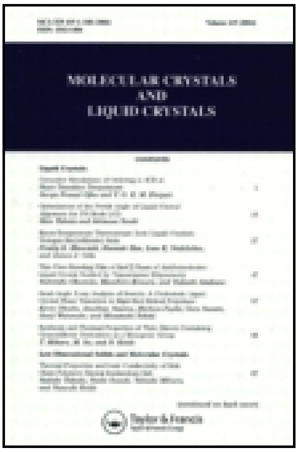

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Preparation of Organic-Inorganic Hybridized Materials using Photopolymerization

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Organic-inorganic semiconductor heterostructures have been successfully fabricated by incorporating a polydiacetylene backbone into layered perovskite compounds by photopolymerization. The γ-ray irradiation caused polymerization of aminodiacetylene cations, RNH_3^+, where $R{=}CH_3(CH_2)_{13}C{\equiv}C\text{-}C{\equiv}CCH_2$, in the solid salts of $(RNH_3)_2PbBr_4$.

Keywords: Layered Perovskite; Photopolymerization; Quantum-well

INTRODUCTION

Recently, two-dimensional layered perovskites, with the general formula $(RNH_3)_2PbBr_4$ (R: C_nH_{2n+1}), have been the subject of growing interest due to their exceptional properties and the tunability of their structures[1-3]. These compounds naturally form a quantum-well structure consisting of a lead bromide semiconductor sheet

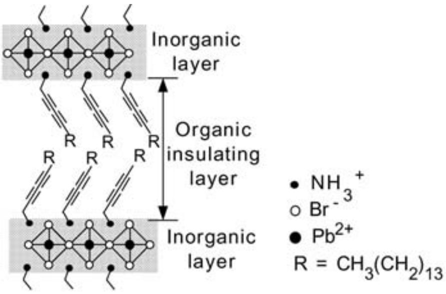

FIGURE 1 Schematic presentation of layered perovskites $(CH_3(CH_2)_{13}C{\equiv}CC{\equiv}CCH_2NH_3)_2PbBr_4$.

sandwiched between organic insulator layers. Because the insulating organic layers have a wide band gap, excitons are confined in the inorganic $[PbBr_6]^{4-}$ layer; these provide strong photoluminescence with high optical nonlinearity, characteristics with potential applications in optical devices[4,5]. Organic-inorganic perovskites have a wide variety of possible combinations of inorganic and organic parts. Organic materials with specific functionality are combined on a molecular scale with an inorganic matrix with other target properties, creating an organic-inorganic composite with either a combination of the useful properties or one in which new phenomena arise from the interaction between the organic and inorganic components[6].

In this study, the incorporation of polydiacetylene systems into layered perovskites replacing insulating organic layers was examined. The incorporation of diacetylenic species into the layered perovskites (Figure 1) provides the potential for topochemical polymerization through the activation of the materials by an external energy source. Herein, we report the solid-state polymerizability of diacetylenic moieties into organic-inorganic perovskites using UV-light and a γ-ray source as energy sources.

EXPERIMENTAL

Aminodiacetylenes $CH_3(CH_2)_{13}C{\equiv}C\text{-}C{\equiv}CCH_2NH_2$ were synthesized accoring to Tsibouklis et al.[7] and Ohba et al[8]. Stoichiometric amounts of hydrobromic acid (HBr. 48 %) and aminodiacetylenes were mixed in a flask that was cooled in a water bath. After the reaction, the water was evaporated, followed by washing with diethylether to obtain $CH_3(CH_2)_{13}C{\equiv}C\text{-}C{\equiv}CCH_2NH_3Br$.

Layered perovskites, $(CH_3(CH_2)_{13}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_2NH_3)_2PbBr_4$, which have aminodiacetylene organic parts, were prepared by treating the diacetylenic amine hydrobromides with a stoichiometric amount of $PbBr_2$ in N, N-dimethylformamide (DMF) at 30 °C. Powder samples were obtained as precipitates by pouring the reaction solutions into acetone. During all reactions, compounds containing diacetylene functional groups were protected from light. Films were spin-coated onto SiO_2 from DMF solutions.

For polymerization, the spin-coated films on a SiO_2 substrate were irradiated by high-energy radiation using a ^{60}Co γ-source at room temperature. The dose rate was approximately 22.3 kGy/h. Specimens were placed in a glass tube, which was evacuated to 10^{-5} Torr in order to avoid oxidation during γ-irradiation. Ultraviolet light at 254 nm from a monochromated Xe lamp was also used as an energy source for polymerization. The polymerization process was followed with UV-Vis spectroscopy.

RESULTS AND DISCUSSION

Organic-inorganic layered perovskite compound, $(CH_3(CH_2)_{13}C{\equiv}C\text{-}C{\equiv}C\text{-}CH_2NH_3)_2PbBr_4$, abbreviated as NDAPbBr, was successfully obtained as both powder and thin films. NDAPbBr exhibited a clear characteristic X-ray diffraction pattern indicative of a layered perovskite structure consisting of inorganic semiconductor layers of lead bromide and organic insulating layers of diacetylenic ammonium $CH_3(CH_2)_{13}C{\equiv}CC{\equiv}CCH_2NH_3^+$.

To investigate the polymerizability of diacetylenic amines in the layered perovskites, NDAPbBr was irradiated with γ-rays in vacuo. Colorless and transparent spin-coated films of NDAPbBr in monomer form turned red after γ-irradiation. The irradiated powder sample also showed a color change to reddish-purple, and became quite insoluble. The optical absorption spectra of NDAPbBr spin-coated films before and after γ-irradiation are shown in Figure 2. The monomer sample exhibited a sharp exciton peak at 378 nm, attributed to the two-dimensional quantum-well structure based on PbBr. After γ-irradiation, a broad peak due to π-π* transitions of polydiacetylene also appeared at around 550 nm, along with the persistent initial exciton peak of perovskite. This implies that red-form polydiacetylene was directly formed and a π-conjugated system was successfully incorporated into the quantum-well layered perovskite structure while maintaining the quantum-well character of the perovskite.

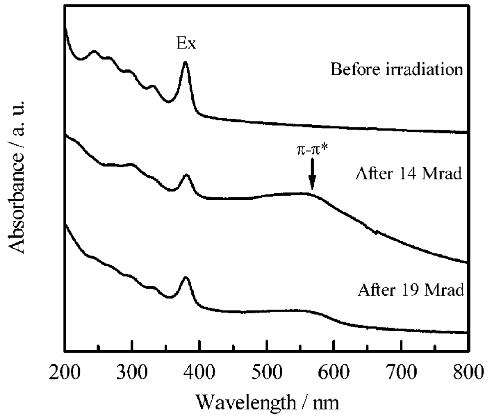

FIGURE 2 Optical absorption spectra of NDAPbBr spin-coated films before and after γ-irradiation.

The π-π* transitions of polydiacetylene were observed at irradiation doses as low as 14 Mrad. Further irradiation caused the absorbance peak attributed to π-conjugated backbone to broaden. Exarhos et al. and other researchers have reported a method of estimating conjugation length by correlating the observed solid state absorption peak of the π-π* transition[9]. By fitting the absorption data obtained for NDAPbBr to their model, we estimate the conjugation length of polydiacetylene introduced into the perovskite structures to be 22 monomer units.

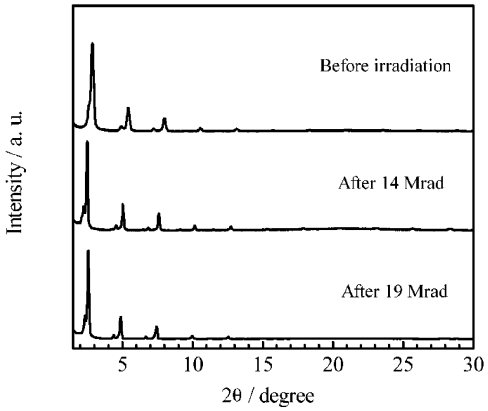

FIGURE 3 X-ray diffraction patterns of NDAPbBr spin-coated films before and after γ-irradiation.

Figure 3 shows the X-ray diffraction patterns of NDAPbBr spin-coated films before and after γ-irradiation. Each spin-coated film produces a series of (001) diffraction patterns, evidence that the layered structure of alkylammonium cations and lead bromide layers remains intact after topochemical polymerization. The powder X-ray diffraction patterns of the polymerized NDAPbBr at 14Mrad, as well as at 19 Mrad, exhibit peaks at 2.60 ° with d = 33.4 Å; however, no peak attributable to the monomer structure was observed. The d-spacing increment of 2.7 Å observed after polymerization occurs as a result of conformation changes such as changes in the tilt angle of alkyl groups and the extent of their interdigitation.

Solid-state polymerization using UV light (at 254 nm) was also attempted for NDAPbBr. Similar results to those for γ-rays were obtained, although the reproducibility of results is poor compared to that for γ-ray irradiation. This difference in reproducibility can be explained by the density of radicals generated by γ-rays and by UV light. Radicals are very sensitive to the defects and become extinct if they trapped by the defects. Because radicals are generated very locally in the case of UV light, the polymerizability of NDAPbBr is very affected by the defects in the sample. On the contrary, because γ-rays can produce radicals broadly and with high density, the polymerizability of NDAPbBr was little dependent on the sample.

In summary, we have successfully incorporated π-conjugated systems into the layered perovskite using the topochemical polymerization. The γ-ray source was more effective for the polymerization than was UV light.

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