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Fabrication of two-dimensional layered perovskite $[NH_3(CH_2)_{12}NH_3]PbX_4$ thin films using a self-assembly method

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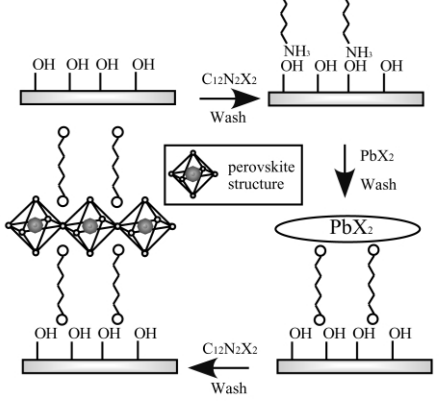
Ultra-thin films of the two-dimensional layered perovskites $[NH_3(CH_2)_{12}NH_3]PbX_4$ (X = Br, I) with the quantum confinement effect have been fabricated by a convenient self-assembly method.

The two-dimensional layered perovskites $(RNH_3)_2MX_4$ (R = alkyl, phenethyl; M = metal; X = halogen) have recently attracted much attention due to their unique electrical and optical properties, along with enormous flexibility in the structure.[1,2] These compounds naturally form a quantum-well structure, in which a two-dimensional semiconductor layer and an organic ammonium layer are alternately stacked.[3,4] Owing to the low-dimensionality of the inorganic semiconductor region, stable excitons have a large binding energy and oscillator strength resulting from the quantum confinement effect and the enhanced dielectric confinement effect, which enables strong excitonic absorption and emission even at room temperature.[5–7] The fabrication of high quality thin films of $(RNH_3)_2MX_4$ is very important from the viewpoint of optical applications such as light-emitting devices and third-order nonlinear optics. Spin-coating, vacuum evaporation, and Langmuir–Blodgett (LB) techniques are employed to prepare well-ordered thin films of these organic–inorganic perovskites.[8–10] However, it is difficult for the spin-coating method to control uniformity and thickness over large areas. The fabrication of various perovskites using different organic molecules is also limited because of the poor solubility of lead halides. In addition, it is difficult for the vacuum evaporation and LB techniques to find empirical conditions of the equipment and processes.

In this work, we tried to prepare the nanostructured films of organic–inorganic perovskites using a self-assembly method. The self-assembly method is based on alternate dipping in solutions of alkyldication halides and lead halides with washing steps to remove excess reactants, as shown in Scheme 1. The benefits of this method are that it is possible to control the thickness in nano order and to construct heterostructures using different organic salts and metal halides.

1,12-Dodecanediammonium dihalides $XNH_3(CH_2)_{12}NH_3X$ (abbreviated $C_{12}N_2X_2$; X = Br, I) were used as organic moieties. While a variety of alkyldiammonium dihalides were examined, $C_{12}N_2X_2$ has been shown to work well for many alkyldiammonium dihalides and alkylammonium halides. The solutions of organic diammonium halides were prepared by dissolving 90 mg of purified $C_{12}N_2Br_2$ in 45 ml of tetrahydrofuran (THF) or 114 mg of $C_{12}N_2I_2$ in 48 ml of 1,4-dioxane. The organic solutions were then diluted with water (5 mM). The solutions of lead halides were obtained by dispersing 45 mg of $PbBr_2$ in 50 ml of dry THF or 42 mg of PbI_2 in 50 ml of dry 1,4-dioxane. The selections of solvents (THF and 1,4-dioxane) for dissolving $C_{12}N_2X_2$ and PbX_2 were critical for fabricating high-quality films of the organic–inorganic perovskites by using the self-assembly method. Obtained $[NH_3(CH_2)_{12}NH_3]PbX_4$ films were identified by FT-IR and Inductively Coupled Plasma (ICP) measurements. The FT-IR spectra recorded from a $[NH_3(CH_2)_{12}NH_3]PbBr_4$ film in the range 500–4000 cm^{-1} exhibited feature characteristic IR bands (C–H at 3000–3180 and 1455 cm^{-1}, and N–H at 3430–3500 cm^{-1}) attributed to 1,12-dodecanediammonium ions. The ICP measurements were made for a self-assembly film with 100 layers, and the content of Pb atoms (29.6%) agreed closely with the theoretical value (28.4%).

Quartz substrates were cleaned in a mixed solution of H_2SO_4 and H_2O_2, followed by rinsing with distilled water and methanol. The hydrophilic quartz substrates were first dipped into a $C_{12}N_2Br_2$ solution for 20 min, followed by immersing in a THF/water mixed solution for 5 min to remove excess organic salts. The substrates were subsequently dipped into a $PbBr_2$ solution for 15 min and then rinsed with THF. This procedure was repeated to obtain the required multilayer self-assembly films. The $[NH_3(CH_2)_{12}NH_3]PbI_4$ self-assembly films were similarly prepared from $C_{12}N_2I_2$ and PbI_2 using 1,4-dioxane as solvent. The conditions and procedure described above are essential in order to generate the material quality and uniformity required to observe stable excitons.



Scheme 1 Schematic presentation of the self-assembly method.

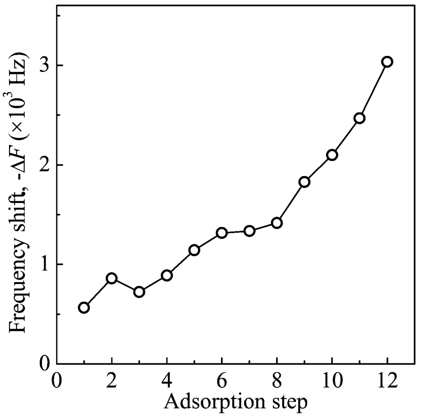


Fig. 1 Averaged QCM frequency shifts due to alternate $C_{12}N_2Br_2$–$PbBr_2$ adsorptions at room temperature by using a self assembly method.

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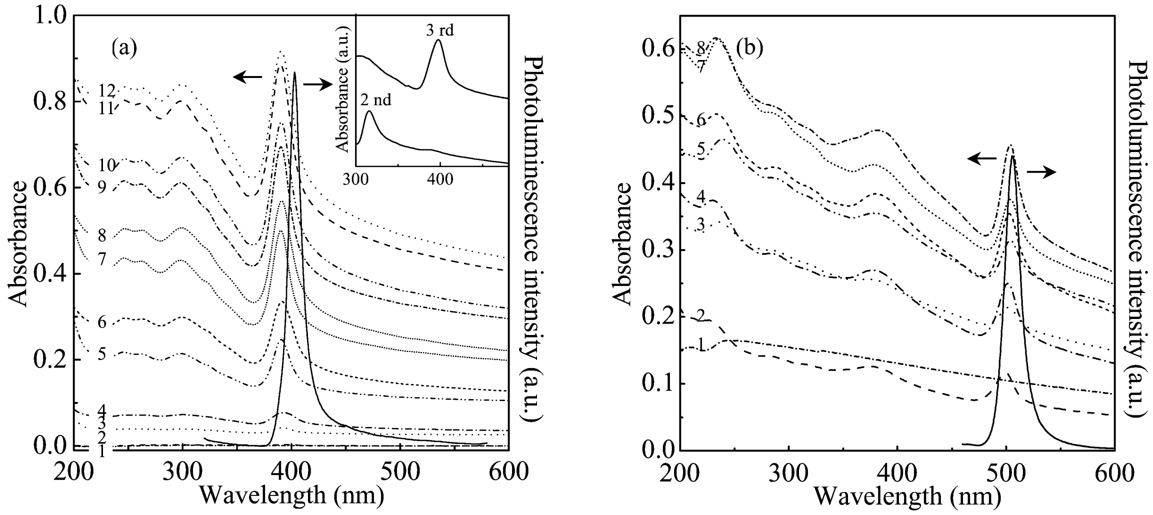

Fig. 2 Room temperature UV-Vis absorption and PL spectra of (a) $[NH_3(CH_2)_{12}NH_3]PbBr_4$ self-assembly film with 12 layers (ex. λ = 300 nm) and (b) $[NH_3(CH_2)_{12}NH_3]PbI_4$ self-assembly film with 8 layers (ex. λ = 380 nm).

The adsorption of each molecule was monitored using a quartz crystal microbalance (QCM).† Fig. 1 shows frequency shifts ($-\Delta F$) of QCM in the successive adsorptions of $C_{12}N_2Br_2$ and $PbBr_2$ layers. The odd-number steps correspond to $C_{12}N_2Br_2$ layers and the even-number steps to $PbBr_2$ layers. After the adsorptions of $C_{12}N_2Br_2$ or $PbBr_2$ layers were saturated, the QCM plate was picked up horizontally to the air phase, and then the ΔF value was measured. A linear increase of the film mass ($-\Delta F$ is proportional to mass) was observed for all the dipping processes. The averaged mass changes were calculated to be Δm = 237 ng cm^{-2} from the averaged ΔF value. The QCM measurements confirmed the highly reproducible and alternate adsorptions on solid substrates resulting from the electrostatic force between organic and inorganic molecules.

Results of X-ray diffraction measurements also supported the construction of the layer-by-layer structure. In both of the self-assembly films, a series of (00*l*) diffraction patterns was observed, indicating that the films are highly oriented with the *c*-axis with respect to the substrate surface. The distance between inorganic layers was estimated to be 17 and 18 Å for $[NH_3(CH_2)_{12}NH_3]PbBr_4$ and $[NH_3(CH_2)_{12}NH_3]PbI_4$ self-assembly films, respectively. This result appears to be the strong proof of the self-organization of layer-by-layer structures.

The fabrication of two-dimensional layered perovskites was confirmed by UV-Vis absorption and photoluminescence (PL) spectroscopies. Fig. 2 shows the UV-Vis absorption and PL spectra of $[NH_3(CH_2)_{12}NH_3]PbBr_4$ and $[NH_3(CH_2)_{12}NH_3]PbI_4$ self-assembly films on quartz substrates. In the second layer of $[NH_3(CH_2)_{12}NH_3]PbBr_4$, an absorption band appeared at 317 nm, which is attributed to lead bromide. In the third layer, the intensity of the absorption band at 317 nm decreased, and a new absorption band appeared at 391 nm. Furthermore, the intensities of absorption bands at 391 nm linearly increased after the fourth layer. The absorption spectra red shifted as the halogen was changed from Br to I. The spectrum features of the $[NH_3(CH_2)_{12}NH_3]PbI_4$ self-assembly films are very similar to those of $[NH_3(CH_2)_{12}NH_3]PbBr_4$. A strong and sharp absorption band was observed at 503 nm. This self-assembly method provides not only the layer-by-layer structures but also the crystallization of PbX_4 perovskites to the ultra-thin films, as shown in Scheme 1.

In addition, the self-assembly film of $[NH_3(CH_2)_{12}NH_3]PbBr_4$ showed a strong and sharp PL at 402 nm even at room temperature. Since the absorption peak is at 391 nm, the PL band overlapped with the absorption band. The PL features of the self-assembly films were independent of the excitation wavelength. The $[NH_3(CH_2)_{12}NH_3]PbI_4$ self-assembly films also exhibited a PL peak at 507 nm. It has been found that these self-assembly films are natural quantum-well systems, in which excitons are confined in the inorganic perovskite layers sandwiched with organic barrier layers.

In this work, we have successfully fabricated the ultra-thin films of the two-dimensional layered perovskites $[NH_3RNH_3]PbX_4$ by the self-assembly method. The organic–inorganic perovskite films are uniform and smooth, and the thickness can be controlled at the nano-meter level. Moreover, they exhibit strong absorption and photoluminescence resulting from stable excitons, which are confined in the layer-by-layer structure of organic and inorganic molecules. This self-assembly technique seems to be promising for the preparation of the low-dimensional materials such as quantum-wires and dots. From the standpoint of such a versatile design, further investigations are currently underway.

Notes and references

† Experimental conditions of QCM: the quartz crystals (8.6 mm diameter, 9 MHz) were covered by vapor deposition of 300 nm thick gold electrodes and were connected to a gain control oscillator. The QCM resonator was coated with 11-mercaptoundecanoic acid. The frequency changes were monitored by a frequency counter (Advantest R5361A). $\Delta F = -2\Delta m F_0{}^2/A(\mu_q\rho_q)^{1/2}$ where ΔF is the measured frequency shift (Hz), F_0 is the fundamental frequency of the QCM (9 MHz), Δm is the mass change (g), A is the electrode area (0.196 cm^2), ρ_q is the density of quartz (2.65 g cm^{-3}), and μ_q is the shear modulus of quartz (2.95 × 10^{11} dyn cm^{-2}).

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