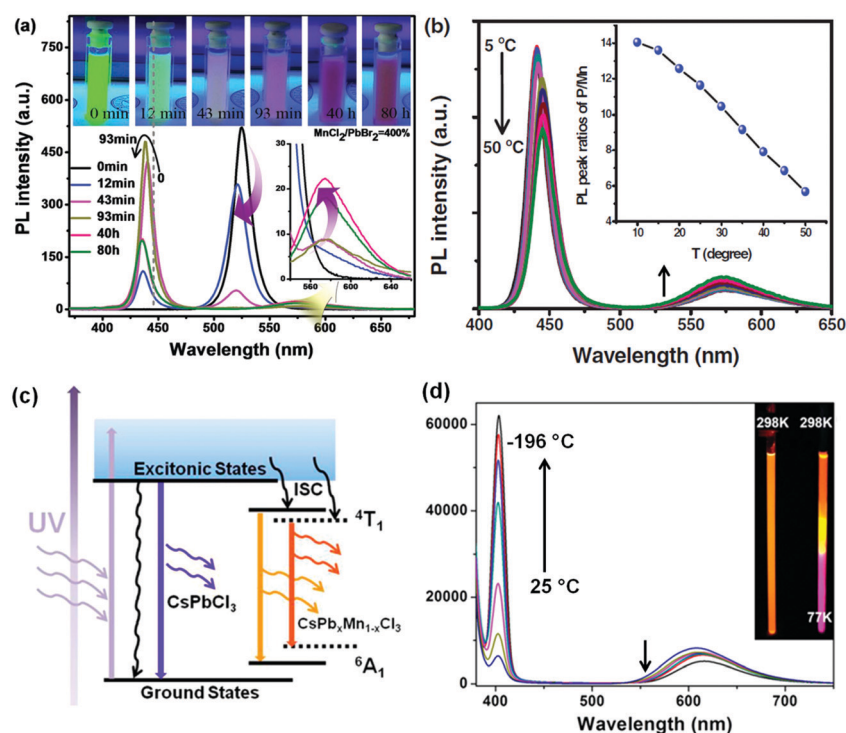
Fig. 13 (a) The bottom panel is the temporal evolution of PL spectra of CsPbBr$_3$ nanocrystals after adding the MnCl$_2$ precursor and the top panel is the corresponding digital photograph at different times under the irradiation of a 365 nm UV lamp. The inset is the blowup spectra between 550–650 nm. (b) PL spectra of CsPb$_{1-x}$Mn$_x$(Cl/Br)$_3$ nanocrystals collected from 5 °C to 50 °C. The inset is the ratio of PL peak intensity between perovskite intrinsic emission at ~438 nm and Mn emission at ~572 nm. Reprinted with permission from ref. 229, copyright 2017, Wiley-VCH. (c) Energy levels and fluorescent mechanism of CsPb$_x$Mn$_{1-x}$Cl$_3$ nanocrystals, where ISC represents intersystem crossing. (d) Temperature-dependent emission spectra of the CsPb$_{0.73}$Mn$_{0.27}$Cl$_3$ nanocrystals collected from 25 °C to −196 °C. Reprinted with permission from ref. 257, copyright 2017, American Chemistry Society.

was at around 520 nm which showed green color under the irradiation of a 365 nm UV lamp (the first digital photograph of "0 min" in the upper panel of Fig. 13a). After 12 min of reaction, a peak at 438 nm appeared and the peak intensity of 520 nm decreased. The peak at 438 nm is an indication of the fast halide exchange, resulting in the formation of $CsPb(Cl/Br)_3$ nanocrystals. After 43 min of reaction, the peak intensities at 438 nm and 520 nm keep increasing and decreasing, respectively, and another shoulder peak at 572 nm becomes visible (see blowup spectra from the inset). The peak at 572 nm indicates Mn^{2+} ligand-field transition emission from $^4T_1$ to $^6A_1$.[229] The notation $^4T_1 \rightarrow \,^6A_1$ refers to a transition between spin–orbit coupled energy levels of Mn^{2+} originated from the Tanabe–Sugano diagram.[251] It took almost 40 h for completely exchange of all the initial $CsPbBr_3$ nanocrystals into $CsPb_{1-x}Mn_x(Cl/Br)_3$ nanocrystals, which is indicated by the complete disappearance of the peak at 520 nm. The long reaction time is due to the difficult diffusion of large sized $MnCl_2$ molecules into the nanocrystal lattice at room temperature (20 °C). Mild heating (50 °C) can dramatically shorten the reaction time from 40 h to 2 h due to accelerated molecular diffusion.[229] Because of the slow diffusion of $MnCl_2$ into the center of the nanocrystals, it was proposed that the three intermediate emission peaks are from mid-states of $CsPbBr_3/CsPb_{1-x}Mn_x(Cl/Br)_3$ core/shell structures. With prolonged reaction time (allowing for diffusion), the domain of $CsPbBr_3$ core will gradually decrease and the PL peak of $CsPbBr_3$ (at 520 nm) will eventually disappear. For HEDCE to occur, the halide exchange and cation exchange between $MnCl_2$ molecules and $CsPbBr_3$ nanocrystals must proceed at the same time and same lattice site. It is for this reason that using separate Mn^{2+} and Cl^- ions from different sources do not lead to Mn doping. The same HEDCE strategy can be repeated in different metal systems, like forming Sn-doped perovskite using $SnCl_2$.[229] The final dual-emitting $CsPb_{1-x}Mn_x(Cl/Br)_3$ nanocrystals have the potential to be used in temperature sensing applications due to temperature-dependent intensity of the two PL peaks. Fig. 13b reveals that the intrinsic emission peak of $CsPb(Cl/Br)_3$ perovskite at 438 nm gradually decreases when the temperature is increased from 5 °C to 50 °C, which is due to thermally activated trapping of charge carriers. The slight red-shift in PL peak position was due to thermal expansion of the crystalline lattice.[229] The emission peak of Mn at 572 nm was enhanced when the temperature increased, which can be attributed to elevated temperature-promoted exciton-to-Mn energy transfer rates, induced by the increased spectral overlap between perovskite donor and Mn acceptor. The slight blue-shift in peak position can be attributed to thermal expansion of the crystalline lattice which changed the strength of the ligand field on Mn ions. The temperature-dependent exciton-to-Mn energy transfer in $CsPb_{1-x}Mn_x(Cl/Br)_3$ nanocrystals was found to exhibit linear ratiometric emission between the intrinsic perovskite (emission at $\sim$438 nm) and Mn (emission at $\sim$572 nm) (the inset of Fig. 13b) and can be used for temperature sensing.[229] A similar temperature-dependent PL study has also revealed the coupling between excitons and the d electrons of the dopants, and it was found that the exciton PL possesses biexponential kinetics where the short-lived emission

is ascribed to the surface trapping state recombination while the long-lived component is due to the band-edge excitonic recombination.[252] $CsPb_xMn_{1-x}(Cl/Br)_3$ nanocrystals can also be achieved by mixing $CsPbBr_3$ and $CsPb_xMn_{1-x}Cl_3$ nanocrystals together and stirred for 1 h to complete the simultaneous Mn^{2+} cation and Cl^- anion exchanges, and the absorption and band edge emission of the as-prepared nanocrystals can be elaborately tuned from 402 nm to 514 nm while the real Pb and Mn contents can be analyzed by inductively coupled plasma-optical emission spectrometer (ICP-OES) analysis.[253] The cation exchange process between Pb^{2+} and Mn^{2+} ions has been proven to be a reversible/interchangeable process that one can obtain $CsPb_{1-x}Mn_xCl_3$ nanocrystals by either adding $MnCl_2$ precursors into $CsPbCl_3$ nanocrystal solution or by introducing $PbCl_2$ precursors into $CsMnCl_3$ nanocrystal solution.[254] Similar to the HEDCE method, Mn doping can also occur through cation exchange driven by the photoinduced halide exchange in dihalomethane (CH_2X_2, X = Cl, Br) solvent.[255] Mn^{2+} post-synthetic ion exchange can also be done via a quasi-solid–solid cation exchange reaction. By adding solid $MnCl_2 \cdot 4H_2O$ precursors to dried $CsPbCl_3$ nanocrystals in the presence of ligands and allowing for a 15 hour reaction, Mn^{2+} heterogenous surface doping of the $CsPbCl_3$ nanocrystals, followed by inward dopant diffusion, has been confirmed by electron paramagnetic resonance (EPR) and optical spectroscopies. It was found that the presence of excess oleylamine ligands is able to activate the Mn^{2+}-precursor and plays an important role in this quasi-solid–solid cation exchange reaction.[256]

Direct replacement of Pb with Mn during colloidal synthesis is easier than using above mentioned post-synthetic processes. It has been demonstrated that by using a phosphine-free hot-injection preparation method, the Mn substitution ratio can reach 46% ($CsPb_{0.54}Mn_{0.46}Cl_3$).[257] The energy transfer of photo-induced excitons from the $CsPbCl_3$ host to the doped Mn greatly enhanced the PLQY of the $CsPbCl_3$ nanocrystals. In the temperature-dependent dual emission study, they decreased the temperature from 298 K to 77 K (from 25 °C to −196 °C) and found that the intensity of the 390 nm emission peak greatly increased, with no significant shift in peak position (Fig. 13d). The intensity of the 580 nm emission peak slightly decreased and the peak position red-shifted to longer wavelengths. The dual PL emission from the Mn-doped $CsPbCl_3$ can be explained by this model (Fig. 13c): $CsPbCl_3$ host absorbs energy from the 365 nm excitation source and emits light at 390 nm via radiative recombination of the excitons. Electron or hole traps lead to nonradiative relaxation (energy loss) with low PLQY. The Mn substitution generates new states that allow exciton-to-Mn^{II} energy transfer from the $CsPbCl_3$ host to the doped Mn^{II} ions. Excitons with sufficient thermal activation energy are allowed to transfer from one excited state to the other via intersystem crossing (ISC) ($^4T_1$–$^6A_1$ transition, d–d transition of Mn^{II} ions).[257] New radiative recombination pathways of exciton-to-Mn^{II} energy transfer result in a longer fluorescent lifetime and emission of light at 580 nm with enhanced PLQY. The PL intensity of $CsPbCl_3$ host is enhanced with decreased temperature due to the restriction of nonradiative relaxation processes, and the PL intensity of the Mn^{II} ion is reduced because fewer electrons

have sufficient thermal energy to undergo the ISC process. The decreased temperature slightly reduced the energy level of the $^4T_1$–$^6A_1$ transition and therefore the emission wavelength of Mn^{II} slightly red-shifts. It was found that a Mn^{II} doping ratio of 27% ($CsPb_{0.73}Mn_{0.27}Cl_3$) obtains the highest PLQY of 54% (Table 4).[257] It has also been found that Mn doping cannot occur when Mn-carboxylates such as manganese(II) acetate ($Mn(Ac)_2$),

manganese(II) acetylacetonate ($Mn(Acac)_2$), and manganese–oleate ($Mn(oleate)_2$) are used as Mn precursors, suggesting that pre-existing Mn–Cl bonds are beneficial for incorporating Mn into the lattice, similar to the prerequisite of HEDCE process mentioned above.[258] Although one can synthesize Mn-doped $CsPbCl_3$ by mixing $PbCl_2$ and $MnCl_2$ during synthesis, the same approach was not successful for $PbBr_2/MnBr_2$ or PbI_2/MnI_2 systems.

Table 4 Summary of the emission peak wavelength, full width at half maximum (FWHM), photoluminescence quantum yield (PLQY), and synthesis method of colloidal metal halide perovskite nanocrystals with different B-site substitutions

Nanocrystals	Emission peak (nm)	FWHM (nm)	PLQY (%)	Ligands	Synthesis method	Ref.
$CsPb_{0.9}Sn_{0.1}Br_3$	519	19	91.9	Oleylamine, oleic acid	LARP	226
$CsPb_{0.7}Sn_{0.3}Br_3$	516	28	62	Oleylamine, oleic acid	LARP	226
$CsPb_{0.5}Sn_{0.5}Br_3$	503	27	41	Oleylamine, oleic acid	LARP	226
$CsPb_{0.3}Sn_{0.7}Br_3$	501	30	30	Oleylamine, oleic acid	LARP	226
$CsPb_{0.1}Sn_{0.9}Br_3$	521	—	9.2	Oleylamine, oleic acid	LARP	226
$Na^+:CsPb_{1-x}Sn_xI_3$	840	~150	~28	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method	241
$CsPb_{0.97}Mn_{0.03}Cl_3$	396/569	—	5	Oleylamine, oleic acid	Hot injection method	257
$CsPb_{0.94}Mn_{0.06}Cl_3$	396/574	—	22	Oleylamine, oleic acid	Hot injection method	257
$CsPb_{0.87}Mn_{0.13}Cl_3$	396/575	—	43	Oleylamine, oleic acid	Hot injection method	257
$CsPb_{0.73}Mn_{0.27}Cl_3$	396/579	—	54	Oleylamine, oleic acid	Hot injection method	257
$CsPb_{0.62}Mn_{0.38}Cl_3$	396/582	—	36	Oleylamine, oleic acid	Hot injection method	257
$CsPb_{0.54}Mn_{0.46}Cl_3$	396/587	—	17	Oleylamine, oleic acid	Hot injection method	257
$Mn^{2+}:CsPbCl_3$	404/600	25/90	12.7	Oleylamine, oleic acid	Hot injection method	378
$Mn^{2+}:CsPbBr_3$	~520	~25	89.6	Oleylamine, oleic acid	Hot injection method	378
$Mn^{2+}:CsPbI_3$	~690	~50	57.1	Oleylamine, oleic acid	Hot injection method	378
$Ca^{2+}:CsPbCl_3$	406.1	~10	77.1	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method	328
$CsPb_{0.7}Ce_{0.3}Br_3$	516	~25	52	Oleylamine, oleic acid	Hot injection method	302
$CsPb_{0.66}Ce_{0.34}Br_3$	~514	~25	64	Oleylamine, oleic acid	Hot injection method	302
$CsPb_{0.65}Ce_{0.35}Br_3$	~512	~25	50	Oleylamine, oleic acid	Hot injection method	302
$CsPb_{0.55}Ce_{0.45}Br_3$	~512	~25	78	Oleylamine, oleic acid	Hot injection method	302
$CsPb_{0.26}Ce_{0.74}Br_3$	510	~25	89	Oleylamine, oleic acid	Hot injection method	302
$Yb^{3+}:CsPbCl_3$	990	~55	170	Oleylamine, oleic acid	Hot injection method	306
$Ni^{2+}:CsPbCl_3$	407	<15	96.5	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method	333
$Ni^{2+}:CsPbCl_{0.99}Br_{2.01}$	470	~20	89	Oleylamine, oleic acid	LARP	334
$Ni^{2+}:CsPbI_3$	~660	~40	79.2	Oleylamine, oleic acid	Hot injection method	208
$Cd^{2+}:CsPbCl_3$	406	~10–12	96 ± 2	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method w/postsynthetic treatment	336
$Cu^{2+}:CsPb(Br/Cl)_3$	459	<40	92.6	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method w/postsynthetic treatment	338
$CsPb_{0.93}Cu_{0.07}(Br/Cl)_3$	453	<30	80	Oleylamine, oleic acid	Hot injection method	337
$Al^{3+}:CsPbBr_3$	456	16	42	Oleylamine, oleic acid	Hot injection method	351
$Bi^{3+}:CsPbBr_3$	517	~20	55	Oleylamine, oleic acid	Hot injection method	344
$MA_3Bi_2Cl_9$	360	50	15	Oleylamine, oleic acid	LARP	355
$MA_3Bi_2Br_9$	423	62	12	Oleylamine, oleic acid	LARP	355
$MA_3Bi_2I_9$	540	91	0.03	Oleylamine, oleic acid	LARP	355
$MA_3Bi_2Cl_9$	370	~50–60	24.7	Octylamine, oleic acid	LARP	364
$MA_3Bi_2Br_3Cl_6$	399	~50–60	22.4	Octylamine, oleic acid	LARP	364
$MA_3Bi_2Br_6Cl_3$	422	~50–60	54.1	Octylamine, oleic acid	LARP	364
$MA_3Bi_2Br_9$	422	~50–60	13.5	Octylamine, oleic acid	LARP	364
$Cs_3Bi_2Cl_9$	393	59	26.4	Oleylamine, oleic acid	Recrystallization method	71
$Cs_3Bi_2Br_9$	410	48	19.4	Oleylamine, oleic acid	Recrystallization method	71
$Cs_3Bi_2I_9$	545	70	0.018	Oleylamine, oleic acid	Recrystallization method	71
$Cs_3Bi_2Cl_9$	380	57	62	Octylamine, oleic acid	LARP	363
$Cs_3Bi_2Br_9$	411	38	22	Octylamine, oleic acid	LARP	363
$Cs_3Bi_2I_9$	526	76	2.3	Octylamine, oleic acid	LARP	363
$Cs_3Sb_2Cl_9$	370	52	11	Oleylamine or octylamine, oleic acid	LARP	356
$Cs_3Sb_2Br_9$	410	41	46	Oleylamine or octylamine, oleic acid	LARP	356
$Cs_3Sb_2I_9$	560	56	23	Oleylamine or octylamine, oleic acid	LARP	356
$CsPb_{0.67}Sn_{0.33}Br_3$	517	~25	83	Oleylamine, oleic acid	Hot injection method	230
$CsSnCl_3$	~490	~100	≤0.14	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method	234
$CsSnBr_3$	~660	~50	≤0.14	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method	234
$CsSnI_3$	~945	~75	≤0.14	Tri-n-octylphosphine, oleylamine, oleic acid	Hot injection method	234
Cs_2SnI_6	~620	—	≤0.48	Oleylamine, oleic acid	Hot injection method	237
$Cs_2AgBiCl_6$	395	68	6.7	Oleic acid	Recrystallization method	375
$Cs_2AgBiBr_6$	465	82	0.7	Oleic acid	Recrystallization method	375
Cs_2AgBiI_6	575	69	<0.1	Oleic acid	Recrystallization method	375

This is probably due to the differences in their bond strengths. The bond dissociation energy of Mn–Cl (338 kJ mol^{-1}) is only 12% higher than that of Pb–Cl (301 kJ mol^{-1}), while the bond dissociation energy of Mn–Br (314 kJ mol^{-1}) is 26% stronger than that of Pb–Br (249 kJ mol^{-1}) and Mn–I bond (282 kJ mol^{-1}) is 46% stronger than Pb–I bond (194 kJ mol^{-1}).[258] It was suggested that the similar bond energy of $PbCl_2$ and $MnCl_2$ favors mixing of these isovalent ions within the lattice, which leads to successfully doped perovskite nanocrystals. In the other two cases, the large disparity in bond energies may favor extended domains of MnX_2 instead of the dispersion of Mn^{2+} within perovskite lattice.[258] Therefore, to obtain Mn-doped $CsPbBr_3$ or $CsPbI_3$ nanocrystals, one will need to first synthesize Mn-doped $CsPbCl_3$ nanocrystals then substitute the halide anion *via* postsynthetic anion exchange by adding excess $PbBr_2$ then PbI_2. The dual emission phenomenon from the energy transfer between the host and the dopant seen in Mn-doped $CsPbCl_3$ systems is less significant in the Mn-doped $CsPbBr_3$ system and can hardly be seen in the Mn-doped $CsPbI_3$ system. This is because of the energy level mismatch in the latter two cases. The energy difference (Δ) between the host perovskite band edge transition (CB-to-VB) and the dopant Mn transition ($^4T_1$-to-$^6A_1$) determine whether it is a forward energy transfer (k_{ET}) or a backward energy transfer (k_{BET}) (Fig. 14).[258] No Mn peak can be seen in the Mn-doped $CsPbI_3$ system (bottom left panel of Fig. 14) because the small band gap of the host $CsPbI_3$ results in backward energy transfer (k_{BET}) from the Mn dopant to the perovskite host. The evolution of the exciton-to-Mn^{2+} energy transfer (ET) efficiency as a function of composition (Br/Cl ratio) and temperature in Mn^{2+}-doped $CsPb(Br/Cl)_3$ nanocrystals has been studied.[259]

The theory of bond dissociation energy difference mentioned above, suggests that the combination of $PbCl_2$ (301 kJ mol^{-1}) and $MnBr_2$ (314 kJ mol^{-1}), instead of $PbBr_2$ (249 kJ mol^{-1}) and $MnCl_2$ (338 kJ mol^{-1}), will create better Mn-doped $CsPb(Cl/Br)_3$ nanocrystals because the difference in their bond dissociation energy is only 4% (much smaller than that of the later combination of 36%). Somewhat surprisingly, many research groups have used a combination of $PbBr_2$ and $MnCl_2$ precursors to achieve Mn-doped $CsPb(Cl/Br)_3$ *via* both a hot-injection approach[260] and room temperature synthesis.[261] Rationale for this seeming contradiction is still under debate. Successful synthetic procedures for doping Mn into $CsPbBr_3$[262] and $CsPbCl_3$[258] nanocrystals are very similar. The procedure for the former and latter are summarized below, respectively: heating a $PbBr_2$/$MnBr_2$/HBr
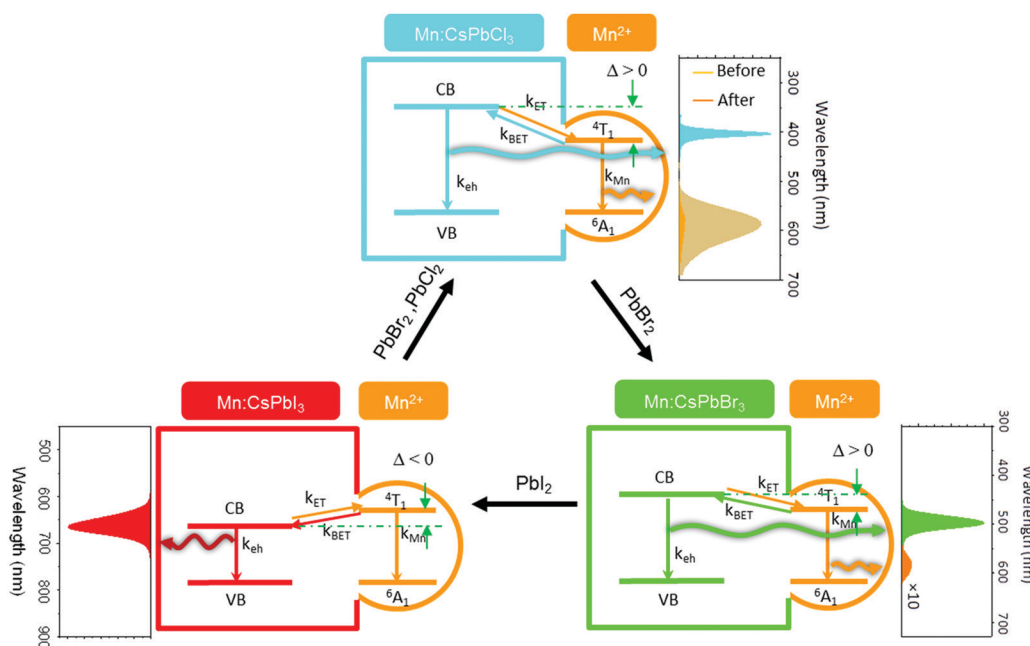

Fig. 14 The evolution of the energy level diagram of Mn-doped CsPbX$_3$ (Mn:CsPbX$_3$) nanocrystals during forward and reverse anion exchange. CB and VB denote the conduction and the valence band of the nanocrystal, respectively. The relative intensities of the two PL features of Mn:CsPbX$_3$ nanocrystals are established by the interplay of rates of several competing processes including: band edge electron–hole recombination (k_{eh}), deactivation of the Mn^{2+}-based d–d transition (k_{Mn}), and forward (k_{ET}) and back (k_{BET}) energy transfer between the nanocrystal and the impurity. The competition between the latter two processes is also strongly influenced by the energy difference (Δ) between the band edge and Mn^{2+}-based transitions. (top panel) The Δ in freshly prepared Mn:CsPbCl$_3$ nanocrystals is large and positive, favoring forward energy transfer and strong Mn^{2+}-based PL (yellow shading spectrum labeled as before in the top right box). After anion exchange with PbBr$_2$, (bottom right panel) the Δ in resulting Mn:CsPbBr$_3$ nanocrystals is still positive but much smaller; and some Mn^{2+} is lost to ion exchange with Pb^{2+}. Both effects lead to reduced Mn^{2+}-based PL (orange shading spectrum in the bottom right box; amplitude multiplied by a factor of 10). After further exchange with PbI$_2$, (bottom left panel) the Δ in the obtained Mn:CsPbI$_3$ nanocrystals is negative, resulting in no Mn^{2+}-based PL (bottom left box). Finally, reverse anion exchange by sequentially exchanging Mn:CsPbI$_3$ with PbBr$_2$ then PbCl$_2$ returns nanocrystals from Mn:CsPbI$_3$ to Mn:CsPbBr$_3$ then Mn:CsPbCl$_3$ (top panel), restoring a large and positive Δ, leading to the re-emergence of Mn^{2+}-based PL. Note that the intensity of the Mn^{2+}-based PL is much smaller compared to the freshly prepared samples (orange shading labeled as After in the top right box), due to the loss of Mn^{2+} when Pb-containing exchange precursors are used. Reprinted with permission from ref. 258, copyright 2016, American Chemistry Society.

mixture with capping ligands first, then swiftly inject Cs–oleate vs. heating $PbCl_2/MnCl_2$ mixture with capping ligands first, then swiftly inject Cs–oleate. The only differences in the previous case compared to the latter are the addition of HBr, some additional capping ligands, and a slightly different heating temperature. Therefore, it is possible that the addition of HBr is key to successfully doping Mn into $CsPbBr_3$ nanocrystals. Their results suggest that Mn luminescent intensity is strongly depended on the amount of HBr used to control the x value in the $L_2[Pb_{1-x}Mn_x]Br_4$ intermediate structure (where L = ligand).[262] Although no other papers mentioned the importance of adding HBr during the Mn doping process, a few papers did mention the importance of adding HCl during the Mn doping process in $CsPbCl_3$ systems.[263–265] While $PbCl_2$ and $MnCl_2$ have been used as the Pb and Mn precursors for most of the Mn-doped $CsPbCl_3$ studies, Xu et al. demonstrated that Mn-doped $CsPbCl_3$ can also be achieved at room temperature through the use of lead(II) acetate $(Pb(Ac)_2)$, manganese(II) acetate $(Mn(Ac)_2)$, and a small amount of HCl acid solution.[263] The acetate ligands in the metal acetate salts will be replaced by oleate ligands and form soluble metal–oleate complexes when dissolved in toluene with the presence of oleic acid and oleylamine. Hydrochloric acid is proposed to play two roles in the room-temperature synthesis of Mn-doped $CsPbCl_3$: (1) protonating the carboxylate groups of the oleate ligand which increases the concentration of active metal monomers, and facilitates generation of $CsPbCl_3$ nanocrystals and (2) providing excess Cl^- to the surface of nanocrystals, increasing the potential binding sites for Mn^{2+}. An optimal amount of HCl exists in order to obtain the highest Mn emission.[263] It was proposed by Adhikari et al. that using alkylamine hydrochloride $(RNH_3Cl$, created by mixing oleylamine and HCl) during synthesis will increase the reactivity of $MnCl_2$ with $PbCl_2$ in the hot-injection method and create more smaller particles, facilitating the slow Mn^{2+} doping process (no fast cooling required).[264] Mn doping by slowly dripping a small volume of $SiCl_4$ into a dispersion of $CsPbCl_3$ nanocrystals (prepared by hot-injection method with the presence of manganese(II) stearate) in toluene at room temperature was also proposed by Lin et al.[265] They found slow incorporation of Mn^{2+} when the reaction proceeded in air and no doping was found for the reaction run under vacuum. They proposed that this was due to the formation of HCl during the hydrolysis of $SiCl_4$ with the water in air (by the reaction of $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$). Under vacuum, there was no air (water) to trigger hydrolysis of $SiCl_4$. HCl serves many purposes in this process: (1) reacts with the manganese(II) stearate precursor releasing Mn^{2+}, (2) etches the surface of $CsPbCl_3$ nanocrystals (by H^+), and (3) reconstructs/passivates the surface of $CsPbCl_3$ nanocrystals (by Cl^-).[265] Halide acid is not always necessary for Mn-doping; one group successfully doped Mn into $CsPbI_3$ without the addition of HI by using hot-injection method with a combination of PbI_2, MnI_2 and Cs–oleate.[266]

In Mn-doped $CsPbCl_3$ nanocrystals, the host exciton can undergo ultrafast nonradiative Auger-like recombination $(\tau_{Aug} = \sim 12$ ps) when co-existing with the long-lived excited Mn-dopant state. Such a fast Auger-like process competes with the exciton-to-dopant spin-exchange internal energy transfer (IET, with $\tau_{IET} = \sim 303$ ps). The generation of multiple Mn-emission sites through consecutive IET

is thus difficult, allowing for Mn-dopant emission from only one Mn^{2+} site per nanocrystal at a time. This is different from the Mn-doped CdS or CdSe quantum dots with consecutive exciton-to-dopant IET processes that generate multiple excited Mn-dopants per nanocrystal. Notably, such a dopant-induced Auger-like recombination corresponds to the broadly observed excitation-dependent saturation of dopant emission in Mn-doped nanocrystals.[267] Mn-doped $CsPbCl_3$ nanocrystals showed an energy transfer time (τ_{ET}) of 380 ps, which is slower than the 70–190 ps energy transfer time of Mn-doped CdS/ZnS core/shell quantum dots.[268] Because the exciton–Mn energy transfer time is longer for Mn-doped $CsPbCl_3$ nanocrystals than Mn-doped CdS/ZnS core/shell quantum dots, it can be concluded that Mn-doped $CsPbCl_3$ nanocrystals have weaker exciton–Mn exchange coupling than Mn-doped CdS/ZnS core/shell quantum dots.[268] This is because, unlike Mn-doped CdS/ZnS core/shell quantum dots, $CsPbCl_3$ nanocrystals (cubes with length of ~ 10 nm in this specific study) are larger than their Bohr radius (the Bohr radius/exciton binding energy of $CsPbCl_3$, $CsPbBr_3$, and $CsPbI_3$ are 2.5 nm/75 meV, 3.5 nm/40 meV, and 6 nm/20 meV, respectively)[5] and therefore quantum confinement has no effect on exciton–dopant exchange coupling. In $CsPbCl_3$ nanoplatelets, where the thickness of the $CsPbCl_3$ nanoplatelets is smaller than their Bohr radius, enhanced dopant–carrier exchange interaction is observed due to strong quantum confinement effects.[269]

Excitation-dependent emission color tuning from an individual Mn-doped $CsPbCl_3$ microcrystal with a wide color tuning range (reversible between orange and blue) has been reported (Fig. 15c). Mn-doped $CsPbCl_3$ microcrystals were grown by immersing a lead(II) acetate $(PbAc_2)$-coated glass slide in a mixed isopropanol solution containing $MnCl_2 \cdot 4H_2O$ and CsCl for about 48 h at room temperature, and exhibit dual-color emission from both perovskite host excitons (blue) and Mn-dopants (orange) via an exciton-to-dopant IET process (Fig. 15a). By simply changing the laser excitation repetition rate or pulse intensity, the relative emission intensity between exciton $(I_{exciton})$ and Mn-dopant (I_{Mn}) can be continuously and reversibly altered from $I_{Mn} \gg I_{exciton}$ to $I_{exciton} \gg I_{Mn}$ with increasing excitation intensity (Fig. 15b). Such emission color tuning is enabled by (1) the saturation of Mn-dopant emission at high excitation intensity through a bottlenecked energy transfer effect mediated by shallow trap states, and (2) a linear dependence of host exciton emission with excitation intensity. It has been demonstrated that this reversible emission color switching is highly photo-stable as the emission color can be switched between orange and blue for more than 300 cycles within a continuous 14 h operation.[270] Up to 2% Mn-doped $CsPbCl_3$ nanoplatelets, with dimensions of 32 nm by 9 nm (length by width) and thickness of 2.2 nm (4 monolayers), can be achieved through room temperature synthesis method (Fig. 16a).[269] Room temperature synthesis of $CsPbCl_3$ nanoplatelets was achieved by modifying the room temperature synthesis of $CsPbBr_3$ nanoplatelets.[271] In Mn-doped $CsPbCl_3$ nanoplatelets, the $CsPbCl_3$ excitonic PL (emission peaks around 400 nm in Fig. 16e) is quenched by the new midgap levels created by Mn d states. At the same time, the excitonic energy transferred from the perovskite host to the Mn^{2+} dopant leads to a
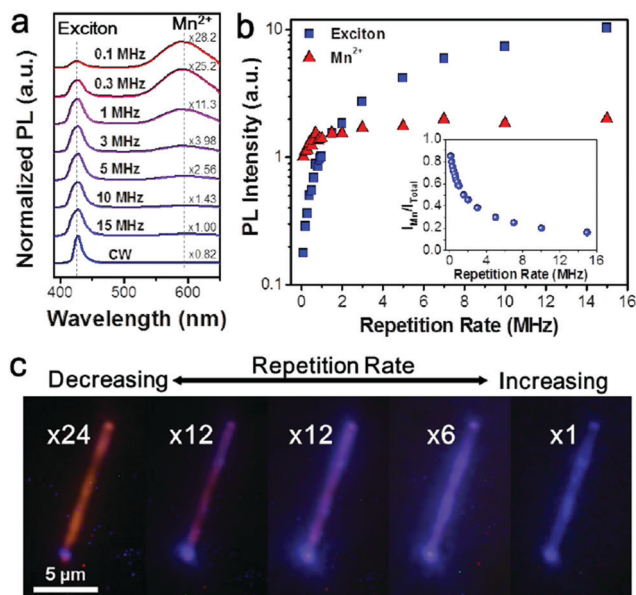
Fig. 15 (a) A set of PL spectra and (b) the corresponding change of integrated emission intensities of host exciton ($I_{exciton}$) and Mn-dopant (I_{Mn}) collected from an individual Mn-doped $CsPbCl_3$ microcrystal excited under various laser repetition rates. The inset is a plot of I_{Mn}/I_{total} (where $I_{total} = I_{Mn} + I_{exciton}$) as a function of excitation repetition rate. (c) PL images of an individual Mn-doped microcrystal showing the continuous change of emission color between orange and blue with increasing/decreasing the excitation repetition rate. The numbers next to the image are the magnification of PL intensity for comparison. Reprinted with permission from ref. 270, copyright 2019, American Chemistry Society.

spin-forbidden $^4T_1$–$^6A_1$ Mn d-electron emission (emission peaks around 600 nm in Fig. 16e) and enhances the PLQY from 2.8% (undoped $CsPbCl_3$ nanoplatelets) to 20% (0.8% Mn-doped $CsPbCl_3$ nanoplatelets). Further increasing the doping ratio from 0.8% to 2% reduces PL efficiency. This decrease is probably due to the increase of intrinsic defects[261] or due to increased interactions between neighboring Mn^{2+} ions, similar to cases of Mn-doped II–VI semiconductors where an optimal Mn-doping concentration exists.[269] Undoped $CsPbCl_3$ nanoplatelets possess a low PLQY of 2.8% (compared to $CsPbBr_3$ nanoplatelets that usually show PLQY as high as 90%), which could be because there is a greater probability of capping molecules forming nonradiative deep midgap states for wider band gap semiconductors. Further anion exchange reactions can convert these Mn-doped $CsPbCl_3$ nanoplatelets into Mn-doped $CsPbBr_3$ nanoplatelets, which still exhibit weak Mn emission.[269] Mn-doped $CsPbBr_3$ perovskite magic sized clusters (PMSCs) and perovskite quantum dots (PQDs) have been synthesized at a room temperature using manganese(II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) and $MnBr_2$ as Mn^{2+} dopant sources and benzoic acid (BA) and benzylamine (BZA) as passivating ligands.[272] The fluorescence of Mn-doped $CsPbBr_3$ PMSCs and PQDs synthesized with 0.10, 0.20, 0.30, and 0.40 mol of $MnCl_2 \cdot 4H_2O$ changed from green to blue, pink and orange (Fig. 17c). Their UV-vis spectra have two or three excitonic absorption peaks at 392/411/464, 395/452, 398/450 and 399/447 nm, respectively (Fig. 17a), and the corresponding PL spectra display multiple emission peaks at 398/412/471/585, 411/455/589,

411/454/590, and 411/455/591 nm, respectively (Fig. 17b), with increasing $MnCl_2 \cdot 4H_2O$ concentration.[272] It may be possible that the Mn and Cl are simultaneously doped into the $CsPbBr_3$ nanocrystals, resulting in Mn-doped $CsPb(Br/Cl)_3$ nanocrystals that show blue-shifted perovskite intrinsic peak with increasing amount of $MnCl_2$ precursors, similar to the HEDCE previously discussed. We note that, in this study, such blue-shifted peak were attributed to the effect of passivation and smaller size nanocrystals formation from the additional Cl^- ions.[272] To this point, it is not known whether room temperature synthesis or hot-injection method is better for incorporating a higher Mn doping ratio. The Mn doping concentration using room temperature synthesis can be as high as 37% ($CsPb_{0.63}Mn_{0.37}Cl_3$),[261] while an Mn doping ratio of 46% ($CsPb_{0.54}Mn_{0.46}Cl_3$) can be achieved by hot-injection.[257] Room temperature synthesis may lead to higher doping ratio than high temperature synthesis because the doped Mn^{2+} ions could be ejected from the surface of nanocrystals (a phenomenon known as self-purification or self-annealing process) when subjected to high temperatures.[261,273–275] Some scientists doubt the presence of the defect self-purification process in nanocrystals because the diffusion barriers for most defects cannot be readily overcome at temperatures used in colloidal synthesis (350 °C and below).[276] Doping Mn^{2+} into traditional II–VI semiconductor quantum dots has been demonstrated to be more difficult than doping into bulk and was also proposed to be a result from the exclusion effect.[258] At typical colloidal synthesis temperatures ($<$350 °C), the impurity diffusion rate into the semiconductor lattice is negligible and therefore the doping is accomplished via control over kinetic factors.[258] A few approaches have been proposed to promote Mn inclusion. One approach is to take advantage of the strong binding of dopant ions to specific crystal facets, followed by material overgrowth. Another approach is to utilize polychalcogenide precursors which feature Mn directly bound to other lattice constituents in a cluster form, which will favor Mn's inclusion.[258] One can tell whether the Mn-doping is substitutional or interstitial via XRD patterns of the perovskite powders/films. If the Mn doping is substitution, the XRD peak will shift to higher 2θ values indicating the incorporation of smaller Mn into the lattice sites of Pb. If the Mn doping is interstitial, the XRD peak will shift to lower 2θ, indicating an expansion of the crystalline lattice due to the insertion of Mn^{2+} ions in the interstices.[277] Mn-doped $CsPbCl_3$ nanocrystals were synthesized by the halide-rich method using manganese(IV) oxide (MnO_2).[278] When fabricated at the molar ratio of Pb/Mn/Cl = 1:1:8, Mn^{4+} (from MnO_2) was witnessed to be reduced to Mn^{2+} (in the form of $MnCl_2$) and dope into the $CsPbCl_3$ lattice.[278] Mn^{2+}-doped $CsPbCl_3$ nanocrystals have been synthesized using a single-step ultrasonic synthesis route, and triethylamine (TETN) was introduced to passivate the surface of Mn:$CsPbCl_3$ nanocrystals.[112] Gram-scale mass production of Mn^{2+}-doped $CsPbX_3$ nanocrystals have been achieved through a microwave-assisted hot injection method[279] and a solvent-free mechano-synthesis approach.[122] Mn^{2+}-doped $CsPbCl_3$ and $CsPb(Br/Cl)_3$ nanocrystals have also been achieved through a room-temperature transformation doping method from Cs_4PbX_6 nanocrystals.[280] Mn-Doped lead-free $Cs_2AgInCl_6$ and Cs_2AgBiX_6 (X = Cl, Br)
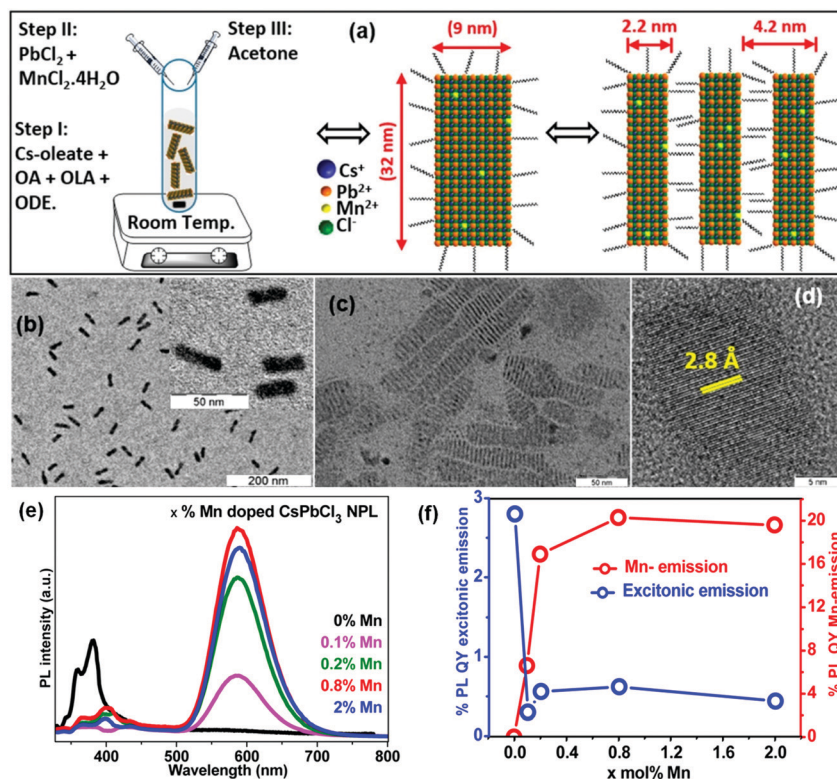
Fig. 16 (a) Schematic representations of synthesis and morphology of 0.8% Mn-doped $CsPbCl_3$ nanoplatelets, which can undergo face-to-face self-assembly. OA, OLA, and ODE refer to oleic acid, oleylamine, and 1-octadecene, respectively. (b) TEM image of nanoplatelets lying flat on the TEM grid. Inset shows a magnified view. (c) TEM image of self-assembled nanoplatelets lying perpendicular to the TEM grid. (d) HRTEM image illustrating lattice fringes for nanoplatelets lying flat on the TEM grid. (e) PL spectra as a function of Mn doping concentration, where absorbance at excitation wavelength for all samples was maintained the same. (f) PLQY for excitonic and Mn emission as a function of Mn doping concentration, where open circles are data points and solid lines are just a guide to the eye. Reprinted with permission from ref. 269, copyright 2017, American Chemistry Society.

double perovskite nanocrystals have also been studied.[281,282] Mn and Ni codoped $CsPbCl_3$ perovskite nanocrystals have also been realized through the addition of $NiCl_2$.[283]

In addition to the Mn-doped $CsPbCl_3$ and Mn-doped $CsPb(Cl/Br)_3$ noted above, Mn-doped organic–inorganic hybrid lead halide perovskites ($MAPbX_3$, X = Cl, Br, I) have also been achieved. Interestingly, all examples of Mn-doped organic–inorganic hybrid lead halide perovskites are based on room temperature synthesis approaches.[258,284,285] It was also interesting to note that the Mn doping ratio in the $MAPbCl_3$ and $MAPb(Br/Cl)_3$ systems can be significantly higher than that of the Mn-doped $CsPbCl_3$ and $CsPb(Br/Cl)_3$ systems. The highest Mn doping ratio in $CsPbCl_3$ and $CsPb(Br/Cl)_3$ systems is 46%, while the Mn doping ratio in $MAPbCl_3$ and $MAPb(Br/Cl)_3$ systems can reach as high as 90% (Fig. 17d–f).[284,285] The stark difference in the possible doping ratios of all-inorganic and organic–inorganic hybrid perovskites is attributed to the flexibility of the organic cation ($CH_3NH_3^+$) network which can preserve perovskite structure better than the rigid inorganic cation (Cs^+).[284] It was found that 90% Mn-doping is roughly the solubility limit, and further inclusion of Mn to 100% will result in the formation of 2D $(MA)_2MnCl_4$ instead of 3D $MAMnCl_3$. The transition is said to occur because Mn is smaller than Pb, and complete substitution will result in an unstable octahedral factor (μ) of less than 0.40.[284] Due to

limited space, many papers regarding Mn-doped perovskite nanocrystals are not covered in this review.[286–293] You may refer to a recent review for a more comprehensive insight into Mn-doped perovskite nanocrystals.[294]

3.3. Lanthanide-based (trivalent substitution) perovskite nanocrystals

Rare-earth element lanthanide ions have widely been used to dope phosphors like Ce^{3+}-doped $Y_3Al_5O_{12}$ (cerium-doped yttrium aluminum garnet, YAG:Ce),[295,296] and up-conversion nano-particles such as Yb^{3+}, Er^{3+} co-doped $KMnF_3$ ($KMnF_3$:Yb,Er)[297,298] and $NaYF_4$ ($NaYF_4$:Yb,Er).[299–301] The radius of Ce^{3+} is similar to that of Pb^{2+} (103 pm and 119 pm for Ce^{3+} and Pb^{2+}, respectively)[302] and has been doped in KPb_2Cl_5 and KPb_2Br_5 ternary lead halides.[303] $CeBr_3$ salt has been incorporated with hot-injection method to successfully dope Ce^{3+} into $CsPbBr_3$ nanocrystals, resulting in an improved PLQY.[302] Modified hot injection has also lead to successful lanthanide doping in Ce^{3+},Yb^{3+} co-doped $CsPbCl_{1.5}Br_{1.5}$ and Yb^{3+},Er^{3+} co-doped $CsPbCl_{1.5}Br_{1.5}$ nanocrystals.[304] Ce^{3+},Yb^{3+} co-doped $CsPbCl_{1.5}Br_{1.5}$ ($CsPbCl_{1.5}Br_{1.5}$:Yb(7.1%),Ce(2%)) nano-crystals show a significantly high PLQY of 146% and a large absorption cross-section, which make them prime candidates for downconversion material.[304] The PLQY can exceed 100% through a mechanism called the quantum-cutting effect, where one
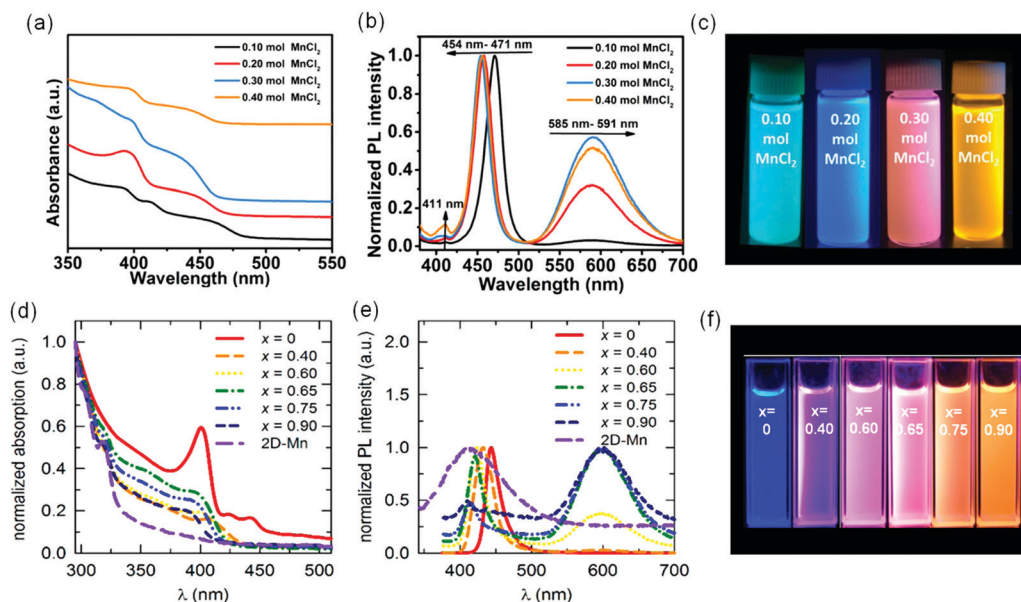
Fig. 17 (a) UV-vis absorption and (b) PL spectra of Mn-doped CsPbBr$_3$ perovskite magic sized clusters (PMSCs) and PQDs prepared using 0.10, 0.20, 0.30, and 0.40 mol of MnCl$_2\cdot$4H$_2$O. (c) Photograph of the Mn-doped CsPbBr$_3$ PMSCs and perovskite quantum dots (PQDs) samples synthesized with 0.10, 0.20, 0.30, and 0.40 mol of MnCl$_2\cdot$4H$_2$O in toluene under UV irradiation (λ_{ex} = 365 nm). Reprinted with permission from ref. 272, copyright 2020, American Chemistry Society. Optical properties of 3-D MAPb$_{1-x}$Mn$_x$Br$_{3-(2x+1)}$Cl$_{2x+1}$ nanocrystals with various Mn doping content (x) and 2-D (MA)$_2$MnCl$_4$ (2D-Mn) nanocrystals with 100% Mn: (d) absorption spectra normalized at 295 nm and (e) normalized PL spectra excited at 365 nm, except for 2-D (MA)$_2$MnCl$_4$ which was excited at 308 nm. The highest emission intensity among the exciton and Mn^{2+} peaks was used for normalization. For $x \leq 0.6$, exciton emission peaks were used for normalization; while for $x > 0.6$, Mn^{2+} emissions were used. The 2-D (MA)$_2$MnCl$_4$ emission was normalized at its emission maximum of 410 nm. (f) Photographs of the corresponding Mn-doped nanocrystals under 365 nm UV light illumination. Reprinted with permission from ref. 284, copyright 2017, American Chemistry Society.

absorbed high-energy photon can downconvert into two emitting low-energy photons.[305] When the two photons are emitted at a wavelength far away from their absorption edge (which means with large Stokes shift), the self-absorption loss can be eliminated and the PLQY can be doubled. Yb^{3+}-doped CsPbCl$_3$ nanocrystals synthesized *via* hot injection method have successfully demonstrated PLQY of 170% (close to the theoretical quantum-cutting limit of 200%), because they have emission in the NIR ($\sim$1000 nm) range while their absorption is in the near UV ($\sim$400 nm) range.[306] It is proposed that the aliovalent Yb^{3+} dopants tend to form a cation vacancy charge-neutral defect complex (Yb^{3+}-V$_{Pb}$-Yb^{3+}), which facilitates trapping the excitation energy from the CsPbCl$_3$ host (therefore almost no excitonic luminescence near absorption edge can be found). The trapped excitation energy is then divided to excite the two neighboring Yb^{3+} dopants followed by luminescent $^2F_{5/2} \rightarrow {}^2F_{7/2}$ f–f transitions of Yb^{3+} ions resulting in quantum-cutting NIR emission with PLQY approaching 200%.[306–309] Density functional theory (DFT) calculation demonstrates that the charge-neutral Yb^{3+}-V$_{Pb}$-Yb^{3+} complex does not create an inter-band gap defect energy level, and therefore different from the previous proposal, the energy donor in the quantum cutting process is actually the "right-angle" Pb atom rather than the Yb^{3+}-induced defect.[310] Yb^{3+} doping can also be achieved *via* postsynthetic exchange using Yb(NO$_3$)$_3\cdot$5H$_2$O in a mixture of methyl acetate : toluene (1 : 3 v/v) as precursor.[311] In order to see the quantum-cutting mechanism of $^2F_{5/2} \rightarrow {}^2F_{7/2}$ f–f transitions, a fundamental energy-conservation threshold of $E_g > 2 \times E_{f-f}$

must exist, meaning that the absorption band gap of perovskite host must be adequately large. When continuously decreasing the band gap by tuning the x value from 0 to 1 in Yb^{3+}-doped CsPb(Cl$_{1-x}$Br$_x$)$_3$ nanocrystals, quantum-cutting effect can be retained for x values as large as $\sim$0.75 then a steep drop of PLQY is observed with larger x values.[312] It has been proposed that the formation of a higher-concentration of defects can facilitate the introduction of a higher-concentration of Yb^{3+} dopant ions.[313] Yb^{3+}-doped Cs$_2$AgInCl$_6$ and Cs$_2$AgBiX$_6$ (X = Cl, Br) double perovskite nanocrystals also exhibit NIR emission at $\sim$1000 nm.[281,314] Although Yb^{3+}-doped perovskite nanocrystals can show PLQY approaching 200% due to quantum cutting process, there is still obstacles preventing them from practical use as solar downconversion materials due to their PL power saturation under modest photoexcitation fluences.[315] Eu^{3+}-Doped CsPbBr$_3$ and Tb^{3+}-doped CsPbBr$_3$ nanocrystals have been synthesized using a one-pot ultrasonication method.[316] Various of lanthanide ions (Ce^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Er^{3+}, and Yb^{3+}) have been systematically studied and successfully doped into the lattices of CsPbCl$_3$ perovskite nanocrystals through a modified hot-injection method using the corresponding lanthanide chloride salts as doping precursors.[317] From the absorption spectra (Fig. 18a), it was found that as the atomic number of the lanthanide ion increased, the band gap of the host perovskite nanocrystals gradually blue-shifted due to lattice contraction, which is in good agreement with common band gap engineering literature.[317] In the emission spectra (Fig. 18b), several peaks associated with the
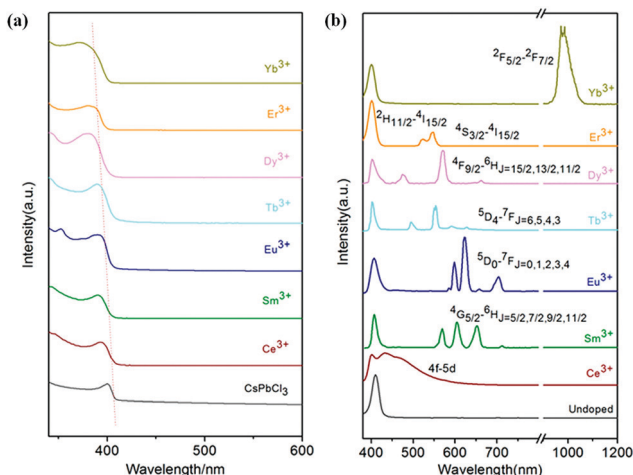
Fig. 18 (a) Absorption spectra and (b) PL emission spectra of $CsPbCl_3$ nanocrystals doped with different lanthanide ions. Reprinted with permission from ref. 317, copyright 2017, American Chemistry Society.

intrinsic electronic transitions of lanthanide ions can be found in the doped systems besides the narrow band-edge emission peak at around 410 nm. The overall PLQY of doped systems is enhanced mainly due to the contribution of intrinsic emissions from the lanthanide ions. Although the energy transfer from exciton of perovskite host to doping ions likely decreases the PLQY of the exciton, some nonradiative recombination pathways (such as Cl vacancy) may be removed during the doping and result in enhanced PLQY of exciton.[317] $LiYbF_4:Tm^{3+}@LiYF_4$ core/shell nanoparticles were used to sensitize $CsPbX_3$ perovskite nanocrystals in order to achieve upconversion luminescence (UCL) through a radiative energy transfer upconversion (RETU) process. Lanthanide-doped core/shell nanoparticles function as the energy donor to convert the NIR excitation light into the UV and visible emission light through successive photon absorption and energy transfer upconversion (ETU) processes, then the emitted light from nanoparticles will be reabsorbed by perovskite nanocrystals.[318] Bright blue light-emitting CsBr lead-free nanocrystals doped with Eu^{2+} have been achieved through hot-injection method.[319] We note that discussion on a few more lanthanide-doped perovskite nanocrystals studies can be found in this review.[320]

3.4. Au (Au(0), Au(ɪ), Au(ɪɪ), Au(ɪɪɪ)) and Ag-based perovskite nanocrystals

Interesting combinations can be observed when incorporating Au into perovskite systems due to the different valence charge states in gold systems. $Cs_2[Au^IX_2][Au^{III}Y_4]$ (X, Y = halogen) gold mixed-valence complexes with mono-halogen (X = Y, *i.e.*, $Cs_2Au_2X_6$)[321] or hetero-halogen (X ≠ Y)[322] with distorted perovskite structures have both been achieved.[323] The perovskite-type gold mixed-valence systems undergo either pressure-induced or photo-induced Au valence transition from the mixed-valence state of $Au^{I,III}$ to the single-valence state of Au^{II}. The electrical properties of mixed-valence $Au^{I,III}$ complexes are attributed to the mobility of bipolarons, the dynamic two-electron exchange between the Au^I and Au^{III} states, and can behave as either an insulator or metal,

depending on pressure or temperature.[321–323] Although the distorted perovskite structures of these $Cs_2[Au^IX_2][Au^{III}Y_4]$ complexes are three-dimensional, the charge transfer interaction between Au^I and Au^{III} within these complexes is two-dimensional through the bridging halogen Y, which sits in the *a–b* plane. Because the bridging halogen Y is responsible for controlling the pressure-induced gold valence transition in the $Cs_2[Au^IX_2][Au^{III}Y_4]$ complexes, the critical pressure for the valence transition from $Au^{I,III}$ to Au^{II} is distinct for different halogen systems.[322,323] Besides the Au(ɪ)/Au(ɪɪɪ) and Au(ɪɪ) states mentioned above, Au can also be incorporated into perovskite systems through Au(0) state.[324] When introducing $AuBr_3$ into a $CsPbBr_3$ nanocrystal/toluene solution, gold nanoparticles can spontaneously form at the edge of $CsPbBr_3$ nanocrystals (Fig. 19a and b, from (1) $CsPbBr_3$ to (2) Au–$CsPbBr_3$). If $AuCl_3$ is introduced to $CsPbBr_3$ nanocrystals, gold nanoparticles will again form on their surface, and an anion exchange process forming Au–$CsPb(Br_{1−x}Cl_x)_3$ nanocrystals will occur (Fig. 19a and b, from (1) $CsPbBr_3$ to (3) Au–$CsPb(Br_{1−x}Cl_x)_3$). It was proposed that the Au(ɪɪɪ) ions can be reduced into Au(0) by the oleylamine on the surface of $CsPbBr_3$ nanocrystals, and subsequently nucleate and grow into Au nanoparticles on the corners of perovskite nanocrystals, without the assistance of any additional reducing agent (Fig. 19b).[324] The PLQY of the nanocrystals is decreased when Au–$CsPbBr_3$ or Au–$CsPb(Br_{1−x}Cl_x)_3$ hybrid structures are formed suggesting that there is a charge-transfer process between the perovskite nanocrystal and the Au nanoparticles.[324] Another study suggested that the formation of Au–$CsPbBr_3$ hybrid structures may not always occur and sometimes a cation exchange process between Au ions and Pb ions may form $Cs_2Au^IAu^{III}Br_6$ nanocrystals, which have absorption in the NIR range (Fig. 19c–f).[325] By introducing some $PbBr_2$ salts at the same time as adding $AuBr_3$ crystals, the existence of excess Pb ions competitively prevents the cation exchange of Au ions for Pb ions and insures there is no formation of $Cs_2Au^IAu^{III}Br_6$ nanocrystals (Fig. 19c–f, from (4) $CsPbBr_3$ to (6) Au–$CsPbBr_3$). The diameter of the deposited Au nanoparticles can be tuned by the concentration of additional Au(ɪɪɪ) ions. The formation of $Cs_2Au^IAu^{III}Br_6$ nanocrystals can be considered an alternative synthetic strategy for Pb-free perovskites *via* a post-synthetic cation exchange process. The formation of Au–$CsPbBr_3$ hybrid nanocrystals can provide improved catalytic activity due to the plasmon–exciton coupling effect and the metal domains of Au–$CsPbBr_3$ hybrid heterostructures can act as electrical contact points for nanoscale optoelectronic devices.[325] Silver ions (Ag^+) have also been proposed to heterovalently dope colloidal $CsPbBr_3$ nanocrystals *via* substituting Pb^{2+} ions and significantly improve the conductivity and charge-carrier mobility by nearly 3 orders of magnitude. Heterovalent doping of Ag^+ has been found to shift the Fermi level downward to the valence band and induce a p-type character in Ag^+-doped $CsPbBr_3$ nanocrystals and significantly improve the conductivity and charge-carrier mobility by nearly 3 orders of magnitude compared to the undoped $CsPbBr_3$ nanocrystals, confirmed by field effect transistor (FET) studies.[326] In another study, however, Ag^+ ions were proposed to replace Cs^+ ions instead of Pb^{2+} ions and claimed to simultaneous dope and surface passivate the $CsPbI_3$ nanocrystals film in LED device.[327]
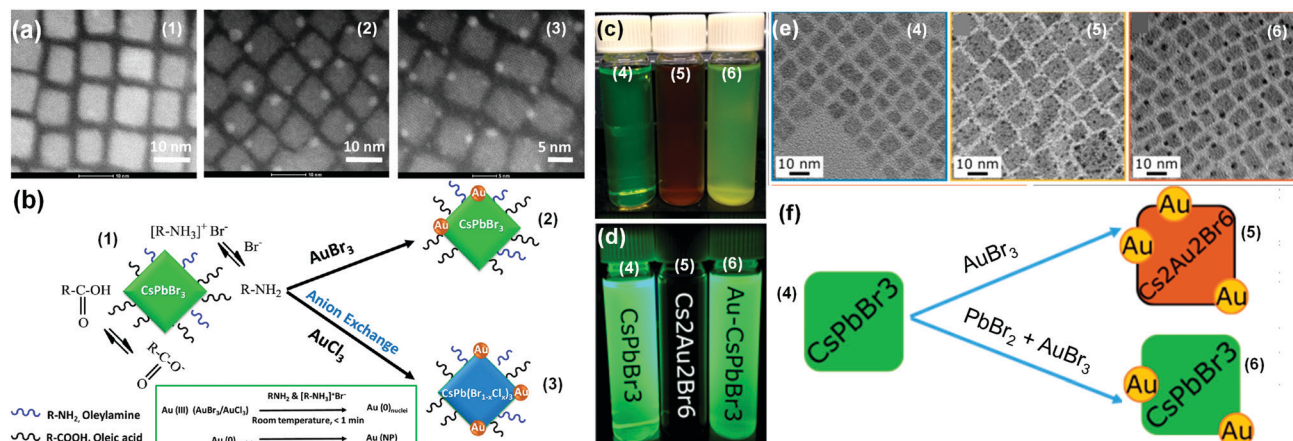
Fig. 19 (a) High-resolution scanning transmission electron microscopy (HR-STEM) images of (1) parent CsPbBr$_3$ nanocrystals, and (2) Au–CsPbBr$_3$ or (3) Au–CsPb(Br$_{1−x}$Cl$_x$)$_3$ hybrid structures after reactions. (b) Schematics of surface amine ligands reacting with the additional AuBr$_3$ (or AuCl$_3$) salts leading to the reduction of Au(III) to Au(0), forming Au nanoparticles at the edge of CsPbBr$_3$ (or CsPb(Br$_{1−x}$Cl$_x$)$_3$, due to the accompanied anion exchange when adding AuCl$_3$ salts) nanocrystal. Reprinted with permission from ref. 324, copyright 2017, American Chemistry Society. Photographs of (4) CsPbBr$_3$, (5) Cs$_2$Au$_2$Br$_6$, and (6) Au–CsPbBr$_3$ nanocrystal solutions under (c) ambient light and (d) UV light excitation, and (e) their corresponding TEM images. (f) Schematics of (4) CsPbBr$_3$ nanocrystals reacting with AuBr$_3$ forming (5) Cs$_2$Au$_2$Br$_6$ nanocrystals (gold cation exchange accompanied with some gold deposition) or (6) Au–CsPbBr$_3$ nanocrystals (purely gold deposition, the existence of excess Pb ions from added PbBr$_2$ can competitively prevent the gold cation exchange from occurring). Reprinted with permission from ref. 325, copyright 2017, American Chemistry Society.

3.5. Other divalent (isovalent) substitution perovskite nanocrystals

Other than the widely studied Sn-doped and Mn-doped systems, a few other divalent cations have also been tested in doping colloidal metal halide perovskite nanocrystals. Alkaline-earth (AE) metals (*e.g.*, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) have been proposed to be used as dopants to substitute Pb^{2+} in halide perovskites through a one-pot synthetic method.[328] AE metal chloride (*i.e.*, MgCl$_2$, CaCl$_2$, SrCl$_2$, and BaCl$_2$) were added to the other precursors during synthesis of CsPbCl$_3$ perovskite nanocrystals, and it was found that the incorporation effectiveness of AE^{2+} ions in CsPbCl$_3$ nanocrystals are quite different. It was found that only Ba^{2+} can be incorporated into the core of nanocrystals, while Ca^{2+} and Sr^{2+} stay at/near the surface of nanocrystals, passivating the nonradiative recombination surface vacancies and significantly enhancing PLQY (pristine CsPbCl$_3$: 0.8%; Ca^{2+}-doped CsPbCl$_3$: 77.1%). Mg^{2+} found to rarely incorporate into the nanocrystals, neither in the core nor at the surface, probably due to its relatively small ionic radius (ionic radius: Mg^{2+} = 0.72 Å, Ca^{2+} = 1.00 Å, Sr^{2+} = 1.18 Å, Ba^{2+} = 1.35 Å, Pb^{2+} = 1.19 Å), which results in a notable self-purification effect that excludes Mg^{2+} outside the lattice.[328] SrCl$_2$ has also been used as a co-precursor during CsPbI$_3$ nanocrystals synthesis to simultaneously dope Sr^{2+} ions and passivate the surface with Cl$^−$ ions. Because Sr^{2+} has a smaller ionic radius (1.18 Å) than Pb^{2+} (1.19 Å), it can cause a slight contraction in CsPbI$_3$ lattice, resulting in improved stability. At the same time, Cl$^−$ ions can passivate surface defects of CsPbI$_3$ nanocrystals, resulting in enhanced PL.[329] SrI$_2$ has also been used to stabilize cubic phase α-CsPbI$_3$ nanocrystals, and a high PLQY of 80% can be maintained even after storage for two months.[330] Ni^{2+}, with the smallest ionic and Shannon radii among all transition metal ions, has been used to dope CsPbI$_3$, CsPbBr$_3$, and CsPbCl$_3$ nanocrystals using NiI$_2$, NiBr$_2$, and NiCl$_2$ as precursors, respectively.[208,331–334] It was found that

Ni^{2+} doping can restrict the phase change of CsPbI$_3$ nanocrystals from α-CsPbI$_3$ to δ-CsPbI$_3$ and significantly improve their stability.[331] While violet emitting CsPbCl$_3$ nanocrystals usually have relatively low PLQYs (<5%),[335] Ni^{2+} doping was found to boost the PLQY of violet emitting CsPbCl$_3$ nanocrystals from 2.4% up to 96.5%.[333] Similarly, postsynthetic treatment of CsPbCl$_3$ nanocrystals using CdCl$_2$ can also boost the PLQY of violet emitting CsPbCl$_3$ nanocrystals from 3% up to 96 ± 2% and maintain its original PL peak position (406 nm) and peak width (FWHM ∼10–12 nm).[336] By adding optimum amount of CuCl$_2$ during hot-injection synthesis of CsPbCl$_3$ nanocrystals, the PLQY of violet-emitting CsPbCl$_3$ nanocrystals can be boosted from ∼0.5% to 60% with an emission peak position (λ_{em}) at 403 nm, and the PLQY of halide-exchanged CsPb(Cl/Br)$_3$ can be boosted from ∼8% to ∼92% (for sample with λ_{em} = 430 nm) and from 22% to 98% (for sample with λ_{em} = 460 nm).[335] All the abovementioned Ni, Cd, and Cu-doped CsPbCl$_3$ and CsPb(Cl/Br)$_3$ nanocrystals exhibit no blue shift in the PL peak position, even though one would be expected from lattice contraction associated with the incorporation of relatively smaller Ni^{2+}, Cd^{2+}, and Cu^{2+} ions. One study demonstrated, however, that doping smaller Cu^{2+} ions can boost the PLQY of CsPb(Br/Cl)$_3$ nanocrystals from 23% to 80% but would also blue shift the wavelength from 466 nm to 453 nm.[337] It has been demonstrated that CsPbCl$_3$ nanocrystals only experience a massive boost in PLQY when treated with Cu(II)X$_2$ precursors (when treated with CuCl$_2$ or CuBr$_2$, the PLQY of CsPbCl$_3$ can be boosted from 2.7% to 12.3% (CuCl$_2$ treatment) and 92.6% (CuBr$_2$ treatment)), and not when treated with Cu(I)X precursors (when treated with CuCl or CuBr the PLQY of CsPbCl$_3$ showed improvements of only 2.7% (CuCl treatment) and 22.3% (CuBr treatment)).[338] Simply by increasing the Cu doping concentration, the emission wavelength of MAPb$_{1−x}$Cu$_x$Br$_3$ can be tuned from 468 nm to 513 nm.[339] Co^{2+} doping in CsPbBr$_3$/Cs$_4$PbBr$_6$

nanocrystals can lead to effective catalytic sites for CO_2 reduction.[80] Partial substitution of Pb^{2+} with Zn^{2+} in $CsPbI_3$ perovskite nanocrystals exhibited an improved, close-to-unity PLQY of 98.5% due to the increased radiative decay rate and decreased nonradiative decay rate.[340] A postsynthetic cation exchange method was used to dope $CsPbBr_3$ nanocrystals with metal(II) ions by dissolving metal(II) bromide salts ($MBr_2 = SnBr_2$, $CdBr_2$, $ZnBr_2$) in oleylamine and adding it to a perovskite nanocrystal–toluene solution at room temperature inside a nitrogen-purged glovebox.[227] Using metal(II) bromide salts ensures that no anion exchange occurs and any change is solely coming from cation exchange. Blue-shifted absorption and PL spectra were observed in all three cases (Fig. 20), but the blue-shift behaviors vary from case to case and strongly depend on the precursor concentration and the type of divalent cation. For the case of postsynthetic reaction with $SnBr_2$, the blue-shift is small for both low and high $SnBr_2$ concentrations. Postsynthetic reactions with $CdBr_2$ and $ZnBr_2$ lead to more pronounced blue-shifts than those seen with $SnBr_2$. The size, shape, high PLQYs (over 60%), and colloidal stability in toluene of parent $CsPbBr_3$ nanocrystals were maintained for at least several months after the reactions with metal(II) bromide salts. 1D powder electron diffraction (PED) patterns (obtained by azimuthally integrating the 2D electron diffraction (ED) patterns) show that the lattice contracts more after reaction with $CdBr_2$ and $ZnBr_2$ salts than with $SnBr_2$ (Fig. 20f and g). This is expected due to the differences in the ionic radii ($r(Pb^{2+}) = 119$ pm, $r(Sn^{2+}) = 118$ pm, $r(Cd^{2+}) = 95$ pm, $r(Zn^{2+}) = 74$ pm, and coordination number (CN) = 6 in all cases).[227] The cation exchange process is often limited by the diffusion rates of the outgoing and incoming cations, which is often attributed to vacancy-mediated migration which is limited by the formation energy of each vacancy. Cation diffusion in perovskites is relatively much slower than that of anions because cations have higher activation energies and lack of interstitial sites for interstitial diffusion. Therefore, the postsynthetic cation exchange in this study is very slow and only partially occurs despite the large excess amount of M^{2+} cations used. It was suggested that the amount of oleylamine added also plays an important role in the ion exchange process because the amount of oleylamine (OLAM) will affect the amount of OLAM–Br complex (between both host perovskite and MBr_2 dopant) and that strongly affects the number of halide vacancy generated (Fig. 21).[227] We note that the abbreviation for oleylamine in the whole paper is not consistent due to the different abbreviations used in different schematic figures. Transition metal halides (FeX_3, CoX_2, NiX_2, CuX_2, and ZnX_2) have also been used to dope $CsPbX_3$ nanocrystals.[341] Similary, metal(II) bromide salts ($MBr_2 = ZnBr_2$, $MnBr_2$, $EuBr_2$) have been used to convert Cs_4PbBr_6 nanocrystals into $CsPb_xM_{1-x}Br_3$ nanocrystals,[342] following an earlier finding that excess $PbBr_2$ would transform Cs_4PbBr_6 nanocrystals into $CsPbBr_3$ nanocrystals.[343]

3.6. Other trivalent (heterovalent) substitution perovskite nanocrystals

Scientists have also considering doping Bi to replace Pb because Bi^{3+} and Pb^{2+} are isoelectronic (i.e., both electron configurations are the same as $[Xe]4f^{14}5d^{10}6s^26p^0$). Incorporating heterovalent Bi^{3+} ions may induce electronic doping (act as electron donor) by increasing the charge carrier density in the lead halide perovskites. Doping heterovalent Bi^{3+} ions in colloidal $CsPbBr_3$ perovskite nanocrystals has been achieved by hot-injection method with a combination of $BiBr_3$, $PbBr_2$, and Cs–oleate (Fig. 22A–D).[344] Through the use of Kelvin probe, time-resolved transient absorption, and photoemission spectroscopy in air (PESA), it was demonstrated that Bi^{3+} doping not only affects the band structure and carrier dynamics of $CsPbBr_3$, but also the interfacial charge transfer between Bi-doped $CsPbBr_3$ and two well-known molecular electron acceptors, tetracyanoethylene (TCNE) and phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$).[344] The driving-force of interfacial charge transport, Gibbs free energy ($-\Delta G$) between the molecular acceptor and donor moieties, can be tuned upon metal doping.[344] Interestingly, band gap broadening (blue-shift) was found in the Bi-doped $CsPbBr_3$ nanocrystals (Fig. 22C), and band gap narrowing (red-shift) was found in most Bi-doped single crystal cases including Bi-doped $CsPbBr_3$ (Fig. 22F),[345] Bi-doped $MAPbBr_3$,[346] and Bi-doped $MAPbCl_3$ single crystals.[347] One study claimed Bi-doping had no effect on the band gap of Bi-doped $MAPbBr_3$ single crystals, but instead significantly increases the sub-band gap density of states, which other studies incorrectly interpreted as band gap narrowing.[348] Though the effect of band gap narrowing or broadening is contradictory to each other in the single crystal and nanocrystal cases, there is no doubt that Bi-doping can affect the electronic properties of the host crystals. By sandwiching a ~ 2 mm thick Bi-doped perovskite single crystal in between two ~ 100 nm thick Au electrodes, the metal–semiconductor–metal configuration demonstrated current–voltage (I–V) characteristics of an Ohmic contact for the undoped single crystal (e.g., $CsPbBr_3$,[345] or $MAPbCl_3$,[347]), and showed that conductivity increased with Bi-doping content, probably due to higher carrier concentration and alteration of the metal–semiconductor band alignment.[345] High-level DFT calculations demonstrate that replacing Pb^{2+} with Bi^{3+} ions in the bulk or on the surface creates deep trap states that remove the defect-tolerant nature of $CsPbBr_3$ nanocrystals and function as nonradiative recombination centers significantly quenching the PL intensity. Conversely, Ce^{3+} ions can stabilize the bulk/surface structure of $CsPbBr_3$ nanocrystals providing band-edge states that leads to PL enhancement.[349] Besides Bi^{3+}, a few other trivalent ions have been examined as heterovalent dopants in lead halide perovskite systems. Sb^{3+} doping in super small blue emitting $CsPbBr_3$ nanocrystals is suggested to reduce the surface energy, improve the lattice energy, passivate the defect states below the band gap, and boosting their blue emitting PLQY from 50.0% to 73.8%.[350] Au^{3+} and In^{3+} have been successfully incorporated into $MAPbBr_3$ single crystals by the addition of $AuBr_3$ and $InBr_3$ salts, however they did not exhibit significant spectral changes (band gap narrowing).[346] They suggested that the outer ns^2 electrons play a critical role in band gap modulation and DFT calculations also suggested that Au and In create deeper, more localized states than Bi.[346] Al^{3+} has been successfully incorporated in $CsPbBr_3$ nanocrystals by the addition of $AlBr_3$ salt, and a blue-shift in the
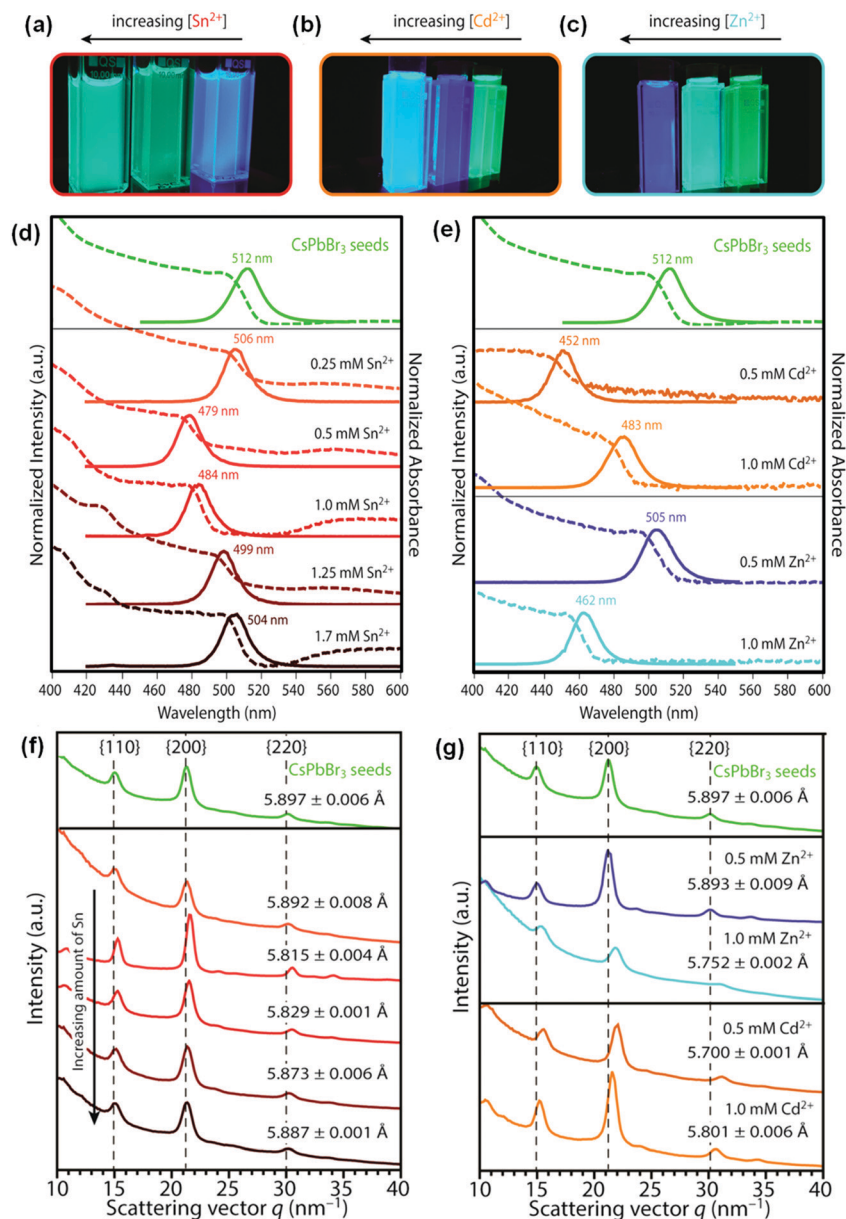
Fig. 20 Photographs of colloidal suspensions of $CsPbBr_3$ nanocrystals upon reaction with different divalent cation bromide salts under UV illumination: (a) $CsPbBr_3$ nanocrystals after reaction with different concentrations of $SnBr_2$ (from right to left: 0.5, 1.25, and 1.7 mM), (b) parent $CsPbBr_3$ nanocrystals (right vial) and product nanocrystals after reaction with different concentrations of $CdBr_2$ (0.5 mM (middle vial) and 1.0 mM (left vial)), and (c) parent $CsPbBr_3$ nanocrystals (right vial) and product nanocrystals after reaction with different concentrations of $ZnBr_2$ (0.5 mM (middle vial) and 1.0 mM (left vial)). PL spectra (solid lines) and absorption spectra (dashed lines) of (d) parent $CsPbBr_3$ nanocrystals (green lines) and product nanocrystals obtained after reaction with different concentrations of $SnBr_2$ (red and brown lines) and (e) parent $CsPbBr_3$ nanocrystals (green lines) and product nanocrystals obtained after reaction with different concentrations of $CdBr_2$ (orange lines) and $ZnBr_2$ (blue lines). In all cases, a blue-shift of both the absorption and the PL emission spectra is observed after reacting $CsPbBr_3$ nanocrystals with divalent cation bromides (MBr_2), while the well-defined absorption features and narrow PL FWHMs ($\sim$80 meV) are preserved. 1D powder electron diffraction (PED) patterns of $CsPbBr_3$ nanocrystals after reaction with MBr_2 obtained from azimuthal integration of 2D electron diffraction (ED) patterns: (f) after reaction with $SnBr_2$ with concentration of 0.25, 0.50, 1.0, 1.25, and 1.7 mM, from top to bottom, respectively, show minor lattice contraction; whereas (g) after reaction with 0.50 and 1.0 mM of $ZnBr_2$ and $CdBr_2$ show larger lattice contraction. Reprinted with permission from ref. 227, copyright 2017, American Chemistry Society.

emission was observed.[351] They suggested that the blue-shifted emission was due to the extended band gap of Al-doped nanocrystals as well as the quantum confinement effect originating from the elongated shape of Al-doped nanocrystals. The bond dissociation energy of Al_2Br_6 (the dimeric form of $AlBr_3$) needs to

be considered during the incorporation because of the possibility of retention of some Al–Br (bridging) bonds.[351] The introduction of foreign Bi^{3+}, Al^{3+}, and In^{3+} ions to $CsPbBr_3$ nanocrystals by adding $BiBr_3$, $BiFeO_3$, $BiCl_3$, $AlBr_3$ or $InBr_3$ into the synthesis precursors will function as capping ligands and led to partial
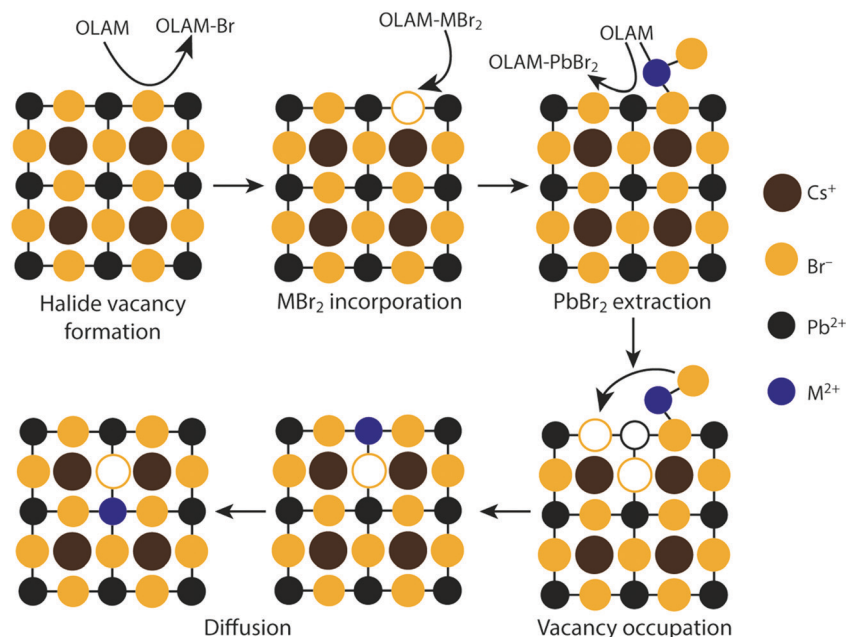
Fig. 21 Schematic representation of the proposed cation exchange reaction mechanism. In the first step, surface halide vacancies are created by oleylamine (OLAM) molecules in solution. In the second step, a Br anion of an OLAM−MBr_2 unit occupies the halide vacancy. In a third step, the bound OLAM molecule extract a $PbBr_2$ unit, leaving a cation and halide vacancy behind, which are occupied by the bound MBr_2 species. Finally, the incorporated divalent guest cation diffuses into the perovskite lattice, leaving behind a halide vacancy at the surface for a second cation exchange process to occur. Reprinted with permission from ref. 227, copyright 2017, American Chemistry Society.
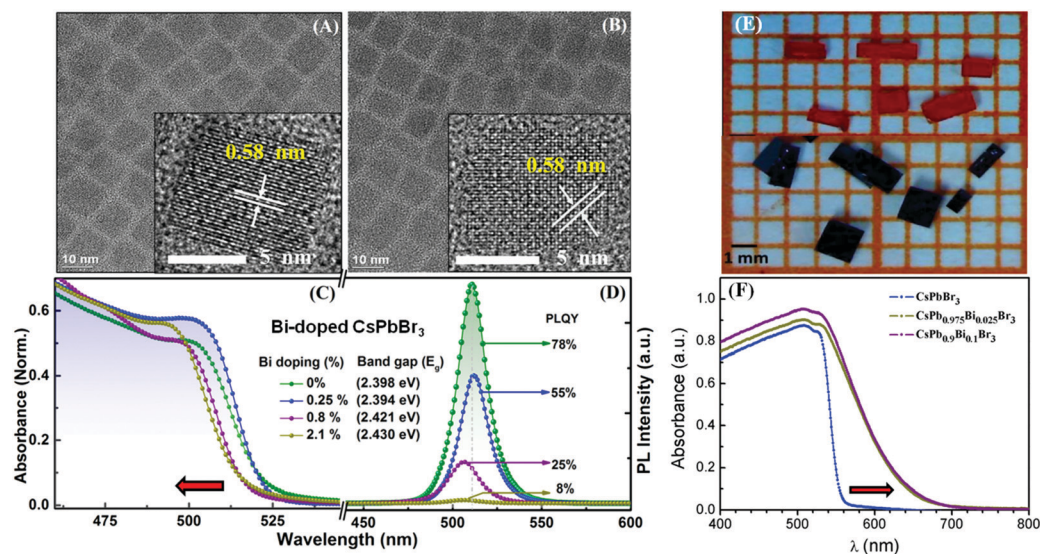
Fig. 22 (A) TEM images of undoped $CsPbBr_3$ and (B) 2.1% Bi-doped $CsPbBr_3$ nanocrystals, with HRTEM images shown in the insets, indicating no change in the average size, shape, or crystal structure upon Bi^{3+} doping. (C) Absorption spectra and (D) PL spectra (λ_{ex} = 365 nm) of undoped and Bi-doped (0.25%, 0.8%, and 2.1%) $CsPbBr_3$ nanocrystals showing the spectral shift and change in the band gap energy (E_g, calculated from Tauc plots). Reprinted with permission from ref. 344, copyright 2017, American Chemical Society. (E) Photographs of $CsPbBr_3$ (top orange crystals) and $CsPb_{0.9}Bi_{0.1}Br_3$ (bottom black crystals) single crystals with reference grid width of 1 mm. (F) Absorption spectra of the $CsPbBr_3$ and $CsPb_xBi_{1−x}Br_3$ single crystals. Reprinted with permission from ref. 345, copyright 2017, Royal Society of Chemistry. The red arrows indicating the directions of increasing Bi-doping content: (C) blue-shifted optical responses were observed in the Bi-doped $CsPbBr_3$ nanocrystals, while (F) red-shifted optical responses were observed in the Bi-doped $CsPbBr_3$ single crystals.

formation of growth-constrained thinner perovskite nanoplatelets with a thickness of 3 inorganic $PbBr_4^{2−}$ octahedron layers. The final products will be a mixture nanoplateles with two different thicknesses, as seen by two well-defined absorption and emission bands.[352] Fe(II)-doped $CsPbBr_3$ nanocrystals can be efficient photocatalysts for reduction of CO_2 without the need of any additional carrier transportation material or heterostructures. During photocatalytic reduction of CO_2, undoped

CsPbBr$_3$ led to CO as the major product while Fe(II)-doped CsPbBr$_3$ led to CH$_4$ as the dominant product.[82] Fe(III)-doped CsPbCl$_3$ nanocrystals shows a pink-colored dual emission consisting of a sharp blue emission at 410 nm from the excitonic peak of CsPbCl$_3$ and a broad red emission at ~580 nm result from the $^4T_1 \rightarrow {}^6A_1$ (d–d) radiative transition of Fe^{3+} dopant.[353] Gadolinium (Gd^{3+}) doping was found to enhance the phase stability of α-CsPbI$_3$ nanocrystals from 5 days to 11 days probably due to the reasons of increased tolerance factor, distorted cubic symmetry, and decreased defect density.[354]

Lower toxicity bismuth (Bi^{3+}), antimony (Sb^{3+}), and indium (In^{3+}) ions are commonly used heterovalent ions for lead (Pb^{2+}) ion substitution in perovksite systems. To meet charge neutrality, the final product of lead-free substitution with trivalent ions will no longer be ABX$_3$ but will be either A$_3$B$_2$X$_9$ (e.g., (MA)$_3$Bi$_2$Br$_9$[355] and Cs$_3$Sb$_2$Br$_9$[356]) or A$_2$B'B''X$_6$ (e.g., Cs$_2$AgBiX$_6$[79,357,358] and Cs$_2$AgInX$_6$[282,359–361]) double perovskite. The structure of A$_3$B$_2$X$_9$ can be visualized by removing every third layer of B atoms along the ⟨111⟩ direction of ABX$_3$ perovskite structure,[356] and the structure of A$_2$B'B''X$_6$ can be thought of as doubling the ABX$_3$ perovskite unit cell and replacing the B atoms alternatively with M$^+$ and M^{3+} cations.[357] CH$_3$NH$_3$Br and BiBr$_3$ were used to prepare the (MA)$_3$Bi$_2$Br$_9$ nanocrystals through a LARP method at room temperature and obtained blue emitting nanocrystals with emission peak at 423 nm, FWHM of 62 nm, and PLQY of up to 12%.[355] Similarly CsBr and SbBr$_3$ were used to prepare the Cs$_3$Sb$_2$Br$_9$ nanocrystals through LARP method and obtained blue emitting nanocrystals with emission peak at 410 nm, FWHM of 41 nm, and PLQY of up to 46%.[356] The emission wavelength of both (MA)$_3$Bi$_2$Br$_9$ and Cs$_3$Sb$_2$Br$_9$ nanocrystals can be tuned between ~360 nm to ~550 nm via halide substitutions. It was proposed that a Br-rich (SbBr$_x$) surface passivation resulted in the relatively high PLQY of their Cs$_3$Sb$_2$Br$_9$ nanocrystals, similar to Br-rich (PbBr$_x$) surface passivation proposed in the CsPbX$_3$ systems.[362] Cs$_3$Bi$_2$Br$_9$ nanocrystals have been synthesized through a similar room temperature LARP method, and it was proposed that after addition of deionized (DI) water, a self-passivating layer of BiOBr was formed which led to enhanced PL and improved stability. Similar improvement was not observed in the (MA)$_3$Bi$_2$Br$_9$ systems.[71] The optical properties of Cs$_3$Bi$_2$X$_9$ nanocrystals[71,363] displayed a rough trend of slightly red-shifting, with slightly higher quantum yield when compared to (MA)$_3$Bi$_2$X$_9$ nanocrystals,[355,364] though some exceptions exist. Cs$_3$Sb$_2$X$_9$ nanocrystals[356] present a wider emission range than both Cs$_3$Bi$_2$X$_9$ and (MA)$_3$Bi$_2$X$_9$ nanocrystals, and possess a much higher quantum yield for the iodide nanocrystals (Fig. 23 and Table 4). Ligand-free Cs$_3$Bi$_2$X$_9$ nanocrystals with emission ranging from 400 nm to 560 nm have been synthesized through a one-pot room temperature method similar to the ligand-capped nanocrystals using various CsX and BiX$_3$ halide salts as precursors (Fig. 24).[365] The ligand-free nanocrystals exhibited much lower PLQYs than ligand-capped nanocrystals but the PLQY of ligand-free Cs$_3$Bi$_2$Br$_9$ nanocrystals can be improved by storing in open air, which probably facilitates perovskite hydrate formation on the nanocrystal surface passivating surface trap-states.[365] Cs$_3$Bi$_2$I$_9$ nanocrystals have been synthesized using a hot-injection method with BiI$_3$ as a precursor, and the coexistence of direct–indirect transitions of their band gap was discussed.[366] Cs$_3$Bi$_2$I$_9$ and Rb$_3$Bi$_2$I$_9$ are considered as 0D and 2D structure, respectively.[367]

In the A$_2$B'B''X$_6$ double perovskite cases, the ionic radii of Bi^{3+} (1.03 Å) and Ag$^+$ (1.15 Å) are similar to that of Pb^{2+} (1.19 Å) and are commonly used for heterovalent substitutions.[368] Double perovskites made from Bi^{3+} could possess defect-tolerance similar to the perovskites made from Pb^{2+} because of the isoelectronic nature of Bi^{3+} and Pb^{2+}.[369] Some other possible candidates for M^{3+} are Sb^{3+} (0.76 Å), In^{3+} (0.80 Å), and Ga^{3+} (0.62 Å) (As^{3+} is less desirable due to its toxicity). Possible candidates for M$^+$ are Cu$^+$ (0.77 Å), Na$^+$ (1.02 Å), and Au$^+$ (1.37 Å).[368,369] Based on calculations, the band gaps for Bi^{3+} and Sb^{3+} double perovskites tend to be indirect and smaller than 2.7 eV,[368] while Cs$_2$InAgX$_6$ tend to be direct band gap, which is more suitable for photovoltaic applications.[359] Mn-doped Cs$_2$AgInCl$_6$ double perovskite nanocrystals have been achieved through a hot injection method.
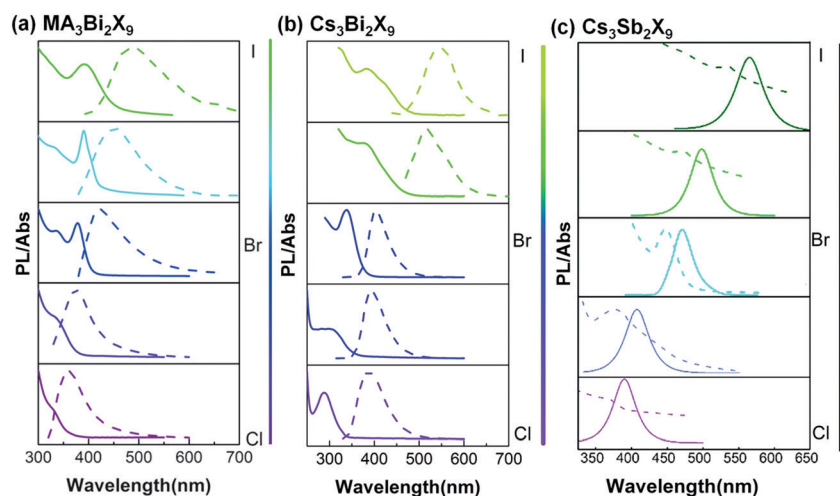
Fig. 23 Absorption and PL spectra of (a) (MA)$_3$Bi$_2$X$_9$, reprinted with permission from ref. 355, copyright 2016, Wiley-VCH. (b) Cs$_3$Bi$_2$X$_9$, reprinted with permission from ref. 71, copyright 2017, Wiley-VCH and (c) Cs$_3$Sb$_2$X$_9$ reprinted with permission from ref. 356, copyright 2017, American Chemistry Society. Nanocrystals with different halide compositions. The summary of their optical properties can be found in Table 4.
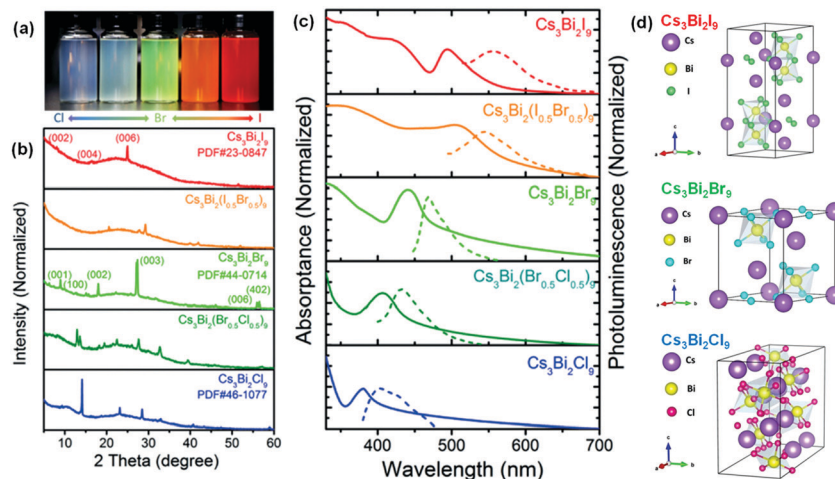
Fig. 24 (a) Photographs, (b) XRD patterns, and (c) steady-state absorption and normalized photoluminescence spectra of the ligand-free $Cs_3Bi_2X_9$ (X = Cl, $Cl_{0.5}Br_{0.5}$, Br, $Br_{0.5}I_{0.5}$, I) nanocrystals. Reprinted with permission from ref. 365, copyright 2017, Wiley-VCH. (d) Unit cell crystal structures of $Cs_3Bi_2I_9$, $Cs_3Bi_2Br_9$, and $Cs_3Bi_2Cl_9$. Reprinted with permission from ref. 71, copyright 2017, Wiley-VCH.

These doped nanocrystals exhibited a bright orange PL emission with PLQY of ~16%, which contrasts greatly with the white PL emission and PLQY of ~1.6% displayed by undoped $Cs_2AgInCl_6$ nanocrystals (Fig. 25a).[282] Direct band gap undoped and Ag-doped $Cs_2NaInCl_6$ double perovskite nanocrystals have been synthesized via hot injection method.[370] Varying the amount of Na alloying in $Cs_2Na_xAg_{1-x}BiCl_6$ (x = 0, 0.25, 0.5, 0.75, and 1) double perovskites leads to increase in their optical band gaps (from 3.39 eV for x = 0 to 3.82 eV for x = 1) and significant improvement in their weak PLs (a 30-fold increment).[371] Study reveals that the Bi^{3+} dopants inside the Bi-doped $Cs_2Ag_{1-x}Na_xInCl_6$ double perovskite nanocrystals introduce $BiCl_6$ states that

localize just below the CBM are essential for observing any PL emission, while the Ag^+ ions in the double perovskite structure give rise to localized $AgCl_6$ energy levels just above the VBM under Na-rich conditions.[372] The color temperatures of white emitting colloidal $Cs_2Ag_{1-x}Na_xIn_{1-y}Bi_yCl_6$ nanocrystals can be tuned by the amount of Na^+ and Bi^{3+} incorporation (x = 0–1, y = 0.03–0.16).[373] Doping with lanthanide ions (Yb^{3+} and Er^{3+}) can further red shift the visible emission of $Cs_2AgInCl_6$ nanocrystals to NIR emission with characteristic f–f transition peaks at 996 nm for Yb^{3+} and 1537 nm for Er^{3+} dopants (Fig. 25b).[360] Cs_2InBiX_6 and Cs_2InSbX_6 In(I)-based double perovskites have been proposed to be intrinsically unstable, because In(I) easily
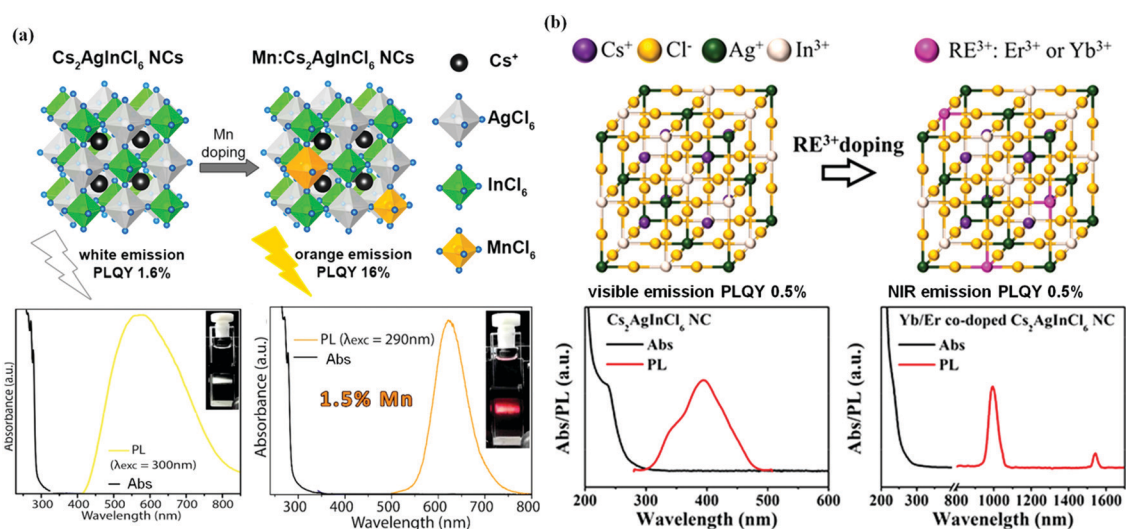
Fig. 25 (a) Schematic of double perovskite structures (top panel) as well as absorption and PL spectra (bottom panel) of $Cs_2AgInCl_6$ (left) and Mn-doped $Cs_2AgInCl_6$ (right) nanocrystals. Insets show corresponding optical photos of PL emission of $Cs_2AgInCl_6$ (left) and 1.5% Mn-doped $Cs_2AgInCl_6$ (right) nanocrystals dispersions in hexane from cuvettes under Xe lamp excitation at 300 nm. Reprinted with permission from ref. 282, copyright 2018, American Chemistry Society. (b) Schematic of double perovskite structures (top panel) as well as absorption and PL spectra (bottom panel) of $Cs_2AgInCl_6$ (left) and Yb^{3+}/Er^{3+}-codoped $Cs_2AgInCl_6$ (right) nanocrystals. RE^{3+} represents rare earth ions. Reprinted with permission from ref. 360, copyright 2019, American Chemistry Society.

oxidizes to In(III).[374] Cs_2AgBiX_6 (X = Cl, Br) nanocrystals have been successfully synthesized through hot-injection approaches using acetates (Cs(OAc), Ag(OAc), Bi(OAc)$_3$) as cation precursors and trimethylsilyl halide (TMSCl or TMSBr),[357] hydrochloric acid (HCl), or bromotrimethylsilane as halide precursors.[358] $Cs_2AgBiBr_6$ colloidal nanocrystals have also been successfully synthesized through hot-injection approaches using Cs_2CO_3, $BiBr_3$, and $AgNO_3$,[79] or AgBr[358] as precursors. Formation of quaternary Cs_2AgBiX_6 colloidal nanocrystals requires careful balancing of the reactivities and chemical potentials of the individual components. If balance is not achieved, impurities such as AgX, CsX, Cs–Bi–X or Cs–Ag–X ternary phases (*e.g.*, Cs_3BiX_6) may form.[357] It was found that addition of a small amount of hydrobromic acid (HBr) is critical to ensure the full ionization of Ag^+, which prevents the formation of AgBr impurity in the final product. The injection temperature and the existence of oleylamine are also key factors for successful synthesis because $BiBr_3$ would remain insoluble at temperatures below 160 °C or without the addition of oleylamine.[79] Ligand-free $Cs_2AgBiBr_6$ nanocrystals have, however, been successfully synthesized using CsBr, AgBr and $BiBr_3$ as precursors through a room temperature anti-solvent recrystallization method without heat treatment or oleylamine.[375] These ligand-free $Cs_2AgBiBr_6$ nanocrystals exhibit a sub-band gap long absorption tail originating from surface defects on nanocrystals and could be suppressed by the addition of oleic acid surfactants.[375] The degradation products of $Cs_2AgBiBr_6$ have been proposed to be a combination of two different ternary cesium bismuth bromides (*i.e.*, $Cs_3Bi_2Br_9$ and Cs_3BiBr_6), elemental silver, and bromine.[358]

3.7. Size-dependent doping regime

Though highly challenging, pinpointing the exact location or distribution of dopants within a host matrix and understanding the underlying mechanisms of doping is of key importance. Whether foreign ions can be fully incorporated within or simply segregate on the surface of the perovskite crystals depends heavily on the dopant's ionic radii. Take the incorporation of divalent alkaline earth metal ions in MA-based perovskite as an example. Theoretical calculations have predicted that Sr^{2+} can replace Pb^{2+} in the perovskite lattice because Sr^{2+} and Pb^{2+} have similar ionic radii (118 pm and 119 pm, respectively) and the tolerance factor of $MASrI_3$ (0.91) falls within the stable 3D perovskite structure range (0.8 to 1.0).[376] Despite that, the synthesis of a pure 3D $MASrI_3$ halide perovskite has not yet been reported. In Sr-doped perovskite films, a Sr-rich secondary phase has been observed to form on the surface.[377] On the other hand, Mg^{2+}, with a smaller ionic radius (72 pm), cannot form stable $MAMgI_3$ as its tolerance factor (1.06) is not within the stable 3D perovskite structure range (0.8 to 1.0).[377] Fig. 26a and b show the grazing incidence X-ray diffraction (GIXRD) patterns of Sr and Mg-doped tetragonal $MAPbI_3$. No additional peaks were seen upon the addition of Sr^{2+} and Mg^{2+}, indicating no new crystalline phases are formed. The lack of an identifiable secondary phase suggested that the surface segregated phase is either amorphous or too thin (or too dispersed) to be detected by GIXRD. Le Bail refinement and the effect of GIXRD patterns

broadening were used to characterise the microstrain due to doping. As schematically shown in Fig. 26c, the microstrain represents a local distortion of the lattice, which can be revealed as a broadening of the peaks. No systematic XRD peak shift was observed, signifying the absence of lattice macrostrain or homogenous changes in the crystal structure. The microstrain evolution of the Sr doping (Fig. 26d) and Mg doping (Fig. 26e) series showed that the perovskite lattice can accumulate distortion up to a critical doping level, after which the lattice relaxes back probably due to the formation of segregated secondary phase. The microstrain of Sr-doped samples reached a maximum value at a doping concentration of 0.2% and quickly droped to a value similar to the undoped sample at higher concentrations. This suggested that phase segregation dominated the doping process, with dopant lattice incorpation only occurring within the low doping regime of 0.2. On the other hand, the microstrain in Mg-doped samples showed a more gradual decrease after the maximum was reached at doping concentration of 1%, implying both lattice incorporation and lattice relaxation due to segregation can occur simultaneously at concentrations higher than 1%. It is hypothesized that dopants are incorporated into the perovskite lattice until a critical distortion is attained, beyond which the dopant starts to segregate at the surface, resulting in a relaxation of the perovskite lattice. The findings that Mg^{2+} has a higher inclusion concentration than Sr^{2+} (despite the more favorable tolerance factor of Sr^{2+}) suggests a plausible scenario of Mg^{2+} inclusion in interstitial positions.[377] The Mg-doped perovskite lattice only shows contraction in the *c*-direction while the Sr-doped perovskite lattice displays uniform changes in both directions. It can be concluded true incorporation of the dopant into the perovskite lattice occurs within the low doping concentration regime (0.1–1 mol%). In contrast, the high doping concentration regime (3–10 mol%, such as those numbers commonly used in the literature) results in surface phase segregation. Moreover, it was also found that, for one dopant (Sr^{2+} or Mg^{2+}), the low doping regime induces a more n-type doping character, yet the high doping regime triggers a less n-type doping feature, which is different from classical doping in silicon system.[377]

4. X-site substitution

Tuning the emission band gap of lead halide perovskite nanocrystals differs from traditional II–VI, III–V, and IV–VI semiconductor quantum dots because instead of altering dimensionality to utilize quantum confinement effects,[6,7,113,126,136,187,190,191,379–385] the emission band gap of metal halide perovskite nanocrystals is primarily tuned by their halide compositions.[5,386,387] For lead halide perovskite, the maximum wavelength difference that can be tuned by quantum confinement effects is roughly 100 nm (Fig. 27a), which is relatively narrow compared to greater than 300 nm range that can be tuned *via* varying halide compositions (Fig. 27b).[191]

4.1. Halide-based perovskite nanocrystals

Compared to cation-exchange, anion-exchange in perovskite systems is relatively fast and easy. Mixed-halide perovskite
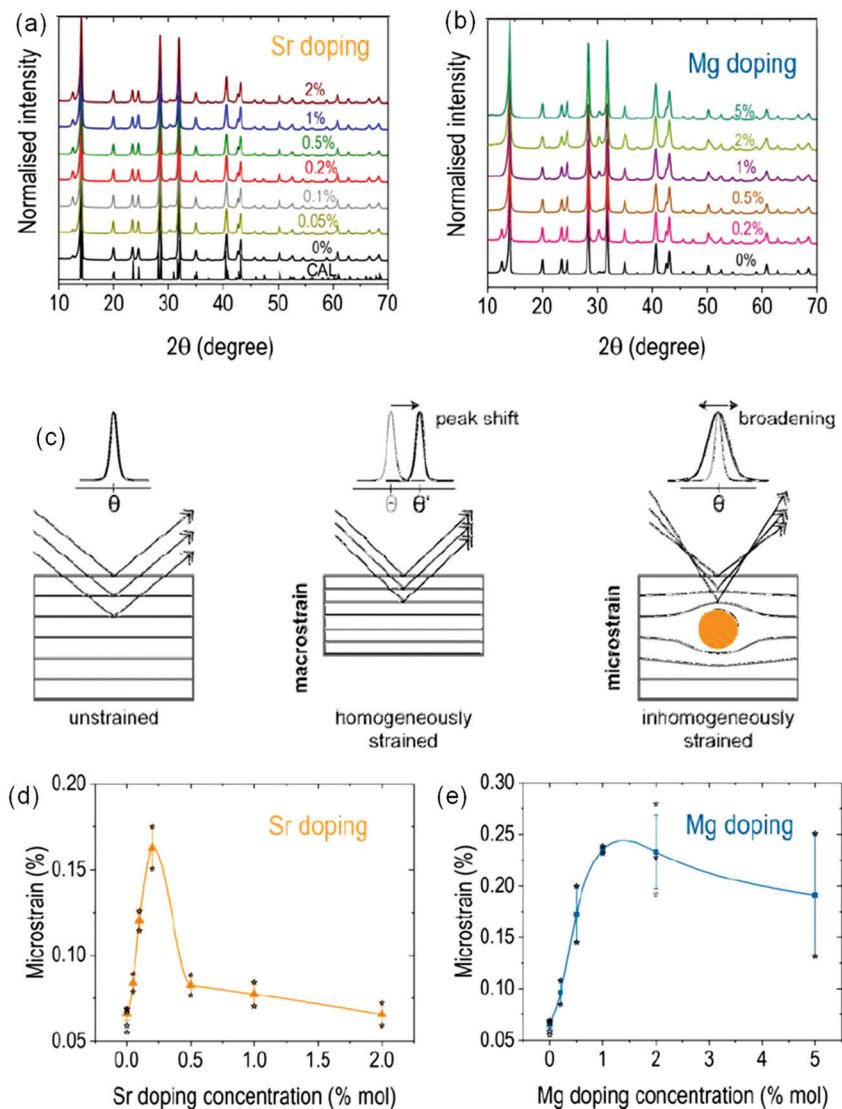
Fig. 26 Grazing incidence X-ray diffraction (XRD) patterns of (a) Sr doping series (CAL is the theoretical calculation of tetragonal MAPbI$_3$) and (b) Mg doping series in MAPbI$_3$. (c) Schematic of no strain (left panel), macrostrain (central panel) which causes a peak shift in XRD pattern, and microstrain (right panel) which induces a peak broadening. (d) Microstrain values obtained by Le Bail refinement of the Sr-doped MAPbI$_3$ and (e) the Mg-doped MAPbI$_3$ samples as a function of nominal dopant concentration. The depicted microstrain values are the mean of at least two different samples (star points next to the mean values), and the error bar represents the standard deviation. Spline fits of the values are shown as a visual guide. Reprinted with permission from ref. 377, copyright 2020, American Chemistry Society.

(e.g., CsPb(Br/Cl)$_3$ or CsPb(Br/I)$_3$) colloidal nanocrystals can be achieved by either direct synthesis strategy of directly using mixed-anion precursors during nanocrystals synthesis, or by postsynthetic strategy of adding excess amounts of Cl or I halide precursors into as prepared colloidal bromide-based perovskite (e.g., MAPbBr$_3$ or CsPbBr$_3$) nanocrystal suspensions.[386] Options for Cl or I halide precursors include: lead halides (PbX$_2$),[386,388] organoammonium halides (such as octadecyl-ammonium halides (ODA-X),[386] oleylammonium halides (OLAM-X)),[386,387,389] and aryl-based aniline hydrohalide (An-HX).[389] Fast anion-exchange kinetics in halide perovskites are likely due to their low defect formation energy, the rigid nature of their cationic sublattice, and the high ion mobility in the lattice due to the prevalence of vacancies.[390,391] Although both chlorine exchange

and iodine exchange of CsPbBr$_3$ nanocrystals are kinetic processes and demonstrate no thermodynamic preference for these two anions, their anion exchange mechanisms are actually different: the chlorine exchange is likely diffusion-limited, whereas the iodine exchange is likely surface-limited.[392] In most cases, the parent CsPbBr$_3$ nanocrystals retain their cubic (Fig. 28a)[387] or orthorhombic (Fig. 28b)[390] structures during their anion-conversion from CsPbBr$_3$ to CsPbI$_3$ or CsPbCl$_3$.[95] There are also cases where CsPbBr$_3$ nanocrystals are transformed from cubic to orthorhombic when increasing the I$^-$ anion-exchange level (Fig. 28c),[388] which indicates that CsPbBr$_{3-x}$I$_x$ nanocrystals do not form a continuous solid solution over the entire I$^-$ anion-exchange range (from $0 \leq x \leq 3$).[95] These contradictory findings may be due to anion-exchanged CsPbI$_3$ nanocrystals
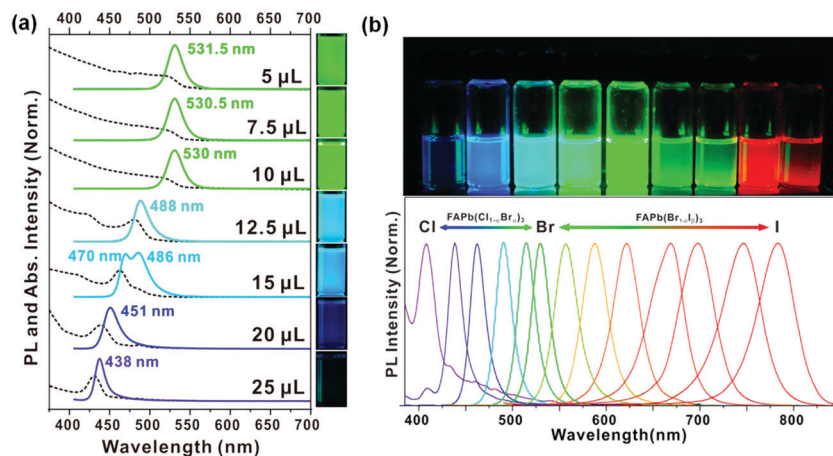
Fig. 27 (a) Absorption (dashed lines) and PL (solid lines) spectra of FAPbBr$_3$ nanocrystals synthesized by varying the amount of oleylamine capping molecule from 5 to 25 μL (70%, Sigma-Aldrich), demonstrating their tunability through quantum confinement effect. (b) PL emission spectra of FAPbBr$_3$ nanocrystals synthesized with different halide anions, demonstrating their tunability through varying their anion species. Photographs in (a) and (b) are their corresponding suspension samples under 365 nm UV irradiation. Reprinted with permission from ref. 191, copyright 2017, American Chemistry Society.
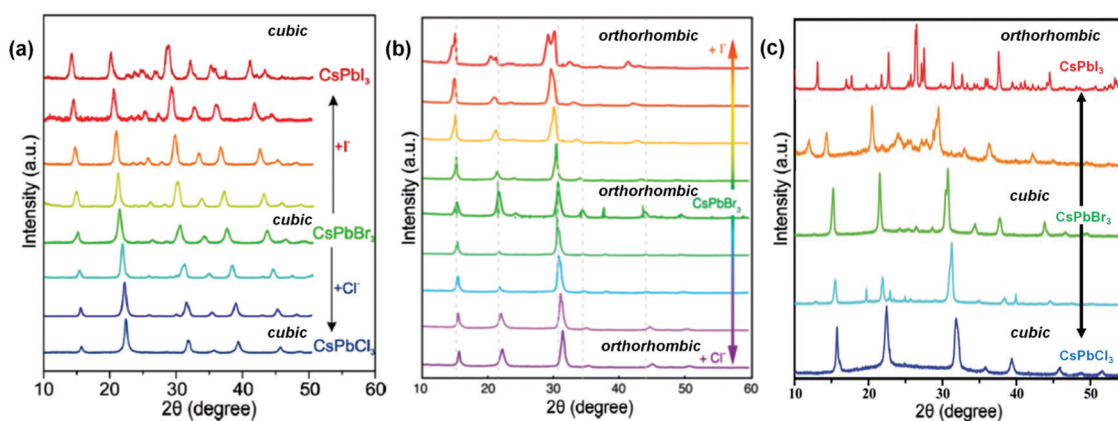
Fig. 28 XRD patterns of the parent CsPbBr$_3$ nanocrystals with (a) cubic structure (reprinted with permission from ref. 387, copyright 2015, American Chemistry Society) and (b) orthorhombic structure (reprinted with permission from ref. 390, copyright 2016, American Chemistry Society) that retain their structures after anion-exchange processes; while in some cases (c) the structure of CsPbBr$_3$ nanocrystals gradually changes from cubic to orthorhombic when increasing the I content during their anion-exchange processes. Reprinted with permission from ref. 388, copyright 2016, Royal Society of Chemistry.

gradually undergoing a phase transition from black cubic phase to their thermodynamically preferred yellow orthorhombic phase.[393] Conversely, the shape and crystal structure of the parent CsPbBr$_3$ nanocrystals is retained while undergoing the Br–Cl exchange process.[388] There are still limitations for band gap tuning *via* halide substitutions. In perovskites, the conduction band (E_c) (electron affinity) and valence band (E_v) (ionization potential) energies are dictated mostly by the atomic orbitals of the cations and anions, respectively.[394] The valence orbitals change from 3p to 4p to 5p with a monotonic decrease in electron binding energy (lower ionization potential) during the halide substitution from Cl to Br to I, with most offset shown in the valence band (ΔE_v).[158] For example, the band gaps for MAPbX$_3$ can only be changed from 3.11, 2.22, to 1.51 eV for X = Cl, Br, and I, respectively,[395] which indicates that in order to obtain perovskites with band gaps smaller than 1.51 eV, an offset in the conduction band is also required, which would require substitution of a B-site cation.

Colloidal metal halide perovskite nanocrystals display fast exchange dynamics in solution, even in the absence of an excess halide source. Simply mixing two different colloidal halide perovskite nanocrystal suspensions in one vial would result in anion-exchange between these two nanocrystals.[386,387] Solution-phase is not a prerequisite for anion exchange, as solid-state anion exchange was also observed when mixing two different halide perovskite dried powders or mixing perovskite powders with other halide containing solids (*e.g.*, KCl, KBr, KI).[396] Only Cl–Br and Br–I couples (and never for Cl–I couples) are attainable in halide exchange. Attempts to yield CsPbCl$_3$ directly from CsPbI$_3$ nanocrystals (or *vice versa*) through anion-exchange or mixing CsPbCl$_3$ and CsPbI$_3$ nanocrystals together to obtain intermediate CsPb(Cl/I)$_3$ nanocrystals have yet to be succeeded. Generally, the PL is completely diminished, suggesting a total dissolution of particles. One possible explanation is that due to the large difference in ionic radii between Cl$^-$ and I$^-$, the direct exchange between Cl$^-$ and I$^-$ would involve a structural stress
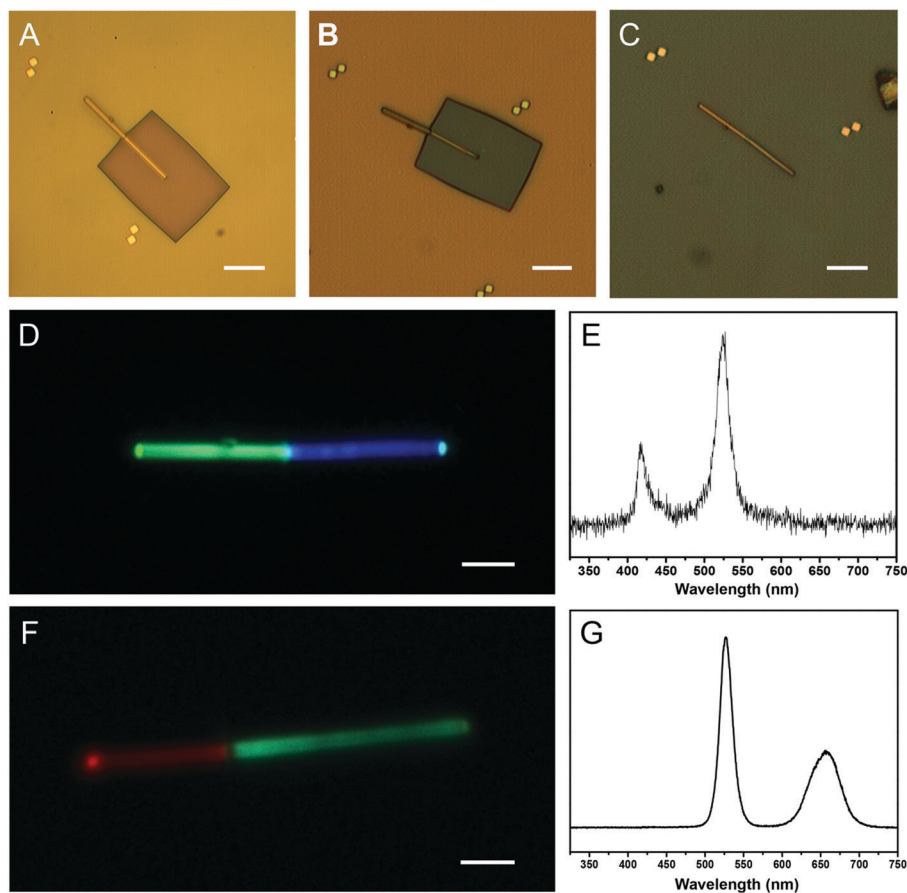
Fig. 29 Fabrication and PL characterization of cesium lead halide perovskite nanowire heterojunctions. (A) Optical microscope image of a $CsPbBr_3$ nanowire partially coated with PMMA before anion exchange. (B) Optical image of the $CsPbBr_3$ nanowire partially coated with PMMA after anion exchange. (C) Optical image of the $CsPbBr_3$ nanowire after anion exchange and after removal of PMMA. (D) Optical image of the partial bromide/partial chloride nanowire under laser excitation, and (E) the corresponding PL emission spectrum. (F) Optical image of the partial iodide/partial bromide nanowire under laser excitation, and (G) the corresponding PL emission spectrum. Scale bars for (A)–(C) are 10 μm, while scale bars for (D) and (F) are 3 μm. Reprinted with permission from ref. 391, copyright 2017, National Academy of Sciences.

on the lattice that cannot be tolerated, resulting in destruction of perovskite nanocrystals.[386] Researchers have demonstrated heterojunction cesium lead halide perovskite nanowires, where different segments of the same nanowire contain of different halide ions. For example, half of the nanowire could be $CsPbBr_3$ while the other half is $CsPbI_3$ or $CsPbCl_3$ (Fig. 29A–G). This heterojunction structure perovskite was achieved by a very delicately controlled anion exchange process where a segment of a nanowire was partially coated in poly(methyl methacrylate) (PMMA) while the other segment underwent anion exchange.[391] Besides using delicate PMMA masking to achieve desired anion exchange patterning, anion exchange patterning *via* photo-excitation has also been demonstrated. Light can trigger photo-induced anion exchange in $CsPbX_3$ nanocrystal–dihalomethane solutions (Fig. 30).[397] The accepted mechanism for this novel phenomenon is that photoexcited $CsPbX_3$ nanocrystals transfer an interfacial electron to a dihalomethane (*e.g.*, dichloro-methane (DCM) or dibromomethane (DBM)) solvent molecule, and halide anions are produced *in situ* by the reductive dis-sociation due to the transferred electron. The extent of photo-induced anion-exchange reaction can be precisely controlled
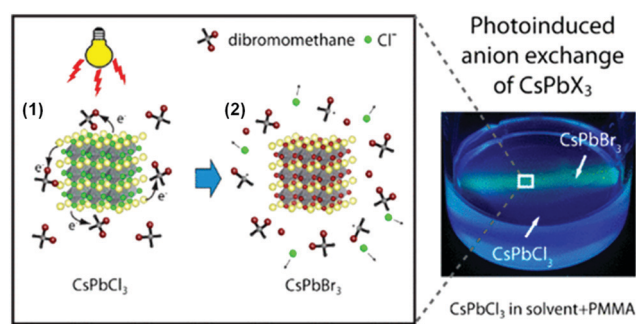
Fig. 30 Optical image of the photoinduced anion exchange of $CsPbX_3$ (X = Cl to Br) nanocrystals in dibromomethane solution (right figure), and schematic of the proposed mechanism for photoinduced anion exchange reaction (left figure): (1) photoinduced electron transfer from $CsPbCl_3$ nanocrystals to dibromomethane solvent, (2) halides from reductive dissociation of solvent causing the anion exchange of perovskite nano-crystals to $CsPbBr_3$. Reprinted with permission from ref. 397, copyright 2017, American Chemistry Society.

by either changing the photon dose or wavelength of the excitation light.[397]

4.2. SCN-based perovskite nanocrystals

Pseudo-halide thiocyanate ions (SCN$^-$, which has a similar ionic radius to I$^-$) were first introduced to partially replace the iodide ions in MAPbI$_3$ thin film solar cells to improve the stability/moisture tolerance of the cells and were found to also increase the crystal size.[398–402] It was found that individual MAPbI$_{3-x}$(SCN)$_x$ crystals demonstrate spatially heterogeneous PL emission, with substantially higher intensity at the grain boundaries as compared to the interior regions of the crystals.[403] Studies have since revealed that the proposed MAPbI$_{3-x}$(SCN)$_x$ 3D-connected perovskite structure may actually be (MA)$_2$Pb(SCN)$_2$I$_2$ 2D-layered orthorhombic structure instead, where Pb is octahedrally coordinated by four I$^-$ ions and two S-bonded SCN$^-$ ligands, while the MA$^+$ cations are situated between the layers of Pb(SCN)$_2$I$_4$ octahedra (similar to a K$_2$NiF$_4$-type structure).[404] DFT calculation has shown that (MA)$_2$Pb(SCN)$_2$I$_2$ has improved chemical stability against phase separation and does not spontaneously decompose into either MAI + Pb(SCN)$_2$ (with $\Delta H = 0.38$ eV) or MA(SCN) + PbI$_2$ (with $\Delta H = 1.97$ eV). As a comparison, it is thermodynamically favorable for MAPbI$_3$ to spontaneously decompose into MAI + PbI$_2$ (with $\Delta H = -0.09$ eV).[405] Another study claimed, because of their observation of red solid phase decomposing into black solid under ambient humidity, that it is possible for 3(MA)$_2$Pb(SCN)$_2$I$_2$ to decompose into 2MAPbI$_3$ + 4MA(SCN) + Pb(SCN)$_2$ by hydration.[406] These 2D-layered (MA)$_2$Pb(SCN)$_2$I$_2$ single crystals displays a reversible piezochromism phenomena. When compressed in a diamond-anvil cell, the color of single crystals changes from translucent red (1 GPa) to opaque black (2.6 GPa), then to translucent yellow (3.9 GPa), and finally retains this color up to 4.3 GPa, suggesting a substantial change in the corresponding band gap.[406] A$'$A$''$Pb(SCN)$_2$I$_2$-type 2D perovskite films have been systematically studied by replacing the cation species (A$'$A$''$) with combinations of MA, FA, and Cs cations.[407] Despite the wide study of thiocyanate-based perovskite films, thiocyanate-based perovskite nanocrystals are rarely studied. SCN-doped CsPbBr$_3$ nanocrystals have been achieved by replacing a small amount of Br$^-$ ions with SCN$^-$ ions forming CsPbBr$_{3-x}$(SCN)$_x$ nanocrystals. This substitution led to an increase in the crystallinity and a slightly blue-shifted PL peak, without significant change in their shapes or crystal structures.[162]

4.3. Split-anion-based perovskite nanocrystals

Some scientists have proposed partially replacing some of the halide anions (Cl, Br, I) in perovskite with chalcogen anions (S, Se, Te), forming a so-called "split-anion" system with mixed chalcogen and halogen anions. This strategy is mostly employed in antimony or bismuth-based perovskites (e.g., MASbI$_2$S,[408] and MABiI$_2$S[409]).[410,411] The potential benefit of such Pb-free perovskites with mixed chalcogen and halogen anions, AB(Ch,X)$_3$ (A = Cs or Ba; B = Sb or Bi; Ch = chalcogen (S, Se, Te); X = halogen (Cl, Br, I)), is that the metal–chalcogenide bonds are more covalent than metal-halide bonds and as such may exhibit an enhanced stability under ambient conditions.[411] Solar cells fabricated from Pb-free perovskites with mixed chalcogen and halogen

anions exist,[408] but this field is still relatively new for colloidal nanocrystals. This new class of split-anion perovskites may broaden the selection pool of elements for designing perovskite nanocrystals by allowing higher valence cations (such as 3$^+$ or 4$^+$ cations instead of 2$^+$) in the place of B-site cation (e.g., MABiSI$_2$ or CsSnS$_2$Cl) due to the introduction of divalent chalcogen anions.[410,411]

5. Applications

Owing to their outstanding optoelectronic properties, doped and ion-substituted colloidal metal halide perovskite nanocrystals show promising potential for many practical applications, including light emitting diodes (LEDs), lasing, perovskite solar cells, photodetectors, among many others.

5.1. LEDs based on doped or ion-substituted perovskite nanocrystals

Due to the excellent stability and appealing optoelectronic properties of Cs-based perovskite nanocrystals, A site doping using Cs$^+$ is recognized as an effective strategy for improving the performance of organic–inorganic perovskite-based LEDs. Cs doped perovskite FA$_{(1-x)}$Cs$_x$PbBr$_3$ nanocrystals with specific Cs content ($x = 0$, 0.1, 0.2, and 0.3) have been applied as the emissive materials for LED devices. The device structure consists of a transparent conductive indium tin oxide (ITO)-coated glass substrate, a hole-transporting layer of poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (PEDOT:PSS) and poly[[9,9-dioctyl-fluorenyl-2,7-diyl]-co-(4,4$'$-(N-(4-sec-butylphenyl)diphenylamine)] (TFB), a photoactive layer of FA$_{(1-x)}$Cs$_x$PbBr$_3$ perovskite nanocrystals, an electron-transporting layer of 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi), an electron injection layer of LiF and a cathode layer of Al (Fig. 31a).[42] The electroluminescence (EL) mechanism of the LED device is described as follows (Fig. 31b): electrons are injected from the lowest unoccupied molecular orbital (LUMO) level of TPBi into the conduction band (CB) of perovskite nanocrystals. Holes are transferred from the highest occupied molecular orbital (HOMO) level of TFB into the valence band (VB) of perovskite nanocrystals, followed by radiative recombination of electron–hole pairs inside the active perovskite layer.[42] Alignment of the energy levels of different components in the LED device is a key factor that significantly affects the performance of LEDs. With increasing Cs content ($x = 0$, 0.1, 0.2, and 0.3), the VB levels of FA$_{(1-x)}$Cs$_x$PbBr$_3$ gradually decreased from -5.88 eV to -5.25 eV which facilitating the hole injection due to the reduced hole injection barrier at the interface between the perovskite and the hole transport layer. The electroluminescence (EL) spectra (Fig. 31c) of the FA$_{(1-x)}$Cs$_x$PbBr$_3$-based perovskite LEDs exhibited gradual blue-shifts as a function of increasing Cs, which is consistent with the PL spectra of the corresponding nanocrystals (Fig. 5e). The inset of Fig. 31c shows a photograph of the best performance LED device based on FA$_{0.8}$Cs$_{0.2}$PbBr$_3$ with a luminance of 55 005 cd m^{-2} (Fig. 31d) and a current efficiency (CE) of 10.09 cd A^{-1} (Fig. 31e), exhibiting 6.4-fold and 3.6-fold improvement, respectively, over those of undoped FAPbBr$_3$.[42] Further increasing the Cs doping
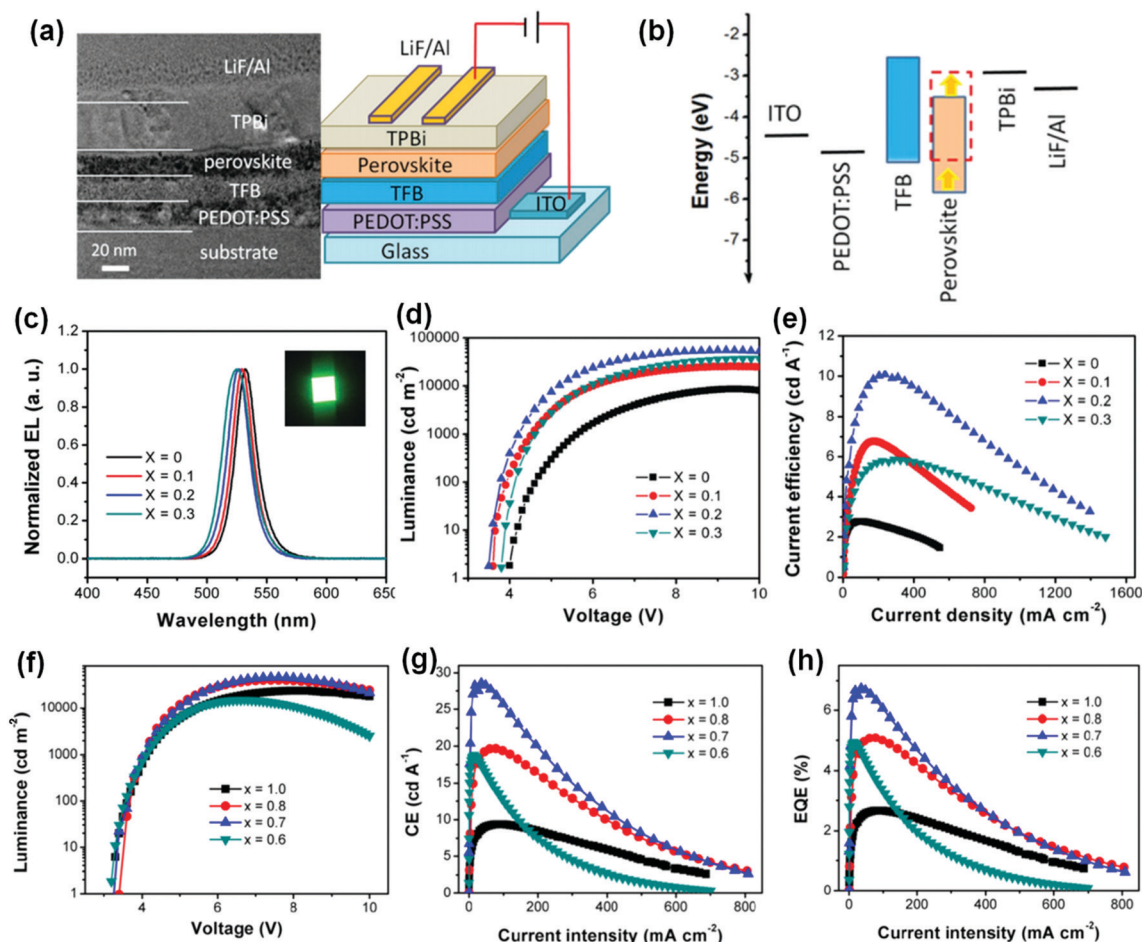
Fig. 31 (a) Cross-section SEM image (left) and schematic illustration (right) of the $FA_{(1-x)}Cs_xPbBr_3$-based perovskite LED device structure. (b) The flat-band energy levels of the different layers in the perovskite LED devices. (c) Electroluminescence (EL) spectra and photograph (inset) of $FA_{(1-x)}Cs_xPbBr_3$-based perovskite LEDs driven at a bias potential of 4 V. (d) Luminance−voltage and (e) current efficiency−current density characteristics of perovskite LEDs, based on $FA_{(1-x)}Cs_xPbBr_3$ (x = 0, 0.1, 0.2, and 0.3). Reprinted with permission from ref. 42, copyright 2017, Wiley-VCH. (f) Luminance−voltage, (g) current efficiency (CE)−current density, and (h) external quantum efficiency (EQE)−current density characteristics of $FA_{0.8}Cs_{0.2}Pb_xBr_3$ less-lead perovskite LEDs (x = 1.0, 0.8, 0.7, and 0.6). Reprinted with permission from ref. 43, copyright 2018, American Chemistry Society.

ratio from x = 0.2 to 0.3 did not improve device performance, indicating an optimized doping content of Cs is crucial in achieving good device performance. The excellent performance of $FA_{0.8}Cs_{0.2}PbBr_3$-based LEDs may be attributed to the high crystallinity, large quantum efficiency and efficient hole injection of Cs-doped $FAPbBr_3$. In another case of Cs-doped $FAPbBr_3$ perovskite, colloidal $FA_{0.8}Cs_{0.2}Pb_xBr_3$ nanocrystals with varied Pb content (x = 1.0, 0.8, 0.7, and 0.6) were fabricated forming stoichiometrically "less-lead" perovskite.[43] As the x value decreased from 1.0, 0.8 to 0.7, the maximum luminance, current efficiency (CE), and external quantum efficiency (EQE) were greatly enhanced (the maximum luminance, CE, and EQE for x = 0.7 were 45440 cd m^{-2}, 28.61 cd A^{-1}, and 6.75%, respectively, while for x = 1.0 were 23720 cd m^{-2}, 9.38 cd A^{-1}, and 2.67%, respectively, Fig. 31f–h), probably due to improved hole injection resulting from the reduced hole injection barrier between the perovskite and hole transport layer. Further decreasing the Pb ratio from 0.7 to 0.6 did not further improve the device performance, indicating the best LED performance stems from the

optimized Pb ratio in $FA_{0.8}Cs_{0.2}Pb_{0.7}Br_3$.[43] It was suggested that the "less-lead" configuration can inhibit nonradiative recombination by diminishing the presence of uncoordinated metallic Pb atoms. It was also found that the improved stability of $FA_{0.8}Cs_{0.2}Pb_{0.7}Br_3$-based LED device can be attributed to the hydrogen-bonding interactions between the organic cation and halide anions, induced by the moderate ambient moisture.[43] When Cs was doped into $MAPbBr_3$ nanocrystals, the performance of $MA_{1-x}Cs_xPbBr_3$-based LEDs were also highly correlated with the Cs content. Notably, $MA_{0.7}Cs_{0.3}PbBr_3$-based LEDs displayed a maximum luminescence of 24500 cd m^{-2}, nearly 10-fold higher than that of previously reported $MAPbBr_3$ nanocrystals.[206] Interestingly, through doping FA into $CsPbI_3$ nanocrystals, it is feasible to achieve stable red-emitting LED.[202]

B-site doped lead halide perovskite nanocrystals have also been used as the active light emitting layer of LEDs. LED devices made from 2.6 mol% Mn-doped $CsPbBr_3$ and 3.8 mol% Mn-doped $CsPbBr_3$ nanocrystals possessed improved maximum luminance of 9971 and 9717 cd m^{-2} under the applied voltages

of 6.2 and 6.5 V, respectively. Their pure $CsPbBr_3$ counterpart had a maximum luminance of 7493 cd m^{-2} under 6.6 V of applied voltage. The EQE and CE values of 2.6 mol% Mn-doped $CsPbBr_3$ device (0.95% and 4.33 cd A^{-1}) and 3.8 mol% Mn-doped $CsPbBr_3$ device (1.49% and 6.40 cd A^{-1}) also outperform the pure $CsPbBr_3$ device (0.81% and 3.71 cd A^{-1}).[378] The EQE and CE values of LED devices made from 7.9 mol% Mn-doped $CsPbI_3$ nanocrystals (0.51% and 0.07 cd A^{-1}) and 21.6 mol% Mn-doped $CsPbI_3$ nanocrystals (1.04% and 0.15 cd A^{-1}) also outperform the pure $CsPbI_3$ device (0.41% and 0.06 cd A^{-1}).[378] Sn^{2+}-doped $CsPbBr_3$ perovskite nanocrystals have also been incorporated in LED devices. The device performance of Sn-doped $CsPbBr_3$ LEDs was found to be closely related to the Sn doping ratio.[223,226,233] The best device based on $CsPb_{1-x}Sn_xBr_3$ nanocrystals exhibited a low turn-on voltage of 3.6 V, maximum luminance of 12 500 cd m^{-2} and EQE of 4.13%, representing the best values among Sn-doped LEDs.[223,230] By varying Ni^{2+} and modulating Cl/Br element ratios, Ni^{2+}-doped $CsPbCl_xBr_{3-x}$ perovskite nanocrystals with tunable emission from 508 to 432 nm were prepared *via* the supersaturated recrystallization method at room-temperature. As depicted in Fig. 32a, a blue-emitting LED (at 470 nm) based on 2.5% Ni^{2+}-doped $CsPbCl_{0.99}Br_{2.01}$ was produced, and displayed a 6-fold improvement of luminance (Fig. 32b) and a 20-fold improvement of EQE (Fig. 32c) over undoped counterparts.[334] Besides isovalent cation-doping, hetero-valent Ce^{3+}-doped perovskite nanocrystals have also been used in LED fabrication. While LED devices with pure $CsPbBr_3$ nanocrystals showed a maximum CE of 12.5 cd A^{-1} at 4 V and EQE of 1.6% at 4.2 V, LED devices with Ce^{3+}-doped $CsPbBr_3$ nanocrystals (with Ce/Pb ratio of 2.88%) displayed an enhanced maximum CE of 14.2 cd A^{-1} and much higher EQE of 4.4% at 3.8 V, which indicates that the nonradiative recombination has been strongly suppressed *via* the Ce^{3+}-doping.[302]

5.2. Lasers based on doped or ion-substituted perovskite nanocrystals

Lead halide perovskites have been intensely investigated as optical gain materials for amplified spontaneous emissions (ASEs) due to their relatively low lasing thresholds and high optical gain.[202,412] It is particularly challenging to obtain perovskite ASEs in the red region due to the thermodynamic instability of

red-emitting iodine-containing perovskites (*e.g.* MAPbI$_3$, FAPbI$_3$, and CsPbI$_3$).[202] In iodide-based $CsPbX_3$ (X = Br/I) nanocrystal lasing, the lasing threshold increases as the ratio of I/Br increases (*i.e.*, red-shifted) under the same testing conditions.[202] By using FAPbI$_3$ or FA-doped CsPbI$_3$ nanocrystals, one can observe ASEs in compact nanocrystal films deposited on glass substrates under 100 fs pulsed excitation at room temperature. ASEs appear as a narrow band with a FWHM of 10–12 nm and are 50 nm and 30 nm red-shifted from the PL maxima of FAPbI$_3$ and $FA_{0.1}Cs_{0.9}PbI_3$ nanocrystals, respectively (Fig. 33a and b). A lasing threshold of 7.5 μJ cm^{-2}, one of the lowest values among red-to-NIR emitting perovskites, was achieved by 100 nm compact films of FAPbI$_3$ nanocrystals with smooth mirror-like surfaces, obtained by repetitive dip-coatings and 90 °C annealing (Fig. 33a). A lasing threshold of 28 μJ cm^{-2} was achieved by films of $FA_{0.1}Cs_{0.9}PbI_3$ nanocrystals obtained by drop-casting and drying at 50 °C (Fig. 33b). It was found that perovskite nanocrystal films exhibited lower lasing thresholds when films were prepared under processing conditions that favored the sintering of perovskite nanocrystals (*e.g.*, ligand desorption by repetitive washing steps and/or annealing the films at a higher temperature of 90–100 °C).[202] Lasing from single crystal perovskite nanowires with tunable wavelength have also been studied by controlling the stoichiometry of both cations and anions. $MAPbBr_yI_{3-y}$ and $MAPbCl_xBr_{3-x}$ single crystal nanowires were synthesized by mixing different stoichiometry of iodide and bromide or bromide and chloride precursors, and the corresponding lasing emission coverd from 500 to 790 nm (Fig. 33c).[23] Single-crystal $MAPbX_3$ perovskite nanowires exhibit lasing quantum yields approaching 100% with the lowest lasing thresholds (220 nJ cm^{-2}) and highest quality factors (Q factors ~3600) yet reported for nanowire lasers.[23] Cation alloying (FA,MA)PbI$_3$ and cation/halide double alloying (FA,MA)Pb(Br,I)$_3$ single-crystal nanowires can fill the lasing gap between 580 and 670 nm which cannot be realized by MA-based perovskite nanowires and can further extend the lasing wavelength all the way to 824 nm NIR region (the wavelengths highlighted in the dashed rectangular boxes in Fig. 33c).[24] The violet-blue wavelength region (420–490 nm) can be satisfied with wide band gap CsPb(Br,Cl)$_3$ nanowires (Fig. 33d).[22] Compared with MA-based lasers, single crystal FAPbX$_3$ nanowire lasers feature red-shifted emission and better thermal stability.[24] Recently, continuous
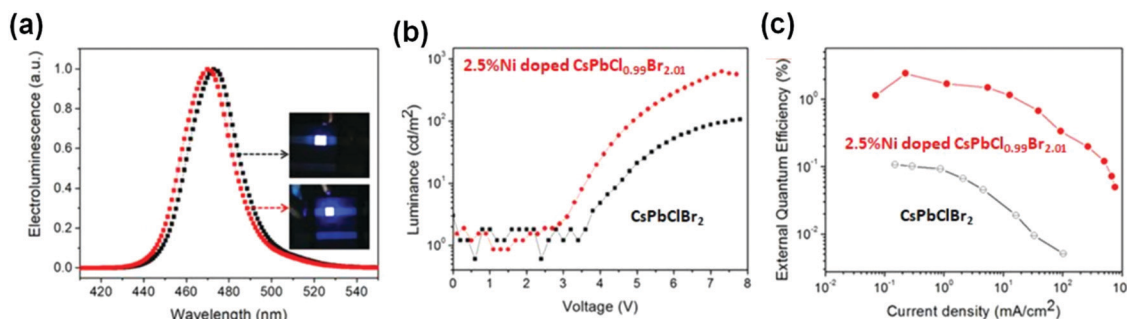
Fig. 32 (a) Electroluminescence spectra, (b) brightness, and (c) EQE curves of LEDs based on CsPbClBr$_2$ (black curve) and 2.5% Ni^{2+}-doped CsPbCl$_{0.99}$Br$_{2.01}$ (red curve) perovskite nanocrystals, respectively. The insets in (a) are photographs of the devices at a voltage of 5 V. Reprinted with permission from ref. 334, copyright 2020, American Chemical Society.
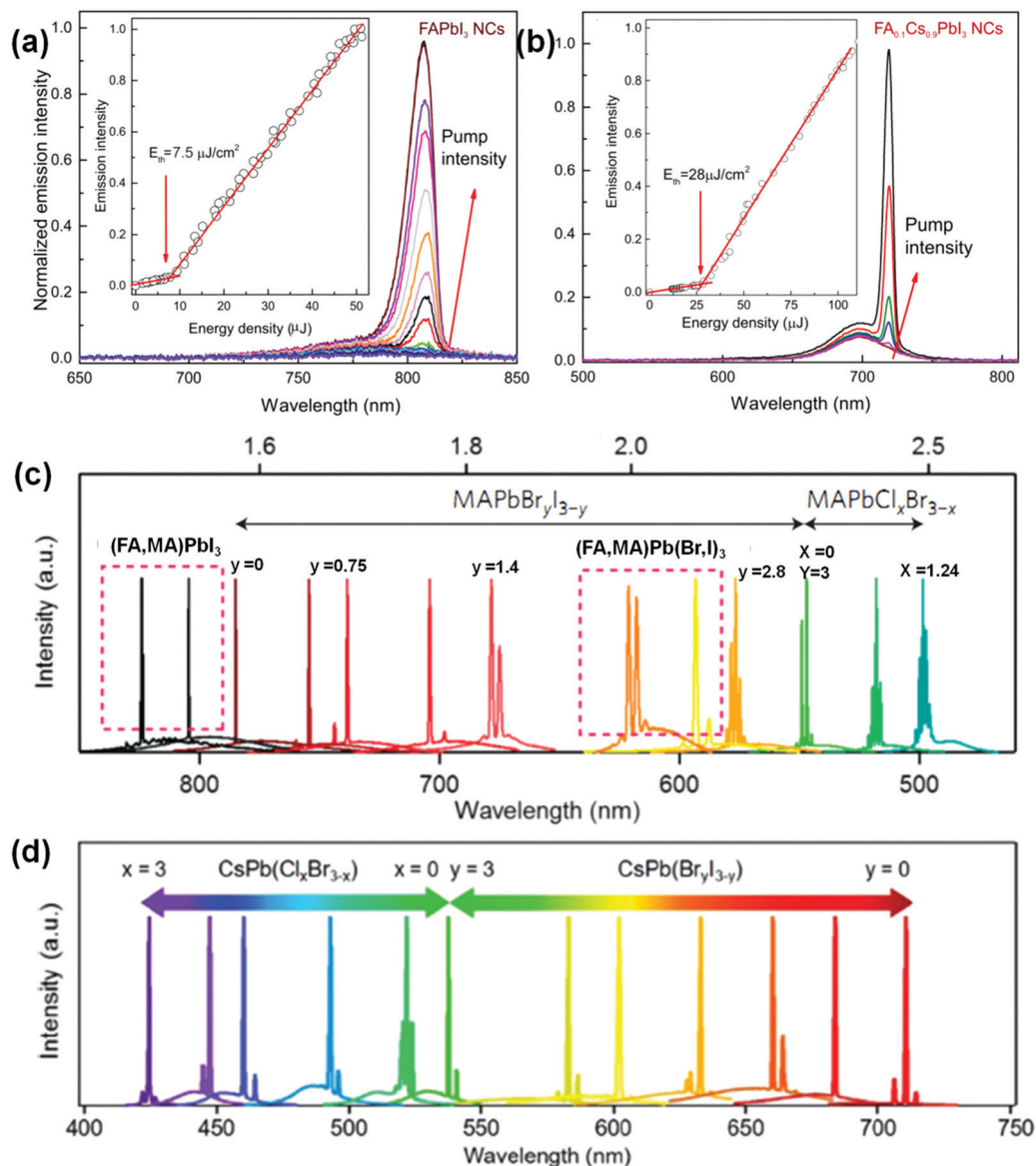
Fig. 33 Amplified spontaneous emissions (ASEs) for perovskite compact films prepared from (a) $FAPbI_3$ nanocrystals using dip-coating with heat treatment at 90 °C showing a 50 nm red-shift of ASE from the PL maxima and a lasing threshold of 7.5 μJ cm^{-2} (inset), and (b) $FA_{0.1}Cs_{0.9}PbI_3$ nanocrystals using simple drop-casting and heat treatment at 50 °C displaying a 30 nm red-shift of ASE from the PL maxima and a lasing threshold of 28 μJ cm^{-2} (inset). Reprinted with permission from ref. 202, copyright 2017, American Chemistry Society. (c) Tunable lasing emission wavelength of single-crystal MA-based perovskite nanowires with mixed halides. The wavelengths marked inside dashed rectangular boxes were obtained from MA-doped FA-based perovskite nanowires. Reprinted with permission from ref. 24, copyright 2016, American Chemistry Society. (d) Tunable lasing emission wavelength of single-crystal Cs-based perovskite nanowires with mixed halides. Reprinted with permission from ref. 22, copyright 2016, American Chemistry Society.

wave (CW) lasers were fabricated from non-stoichiometric Cs, MA and FA mixed cations perovskite thin films,[413] which is worth further studying in nanocrystals form. In addition, single-mode lasers based on $CsPbX_3$ submicron spheres are other interesting devices that merit further investigation.[414]

5.3. Solar cells based on doped or ion-substituted perovskite nanocrystals

Perovskite solar cells have witnessed a rapid increase in power conversion efficiency (PCE) and long-term stability over the past decade.[415] Doping with different cations in the A-site and

incorporating different halides in the X-site have been regarded as feasible strategies for substantially enhancing the stability and PCE of film-based perovskite solar cells.[416] Doped perovskite nanocrystals have also been extensively studied in photovoltaic applications. Though Sn-based perovskite solar cells are unstable due to easy oxidation, alloyed $CsSn_{1-x}Pb_xI_3$ nanocrystals possess far superior phase-stability to both parent $CsSnI_3$ and $CsPbI_3$ nanocrystals (degradation over months, not days).[10] Photoexcited electrons from alloyed $CsSn_{1-x}Pb_xI_3$ nanocrystals can be injected into TiO_2 at a fast rate of 1.12×10^{11} s^{-1}, which may facilitate high photocurrent generation when applied in solar cells. As a

proof of concept, alloyed $CsSn_{1-x}Pb_xI_3$ nanocrystals have been employed as the sensitizer in a quantum dot-sensitized solar cell (QDSC) configuration, with the use of liquid-state iodide/triiodide (I^-/I_3^-) electrolyte. The device delivered a short-circuit current (J_{sc}) of 10.13 mA cm^{-2}, open-circuit voltage (V_{oc}) of 0.63 V, fill factor (FF) of 0.46, and an overall power conversion efficiency (PCE) of 2.9%.[10] $CsSnI_{2.95}F_{0.05}$ with and without SnF_2 doping have been used to replace the liquid-state iodide/triiodide (I^-/I_3^-) electrolyte in the dye-sensitized solar cell (DSSC) and serves as the hole conduction layer to realize a novel all-solid-state photovoltaic cell structure.[242] $CsSnX_3$ quantum rods synthesized by solvothermal process have also been used as the absorbing layer to fabricate solar cells, and those devices reached power conversion efficiencies of 9.66%, 10.46%, and 12.96% from $CsSnCl_3$, $CsSnBr_3$, and $CsSnI_3$ devices, respectively.[235]

Solar cells based on colloidal perovskite nanocrystals generally have the following structure: a transparent conductive oxide (TCO) substrate (*e.g.*, indium tin oxide (ITO) or fluorine-doped tin oxide (FTO))/electron transport layer (ETL) (*e.g.*, TiO_2 or SnO_2)/perovskite active layer/hole transport layer (HTL) (generally spiro-OMeTAD)/metal contact electrode (*e.g.*, Au or Al).[8,9] When employing colloidal quantum dots or nanocrystals in solar cell devices, the insulating ligands on the surface of colloidal nanocrystals are considered to be a major limiting factor. Due to the ionic nature of perovskite nanocrystals, the polarity of the antisolvent used for nanocrystal surface treatment needs to be deliberately chosen in order to remove the surface ligands without damaging the integrity of the nanocrystals. Water, methanol, ethanol, and isopropanol are classified as "grade I" solvents that can completely destroy the ionic bonds in $FAPbI_3$ nanocrystals; *t*-butanol, 2-pentanol, acetonitrile/toluene (v:v 2:3), and ethyl

acetate are classified as "grade II" solvents that can gradually remove the surface ligands without destroying the integrity of $FAPbI_3$ nanocrystals; and chlorobenzene, toluene, octane, and hexane are classified as "grade III" solvents that are not able to remove the surface ligands on $FAPbI_3$ nanocrystals.[9] Therefore, a photovoltaic device using $FAPbI_3$ colloidal quantum dots (CQD) as a photoactive layer (Fig. 34a) was fabricated by employing a set of three different "grade II" solvents with gradually reducing polarity, and the ligand density can be sequentially decreased while maintaining the integrity of $FAPbI_3$ nanocrystals. The J_{sc}, V_{oc}, and external quantum efficiency (EQE) of the $FAPbI_3$ CQD-based solar cell gradually increased after each surface treatment cycle due to the progressive removal of insulating surface ligands (Fig. 34b and c).[9] A maximum PCE of 8.38% was achieved with a J_{sc}, of 11.84 mA cm^{-2}, a V_{oc} of 1.10 V and a FF of 0.64. It is worth noting that the high defect tolerance of perovskite materials accounts for the large V_{oc} of $FAPbI_3$ CQD-based solar cells, which in turn leads to favorable carrier transport.

In addition to removing the surface ligands using polarity controlled antisolvents, one can also boost solar cell performance by post-treatment with an A-site cation halide salt (AX, where A = formamidinium (FA$^+$), methylammonium (MA$^+$), or cesium (Cs$^+$) and X = I$^-$ or Br$^-$).[8] Postsynthetic addition of A-site cation halide salts (AX) (such as formamidinium iodide (FAI)) has been shown to improve the coupling between nanocrystals, passivate the surface, tune the device energetics, and improve stability of perovskite solar cells. A perovskite solar cell was fabricated by sequentially deposited $CsPbI_3$ nanocrystal film *via* a spin coating method. The film was immersed in a saturated lead(II) nitrate $[Pb(NO_3)_2]$ solution in methyl acetate (MeOAc) after each coating to partially remove the native ligands and allow for further layers
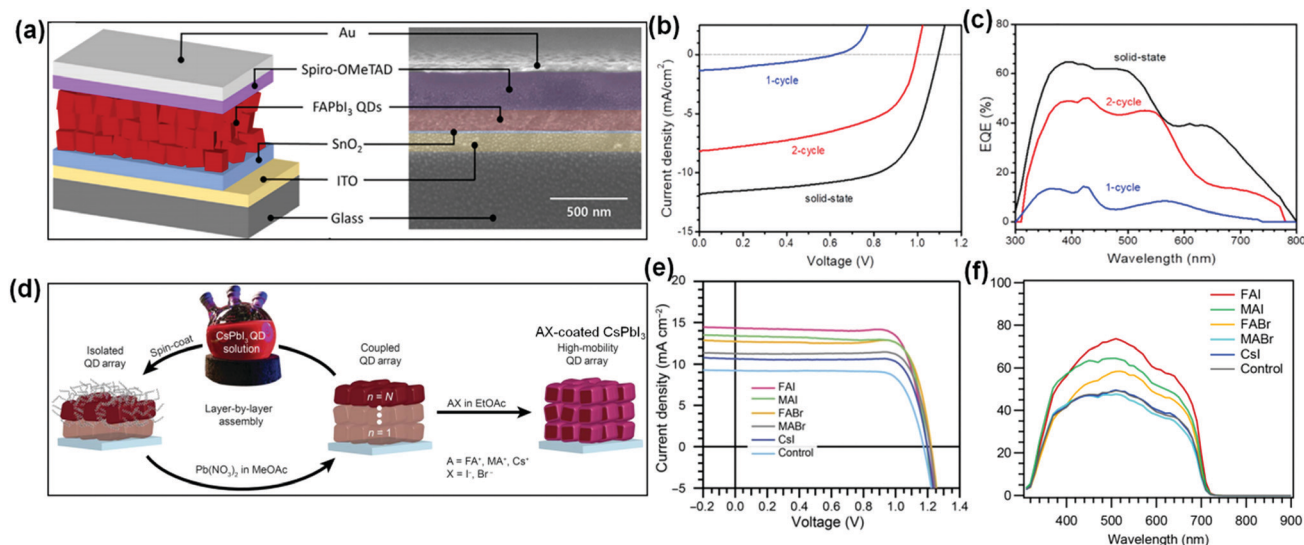
Fig. 34 (a) Schematic of the $FAPbI_3$ nanocrystals–based solar cell device structure and the corresponding device cross-sectional SEM image. (b) Current density−voltage (J−V) curves, and (c) external quantum efficiency (EQE) curves of the devices based on $FAPbI_3$ colloidal nanocrystals with increasing cycles of surface treatment (two cycles in solution phase and one cycle in solid state). Reprinted with permission from ref. 9, copyright 2018, Elsevier. (d) Schematic of layer-by-layer deposition process of $CsPbI_3$ nanocrystal film and the AX salt post-treatment. (e) J−V characteristics and (f) EQE curves of $CsPbI_3$ nanocrystals–based devices treated with different AX salts. Reprinted with permission from ref. 8, copyright 2017, American Association for the Advancement of Science.

to be deposited without re-dispersing the existing layers. After three to four deposition cycles, a $CsPbI_3$ nanocrystal film with a thickness of 200 to 400 nm was built and then immersed in a saturated AX salt solution in ethyl acetate (EtOAc) for $\sim$10 s to yield AX coated $CsPbI_3$ active layer (Fig. 34d). The highest PCE of 13.4% was obtained by FAI treatment with a J_{sc} of 14.37 mA cm^{-2}, which was significant higher than that of treatment in pure EtOAc (9.22 mA cm^{-2}). Notably, other AX salt (*i.e.*, FABr, MAI, MABr, CsI) treatments also displayed improved J_{sc} over the control sample (*i.e.*, pure EtOAc treatment) (Fig. 34e). However, all AX salt treatments displayed little impact on the V_{oc} (1.17–1.22), FF (0.78–0.82), and EQE onset ($\sim$700 nm) (Fig. 34f), indicating the improvement of PCE is largely attributed to the increased J_{sc}. The possible reason for the increased J_{sc} was found to be related to the higher charge carrier collection efficiency in the $CsPbI_3$ quantum dot films after post-treatment by AX salts.[8] Despite the fact that solar cells made from FAI-coated $CsPbI_3$ nanocrystals outperformed neat $CsPbI_3$ nanocrystals in the abovementioned study, the devices fabricated from $Cs_{1-x}FA_xPbI_3$ mixed A-site perovskite nanocrystals did not perform better than those made with $CsPbI_3$ nanocrystals.[417] Notably, surface passivation seems to play a more important role than alloying in nanocrystals-based perovskite solar cells. For instance, solar cells based on $CsPbI_3$ nanocrystals with a GeI_2 additive showed better stability than the ones without GeI_2, which was believed to be due to the efficient surface passivation of the quantum dots upon the addition of GeI_2.[418] It is notable that the best performance research cells reported by the National Renewable Energy Laboratory (NREL)[49] are all mixed perovskite cells, either employing mixed cations or mixed anions. This is likely because light absorbing films grown under iodine-rich conditions are prone to a high density of deep electronic traps, which act as recombination centers. Thus the use of bromide or chloride precursors mitigate or suppress the formation of these key defects.[144] It is important to note that although the PCEs attained from nanocrystal-based perovskite solar cells have not exceeded those of film-based cells due to the insulating ligands that results in the lower J_{sc}, the V_{oc} accessed by nanocrystal-based devices possesses a lower V_{oc} loss than film-based cells and is closer to the theoretical thermodynamic limit of single-junction cells based on the Shockley–Queisser (SQ) analysis.[417]

5.4. Energy down-conversion coatings based on doped or ion-substituted perovskite nanocrystals

In addition, doped perovskite nanoscrystals can also be utilized as energy converting coating. For example, Mn-doped $CsPbCl_3$ (or $CsPbCl_3$:Mn) nanocrystals were used as energy down-converters to change the normally un-harvestable ultraviolet (UV) radiation (wavelengths 300–400 nm) into harvestable visible light.[67] $CsPbCl_3$:0.1Mn (meaning 10% Mn substitution) nanocrystals were synthesized *via* a hot-injection method by swiftly injecting Cs–oleate precursor into a mixture of $PbCl_2$ and $MnCl_2$. These $CsPbCl_3$:0.1Mn nanocrystals displayed a large Stokes shift ($>$200 nm) and had yellow emission centered at $\sim$590 nm. The Stokes shift can be explained by the energy transferred from the conduction band (CB) of $CsPbCl_3$ host to Mn^{2+} ions *via* $^4T_1$–$^6A_1$ transition.[67] Different concentrations of $CsPbCl_3$:0.1Mn nanocrystal solutions were spin-coated onto the transparent side of $CH_3NH_3PbI_3$ perovskite solar cells (Fig. 35a), and it was found that devices with the optimized concentration of 5 mg mL^{-1} saw a 3.34% improvement in PCE (increased from 17.97% to 18.57%) (Fig. 35b). Devices coated with $CsPbCl_3$:0.1Mn nanocrystal also showed enhanced stability, illustrated by their 97% retention of initial PCE after 100 h of continuous UV LED irradiation while the PCE for devices without coating dropped to 85% of its initial efficiency (Fig. 35c). It is possible that the energy-down-converting $CsPbCl_3$:0.1Mn coating can reduce the UV-induced degradation and therefore improve the device stability.[67] Similar down-converting coating strategies have also been applied in photodetectors. The UV response of photodetectors can be markedly enhanced by depositing a layer of colloidal $CsPbX_3$ perovskite nanocrystals on the surface and tuning the PL emission wavelength *via* the halide composition to fall within the maximal EQE response region of the detector.[16]

5.5. Color conversion coatings based on doped or ion-substituted perovskite nanocrystals

Similar to the above application as energy down-converters from UV to visible light, perovskite nanocrystals can also be used as down-conversion luminescent phosphors by down converting light from blue LED chips into different visible light
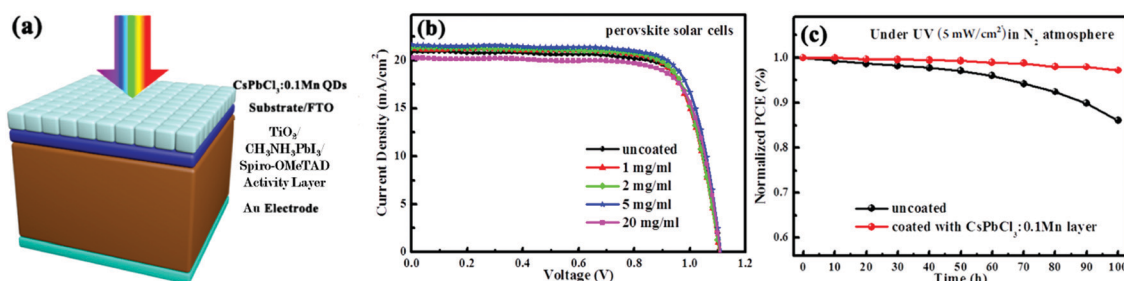
Fig. 35 (a) Schematic structure of a $CH_3NH_3PbI_3$ perovskite solar cell coated with a layer of $CsPbCl_3$:0.1Mn nanocrystals. (b) Current density–voltage curves for reference and perovskite solar cells assisted with a coating of $CsPbCl_3$:0.1Mn nanocrystals with different coating concentrations (associated with different coating layer thicknesses). (c) Aging test results of the reference perovskite solar cell and $CsPbCl_3$:0.1Mn nanocrystal-coated cell under continuous UV irradiation (5 mW cm^{-2}) for 100 h in a N_2 atmosphere. Reprinted with permission from ref. 67, copyright 2017, American Chemistry Society.
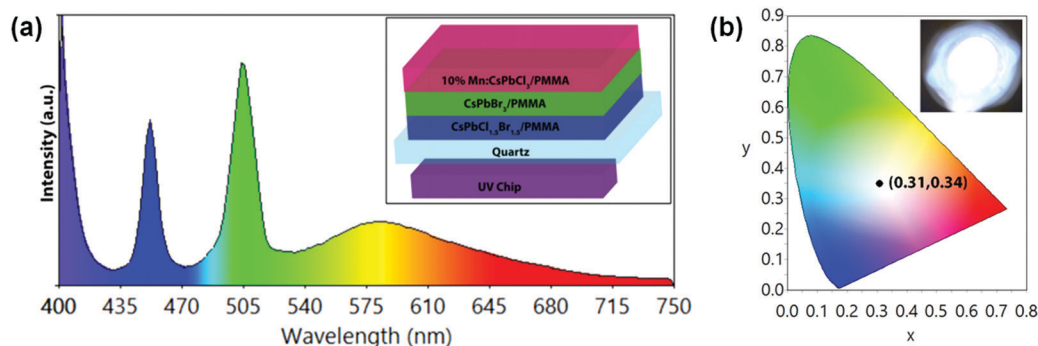
Fig. 36 (a) EL spectrum of a WLED device based on a 10% Mn-doped $CsPbCl_3$/$CsPbBr_3$/$CsPbCl_{1.5}Br_{1.5}$ nanocrystals/PMMA composite film on top of a 396 nm UV LED chip. The device structure is shown as an inset. (b) Chromaticity diagram of the CIE coordinates of the WLED and its digital photograph (inset). Reprinted with permission from ref. 420, copyright 2020, Elsevier.

(green, yellow, orange, or red) to obtain desired color temperature white lights for lighting or display applications.[68–71] Green emitting $Cs_{0.1}FA_{0.9}PbBr_3$ and red emitting $Cs_{0.1}FA_{0.9}PbBr_{1.5}I_{1.5}$ mixed-cation perovskite nanocrystals–PMMA polymer composite films have been used as color converters on a blue LED chip to achieve white light LED.[419] Likewise, a bright pure white light-emitting device (WLED), with corresponding CIE color coordinate (0.31, 0.34) (note that pure white light is (0.33, 0.33)), was assembled by stacking a 10% Mn-doped $CsPbCl_3$/PMMA composite film as an orange-red emitting layer, a $CsPbBr_3$/PMMA composite film as a green-emitting layer, and a $CsPbCl_{1.5}$ $Br_{1.5}$/PMMA composite film as a blue-emitting layer on top of a 396 nm UV LED chip (Fig. 36).[420] The orange-red emission from the Mn-doped perovskite nano-crystals can be used as color conversion coatings by mixing dual emission Mn-doped $CsPbCl_3$ or Mn-doped $CsPb(Cl/Br)_3$ nanocrystals with polymer and depositing these polymer–nano-crystals composites on the surface of blue LED chips.[257,261] In order to achieve the desired color temperature from these dual emission Mn-doped nanocrystals, sometimes it is crucial to fine tune the host perovskite emission peak position (by tuning the ratio of Cl/Br content) as well as the relative peak intensity ratio between the host perovskite emission and the dopant Mn emission. This complex design is sometimes difficult to achieve during the synthesis process and may need to be further fine-tuned through postsynthetic processes. By utilizing the distinct exchange rates of the cation (slow) and anion (fast) and control (terminate) the ion exchange by purification at different reac-tion times, one can easily obtain the desired color temperature from these Mn-doped $CsPb(Cl/Br)_3$ nanocrystals.[421] For lighting or display applications it is beneficial to choose a phosphor material that has a larger Stokes shift (which means there is a significant difference between the absorption and emission peak) to minimize the potential for self-absorption. $MA_3Bi_2X_9$ and $Cs_3Bi_2X_9$ systems both show a slightly larger Stokes shift, which makes them prime candidates for lighting applications.[355]

There are many other applications that have capitalized on either colloidal perovskite nanocrystals or doped perovskite nanocrystals, such as $CsPbI_3$-based photodiodes,[12] Cs_2SnI_6 and Ag-doped $CsPbBr_3$-based FETs,[237,326] $CsPbCl_3$/graphene and $FA_xMA_{1-x}PbI_3$/MoO_x FET heterojunction photodetectors,[18,422]

$CsPbX_3$-based X-ray detection scintillators,[75] Yb^{3+}-doped $CsPbCl_3$ luminescent solar concentrators (LSCs),[307,308] chemical probes for TNP, TOAX, or HCl detections,[72–74] hydrogen (H_2) generation,[76] photocatalytic CO_2 reduction,[77–83] fluorescent inks for anti-counterfeit/encryption printing purposes,[84–86] and luminescence probes for bioimaging applications.[87]

6. Summary and outlooks

This review summarized the general background of perovskite nanocrystals, discussed the fundamentals of doping and ion substitution in the A-, B-, and X-site of ABX_3 type 3D perovskite nanocrystals, examined their stability, and outlined their appli-cations. Particularly, various dopants and doping strategies have been discussed as summarized as follows: first, for A-site doping, Cs, MA, and FA are the three commonly used cations that can sustain stable 3D perovskite structure. The size and optical properties of MA lie in between those of FA and Cs cations. Introducing smaller Cs cations contracts the lattice and reduces the cubo-octahedral volume, thereby inducing stronger interaction between the cations and halides which increases (i.e. blue-shifts) the band gap, and in turn facilitates the formation of highly crystalline perovskite crystals at a low temperature. In contrast, incorporating larger FA cations causes lattice expansion, achieves a tolerance factor closer to 1, and forms hydrogen bonds which stabilize the pseudocubic structure, thus resulting in superior solar cell performance due to red-shifted absorption (i.e., reduced band gap) and improved charge transport. Moreover, Rb and Tl have also been used for A-site doping and exhibited a relatively lower PLQY. Second, for B-site doping, partial substitution of Pb^{2+} with a smaller B-site cations reduces the B–X bond length and stabilizes the lead iodide perovskite by reducing the extent of octahedral rotation or distortion, leading to: a larger tolerance factor (improved phase stability), a larger formation energy (improved thermal stability), and reducing the toxic lead content at the same time. Sn^{2+}-containing perovskite nanocrystals display relatively red-shifted optical properties (compared with their Pb-based counterparts) due to higher Pauling electronegativity for Sn^{2+} than Pb^{2+} ions. However, Sn^{2+} easily oxidizes to Sn^{4+} causing

their persistent instability. Intriguingly, Mn-doping and lanthanide-doping both demonstrate multi-peak emission with PL peaks related to transitions from energy levels of the dopant ions. Depending on the dopant levels, Mn^{2+}-doped perovskites possess a dopant PL at ~ 600 nm while Yb^{3+}-doped perovskites show a dopant PL at ~ 1000 nm with PLQY exceeding 100% due to the quantum-cutting effect. Notably, metal(II) halide salts (MX_2) have been commonly employed for isovalent substitutions such as doping alkaline-earth metals and transition metals, and have various impacts based on the size of the metal ions. Furthermore, heterovalent substitutions also exert very different influences, depending on the ion used, and occasionally may produce structures other than ABX_3 (*e.g.*, $A_3B_2X_9$ or $A_2B'B''X_6$) in order to satisfy charge neutrality. Finally, for X-site doping, halide substitution has been widely exploited for tailoring the band gap of perovskite nanocrystals as it can readily change the optical responses throughout the whole visible range (~ 300 nm); this contrasts greatly the range that can be tuned *via* the quantum confinement effect (only roughly 100 nm). In particular, the incorporation of Cl^- or I^- anions blue-shifts or red-shifts the optical properties of Br^--based perovskite nanocrystals, respectively. It is also noteworthy that SCN^--doped and chalcohalide split-anion perovskites have been investigated in thin film solar cells yet are relatively new for colloidal nanocrystals.

Doping and ion substitution has been shown to alter the optical properties of perovskite nanocrystals, improve their stability, and reduce their toxic lead content. The extremely high PLQY, ease of synthesis, and the potential of roll-to-roll printing or low temperature solution mass production of perovskite nanocrystals render them as promising candidates for next-generation optoelectronic devices. Nonetheless, for commercialization of perovskite nanocrystals-based materials and devices, a few issues merit further investigation and improvement. The major challenges facing perovskite nanocrystals include: increasing stability,[423] broadening the band gap (*i.e.*, extension of absorption from visible to UV and NIR), eliminating toxic lead content,[424] minimizing phase segregation (ion migration and hysteresis),[194,425] and reducing self-absorption (*i.e.*, increasing Stokes shift).[426,427] Peculiarly, the stability remains a key issue among all challenges, including colloidal stability, color stability, structural stability, phase stability, photo (UV) stability, thermal stability, as well as moisture and air stability.[428] Generally, the stability of colloidal perovskite nanocrystals could be largely raised by the following strategies: (1) deliberate selection of low polarity solvent/anti-solvent and stronger binding ligands to minimize the detachment of ligands and reduce the number of surface defects.[429] (2) Encapsulation *via* creating core–shell (or core/shell 1/shell 2) structures or impregnating in water resistant organic or inorganic matrix to prevent direct contact with the surrounding environment and passivate surface defect sites.[430] (3) Intrinsic structural engineering (*e.g.* compositional tuning, double perovskite, or other low-dimensional structures) to tailor the tolerance factor and thus enhance the formation energy. The desorption of surface ligands during washing is recognized as one of the main causes for the instability in colloidal perovskite nanocrystals. Stronger binding ligands such as multidentate ligands (*e.g.*, compounds with concurrent polyamine and polyacid functional groups),[431] pre-formed alkylammonium halide salts,[432,433] or ligated star-like polymer nanoreactors[99,100] represent promising research directions for enhanced stability.[434] Seeking alternative solvents that do not require the removal of solvent prior to employing nanocrystals for applications may stand out as the other possible research effort to avoid ligand detachment.[435]

We note that the general research endeavors towards mixed-cation/anion colloidal metal halide perovskite nanocrystals practically follow that of thin film perovskites, including multi-site ion substitutions (*i.e.*, simultaneous substitution of A-site & B-site ions, *e.g.*, $(FA/Cs)(Pb/Sn)X_3$[436] and $(MA/FA)(Pb/Sn)X_3$;[437,438] A-site & X-site ions, *e.g.*, $(FA/Cs)Pb(I/Br)_3$[203,204,439] and $(FA/MA)Pb(I/Br)_3$;[201,440–442] or B-site & X-site ions, *e.g.*, $MA(Pb/Sn)(I/Br)_3$[443] and $MA(Pb/Sn)(I/Cl)_3$[444]), and can be further expanded to concurrent substitution of all three sites (A-site, B-site, and X-site) such as $(FA/MA)(Pb/Zn)(I/Br)_3$.[445] Triple-cation perovskite (*e.g.*, $(Cs/MA/FA)PbX_3$[446–448] and $(K/MA/FA)PbX_3$[449]) and quadruple-cation perovskite (*e.g.*, $(Rb/Cs/MA/FA)PbX_3$[156,447,448] and $(K/Cs/MA/FA)PbX_3$[450]) have already been widely studied in thin film solar cells to improve device performance, enhance thermal stability, and reduce hysteresis. Nonetheless, to date no colloidal perovskite nanocrystals based on triple- or quadruple-cation have been synthesized. Exotic A-site cations $C_4H_9NH_3^+$ (*n*-butylammonium, BA),[451] $(CH_2)_3NH_2^+$ (azetidinium, Az),[452] $C_2H_4(NH_3)_2^{2+}$ (ethylene-diamine, EDA^{2+}),[453] $C(NH_2)_3^+$ (guanidinium, Gua),[454] $C_6H_{13}NH_3^+$ (*n*-hexylammonium, HA),[455] $C_8H_9NH_3^+$ (phenylethylammonium, PEA),[456] thiourea (TU),[457] and aromatic derivatives ($R–NH_3^+$, where R is naphthalene, fluorine, anthracene, pyrene, or perylene)[458–460]) have been exercised in mixed-cation perovskite thin film solar cells. However, the synthesis in the form of perovskite nanocrystals containing these A-site cations noted above has not yet been explored. This represents an important area and can be pursued. It is worth noting that the incorporation of some of these complex yet bigger organic cations may induce low-dimensional (quasi-2D layered, 2D, 1D, and 0D) structures instead of 3D structure.

On the other hand, the concrete mechanisms of doping and ion substitution remain elusive and merits more thorough investigation. For example, it is challenging to pinpoint the exact location or distribution of the dopant within the host matrix. To this end, it invokes a combination of several different techniques such as X-ray photoelectron spectroscopy (XPS), extended X-ray absorption fine structure (EXAFS) spectroscopy, and high-resolution synchrotron XRD, in conjunction with the first-principles calculations to clarify the underlying doping mechanism.[328] The ability to scrutinize the actual position of dopant ions in the lattice is the key to derive accurate conclusions. For example, when adding metal halide salts (*e.g.*, $SbCl_3$, $BiCl_3$, VCl_3, $NiCl_2$, $ZnCl_2$, $SnCl_2$, $SnCl_4$, $PbCl_2$, and CuCl) as dopants to $CsPbCl_3$ nanocrystals, the difference in the PLQY enhancements are not due to the doping of these dissimilar metal ions, yet because of the varied ability of these metal salts to release active chloride ions for surface passivation, as proven by control experiments with metal acetate salts showing no increase in the PLQY.[433]

Investigation into the PL decay kinetics is also of key importance in determining how surface defects, functioning as recombination centers, affect the PLQY of perovskite nanocrystals. For instance, a biexponential PL decay transforming to a monoexponential decay signifies the efficient passivation of surface defects.[327,461] Transient absorption, time-resolved PL, and time-resolved fluorescence quenching spectroscopies represent some robust techniques to explore the energy transfer process in perovskite nanocrystals, including examining the exciton diffusion length and probing the energy transfer rate between neighboring nanocrystals. Nonetheless, these are critical measurements to identify whether these nanocrystals are suitable to be utilized in certain applications.[462] Such fundamental studies may also be beneficial for improving the PLQY of Cl-based and lead-free perovskite nanocrystals as they possess low PLQY.[335] The ferroelectric and piezoelectric properties of perovskite nanocrystals and their corresponding applications may also be worth further study.[463]

Colloidal nanocrystals afford many unique tunable physical properties rendered by the control over their size, shape, architecture (e.g., core–shell structure, Janus structure, nanowire/nanorod, etc.), and surface capping ligands. Clearly, advanced architecture engineering integrated with composition tailoring may constitute a future research direction. For example, some interesting future exploration may involve doping one material in the core and doping the other material in the shell in core/shell nanocrystals[464] or doping two dissimilar materials of interest in the respective half of a Janus nanostructures (e.g., Janus nanoparticles and nanorods) to yield interesting polarized optic or catalytic effects.[465] In addition to fine tuning the doping condition to improve the doping efficiency, the ability to capitalize on doping and ion substitution to alter the optoelectronic properties, enhance the stability, and reduce the toxicity of colloidal metal halide perovskite nanocrystals makes them very appealing for broadened use in many future applications. For instance, due to the ease of wavelength tuning and near unity PLQY, perovskite nanocrystals are ideal candidates as luminescence probes for bioimaging.[87–94] Unfortunately, only toxic lead-containing perovskite nanocrystals are found to possess a sufficiently high PLQY, with safer lead-free perovskite nanocrystals usually displaying a relatively low PLQY. Doped or ion-substituted perovskite nanocrystals with lower cytotoxicity yet retaining high PLQY may stand out as outstanding alternatives for use in bioimaging when they are well-encapsulated within water-resistance matrix.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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