Ion exchange for halide perovskite: From nanocrystal to bulk materials

Haotian Jiang | Siqi Cui | Yu Chen | Haizheng Zhong

1 MIIT Key Laboratory for Low-Dimensional Quantum Structure and Devices, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing, China
2 Beijing Institute of Technology, Shenzhen Research Institute, Nanshan District, Shenzhen, China

Correspondence
Yu Chen, MIIT Key Laboratory for Low-Dimensional Quantum Structure and Devices, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
Email: chenyubit@bit.edu.cn

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Abstract
Halide perovskite, an ionic semiconductor, with the typically structural composition of ABX$_3$ has become the extremely popular star in optoelectronics due to its superior photophysical properties and easily solution processing. In comparison with the traditional semiconductors, the perovskite possesses a low crystal formation energy with facile solution synthesis, which results into its soft and dynamic crystal lattice. Therefore, the post-synthetic composition tuning via ion exchange has been proved to be an effective technique to introduce heteroatoms into perovskite lattice. In this review, we summarize the recent progress on ion exchange of halide perovskites, including mechanisms, methods, as well as different scales from low-dimensional nanoscale to bulk crystal. Besides, we also briefly discuss the prospective of ion exchange for halide perovskites, and hope it benefit for the structural design and compositional optimization in halide perovskites for various optoelectronic applications.

KEYWORDS
bulk materials, halide perovskite, ion exchange, nanocrystal, post-synthesis

1 INTRODUCTION

Halide perovskite materials have the typically chemical structure of ABX$_3$, which the A-site cation (generally methylammonium MA$^+$, formamidinium FA$^+$ and Cs$^+$) occupies the cage surrounding by the corner-sharing metallic halide [BX$_6$]$^{4–}$ octahedra.$^{[1–5]}$ This particular lattice structure was primarily discovered in calcium titanate by Gustav Rose in 1839 and named in honor of Lev Perovski (1792-1856). After a quiet period of 150 years, perovskite and its derivatives burst into prosperity during the past decade, especially the halide perovskites have made remarkable achievements in various fields, such as photocatalytic,$^{[6]}$ photovoltaic,$^{[7–8]}$ light emitting diodes (LED),$^{[9]}$ photodetector,$^{[10]}$ information encryption,$^{[11]}$ scintillator,$^{[12]}$ laser,$^{[13]}$ and so on. Out of the ordinary, the band structure of halide perovskite is opposite to the well-known conventional semiconductors, for example, GaAs, in which the conduction band (CB) and the valence band (VB) are formed by its p and s orbitals, respectively. The VB of halide perovskite is composed of the outermost p-orbital of halogen anion and the outermost s-orbital of centered metallic cation, while the CB mainly consists of the outermost p-orbital of centered metallic cation.$^{[14–23]}$ Therefore, the band gap of halide perovskite can be easily tuned by altering either component in its crystal lattice.
2.1 | Diffusion

The mass transfer indicates that the ion exchange must firstly involve the interacting diffusion between outside ions and the parent compound. Diffusion refers to the migration of atoms, ions or molecules in substances originated from the thermal motion, the kinetic of which is usually described with the Fick’s law. In an ideal steady-state diffusion case, the volume of diffused substance passing through the unit cross-sectional area perpendicular to the diffusion direction per unit time (known as diffusion flux) is proportional to the concentration gradient at the cross section:

$$J = -D \nabla C$$

where $J$ is diffusion flux, $D$ is diffusion coefficient, and $C$ represents concentration may be the number of diffused atoms per volume, or it may be the number of grams per atom or any other units of the number of substances (the diffusion flux also takes the corresponding unit). In practice, the concentration distribution of diffused substances tends to vary with time. On the basis of Fick’s first law, the divergence of concentration is combined with the continuity equation to obtain Fick’s second law:

$$\frac{\partial C}{\partial t} = D \nabla^2 C$$

According to Fick’s law, the diffusion coefficient is an important parameter that describes the mass or number of moles of a substance diffused vertically through unit area along the diffusion direction in the condition of unit concentration gradient per unit time. The experiment shows that the diffusion coefficient $D$ follows the Arrhenius formula in a certain temperature range:

$$D = D_0 e^{-E_A/RT}$$

where $D_0$ is pre-exponential factor, $R$ is gas constant, $E_A$ is a constant called diffusion activation energy, and $T$ is temperature. It suggests that diffusion is closely dependent on temperature.

Atom migration in the lattice mainly includes vacancy diffusion mechanism and interstitial diffusion mechanism. The hopping transfer of vacant and interstitial atoms in the lattice depend on the thermal fluctuation. The number of such hopping per second called hopping rate is expressed as follows:

$$v = v_0 e^{-\varepsilon/k_B T}$$

where $v_0$ is lattice vibration frequency, $\varepsilon$ is the barrier of atom transfer, and $k_B$ is Boltzmann’s constant. In halide...
perovskite, for example, MAPbI$_3$, the intrinsic concentrations of I$^-$, Pb$^{2+}$, and MA$^+$ vacancies are predicted to exceed 0.4% at room temperature$^{[48]}$, which makes the major process of vacancy mediated diffusion in MAPbI$_3$ perovskite. Figure 1 introduces four vacancy diffusion mechanisms in halide perovskites. It needs to point out that we here employed the projection drawing of metallic halide framework in order to briefly elucidate the vacancy diffusion paths rather than the real ion migration in halide perovskite in Figure 1. Different from the covalent bond construction in metallic halide, the A-site cation is just ionically linked within the lattice of halide perovskite, but its migration is also influenced by such vacancy assisted pathway$^{[49]}$.

Except for the aforementioned kinetic factors, the diffusion impetus can be described by the Nerst-Einstein equation$^{[50]}$, which introduce a thermodynamic parameter of diffusion coefficient:

$$D_i = B_i RT \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln N_i}\right)$$

where $D_i$ is the diffusion coefficient of component $i$, $B_i$ is the average velocity of mass point of component $i$, $1+\partial \ln \gamma_i/\partial \ln N_i$ is the diffusion coefficient thermodynamic factor, $\gamma_i$ is the activity coefficient of component $i$, and $N_i$ is the mole fraction of component $i$. The Nerst-Einstein equation states that the chemical potential gradient can act as the driving force of the diffusion reaction. In the perovskite ion exchange reaction, when $1+\partial \ln \gamma_i/\partial \ln N_i > 0$, that is, the conventional diffusion process from high concentration to low concentration occurs, and the solid phase template and environmental components are homogenized. Instead, $1+\partial \ln \gamma_i/\partial \ln N_i < 0$ may cause the invert diffusion process that ions transfer from low concentration to high concentration. Eventually, it leads to segregation or phase separation.

Assuming a crystal lattice is made up of one kind of atoms, this lattice contains $N$ atoms and $n$ vacancies. As a practical matter, $n<<N$, the statistical equation of vacancy at equilibrium can be obtained:

$$n \approx N e^{-\omega/k_BT}$$

where $\omega$ is the energy required to place atoms at a lattice point inside the crystal on the crystal surface, called the vacancy formation energy. Thus, hopping rate can be written as follows:

$$v = v_0 e^{-(\epsilon+\omega)/k_BT}$$

And the diffusion coefficient $D$ is derived:

$$D = D_0 e^{-E_A/RT}$$

$$D_0 = v_0 d$$

$$E_A = N_0 \times (\epsilon + \omega)$$

where $N_0$ is Avogadro constant, and $d$ is the distance between the neighboring atoms. According to the above derivation, several special factors affecting ion diffusion of halide perovskites can be summarized below:

**Lattice sites of ion exchange**

X-site halogen anion has the lowest activation energy due to the favorable vacancy-assisted diffusion.$^{[49]}$ A-site cation migration involves motion through the unit cell face or bottleneck comprising four X-site ions, which leads to a higher activation energy in comparison with X-site anion. More importantly, the A-site cation usually possesses a large volume, especially in organic-inorganic hybrid perovskite. The migration of A-site cation will directly affect the crystalline stability of perovskite.$^{[24]}$ The B-site ion as the center ions of the cation sublattice structure in perovskite shows the highest migration energy barrier. For example, in the case of MAPbI$_3$, the activation energy at A, B, and X-site are calculated to 0.84, 2.31, and 0.58 eV, respectively.$^{[49]}$

**Ionic radius**

The ionic radius has a great impact on the structure distortion and stability according to the Goldschmidt’s tolerance factor $\tau$.$^{[51]}$

$$\tau = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}$$

where $R_A$, $R_B$ and $R_X$ are the ionic radii for corresponding ions, respectively. The halide perovskite structure can keep stable if $\tau$ is between 0.813 and 1.107. Especially, it is
generally believed that $\tau$ between 0.9 and 1 is conducive to form a cubic phase.\textsuperscript{[52,53]} In other words, A-site ion with too large or too small radius may result into the distortion or even collapse of perovskite configuration.\textsuperscript{[24]} In addition to the tolerance factor, the octahedral factor $\mu$ is another semi-empirical geometric parameter used to evaluate octahedral stability.\textsuperscript{[54]}

$$\mu = \frac{R_B}{R_X}$$

The range of $\mu$ between 0.442 and 0.895 is conducive to the stable $[BX_6]^{4-}$ octahedral.

**Defects**

Defects are the most important factor for ion diffusion, which can reduce the activation energy of diffusion and provide more feasible pathways for inter diffusion of ions.\textsuperscript{[55]} Due to the low formation energy, the facile solution-based processes for halide perovskites inevitably lead to abundant surface and bulk crystal defects, no matter in nanosize or in bulk crystalline. Case in point, the bulk trap density in such polycrystalline thin films is measured in the range of $10^{16}$–$10^{18}$ cm$^{-3}$.\textsuperscript{[56–57]} However, solution-grown perovskite single crystals usually have an extremely low trap density around $10^{10}$ cm$^{-3}$, which is comparable with that of the best value reported in intrinsic crystalline silicon (c-Si).\textsuperscript{[58]} For example, based on the first principles calculations for CH$_3$NH$_3$PbI$_3$, all the defects with low formation energies including CH$_3$NH$_3$ interstitials (MAi), Pb vacancies (VPb), CH$_3$NH$_3$ molecules on Pb sites (MAPb), I interstitials (Ii), I vacancies (Vi), and CH$_3$NH$_3$ vacancies (VMA) were found to have transition energies less than 0.05 eV with respect to the VBM or CBM, indicating that the dominant defects in CH$_3$NH$_3$PbI$_3$ are shallow defects.\textsuperscript{[59]}

### 2.2 Ion exchange reaction

The ion exchange reaction describes the progress that the new ions enter the parent crystal meanwhile the original counterpart ions diffuse out. Take the cation exchange reaction in halide perovskite, for example:\textsuperscript{[29,60]}

$$ABX_3 + X^-_{(sol)} \rightarrow ABX_2X^- + X^-_{(sol)} \cdots \cdots \rightarrow ABX'_{3}$$

1. $ABX_2 - X \rightarrow ABX_2 + X$ (dissociation)
2. $X^- \rightarrow X'$ (desolvation)
3. $ABX_2 + X' \rightarrow ABX_2 - X'$ (association)
4. $X \rightarrow X^- (solvation)$
5. $\cdots \cdots \rightarrow ABX'_{3}$

Since the ion exchanges for halide perovskites are often processed within solution phase, the cation exchange can be divided into such four steps: Step 1 and Step 3 present the crystal energy variation, including Born-Lande lattice energy and surface energy. Strain and dislocation energies between the parent and product phases of perovskite also affect the thermodynamics and kinetics of the anion exchange reaction. Specifically, the decreased crystal energy in product perovskite may result in a thermodynamically spontaneous ion exchange reaction. Step 2 and Step 4 illustrate the desolvation and solvation energies for ingoing cations and outgoing cations, respectively. The desolvation and solvation steps are closely related to the solubility of the ions in the solvent, indicating the reaction is more prone to proceed if the parent cation is better solvated in the reaction solvent than the ingoing cation.\textsuperscript{[26,61]} Therefore, the thermodynamic impetus can be estimated by integrating all the contributions of variation in crystal lattice energy, interfacial strain energy, dislocation energy, dissociation, and solvation energy. Besides, reaction temperature also plays a role of importance for the ion exchange reaction in light of the Arrhenius equation.

### 3 THE STRATEGIES OF ION EXCHANGE SYNTHESIS

The common vertex connection of $[BX_6]^{4-}$ octahedron in perovskite lattice has larger lattice gap than that of common edges and common planes. Such structural characteristics not only enable perovskite materials to maintain structural stability with a great quantity of lattice defects, but also facilitate the diffusion and migration of ions in perovskite lattice. This feature is highly compatible with the ion exchange method. In this section, we classify the synthesis strategies of ion exchange for halide perovskite into solid phase, liquid phase, and gas phase ion exchange reaction according to the different reaction conditions (Figure 2).

The solid-phase synthesis refers to the strategy of ion exchange reaction between ion source compound and parent perovskite in solid state. The ion exchange occurs from the interface, and the exchanged ions gradually become homogenized within both of the ion source compound and product perovskite. The solid-phase ion exchange has been conducted between perovskite films with different composition, and by depositing the perovskite quantum dots onto the distinct perovskite films.\textsuperscript{[62–63]} However, due to the diffusion limitation, it seems difficult to achieve totally ion exchange thermodynamically in solid-phase reaction.

The liquid-phase synthesis is defined as the ion exchange for parent perovskite reacting with ion source dissolving in the liquid phase. This strategy is the most
FIGURE 2  Schematic diagrams of solid, liquid, and gas phase process

commonly used for ion exchange of perovskite NCs. Simply dissolve the ion source through ligands in the dispersed solution of perovskite NCs, and the ion exchange can be achieved in a few seconds. It is worth mentioning that ion exchange for all three sites in perovskite NCs can be realized by liquid phase synthesis. In addition, the liquid-phase ion exchange is also widely applied for bulk perovskite, but it usually suffers from the contradiction between the solubility of ion source compound and polarity of solvent.

The gas-phase synthesis means the parent perovskite exchanges ion with the corresponding ion source in the form of gas. There is no special requirement for the size and composition of parent perovskite except for gasifying the ion source compound in high temperature and low pressure.

4  |  ION EXCHANGE FOR ZERO-DIMENSIONAL (0D) PEROVSKITE NANOMATERIALS

In regard to the perovskite in different dimensions, it can be classified by the crystal size (e.g., the 0D scale of nanocrystals (NCs), quantum dots (QDs), 1D scale nanowires or nanorods, 2D scale of nanoplates and 3D scale of bulk single crystals or polycrystals) as well as the crystalline structures (usually defined as the “pseudo-perovskite structures” referring to the different connections of [PbX₆]⁴⁻ octahedra). In this review, unless otherwise noted, the discussed perovskites in various dimensions are all referring to the crystal size with ABX₃ perovskite composition.

Depending on the ultrahigh photoluminescence quantum yield (PLQY), narrow emission FWHM and highly emissive tunability, the 0D perovskite nanomaterials with quantum confinement size have attracted much attentions and made great strides in the past several years, such as the successful display applications recently reported by Zhong et al. Except for the size control achieved within the synthesis procedure (thermal injection, ligand-assisted reprecipitation, and so on), ion exchange provides an additional path to modify the physicochemical properties of 0D halide perovskites. We will discuss the ion exchange for 0D halide perovskites according to the different crystallographic components in this section.

4.1  |  X-site anion exchange

As aforementioned in Chapter 2, the X-site halogens of perovskite have the lowest activation energy for the substitutional reaction comparing with other ions in
perovskite. Kovalenko et al. reported fast and low-temperature anion exchange using organometallic Grignard reagents (MeMgX), lead halide (PbX\textsubscript{2}), or oleylammonium halides (OAm-X) as halogen source (Figure 3A). Almost at the same time, Manna et al. demonstrated a range of different halogen sources were used to turn the chemical composition and the optical properties of pre-synthesized CsPbBr\textsubscript{3} (Figure 3B). By adjusting the halide ratio in the colloidal nanocrystal solution, bright photoluminescence could be regulated over the whole visible spectral region while maintaining a high PLQY and a narrow emission line width.

To date, various halide precursors have been utilized for halogen exchange in halide perovskite. Figure 4 summarized some typical halide precursors for perovskite X-site ion exchange. PbX\textsubscript{2} is a halogen source compound of importance for anion exchange of 0D perovskites. Yang et al. used PbX\textsubscript{2} to prepare CsPbCl\textsubscript{3}, CsPbI\textsubscript{3}, and mixed-halide perovskite nanoparticles by anion exchange, which could continuously tune the spectrum over the whole UV-visible spectral region (360-610 nm), meanwhile keep their PLQY up to 80%. Qu et al. developed an in-situ method for synthesizing CsPbX\textsubscript{3} (X = Cl, Br, I) NCs by dissolving PbX\textsubscript{2} in octane with oleic acid (OA) and oleylamine.
(OLA). The synthesized CsPbX₃ NCs had 12–44 nm wide emission and over 90% PLQY. Moreover, anion exchange with PbX₂ can also be applied to the doped perovskite NCs. Klimev et al.⁷⁹ first demonstrated post-synthesis anion exchange with PbX₂ could regulate the band gap of the Mn²⁺ doped perovskite NCs over a wide range of energies (1.8-3.1 eV). The varied halide composition would tune the intrinsic band-edge and Mn emission according to the energy transfer between the Mn ion and host perovskite. Zhao et al.⁸⁰ synthesized Mn²⁺ doped perovskite NCs with varied Br compositions by PbBr₂ assisted anion exchange. The photoluminescence (PL) intensity of the Mn²⁺ emission band was significantly enhanced with Br⁻ substitution. Especially at low temperature (80 K), the PL intensity ratio of Mn²⁺ emission to band-edge emission increased almost 80 times in Mn²⁺:CsPbCl₂.₁₅Br₀.₈₅ NC compared with that of Mn²⁺:CsPbCl₃ NCs. The temperature-dependent energy-transfer efficiencies of Mn²⁺:CsPbCl₃ and Mn²⁺:CsPbCl₂.₁₅Br₀.₈₅ NCs from excitons in NCs to Mn²⁺ were obtained. In addition, Song et al.⁸¹ demonstrated the use of PbBr₂ for anion exchange of Eu³⁺:CsₓK₁₋ₓPbCl₃ NCs. The anion exchange reactions in Eu³⁺:CsₓK₁₋ₓPbCl₃ NCs caused gradually substituting Cl⁻ by Br⁻, and obtained precisely tunable emissions from 408 nm to 495 nm. Some other metal halides (MX₂, M = Zn, Mg, Cu, or Ca; X = Cl, Br, or I) also can work as solid halogen sources without pretreatment and greatly simplify the reaction process. Li et al.⁸² reported an anion exchange reaction by introducing ZnX₂ to directly convert parent CsPbX₃ NCs at room temperature without any preprocess. The addition of OA and OLA could significantly accelerate the reaction, because OA reduced the activation energy of exchange reaction and OLA greatly enhanced the solubility of ZnCl₂ in toluene solution. Wang et al.⁸³ demonstrated a new halogen source consisting of copper halide- (CuX₂-) OLA complexes. This economical method obtained perovskite NCs with high crystallinity at room temperature during a recrystallization process. Meanwhile, the yielded CuCl₂ could passivate the surface defects so as to increase the PL intensity of obtained CsPbCl₂.₁₅Br₀.₈₅ NCs.

Since the colloidal perovskite NCs must be stabilized by organic ligands, halide ligand becomes another important halide precursor for ion exchange of 0D perovskite materials, such as OAm-X⁶⁴,⁸⁴ and aniline hydrohalide (C₆H₁₃NH₃X, An-HX).⁸⁴-⁸⁵ Ren et al.⁶⁴ regulated the blinking behavior of the CsPbX₃ NCs through varying halide composition with OAm-X. They investigated the ensemble and single particle optical properties of CsPbBr₃₋ₓXₓ and CsPbBr₃₋ₓIₓ NCs via two different anion exchange routes (Br⁻ to I⁻ and I⁻ to Br⁻). Under optimum conditions, the percentage of “non-blinking” CsPbBr₃₋ₓIₓ NCs (the “on time” fraction > 99% of the observation time) was about 71%. Kido et al.⁸⁴ reported highly efficient red perovskite NCs fabricated by anion exchange of CsPbBr₂ with halide alkylammonium and aryllammonium. The obtained NCs exhibited the PL emission shifts from green to a deep-red at 649 nm as well as higher PLQY. Furthermore, comparing with the aryllammonium, the iodized alkylammonium exchanged perovskite NCs showed higher external quantum efficiency, color purity and stability in LED performance due to the lowered surface ligand density. Yu et al.⁸⁵ used An-HX for anion exchange of Ce³⁺ doped CsPbX₃ NCs, which could tune the emission from red (600 nm) to purple (470 nm) and preserve the PLQY of 22–87% after ion exchange. Aside from the ligand-assisted anion exchange reaction, attentions also need to be attracted on purification of product perovskite NCs.⁸⁶ The use of halide ligands for anion exchange may weaken ligand binding strength and result in undesirable decreased PLQY. For this reason, Maye et al.⁸⁷ reported a three-step method to conduct purification and tune the composition of CsPbBr₂₋ₓIₓ perovskite NCs. The addition of acid and base ligands plays an important role in preserving the as-synthesized properties during purification and anion exchange. Due to the composition-dependence of surface ligand binding, the increased iodide content in CsPbBr₂₋ₓIₓ could decrease the ligand density, and consequently affect PLQY of the resultant mixed-halide perovskite NCs. Considering the colloidal synthesis for most of the 0D perovskite, organic halide ligands greatly enrich the selectivity of halide precursors for anion exchange.

Although PbX₂ and halide ligands are most commonly used for anion exchange of perovskite NCs, the issues of their poor solubility in non-polar solvents or low reactivity at room temperature still need to be addressed. In recent years, some other halide compounds are used as anion sources for anion exchange of 0D perovskite materials. Manna et al.⁵² reported that benzoyl halides could be used as halogen sources for efficient anion exchange of CsPbX₃ NCs. The CsPbBr₃ NCs could be transformed into CsPbCl₃ or CsPbBr₂ NCs through ion exchange with corresponding benzoyl halides, and reversely back-exchange from CsPbCl₃ or CsPbBr₂ to CsPbBr could also be achieved with benzoyl bromide. The halide precursor of trimethylsilyl halide (TMS-X) possesses a number of advantages beyond commonly used halide reagents. The solubility in nonpolar solvents allows more reliable ion exchange and the easy evaporation property may provide a simple post-processing way by drying the product perovskite NCs in vacuo without additional workup. The difference in bond energies of TMS-X (TMS-Cl > TMS-Br > TMS-I) becomes the thermodynamic driving force of anion exchange reaction, and generally a slight excess of the TMS-X reagent (< 1.5x) is necessary to guarantee
the completion of anion exchange reaction. Gamelin et al. [88] first reported the TMS-X could be employed for anion exchange of perovskite NCs. They synthesized Yb$^{3+}$ doped CsPbCl$_{3-x}$Br$_x$ via anion exchange with TMS-Br. The obtained Yb$^{3+}$:CsPbCl$_{3-x}$Br$_x$ NCs with mixed halide compositions could keep Yb$^{3+}$ concentration unchanged. Besides, they also carried out ion exchange with TMS-Br in Mn$^{2+}$ doped CsPbCl$_3$. By using a combination of X-band electron paramagnetic resonance (EPR) and PL spectroscopies to monitor the Mn$^{2+}$ dopants in Mn$^{2+}$:CsPbCl$_3$ NCs during anion exchange progress, they found the migration of Mn$^{2+}$ during anion exchange to form clusters, and the Monte Carlo simulation and analysis of the Mn$^{2+}$:CsPbCl$_{3-x}$Br$_x$ lattice with different halide compositions were conducted to support this conjecture.

As the simplest halide, hydrogen halide (HX) provides an ideal model for studying ion exchange mechanism and the effect of halide ions doping in perovskite. Huang et al. [91] first proposed HCl in anion exchange of Mn$^{2+}$:CsPbCl$_3$ NCs (Mn$_x$-NCs). With additional HCl, Cl$^-$ was facilitated to diffuse into CsPbCl$_3$ NCs and possibly exchanged with remained OAc$^-$, then the released OAc$^-$ would be removed gradually through centrifugations and solvent washing. This strategy could effectively reduce the defect density, mitigate the lattice distortion, facilitate energy transfer to dopants, and resultantly enhance the Mn emission efficiency.

Except for the extra halide precursors, the anion exchange could also occur between perovskites with different halogen composition. The migration of anions has been proven by “Tubant’s method” in halide perovskite, such as CsPbBr$_3$ and CsPbI$_3$. Islam et al. [49] verified the X-site had low activation energy, which was derived 0.60-0.68 eV from photocurrent relaxation at biased preconditioning. This data was close to their calculated result. The high flexibility of ion migration in X-site could enable the perovskite itself to serve as a halogen source. It has been reported that anion exchange could be achieved by mixing solutions containing perovskite NCs with different halide compositions, and the PL spectrums could be regulated by the homogenization of different perovskite NCs. Zeng et al. [62] reported a composite interface of MAPbI$_3$ film and CsPbBr$_3$ NCs (Figure 5A). The transition from CsPbBr$_3$ NCs to CsPbBr$_x$I$_{3-x}$ NCs was achieved by ion migration, and the PL emission of CsPbBr$_x$I$_{3-x}$ NCs gradually shifted from green to red. Meanwhile, the ligand density of OLA and OA was proved to tune the anion exchange process between CsPbBr$_3$ NCs and MAPbI$_3$ film. As a result, the continuous emission modulation in the microscale area could be realized. Huang et al. [93] put forward a new strategy using the inorganic perovskite NCs as the halogen source to introduce Br$^-$ and I$^-$ passivation into Cl$^-$ modified PbSe NCs. When the PbSe NCs and CsPbX$_3$ (X = Br, I) NCs coexisted in the same solution, the Cl$^-$ of PbSe NCs was partially exchanged with the Br$^-$ of CsPbBr$_3$ NCs and a CsPbCl$_y$Br$_{3-y}$ alloy could be obtained. In the case of CsPbI$_3$, I$^-$ ions were observed migration to PbSe NCs, while the CsPbI$_3$ NCs would disintegrate rather than...
maintain their crystal structure after ion exchange (Figure 5B). The PLQY of the PbSe NCs treated by CsPbX3 NCs significantly improved, and the solar cells fabricated with these post-passivated PbSe NCs achieved a 12.3% increase power conversion efficiency (PCE) and better air stability in comparison with the pristine devices. Liu et al.94] combined CsPbI3 NCs with CsPbBrI2 films as active layers for photovoltaic application, in which anion exchange occurred at the CsPbBrI2 /CsPbI NCs interface due to the difference halogen composition. This strategy achieved proper band-edge bending as graded bandgap for improved carrier collection, thus realized the optimal device performance. They also utilized a series of organic iodine salts to post-treat the interfaces of CsPbI2Br perovskite films.95] Exchanged I– led to a proper band edge bending, and capped organic cations decreased surface defects. Among them, the FAI-treated device yielded the best PCE of 14.14% proved it an efficient method for the optimization of planar heterojunction PSCs.

Although the versatile anion exchange strategies have been achieved for 0D perovskite, the corresponding research on reaction mechanism lags behind the chemical reaction and methodology. Alivisatos et al.96] proposed the presence of two distinct mechanism of anion exchange in CsPbX3 NCs, ranging in size from 6.5 to 11.5 nm, for transformations from CsPbBr3 to CsPbCl3 or CsPbI3. The iodine exchange presented surface-reaction-limited exchanges allowing all anionic sites within the NCs to appear chemical consistency, whereas the chlorine exchange presented diffusion-limited exchanges proceeding through a more complicated exchange mechanism (Figure 5C). Santra et al.97] introduced variable energy hard X-ray photoelectron spectroscopy (HAXPES) to researched the internal structure of CsPbBr3 NCs ion-exchanged with iodide ions. The partial anion exchange NCs showed an inhomogeneously alloyed heterostructure with a higher concentration of exchanged I– ions on the surface. Even if the ion exchange of CsPbBr3 NCs completely finished and the PL emission peak no longer shifted, a significant amount of bromide ions was still present in the core of the obtained NCs. These new insights regarding the internal heterostructure helped understand the intrinsic optical properties of these anion-exchanged perovskite NCs, and also provided methods and theoretical supports for materials with gradient chemical composition.

### 4.2 B-site cation exchange

The B-site cation exchange is the most difficult compared to other sites owing to its large $E_A$.98] Moreover, the rigid cationic sublattice stabilizes the perovskite lattice, which would further restrain the metallic cation exchange.96] There are some metallic ions have been tried for B-site cation exchange, such as the conglomerates of Pb2+ (Sn2+), transition metal ions (Zn2+, Cd2+, Ni2+), and heterovalent metal ions exemplified by rare earth ions (Al3+). Mello Donega et al.99] first reported a method that allowed partial cation exchange in colloidal CsPbBr3 NCs. Several cations isovalent to Pb2+ were used for cation exchange to form CsPb1-xMxBr3 NCs (M = Sn2+, Cd2+, Zn2+, 0 < x ≤ 0.1) with sub-monolayer coverage on the surface. Yang et al.100] demonstrated a fast and controllable cation exchange of CsPbX3 NCs by use of various Sn2+ halides (Figure 6A). The cation exchange reaction could be accelerated if the SnX2 halide precursor and CsPbX3 NCs contained different halogen component. The produced CsSnI3 NCs with a high stability and optical performance proved this anion-exchange-promoted cation exchange strategy could be an efficient versatile means to produce Sn2+:CsPbX3 NCs. Sheldon et al.101] demonstrated two different products prepared with CsPbBr3 NCs and AuBr3. Cation exchange with sole AuBr3 would lead to Cs2AuIAuIIIBr6 NCs with a tetragonal crystal structure, while another heterostructure NPs with Au deposited on the surface of CsPbBr3 (Au-CsPbBr3) was obtained by use of PbBr2. They102] further studied the exchange reaction between CsPbX3 NCs and Au halides with different valences. The reaction between CsPbX3 and Au+ halide resulted in the deposition of Au on the surface of CsPbX3 NCs with considerable high PLQY. Comparatively, CsPbX3 NCs and Au+ halide could produce complete Au substitution and formed in Cs2AuIAuIIIX6 NPs (X = Cl, Br) with no visible photoluminescence. Deng et al.103] reported a rapid visual detection of ultra-trace Hg2+ real- ized ion exchange of MAPbBr3 NCs. As shown in Figure 6B, the green photoluminescence of MAPbBr3 NCs was gradually quenched along with substituting Pb2+ with Hg2+. This phenomenon was applied for Hg2+ sensing with the detection limit of 0.123 nmol L–1 (24.87 ppt) in the range of 0 to 100 nmol L–1.

The similar bonding energy between Mn–Cl and Pb–Cl allowed Mn2+ to easily incorporate in CsPbCl3 frameworks.79] The Mn2+ doped CsPbCl3 NCs had an additional fluorescence peak in 550–590 nm due to the d-electron emission of Mn2+, and the high PLQY of the Mn2+:CsPbCl3 NCs provide this dual emission material potential applications for lighting.79,99,104] Chen et al.105] reported a one-step dual ion exchange method to synthesis Mn2+:CsPbCl3 NCs, in which the metallic cation and halide anion exchange happened simultaneously between CsPbBr3 NCs and MnCl2. Subsequently, KCl was used as the matrix for Mn2+:CsPbCl3 NCs to offered robust protection from photooxidation and thermo-degradation (Figure 7A). Xia et al.106] developed a co-substitution...
of cation and anion strategy by mixing CsPbBr$_3$ and CsPb$_{1-x}$Mn$_x$Cl$_3$ NCs in n-hexane, which could make the chemical composition of the NCs homogenized. This in situ ion exchange method could adjust the optical properties in a wide range and avoid the additional unfavorable purification process for NCs (Figure 7B). Cui et al.$^{[107]}$ demonstrated another way of halide exchange-driven cation exchange (HEDCE) to achieve partial Mn$^{2+}$ cation exchange in perovskite. MnCl$_2$ was dissolved into N,N-dimethylformamide (DMF), and then dipped into the CsPbBr$_3$ NCs toluene solution. The cation and anion exchange occurred simultaneously between CsPbBr$_3$ NCs and MnCl$_2$ instead of reaction with Mn$^{2+}$ and Cl$^-$. The synthesized Mn$^{2+}$:CsPb(Cl/Br)$_3$ NCs had a
temperature-dependent ratiometric emission that possessed potential application for temperature sensors (Figure 7C). A photoinduced post-synthesis method of Mn$^{2+}$ doping perovskite NCs was addressed by Son et al.\[108\]. Photogeneration halide ions from dihalomethane (CH$_2$X$_2$, X = Cl, Br) driven the Mn$^{2+}$ exchange, and the extent of cation exchange could be controlled by the intensity of irradiation. This photoinduced cation exchange strategy might be further expended to other cations which were hard to process with conventional ways. Except for the forward Mn$^{2+}$ doping CsPbX$_3$ NCs, Chen et al.\[109\] reported a reverse synthetic strategy of CsPb$_{x}$Mn$_{1-x}$Cl$_3$ NCs by cation exchange of CsMnCl$_3$ NCs. Doped with Pb$^{2+}$, the hexagonal CsMnCl$_3$ firstly transformed to rhombohedral Cs$_4$Pb$_5$Mn$_{1.5}$Cl$_6$, and then continued to form into cubic CsPb$_3$Mn$_{1.5}$Cl$_6$. The structural conversion was depended on the ratio of Mn$^{2+}$ and Pb$^{2+}$ in precursor as well as the reaction time. In addition, the concentration of Br$^{-}$ in precursor could also control the structural conversion, so that replacing PbCl$_2$ with PbBr$_2$ made the incomplete phase transformation of Cs$_4$Pb$_5$Mn$_{1.5}$(Cl/Br)$_6$. The simultaneous ion exchange of Pb$^{2+}$ with Mn$^{2+}$ and Br$^{-}$ with Cl$^{-}$ were conducive to the realization of tunable multicolor luminescence. As the metallic cation in perovskite mainly refers to the toxicity issue and intrinsic band structure, the B-site cation exchange still needs further exploration.

### 4.3 A-site cation exchange

The mixed A-site cations have been demonstrated for ameliorating the long-term stability of halide perovskites, such as the Cs-rubidium (Rb) based perovskite cells.\[110–111\] Chen et al.\[112\] first demonstrated the A-Site cation exchange of MAPbX$_3$ NCs with FA$^{+}$. By adding the formamidinum acetate (FA(ac)) into MAPbBr$_3$ NCs toluene solution, the FA$^{+}$ cation exchange reaction was carried out. The low solubility of FA(ac) in toluene allowed the cation exchange to proceed slowly, and retained a cubic lattice with a high PLQY of 69%. (Figure 8).

The potassium ions (K$^{+}$) with small radius were considered to have low tolerance factor to establish perovskites.\[110\] Nevertheless, Cs$_{0.925}$K$_{0.075}$PbI$_2$Br perovskite cells were studied to possess longer operational lifetime than that of CsPbI$_2$Br.\[113\] This result implies that K$^{+}$ could improve the stability of CsPbX$_3$ NCs as well. Li et al.\[114\] reported using K$^{+}$ exchange to improve the optical properties and stability of CsPbBr$_3$ NCs. The monodisperse K$^{+}$ doped CsPbX$_3$ NCs (K-CPB-NCs) exhibited significantly higher photothermal stability, and the PLQY could be increased from 65% to 83% by strictly controlling the using amount of potassium oleate (K/Cs mole ratio of 1.5/1). Moreover, the K-CPB-NCs could almost maintain 100% PL intensity in 50°C and relative humidity 60% after 153 hours, while the PL intensity of controlled CsPbX$_3$ NCs decreased to 50% only after 45 hours (Figure 8B).

5 | ION EXCHANGE FOR ONE-DIMENSIONAL (1D) PEROVSKITE NANOMATERIALS

The one-dimensional halide perovskites with well-defined configurations possess impressive optical properties, high carrier mobilities, and long carrier diffusion length.\[115–117\] Similar to 0D perovskites, the anion exchange can also provide multivariant ways to post-modulate the physicochemistry properties of 1D perovskites. Jin et al.\[118\] connected a MAPb$_3$ nanowire to a bulk MAPbBr$_3$ single crystal and realized the structural transition of nanowire from CH$_3$NH$_3$PbI$_3$ to CH$_3$NH$_3$Pb$_x$I$_{3-x}$ due to the anion diffusion. The terminal of the obtained nanowire closed to MAPbBr$_3$ single crystal was bromine-rich and the opposite was iodine-rich, in which a long carrier diffusion could be achieved because of the gradient bandgap distribution.
FIGURE 9  

(A) Halide-gradient MAPbBr$_{3-x}$ perovskite nanowires comprising a bromide-rich region and an iodide-rich region. (Reprinted with permission from 2016 American Chemical Society[118]).

(B) Schematic illustration of the synthesis of CsPbX$_3$ nanowires. (Reprinted with permission from Science China Press and Springer-Verlag Berlin Heidelberg 2017[120]).

(C) Schematic of the vapor conversion of CsPbBr$_3$ nanostructures into perovskite CsPb(Br,I)$_3$ alloys. (Reprinted with permission from The Royal Society of Chemistry 2017[125])

Figure 9a. However, it spent 15 days realizing such anion exchange via solid phase reaction. By aligning CsPbBr$_3$ nanowires on epitaxial CsPbCl$_3$, MAPbI$_3$, or MAPbBr$_3$ microplates as platforms, Jin et al.[119] first quantitatively analyzed the interdiffusion coefficients of the chloride-bromide couple and calculated out an activation energy of 0.44±0.02 eV for ion diffusion from temperature-dependent studies. In contrast, iodide-bromide interdiffusion was limited due to the complex phase behaviors of mixed halogen perovskite, and the A-site cation interdiffusion across the MAPbBr$_3$/CsPbBr$_3$ junctions was barely observed at room temperature.

In comparison with solid phase reaction, the relatively large surface-to-volume ratio of perovskite nanowires makes it easily carried out in solvents. Kuang et al.[120] transformed the CsPbI$_3$ nanowires to CsPbBr$_3$ nanowires with a diameter of 50–100 nm by immersing in CsBr methanol solution and post annealing (Figure 9B). They applied the formed CsPbI$_3$ and CsPbBr$_3$ nanowires for the first time to perovskite solar cells and found the inorganic CsPbBr$_3$ nanowire solar cells showed better stability. Graetzel et al.[121] proposed a facile way for MAPbI$_3$ and FAPbI$_3$ nanowire preparation by dipping PbI$_2$ films into isopropanol solutions containing MAI or FAI, and DMF (for structure-directing role). This method also allowed the further compositional modification of obtained nanowires via an ion-exchange to form MAPbBr$_3$, MAPbCl$_3$, and FAPbBr$_3$ nanowires.

In comparison to CsPbBr$_3$ nanowires, direct synthesis of chlorine and iodine-based perovskite nanowires usually suffers from the low yield, poor diameter control or undesirable optical properties. Yan et al.[122] obtained CsPbCl$_3$ and CsPbI$_3$ nanowires by anion exchange of CsPbBr$_3$ as a template in corresponding precursors solution in OLA/OA/ODE. Tunable photoluminescence covered almost the entire visible spectrum, and anion exchange did not significantly increase the defects density in nanowires. They further developed a stepwise purification strategy to synthesize a highly uniform and ultrathin CsPbBr$_3$ nanowire, and carried out the composition modulation by anion exchange without changing the morphology.[122]

Unlike solid-phase and liquid-phase reaction, the gas-phase ion exchange requires that the substance is reacted in a gaseous state. Fu et al.[124] used an antisolvent-vapor-diffusion induced crystallization method for CH$_3$NH$_3$PbCl$_3$ nanowires. By exposing the nanowires to HX (X = Br, I) gas, the interconversion among MAPbCl$_3$, MAPbBr$_3$, and MAPbI$_3$ was realized, meanwhile the high crystallinity and morphology of the nanowires were still maintained. Gaseous ion exchange reaction for perovskite usually cannot proceed thoroughly and results into the mixed composition. By using argon as
carrier gas, Jin et al. [125] carried out the conversion reaction from CsPbBr3 nanowires to CsPbBr3-xIx nanowires with n-butylammonium iodide (n-C4H9NH3I) vapor under a vacuum condition (Figure 9C). The volatile excessive iodide precursor in the vapor phase provided enough driving force for the conversion, and the low pressure environment in the reactor facilitated the fast removal of the volatile bromide product. Yan et al. [126] used desynchronized deposition of metal halides and made temperature-controlled anion exchange to obtain CsPbBr3, I3-x nanowires. The temperature, pressure, and precursor ratio were well controlled to adjust the composition of the spatial distribution. The resulting nanowires increased in Br/I ratio from the center to the end and therefore induced a blueshifted emission to achieve tunable two-color laser performance.

For the facile composition variation, ion exchange can be utilized to design the nanowire heterostructures. Yang et al. [127] employed electron beam lithography to make some parts of CsPbBr3 nanowires protected by PMMA and other parts exposed. After immersing in a halogenated oleylammonium solution, the exposed parts underwent ion exchange reactions, but the others remained unchanged. Finally, a nanowire heterostructure with a heterostructure pixel size of 500 nm could be obtained, the photoluminescence of which was tuned throughout the visible spectrum. Li et al. [128] used gaseous ion exchange to convert CsPbI3 to CsPbBr3 with tetrabutylammonium bromide (TBABr). In order to prevent the organic solvents damaging perovskite, they designed an in situ converting and electrode fabrication process, which produced a self-powered lateral photodetector based on CsPbI3-CsPbBr3 heterojunction nanowire arrays.

In addition to nanowire, nanorod is another 1D nanocrystal with a smaller aspect ratio and linearly polarized optical properties. Rogach et al. [129] used polar alcohols to synthesize CsPbBr3 nanorods with high PLQY of 60-76% and emission anisotropy of ~0.2. Both CsPbCl3 and CsPbI3 nanorods with similar dimensions were derived from the CsPbBr3 nanorods by anion-exchange reactions. Yang et al. [130] placed CH3NH3PbBr3 nanorod arrays with a length of more than 1 µm and a diameter of more than 100 nm in CH3NH3I gas. Excess MAI could provide driving force for anion exchange reaction, the CH3NH3PbI3 nanorod array with intact morphology could be obtained after annealed at 150°C. Structural transformation from nanowire to nanorod can also be achieved by ion exchange reactions. Polavarapu et al. [131] obtained CsPbI3 nanorods with an aspect-ratio mainly ranging from 2.5 to 3.5 by adding PbI2-ligand solution to CsPbBr3 nanowires. The shape transition from nanowires to nanorods could lead to improved photoluminescence efficiency owing to a decrease of nonradiative decay rates. Moreover, they found that the perovskite nanorods exhibited single photon emission, while it was not detected in parent nanowires.

6 | ION EXCHANGE FOR TWO-DIMENSIONAL (2D) PEROVSKITE NANOMATERIALS

Freestanding 2D nanoplates provides an interesting nanocrystal geometry for photophysical studies of semiconductors due to their increased exciton binding energy, enhanced absorption cross sections with respect to bulk, low threshold stimulated emission, and notable optical nonlinearity. [132–134] Alivisatos et al. [135] discovered the synthesis of CsPbBr3 nanoplates tended to strongly favor asymmetric growth producing quasi 2D geometries by thermal injection between 90°C and 130°C. After a ligand-assisted anion exchange, the composition of nanoplates could be widely tuned but the geometries were still preserved. Similarly, Manna et al. [136] reported a room temperature synthesis scheme for CsPbBr3 nanoplatelets. Followed by the injection of Olam-I or TBA-Cl, the anion exchange of crude CsPbBr3 nanoplatelet solutions swiftly happened, but the size and shape of the starting particles were maintained (Figure 10A). They also conducted the anion exchange on the CsPbBr3 nanosheets with lateral size controlling up to the micrometer. [137] Zhong et al. [100] used a pre-dissolution assistant solvothermal reaction for CsPbBr3 nanoplatelets, however, the counterparts of Cl or I perovskite nanoplates within the same procedure failed to precisely control the thickness of products. By anion exchange CsPbBr3 nanoplatelets with PbX2 precursors, the narrower emission FWHM could be observed in comparison with that synthesized by solvothermal reaction due to the uniform thickness distribution. Besides of the post treatment, ion exchange can also be used to synthesize nanoplates with different compositions. Zeng et al. [138] proposed an ion-exchange-mediated self-assembly strategy for preparing FAPbBr4 nanoplates at room temperature, in which 2D layered OA2PbBr4 nanoplates could transform into FAPbBr3 nanoplates through a OA+-to-FA+ exchange induced self-assembly perovskite monolayers (Figure 10B). A c-axis crystalline shrinkage was found due to the difference in lattice parameters of OA and FA.

Comparing with solution reaction, it is easier to study the kinetics of ion exchange in perovskite nanoplates with gaseous reaction by rapidly quenching the reaction for optical characterizations. Yang et al. [139] synthesized low defect density CsPbBr3 nanoplates with an improved chemical vapor transport (CVT) growth method, and studied the anion exchange kinetics by converting it into
CsPb(Br$_{1-x}I_x$)$_3$ and CsPbI$_3$. It was found that the anion exchange on the nanosheets was related to the reaction time and plates thickness. In addition, they proposed there were two steps within ion exchange reaction: the first was the surface reaction of anion exchange between N-C$_4$H$_9$NH$_3$I vapor and CsPbBr$_3$ nanoplates, and the second was the solid-state diffusion of I$^-$ into CsPbBr$_3$ nanoplates.

7 | ION EXCHANGE FOR THREE-DIMENSIONAL (3D) BULK PEROVSKITES

Polycrystalline films are the most widely studied types of bulk halide perovskite because of their unique advantages, such as large absorption coefficient, high charge carriers mobility, low exciton binding energy, and so on. A polycrystalline perovskite thin film can be easily obtained by spin-coating the precursor solution. In addition to modulating the photophysical properties, the ion exchange in polycrystalline perovskite needs to keep the parent film intact since the crystallinity and morphology of the perovskite polycrystalline film are the main factors affecting the performance of the perovskite device. Gratzel et al.\cite{140} realized a rapidly mutual conversion of halide perovskites infiltrated in a mesoscopic oxide scaffold, in which the halide substitution on perovskite lattice could be completed within seconds or minutes after contacting with the halide solution. However, gradual substitution on the perovskite lattice could be achieved with Br/Cl and Br/I through in situ halide exchange, while the co-insertion of I/Cl anions was not observed due to the drastic structural changes and lattice mismatches. Kamat et al.\cite{141} studied the transition from CsPbBr$_3$ film to CsPbI$_3$ film in a heated PbI$_2$ solution (\textbf{Figure 11A}). They found that the anion exchange reaction had a strong dependence on temperature according to the Arrhenius relationship. The fitted activation energy was 44±6 kJ mol$^{-1}$, indicating the apparent activation energy was required to expand the lattice to fulfill iodide anion substitution. Buecheler et al.\cite{142} reported a simple partial ion exchange method to achieve a composite gradient perovskite film by converting MAPbI$_3$ to MAPbI$_3-x$Br$_x$. The reaction was facially completed by spin coating the organic bromide (MABr or FABr) solution on primary absorbers (MAPbI$_3$ or FAPbI$_3$) (\textbf{Figure 11B}). The resulting Br concentration gradient over the entire thickness induced a bandgap grading that could facilitate charge collection and reduce interface recombination. Similarly, Zou et al.\cite{143} obtained a CH$_3$NH$_3$PbI$_3-x$Br$_x$ thin film by dripping MABr solution onto parent CH$_3$NH$_3$PbI$_3$ thin film, the obtained mixed halogen perovskite film exhibited increased grain size, prolonged charge carrier lifetime, and higher PCE of solar cells. Park et al.\cite{144} used FAPF$_6$ solution to convert FA$_{0.88}$Cs$_{0.12}$PbI$_3$ to FA$_{0.88}$Cs$_{0.12}$PbI$_{3-x}$(PF$_6$)$_x$. Due to the lattice expansion and narrowed bandgap resulting from the larger volume of PF$_6^-$, they found that the anion exchange could reduce the defect density, increase the carrier life, and improve the photovoltaic performance.

Besides of halide anions, cations exchange can also be facilely carried out for bulk perovskites. Snaith et al.\cite{145} immersed the MAPbI$_3$ or FAPbI$_3$ in solutions of FAI or MAI, and adjusted the band gap of the film from 1.57 to 1.48 eV through cation exchange. By applying this technology to a solar cell device, the performance of a single cation device could be improved. Pang et al.\cite{146} reported a methylammonium-mediation approach by simple addition of excess MA$^+$ cations (MACl was used here) into a stoichiometric perovskite precursor solution (\textbf{Figure 11C}). Since FA-rich organic-inorganic hybrid perovskites are more thermodynamically stable phase at high temperature, spontaneous ion exchange reaction allowed the redistribution/movement of the cations and transformed into MA/FA mixed composition. This process could avoid the formation of the undesirable “yellow” δ-phase because the initially formed MA$^+$-rich perovskite did not energetically favor its existence of non-perovskite δ-phase. You et al.\cite{147} reacted CsPbI$_3$ with FAI in N-methylimidazole to obtain
a Cs$_x$FA$_{1-x}$PbI$_3$ film, in which the N-methylimidazole could improve the crystallization process and result into increased grain size. Dai et al. [148] introduced mixed-cation post-substitution to realize “partial nucleation” before annealing, which effectively promoted the analogous ion-exchange process on a pre-deposited intermediate film via intramolecular cation substitution. The defects density was substantially reduced in the final FA$_{0.92}$MA$_{0.08}$PbI$_3$ perovskite because the analogous molecular structure initiated ion exchange and advanced partial nucleation in the post-processed perovskite film. Moreover, heterogeneous perovskite structure with different dimensions can be formed through cation exchange. Xu et al. [149] realized the transformation from FAPbI$_3$ to (FAPbI$_3$)$_{1-x}$(MAPbBr$_3$)$_x$ by using the dual ion exchange method (DIE). Excessive MA$^+$ and Br$^-$ ions could fill the vacancies of the grain boundary firstly, and then exchanged with FA$^+$ and I$^-$ uniformly. Due to high crystallinity and passivation of the grain boundaries, the perovskite solar cells prepared by the DIE method had reliable reproducibility and impressive PCE for solar cells. All-inorganic perovskites generally have higher stability than organic-inorganic hybrid perovskites. Qi et al. [150] immersed FAPbI$_3$ film the film in a CH$_3$COOCs solution to obtain a Cs$_x$FA$_{1-x}$PbI$_3$ film (Figure 11D). With a Cs$_{0.07}$FA$_{0.93}$PbI$_3$ composition, the improved PCE as well as device stability could be found due to the increased grain size and stability of the perovskite phase. Zaban et al. [151] made Cs$^+$ incorporation by directly dipping the MAPbI$_3$ film in the CsI isopropanol solution. With incrementally replacing MA$^+$ in a time-resolved dipping process, the film exhibited a discontinuity during the conversion. Although small amounts of Cs$^+$ were incorporated into the structure, the Cs content approached a limitation after a few minutes and grains of δ-CsPbI$_3$ occurred, indicating a substitution limit. Since metallic cations have a much higher active energy in comparison to the others in perovskite lattice, there is few work reported for metallic cation exchange in bulk halide perovskite. Ginger et al. [98] converted the FASnI$_3$ film into FASn$_x$Pb$_{1-x}$I$_3$ or FAPbI$_3$ depending on immersing the parent FASnI$_3$ in a hot trioctylphosphine solution with a large excessive concentration of PbI$_2$ for 72 hours. This work provided strong evidence for long-time scale mobility of the B-site metallic cations in perovskites, but it also indicated the centered metal cation could not be exempt from ionic motion under some harsh conditions.

On account of different reaction conditions, gaseous and solid reaction could also be employed for ion exchange bulk halide perovskites. Karunadasa et al. [152] proved that halogen gas could be used to exchange halide composition of MAPbX$_3$ and produce some gas by-products only. Padture et al. [153] exposed as-synthesized MAPbI$_3$ films to FA
gas at 150°C leading to a rapid displacement of the MA\(^+\) cations by FA\(^+\) cations in the perovskite structure, and the microstructural morphology could be well preserved. Kwok et al.\[154\] realized the mutual conversion between MAPbI\(_3\) and MAPbBr\(_3\) with the vapor of MABr or MAI. It was found that gaseous anion exchange would not cause lattice transformation, morphological reconstruction as well as any significant defects. Song et al.\[155\] reacted MAPbBr\(_3\) with MAI gas in a chemical vapor deposition (CVD) tube for pursuing anion exchange. The bandgap of the perovskite film moved in the region between 2.25 and 1.6 eV depending on the mixed halide components. Choi et al.\[156\] put the MAPbI\(_3\) film in a concentrated HBr circumstance, where HBr volatilized and reacted with oxygen to form Br\(_2\). The anion exchange would happen along with the reaction between Br\(_2\) and MAPbI\(_3\), and the obtained MAPbI\(_3-x\)Br\(_x\) with Br concentration gradient possessed accelerated hole extraction and enhanced lifetime (Figure 12A). Jiang et al.\[157\] converted the HASnI\(_3\) film into MASnI\(_3\) in a methylamine (MA) atmosphere. This process increased the grain size and crystallinity. During the conversion process, hydrazine released from the film could effectively inhibit harmful oxidation. Recently, Kamat et al.\[63\] clamped two MAPbBr\(_3\) and MAPbI\(_3\) films to each other and kept them at 100°C for 21 hours to achieve uniformity (Figure 12B). It is found that the ion diffusion rate and temperature followed the Arrhenius equation, and the activation energy of 51 kJ mol\(^{-1}\) was obtained by plot fitting.

Except for composition variation, ion exchange could also be achieved by transformation of perovskite lattice. Jen et al.\[158\] dipped PEA\(_2\)PbBr\(_4\) film in MAI iso-propanol solution (Figure 13A), the low-dimensional PEA\(_2\)PbBr\(_4\) could be converted into MAPbBr\(_3\) through ion exchange. Thanks to the preferential growth of PEA\(_2\)PbBr\(_4\) in the [001] direction, the exchanged MAPbBr\(_3\) showed a higher orientation. This result elucidated the potential of ion exchange in conjuction with a 2D perovskite
growth template as a new processing method to fabricate high-quality perovskite films for optoelectronic applications. Zhao et al.\[159\] found Cl/I and H/MA(MA) ion exchange reactions could induce the rapid transformation of HMA$_{1-x}$FA$_x$Pb$_3$I$_5$Cl perovskite-like films into MA$_3$Pb$_3$I$_5$ films. However, the HMA$_{1-x}$FA$_x$Pb$_3$I$_5$ structure was not stable and quickly transformed into a three-dimensional structure, so the structural evolution was not studied at this stage.

Single crystal is another typical existence of bulk perovskites. As is known to us all, single crystals have no grain boundaries, so perovskite single crystals show enhanced intrinsic semiconductor properties due to the slight influence of surface and minimal grain boundary defects. Compared with polycrystalline materials, single crystals have greatly improved carrier mobility and carrier diffusion length, and have been widely used in optoelectronic devices. Kuang et al.\[160\] fabricated halide-gradient heterojunction via a post gaseous anion exchange process. This graded halide distribution not only extended the absorption range to a panchromatic spectrum, but also expedited the interior carrier separation along with the hole transfer process. Tao et al.\[161\] conversed NH$_2$(CH$_3$)$_2$PbI$_3$ single crystal to MAPbI$_3$ single crystal with gaseous MA. The optical band gap of obtained single crystal was significant decrease. Meanwhile, they designed this novel strategy to form hybrid perovskite single crystals with a desired morphology. So et al.\[162\] synthesized the MAPbBr$_3$ single crystal by inverse solubility method. The MAPbBr$_3$ single crystal was immersed in a MAPbI$_3$ solution to form a MAPbI$_3$ epitaxial layer. The study found that the thickness of the iodine-rich surface layer increased with the increase of the immersion time (Figure 13B), and finally caused changes in photoluminescence and absorption spectrum. This is the first report of the formation of high-quality single crystal heterojunctions in organic halide perovskite materials. Similarly, Etgar et al.\[163\] discovered that methylammonium lead bromide macroscale perovskite single crystals may exchange ions with MAI/MACl ethanol solution of while maintaining their original morphology. The work provided first evidence of halide exchange reactions in macroscale perovskite single crystals.

8 | SUMMARY AND PERSPECTIVE

This review summarized the general background for ion exchange in halide perovskites, including the structural factors, ion exchange mechanism and reaction conditions. The unique lattice characteristics of halide perovskite make them highly compatible with the versatile ion exchange methods. Due to the particular energy band structure, the optical properties of halide perovskites can be easily altered by atomic substitution, especially for metallic B-site cation and halide X-site anion. In addition, the ion exchange can also improve the crystalline stability, reduce the toxicity (e.g., substitution of non-lead divalent metal), and so on. Then we discussed the ion exchange in terms of different dimensions, from nanoscale (0D, 1D, and 2D) to bulk size (3D). Depending on the strong quantum confinement effect, the halide perovskite in nanoscale usually possesses excellent luminescent properties, which can be facely modulated by ion exchange. Moreover, with extremely large specific surface area and ligands encapsulation, the halide perovskite nanocrystals can undergo various methods to achieve precise either cation or anion exchange, so that their emission characteristics can almost cover the whole visible region with a narrow FWHM. Regarding the bulk size crystals, drastically decreased specific surface area slows the exchange reaction dynamics, and meanwhile, inward energy barrier for exchanged ion diffusion also impedes the substitution progress. Hence, in comparison with low-dimensional scales, the ion exchange for bulk halide perovskites usually suffers from the relative poor controllability, slow exchange dynamic, harsh reaction conditions or incomplete exchange extent. Besides, morphology variation is another factor of importance needs to be concerned, since the morphology of halide perovskite plays a crucial role for the device applications.

To date, ion exchange has been successfully utilized to modulate the optoelectronic properties and optimize the device performance of halide perovskites. However, there are several open issues to be addressed so that we can further expand the ion exchange strategy to develop the applications of halide perovskites. (1) Precise ion exchange control. Ion exchange has achieved great success for nanomaterials because of their extreme specific surface area and unique chemical configuration, however, ion exchange in bulk structure usually suffers from restrained controllability because of the insufficient grain boundaries and thermodynamic/kinetic issues, especially for single crystals. It needs to optimize the ion exchange reactivity and lower the diffusion energy barrier so as to achieve fast, complete, and controllable ion exchange in bulk structures. (2) New ion exchange precursors. On the one hand, ligands assistance is solely available for the nanocrystals, while most of the perovskite precursors can only be dissolved in polar solvents, which are apt to deteriorate the morphology of bulk perovskites. On the other hand, regarding the structural diversity in halide perovskite lattice, it will be possible to make a wide variety of novel halide perovskite constructs by ion exchange with other compatible ions, such as complex heterostructures, metastable phases, and hitherto undiscovered compositions. (3) Definite ion exchange mechanisms.
Different ionic precursors defined the distinct ion exchange mechanisms. The mechanism illustration of ion exchange in halide perovskites still stay in the resultant observations rather than the thermodynamics and kinetics analysis. The in-depth interpretation can help further precisely control the ion exchange reactions in halide perovskites towards the designed compositions or crystalline structures. Further study in this field should be continued to build the library of ion exchange for halide perovskites, making each resultant product with given composition and crystallography clearly refer to the corresponding ion exchange precursors, reaction conditions and other factors. With these advances, ion exchange can broaden the realm of halide perovskite in diverse applications.

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