

Formation of PbBr-Based Layered Perovskite Structure Having Poly(thiophene) as an Organic Layer by Soaking Thin Film of Hydrogen Bromide Salt of Poly(3-aminododecylthiophene) in Aqueous Lead Bromide Solution

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(Received November 11, 2002; CL-020958)

When a spin-coated film of hydrogen bromide salt of poly(3-aminododecylthiophene), PC12T·HBr, was soaked in an aqueous solution of PbBr_2 , PbBr-based layered perovskite structure combined with a semiconductor layer of two-dimensional sheets of PbBr_6 octahedra and an organic semiconductor layer of poly(thiophene) was formed.

Lead halide-based layered perovskites, $(\text{RNH}_3)_2\text{PbX}_4$, self-organize an organic-inorganic superlattice structure where an inorganic semiconductor layer of corner-sharing lead halide PbX_6 octahedra and organic ammonium RNH_3 layer are alternately piled up (Figure 1).¹ Owing to their low-dimensional semiconductor structure (quantum-well), they form a stable exciton with a large binding energy of several hundreds meV, and exhibit attractive excitonic properties such as efficient exciton emission, electroluminescence and optical nonlinearity due to the exciton.²⁻⁴

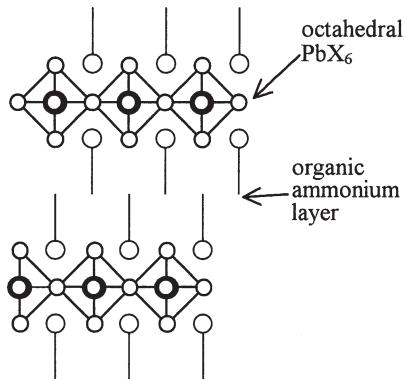


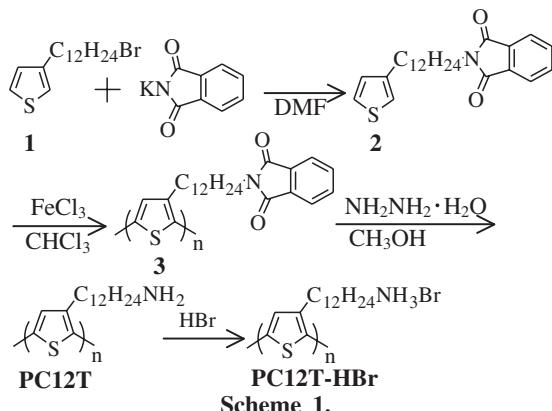
Figure 1. Schematic structure of lead halide-based layered perovskite with alkyl ammonium molecule as an organic layer.

So far, alkyl ammonium molecules, which play only the role of a barrier layer in the layered perovskite superlattice materials, have been employed as an organic layer. In the viewpoint of material design, employment of functionalized organic ammonium molecules is very attractive; one can expect to attain novel functionality combined of inorganic semiconductor and functionalized organic molecules.⁵⁻⁷

Incorporation of π -conjugated polymers into the layered perovskites is an attractive approach to construct new hybrid superlattice materials; the approach provides hybrid superlattice materials combined with properties of organic semiconductor (mechanical flexibility, high optical density, efficient lumines-

cence etc.) and inorganic semiconductor (mechanical and thermal stability, high mobility, magnetism etc.). The hybrid superlattice is expected to apply to electronic devices such as thin film transistor (TFT), solar cell, electroluminescent device and so on. In addition, optical nonlinearity is theoretically predicted to be extremely enhanced by exciton-coupling in hybrid superlattice combined with organic and inorganic semiconductors.⁸ The PbBr-based layered perovskite with π -conjugated polymer as an organic layer is a promising model material of the exciton coupling.

In this letter, we report that PbBr-based layered perovskite structure with poly(thiophene) as an organic layer is formed by soaking thin films of hydrogen bromide salt of poly(3-aminododecylthiophene) in an aqueous lead bromide solution.



Scheme 1.

Synthetic route to PC12T·HBr is shown in Scheme 1. The compound **2** was obtained from the reaction between potassium phthalimide and 3-(12-bromododecyl)thiophene (**1**) which was prepared according to Ref. 9. Then, the compound **2** was polymerized in chloroform by using FeCl_3 as catalyst.¹⁰ Reaction of the obtained polymer (**3**) in methanol with hydrazine monohydrate gave poly(3-aminododecylthiophene), PC12T. Finally, PC12T was treated with aqueous HBr solution to give the hydrogen bromide salt of PC12T (PC12T·HBr).

One of useful techniques to prepare thin films of lead halide-based layered perovskite is spin-coating from the solution in which stoichiometric amounts of lead halide and organic ammonium halide are dissolved. However, stoichiometric mixture of PC12T·HBr and lead bromide was not soluble in conventional solvents. Then, it was not successful to prepare the layered perovskite thin films using the conventional spin-coating technique. Accordingly, we made an attempt to obtain thin films of PbBr-based layered perovskite with poly(thiophene)

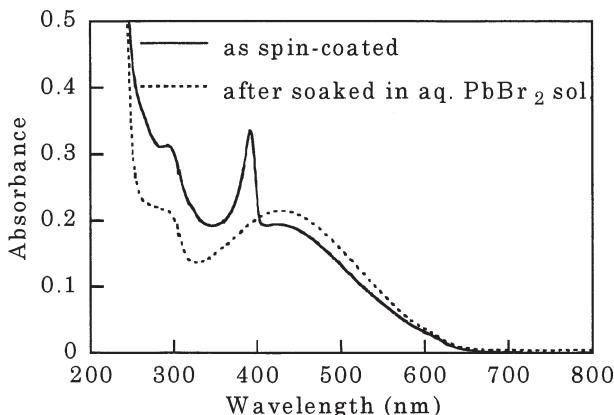


Figure 2. Absorption spectra of thin film of PC12T-HBr: dotted curve, as spin-coated; and solid curve, after soaked in an aqueous PbBr_2 solution.

as an organic layer by the following procedure. First, PC12T-HBr was spin-coated on fused quartz substrates from dimethylformamide solution. Then, the PC12T-HBr films were soaked in a saturated aqueous solution of PbBr_2 . To form layered perovskite structure, the PC12T-HBr films were allowed to stand for more than 10 h in the PbBr_2 solution.

Figure 2 shows absorption spectra of a thin film of PC12T-HBr as spin-coated (broken curve) and after soaked in a PbBr_2 solution (solid curve). After the soaking treatment, the spin-coated film exhibits sharp and intense absorption around 390 nm in addition to the broad absorption due to π -conjugated thiophene sequences in visible region. The sharp absorption corresponds well to the exciton band which is characteristic of PbBr -based layered perovskite. The appearance of the exciton absorption demonstrates that PbBr -based layered perovskite structure was surely formed in the spin-coated film of PC12T-HBr after the soaking treatment.

Figure 3 shows X-ray diffraction profiles of a thin film of PC12T-HBr. In the profile of the spin-coated film, two diffraction peaks corresponding to a layer spacing of 2.0 nm are observed. The diffraction peaks suggest that a layer structure was formed in

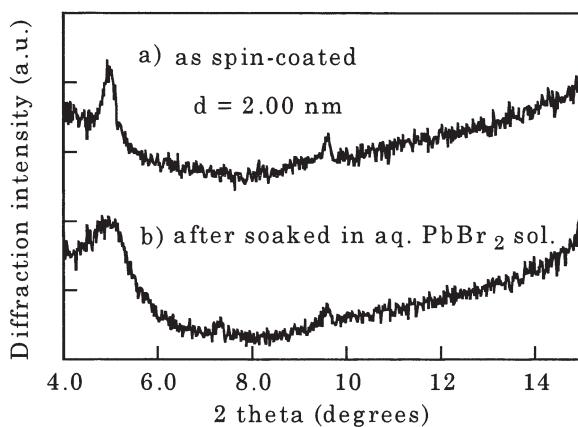


Figure 3. X-ray diffraction profiles of thin film of PC12T-HBr; a) as spin-coated; and b) after soaked in an aqueous PbBr_2 solution.

the spin-coated film. After the soaking treatment, the diffraction peaks are broadened. From the X-ray diffraction profiles, it is supposed that the layered perovskite structure was formed through penetration of Pb^{2+} and Br^- ions into the layered structure in the spin-coated film and that the layer structure was disordered during the formation process.

On the other hand, diffraction peaks corresponding to layer spacing of the perovskite structure are not observed in the diffraction profile of the soaked film; from the length of aminododecyl group of PC12T-HBr, the (001) peak is expected to appear in the 2 theta region less than 4 degrees. The result demonstrates that ordered layer structure of the perovskite was not developed in the spin-coated film. The layered perovskite structure was most likely to be formed in a very short range, and the small domains of the layered perovskite were randomly oriented.

In this work, we demonstrated that the PbBr -based layered perovskite structure with a poly(thiophene) as an organic layer was formed by soaking spin-coated films of HBr-salt of poly(3-aminododecylthiophene) in saturated aqueous solution of PbBr_2 . However, X-ray diffraction measurement demonstrated that well-defined and ordered layer structure of the layered perovskite was not formed in the soaked films. Now, we are continuing the study on optical nonlinearity of thin films of the PbBr -based layered perovskite with poly(thiophene) as an organic layer, in addition to the effort to prepare the highly ordered films of PbBr -based layered perovskite with poly(thiophene) as organic layer by using the Langmuir-Blodgett technique.¹¹

This work is partly supported by the Core Research for Evolutional Science and Technology Program from Japan Science and Technology Corporation (CREST/JST), Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Sports, Science and Culture of Japan and the Scientific Research Fund from the Cooperative Program between Kyushu National Industrial Research Institute and Saga Graduate School.

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