High-quality formamidinium lead iodide (FAPbI₃) perovskite thin films are fabricated via organic cation exchange. With ammonia lead iodide (NH₄PbI₃) as the starting material, the NH₄⁺ in NH₄PbI₃ could be gradually substituted by FA⁺ in formamidine acetate (FA-Ac) and simultaneously transformed to the pure phase α-FAPbI₃ at elevated temperature.

In recent years, perovskite solar cells have attracted tremendous attention due to its increasing light-to-electricity conversion efficiency. The efficiency record has been continuously broken, rocketing from 3.81% in 2009 (CH₃NH₃PbI₃ as the sensitizer) to 21.0% by the end of 2015 (composite perovskite as the active layer).¹² CH₃NH₃PbI₃ (MAPbI₃) is the pioneering material and plenty of deposition methods have been developed, such as the typical one-step solution deposition,³ sequential deposition,⁴ and other derivative techniques.⁵–¹⁰ Almost all these methods start with lead halide (PbX₂) and methylammonium iodide (MAI) as the precursors.¹¹ In comparison to MAPbI₃, the more recently developed FAPbI₃ perovskite is less studied. The preparation of the high-quality black α-FAPbI₃ perovskite film is still a challenge, because the yellow δ-FAPbI₃ non-perovskite polymorph phase formed from one-step solution processing at room temperature is very hard to remove. The unique crystal structure character of FAPbI₃ is attributed to the larger ion size of FA⁺ (the ionic radii of FA⁺ and MA⁺ are 2.79 Å and 2.70 Å, respectively) compared to MA⁺.¹² Theoretically, the yellow δ-FAPbI₃ non-perovskite polymorph phase can transform to the photoactive black α-FAPbI₃ phase at elevated temperature (＞140 °C). Actually, it is not easy to for δ-FAPbI₃ to fully transform to α-FAPbI₃ when it fills the scaffold layer probably because of the stress from the substrate.¹³

Among all the solution deposition methods, the sequential deposition method can directly lead to the α-FAPbI₃ phase, but it always produces a large surface roughness because of the volume expansion behaviour and also results in the formation of some unreacted PbI₂ residues,¹⁴ which dramatically decrease the stability of the devices.¹⁵ The recently developed intramolecular exchange strategy by replacing the dimethylsulfoxide (DMSO) molecule with formamidinium iodide (FAI) from the DMSO–PbI₂ complex can directly produce full coverage α-FAPbI₃ films,² implying that molecule or even ion exchange may be a promising direction for the direct synthesis of α-FAPbI₃ without the formation of the yellow δ-FAPbI₃ non-perovskite polymorph.

In this communication, we presented an organic cation exchange method to directly grow α-FAPbI₃ perovskite films, using NH₄PbI₃ and FA-Ac as precursors using the CVD technique. NH₄PbI₃ is selected as the precursor for its high solubility in N,N-dimethylformamide (DMF). The organic cation exchange process is schematically depicted in Fig. 1. An equimolar amount of PbI₂ and NH₄I was firstly dissolved in DMF. Then the precursors were spin-coated onto the as-prepared substrate. These as-obtained films were put into the upper center of the CVD tube furnace, while FA-Ac was placed just under the films. Then the quartz tube was evacuated to under 10⁻² Pa, and at the same time heated up to 160 °C. The black α-FAPbI₃ polymorph phase was obtained during the exchange process between FA⁺ and NH₄⁺. NH₄Ac as the product of cation exchange is more volatile than FA-Ac, which is beneficial for the occurrence of the cation exchange.

The crystal structure of the NH₄PbI₃ has been confirmed by X-ray diffraction (XRD) measurements. Fig. 2A shows the indexed XRD pattern deposited on the FTO/compact

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**Fig. 1** Schematic illustration of the proposed cation exchange process.
The structure of $\alpha$-FAPbI$_3$ was confirmed by XRD and UV-vis absorption measurements. All the peaks are in good agreement with those reported for $\alpha$-FAPbI$_3$. It shows that the as-prepared $\alpha$-FAPbI$_3$ film has a very strong (111) orientation diffraction peak at 13.8° in comparison with the $\alpha$-FAPbI$_3$ powder sample. The UV-vis absorption spectra of the NH$_4$PbI$_3$ film and the film after the cation exchange process are presented in Fig. 3. They show the total absorption in the visible spectral range for the film after the reaction. The linear fits of the absorption edge of the as-synthesized NH$_4$PbI$_3$ has the lattice parameters of $a = 10.308$ Å, $b = 4.378$ Å, and $c = 17.281$ Å, with the space group of $Pmn2_1$, which is in good agreement with the reported results.

In order to gain insight into the cation exchange process, Fourier transform infrared spectroscopy (FTIR) was used to investigate the as-obtained film with different reaction times (Fig. 4A). No new stretching vibration peak of Ac$^-$ (1540–1620 cm$^{-1}$) during the whole reaction process was observed, which indicates that the Ac$^-$ could not insert into the film and the cation exchange probably happens only on the film surface. We can see that a strong stretching vibration of C–N from FA$^+$ appears at 1712 cm$^{-1}$ when the reaction proceeds for 20 min. At the same time, two other peaks at 3267 cm$^{-1}$ and 3401 cm$^{-1}$ appear, which belong to the stretching vibrations of N–H for FA$^+$. In addition, the stretching vibration of N–H for NH$_4^+$ at 3150 cm$^{-1}$ almost disappears at 40 min. This FTIR spectrum is similar to that of the standard FAPbI$_3$ perovskite film. The absorption peaks indicate that the cation exchange process was complete at ~40 min and no more FA$^+$ could be inserted into the starting film by extending the reaction time.

To clearly check the gradual change of composition during the ion exchange reaction, a thicker NH$_4$PbI$_3$ film was deposited for the cross-sectional measurements. The energy-dispersive X-ray (EDX) spectra of the film after the reaction proceeded for 10 min are shown in Fig. 4B. Two elements which change more obviously are carbon and iodine. There is no carbon in the NH$_4$PbI$_3$ precursor film; therefore, the appearance of carbon is attributed to the replacement of NH$_4^+$ with FA$^+$. The high concentration of FA$^+$ near the surface further indicates that the substitution of NH$_4^+$ with FA$^+$ occurs at the film surface. Compared with the carbon element, the opposite trend of iodine in the film is because of the relatively high iodine concentration in NH$_4$PbI$_3$ compared with that in FAPbI$_3$. Based on the above analysis, we can surmise that the cation exchange between FA$^+$ and NH$_4^+$ occurs at the film surface, then the FA$^+$ ions could diffuse inside and the NH$_4^+$ ions diffuse to the surface and sequentially exchange with FA$^+$. The inside diffusion and surface ion exchange are carried out simultaneously until all the NH$_4^+$ ions are exchanged with FA$^+$ ions.

Solar cells based on the as-prepared $\alpha$-FAPbI$_3$ were constructed using mp-TiO$_2$ as the electron transport layer and 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spiro-biofluorine (spiro-OMeTAD) as the hole transport layer (Fig. 5A). Dense, uniform and black films are obtained at 160 °C for a reaction time of 60 min as can be seen from the scanning electron microscopy (SEM) image in Fig. 5B. The AFM topographical image...
(20 × 20 μm²) of the z-FAPbI₃ reveals a root mean square (RMS) roughness of approximately 36 nm (Fig. 5C). The photocurrent density as a function of bias voltage is measured under standard AM 1.5 sunlight at a humidity of about 30%. Fig. 5D shows the values of the champion device with the reverse scanning direction (from the open-circuit voltage ($V_{oc}$) to the short-circuit current ($J_{sc}$)) and forward scanning direction (from $J_{sc}$ to $V_{oc}$). The device exhibits an efficiency of 12.4% with no hysteresis. The statistics of PCEs are presented in Fig. S1 (ESI†), showing the high reproducibility of the cation exchange method. For comparison, the FAPbI₃ and MAPbI₃ devices are also fabricated and measured as shown in Fig. S2 and Table S1 (ESI†), indicating that the proposed cation exchange method is a viable approach towards preparation of high-quality FAPbI₃ perovskite films. Other than the extended light absorbance range, the z-FAPbI₃ film also delivers an improved thermal stability. Fig. 6 shows the thermal stability comparison between the z-FAPbI₃ and MAPbI₃ films. Both of the films were obtained using the CVD method (the preparation procedure of the films of MAPbI₃ can be seen in the ESI†). A series of z-FAPbI₃ and MAPbI₃ films (without HTM and electrodes) were heated at 140 °C in an argon-filled glove box for 1–7 h. Then the corresponding devices were assembled and studied. The PCEs of z-FAPbI₃-based cells decreased only ca. 5% when the perovskite film was heated to 140 °C for up to 7 h, while the MAPbI₃-based devices decrease to ca. 11% after heating for 4 h and to zero after heating for 6 h. As shown in Fig. S3 (ESI†), the MAPbI₃ phase begins to decay after heating for 4 h and completely decomposed after heating for 7 h. However, the colour of the z-FAPbI₃ film stays almost the same even after heating for 7 h. The SEM images in Fig. 6(B, C) and Fig. S4 (ESI†) show the change of the morphology of the films before and after long-time heating treatment. In contrast to the stable z-FAPbI₃, the MAPbI₃ films obviously shrink after heating for 7 h.

Moreover, the presented cation exchange method was also performed on HPbI₃ and MAPbI₃ films. HPbI₃ was prepared according to a reported procedure, 22 and the preparation procedure of MAPbI₃ films can be seen in the ESI†. The XRD patterns (Fig. S3, ESI†) and the UV-vis absorption spectra (Fig. S6, ESI†) strongly confirm the successful fabrication of the FAPbI₃ films.

In conclusion, we have demonstrated an organic cation exchange concept for the preparation of high-quality z-FAPbI₃ films using the CVD method. The PCE of the champion device was 12.4% based on the mesoscopic structure with no hysteresis. We also demonstrated that this cation exchange concept could also be used to prepare z-FAPbI₃ thin films by replacing H⁺ and MA⁺ in HPbI₃ and MAPbI₃ with FA⁺. This concept will be an alternative route for the development of highly efficient FAPbI₃ solar cells.

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Notes and references