Intercalated formation of two-dimensional and multi-layered perovskites in organic thin films

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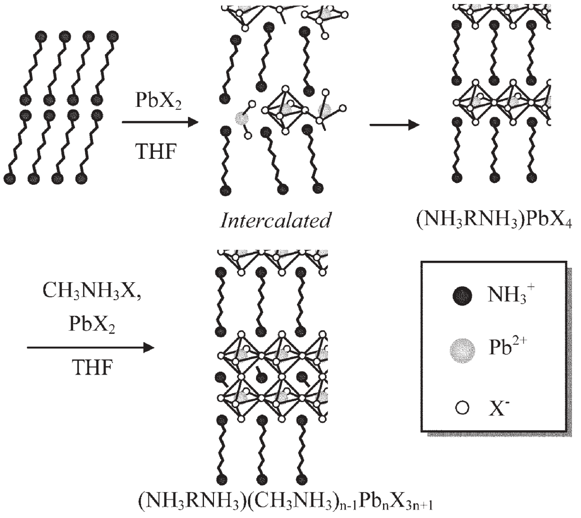
Two-dimensional and multi-layered perovskites, $[NH_3(CH_2)_{12}NH_3]PbBr_4$ and $[NH_3(CH_2)_{12}NH_3](CH_3NH_3)_{n-1}Pb_nBr_{3n+1}$, with a quantum confinement effect have been naturally formed by intercalating lead bromide into organic alkyldiammonium bromide frameworks.

A great deal of attention has been paid to the preparation and characterization of organic–inorganic layered perovskites $(NH_3RNH_3)PbX_4$ (R = alkyl; X = halogen) because of their unique electrical and optical properties, along with their enormous flexibility in construction of quantum confinement structures.[1,2] These compounds naturally form a quantum-well structure, in which a two-dimensional lead halide semiconductor layer and an organic ammonium layer are alternately stacked. Due to the low dimensionality of the inorganic semiconductor region, the stable excitons have large binding energy and oscillator strength resulting from the quantum confinement effect and the enhanced dielectric confinement effect. Such properties enable strong excitonic absorption and emission even at room temperature.[3,4]

The desired optical and electrical applications require simple and proper processing to obtain thin films with controllable thickness and uniformity. Solution chemistry techniques such as crystal growth and spin-coating techniques are predominantly employed to prepare the crystals and well-ordered thin films for fundamental research. However, these solution methods are not always suitable to fabricate various perovskites with novel functional organic materials and/or other metal halides due to problems with solubility, high boiling temperature, and chemical stability in the solution state.[5,6]

The intercalation method has been known as a versatile tool to synthesize organic–inorganic layered compounds.[7] Recently, Mitzi *et al.* reported intercalated hybrid perovskites stabilized by fluoroaryl–aryl interactions.[8] Guest molecules intercalate at a site sandwiched between aryl or fluoroaryl groups of arylamines within the crystals. In this work, we also attempted to prepare ultra-thin films of the two-dimensional layered perovskites by two-step procedures involving conventional spin-coating and intercalation of lead bromide into organic ammonium framework films (Scheme 1). We selected alkyldiammonium compounds as the organic framework to be prepared *via* spin-coating. These alkyldiamines themselves form a bilayer structure; they are weakly interacting with each other through hydrogen bonding and hydrophobic interactions. Due to the flexibility and strong self-organization of these materials and structures, the interlayer ammonium ions act as a host moiety for molecular polar guest species by means of intercalation. We report herein a novel intercalation method for preparing organic–inorganic hybrid thin films of perovskites with various halides and multilayered inorganic sheets that are inaccessible by conventional methods.



Scheme 1 Schematic presentation of a self-intercalation method.

1,12-Dodecanediammonium dibromide $NH_3Br(CH_2)_{12}NH_3Br$ was used as the organic species. A saturated methanol solution of $NH_3Br(CH_2)_{12}NH_3Br$ was used for preparing spin-coated films. Hydrophilic glass was used as a substrate. Spin-coating was performed in a clean booth, and the spin rate was electronically controlled to 1000 rpm for the first step and 2000 rpm for the second step. The intercalation solution of lead bromide was obtained by dissolving 45 mg of $PbBr_2$ in 50 ml of dry tetrahydrofuran (THF). The selections of solvent and alkyldiammonium compounds were critical for fabricating high-quality intercalated films of organic–inorganic perovskites. In most cases, a $NH_3Br(CH_2)_{12}NH_3Br$ spin-coated film was immersed into a $PbBr_2$ solution for 10 min and then rinsed with fresh THF. These thin films were characterized by X-ray diffraction, atomic force microscopy (AFM), UV-Vis absorption, and photoluminescence spectroscopies.

Fig. 1 shows the X-ray diffraction patterns of a spin-coated film of $NH_3Br(CH_2)_{12}NH_3Br$ (a), and of intercalated films immersed in a $PbBr_2$ solution for 10 s (b), and 10 min (c), respectively. The $NH_3Br(CH_2)_{12}NH_3Br$ spin-coated film showed an X-ray diffraction peak at 4.6°. Since dodecyldiammonium ions have only weak

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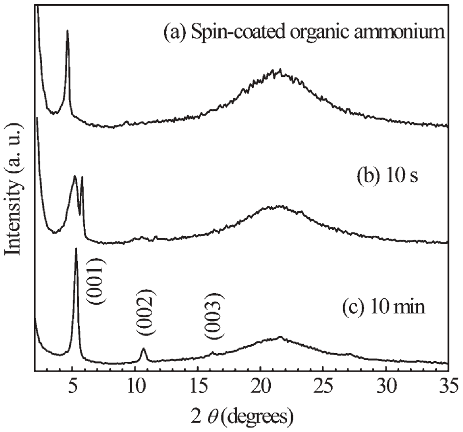

Fig. 1 X-Ray diffraction patterns for (a) a spin-coated dodecyldiammonium bromide film, and for intercalated $[NH_3(CH_2)_{12}NH_3]PbBr_4$ films prepared by dipping a $NH_3Br(CH_2)_{12}NH_3Br$ film into a $PbBr_2$ solution for (b) 10 s and (c) 10 min, respectively.

molecular interactions, the spin-coated $NH_3Br(CH_2)_{12}NH_3Br$ film appears to be less organized with *c*-axis orientation, as indicated by the absence of higher order diffraction. When the $NH_3Br(CH_2)_{12}NH_3Br$ film was dipped into a $PbBr_2$ solution, the X-ray diffraction patterns dramatically changed, as shown in Fig. 1(b) and (c). After 10 min dipping, a new sharp X-ray diffraction peak developed at 5.3° (d = 16.7 Å) with higher order diffraction peaks, while no peak attributable to the original organic framework was observed. The enlargement of *d*-spacing values is also consistent with that of the $[NH_3(CH_2)_{12}NH_3]PbBr_4$ framework prepared by the conventional spin-coating method. Thus, the intercalation of lead halide and the formation of the perovskite framework in these intercalated films have been proved.

The morphology and microstructure of the intercalated $[NH_3(CH_2)_{12}NH_3]PbBr_4$ films were investigated by AFM observations. The surface of the spin-coated $NH_3Br(CH_2)_{12}NH_3Br$ film had needle-like crystals evenly distributed over the film surface, as shown in Fig. 2(a). After the film was dipped in a $PbBr_2$ solution, the needle-like crystals completely disappeared, and smaller and denser plate-like crystals appeared. The plate-like crystal grains are oriented almost parallel to the film surface and finally form polycrystalline sheets. These AFM observations and X-ray diffraction data clearly show that $NH_3Br(CH_2)_{12}NH_3Br$ molecules in the organic framework completely react with $PbBr_2$ molecules which had penetrated from the solution, and that the reacted organic–inorganic hybrid is self-reorganized to form well-defined perovskite crystals. This self-reorganization mostly reflects the highly crystalline and self-organized nature of $(NH_3RNH_3)PbX_4$. The guest molecule penetration and the reorganization are complete within minutes whilst typical crystallizations of organic materials need several days. From our detailed studies, it was proved that at least 5 min intercalation time is necessary for all organic ammonium films examined, to be completely converted into the perovskite structure.

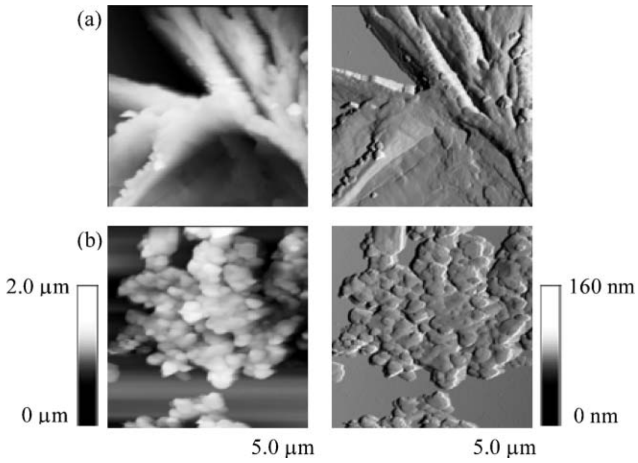

Fig. 2 AFM images: The left frames are topology images and the right frames are amplitude images for a $NH_3Br(CH_2)_{12}NH_3Br$ spin-coated film (a) before and (b) after being dipped into a $PbBr_2$ solution for 10 min.

Results of UV-Vis absorption measurements also supported the construction of organic–inorganic layered perovskites by using the self-intercalation method. Fig. 3(a) and (b) show the UV-Vis absorption spectra of a $NH_3Br(CH_2)_{12}NH_3Br$ spin-coated film before and after it was dipped into a $PbBr_2$ solution for 10 min. Although there is no prominent peak for the spin-coated alkylammonium film in the visible region, the intercalated film exhibited a characteristic exciton peak at 400 nm. The intercalated film showed a strong and sharp photoluminescence at 404 nm even at room temperature, regardless of the excitation wavelength. Thus, we have found that the intercalation process easily provides natural quantum-well systems, in which excitons are confined in the inorganic layers sandwiched with organic barrier layers.

By using the self-intercalation method, we can also prepare layered perovskite compounds: $[NH_3(CH_2)_{12}NH_3]PbCl_4$, $[NH_3(CH_2)_2NH_3]PbBr_4$ and $[NH_3(CH_2)_{12}NH_3](CH_3NH_3)_{n-1}Pb_nBr_{3n+1}$, which are difficult to obtain from conventional methods because of low self-assembling and solubility. The inorganic species successfully diffused and reacted to form the perovskite structures because we had constructed the frameworks of these organic components in advance. In the case of $[NH_3(CH_2)_{12}NH_3](CH_3NH_3)_{n-1}Pb_nBr_{3n+1}$, the intercalated $[NH_3(CH_2)_{12}NH_3]PbBr_4$ film was simply dipped into a mixed THF solution of $PbBr_2$ and methylamine for 10–70 min. Dipping time can be used to control the nature of the confined inorganic

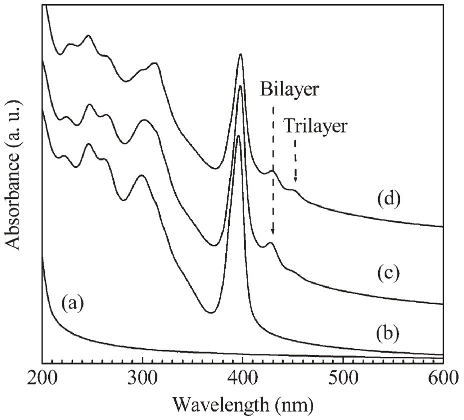

Fig. 3 Absorption spectra of a $NH_3Br(CH_2)_{12}NH_3Br$ spin-coated film (a) before and (b) after being dipped into a $PbBr_2$ solution for 10 min and for a film additionally dipped into a mixed solution of $PbBr_2$ and methylamine for (c) 20 min and (d) 30 min.

perovskite layer. The characteristic absorption bands that resulted from bi- and tri-layers of $PbBr_4$ were successfully achieved after a critical dipping time (20 min for the bilayer and 30 min for the trilayer), as shown in Fig. 3(c) and (d), respectively.

In this work, we successfully fabricated ultra-thin films of the two-dimensional layered perovskites $(NH_3RNH_3)PbBr_4$ by the self-intercalation of lead halide into an organic ammonium framework. This solution technique enables not only simple processing of organic–inorganic hybrid materials but also tailoring of the quantum confinement structures. From the standpoint of promoting such a simple and versatile process, further investigations are currently underway.

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