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Highly Luminescent Lead Bromide Perovskite Nanoparticles Synthesized with Porous Alumina Media

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Nanocrystalline lead bromide perovskite was synthesized by rapid self-organization on a mesoporous aluminum oxide film. With UV excitation, the film exhibited an intense green emission with a narrow bandwidth. The photoluminescence intensity is optimized for the conditions of synthesis and the kind of metal oxide.

High surface areas and activities realized by nanotextured materials create efficient media for energy conversion with use of small amounts of resources such as metals, semiconductors, and organic compounds.[1] Among semiconductive material, metal halide perovskites have been investigated as a low-dimensional layered compound, in which perovskite units are surrounded by organic methyl- or phenylammonium groups. These materials possess semiconductivity with band-gap structures confined by the organic molecule, exhibiting attractive optical and electrical properties due to quantum size effects. To date, quantum wells,[2,3] wires,[4] and dots[5,6] characterized as organic–inorganic perovskite compounds have also been synthesized. There are only a few reports on zero-dimensional pure perovskite nanocrystals without organic insulator layers[7] because it is difficult on synthesis to control their dimension. Among lead halide type perovskites, bulk crystals, $CH_3NH_3PbX_3$ (X = Br, Cl, and I),[8,9] can be synthesized from CH_3NH_3X and PbX_2 by solid-phase or solution-based self-organization techniques. Such preparation methods, however, have not been successfully applied to nanocrystallization of lead halide perovskite.

In our previous report, we have shown for the first time photoelectric conversion using the perovskite nanocrystals $CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$ as visible light sensitizers to an n-type semiconductor, TiO_2.[10] High quantum conversion efficiency, i.e., electron injection from these perovskites to TiO_2 surfaces, was realized by formation of perovskite nanocrystalline particles with a diameter of 2–3 nm successfully synthesized by a solution technique. Here, we report fabrication of an efficient light emission medium created with the $CH_3NH_3PbBr_3$ nanoparticles. Self-organized within an oxide mesoporous film, the nanocrystals proved to be capable of high intensity, green photoluminescence. In this study, a thin Al_2O_3 film was chosen as a mesoporous medium, which, as an insulator, possess a large energy band gap of 8.7 eV[11] and high ionization potential[12] so that photonic energy absorbed by $CH_3NH_3PbBr_3$ can be fully converted to luminescence.

A low-viscosity Al_2O_3 paste was prepared by mixing 2.4 g of Al_2O_3 nanopowder (spherical particle with size 40–50 nm, Wako Pure Chemical), 1.5 mL of acetylacetone, 3 mL of purified water, 14 mL of ethanol, and 2 g of poly(ethylene glycol) (average molecular weight: 20000 ± 5000) and subsequent grinding with an agate mortar. The paste was spin-coated onto a quartz glass substrate (2.5 cm × 2.5 cm) at 4000 rpm followed by sintering at 500 °C for 1 h in air. The resultant porous film is mostly amorphous and has thickness of about 1 μm as confirmed by scanning electron microscopy observations. Semiconductor materials were also examined for comparison. Pastes of SnO_2 (22–43 nm, Wako) and ZrO_2 (<100 nm, Aldrich) were prepared by the same method. TiO_2 paste (ca. 13 nm for nanocrystal) was a commercial grade (Ti-Nanoxide D, Solaronix SA). Nanocrystalline $CH_3NH_3PbBr_3$ particles were deposited onto a porous Al_2O_3 film by the solution technique for crystallization.[10,13] A precursor solution comprising stoichiometric CH_3NH_3Br and $PbBr_2$ in *N*,*N*-dimethylformamide was spin-coated on the moderately heated porous Al_2O_3 film (<50 °C). With drying off the solvent, crystallization of $CH_3NH_3PbBr_3$ was completed in a short time (<1 min).

Reflectance spectra of a $CH_3NH_3PbBr_3$-deposited mesoporous thin Al_2O_3 film ($Al_2O_3/CH_3NH_3PbBr_3$) prepared from 10 and 1 wt% of precursor solutions are shown in Figure 1. Onset of an intense absorption at 550 nm obtained for 10 wt% preparation is attributed to band-gap absorption edge of $CH_3NH_3PbBr_3$.

A large absorbance decrease for the 1 wt% precursor solution indicates a decrease in the amount of loaded $CH_3NH_3PbBr_3$. It is noted that the dilution of the precursor

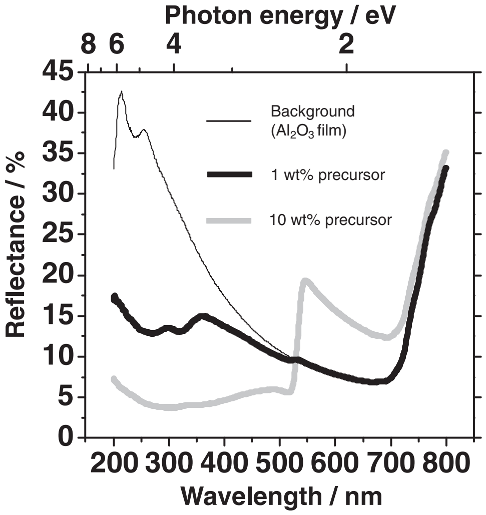

Figure 1. Reflectance spectra of $CH_3NH_3PbBr_3$ on a mesoporous Al_2O_3 film, prepared from 10 and 1 wt% of precursor solutions.

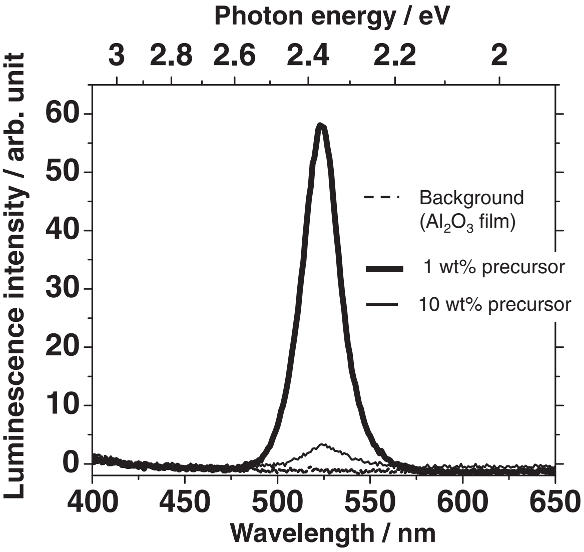

Figure 2. Emission spectra for $CH_3NH_3PbBr_3$ on a mesoporous Al_2O_3 film prepared from 10 and 1 wt % precursor solutions (excitation wavelength: 350 nm).

solution causes a significant blue shift of the absorption peak (edge) to 360 nm.

The spectral shift is assumed to be due to the quantum size effect. Takeoka et al. reported based on optical analysis that the zero-dimensional organic–inorganic perovskite of $(C_4H_8N_2H_4)_2PbBr_6 \cdot 2H_2O$ is assigned with an absorption peak of 312 nm.[5] In this respect, it is thought that molecular size $CH_3NH_3PbBr_3$ particles could also be formed within the Al_2O_3 pore on sufficiently high dilution of the precursor.

Figure 2 and Table 1 show emission spectra and characteristics of $Al_2O_3/CH_3NH_3PbBr_3$ films with 350-nm excitation light. Several samples were prepared by changing the concentration of precursor solution. The emission peak was observed around 523 nm. The emission intensity tends to increase with diluting the concentration of precursor solution. Experiments with different concentrations showed that the samples prepared with conditions above 4 wt % show a very weak emission, as shown in Table 1. This may indicate that high precursor concentrations result in formation of bulk $CH_3NH_3PbBr_3$ which is too large to come into the mesoporous surface. As a result, the highest emission intensity is obtained with 1 wt % precursor. As to the photoluminescence properties of metal halide perovskites, Kitazawa and co-workers showed that microcrystalline $CH_3NH_3PbBr_3$ is capable of photoluminescence at room temperature although its intensity is weak.[13,14] In contrast, strong luminescence occurs with the nanocrystalline particles prepared in our method.

The cross-section image of $Al_2O_3/CH_3NH_3PbBr_3$ film clearly shows that perovskite nanoparticles (ca. 5 nm) were separately deposited on the spherical Al_2O_3 as shown in Figure 3. Regarding the connection of the semiconductive nanoparticles on the metal oxide surface, the procedure using bifunctional molecules to form chemical bonding has been reported.[15] In this study, the perovskite nanoparticles, synthesized in situ without use of any linker molecules, are believe to be making physical contact with the Al_2O_3 surface.

Table 1. Luminescence characteristics of $Al_2O_3/CH_3NH_3PbBr_3$ films prepared with various precursor solutions

Precursor concentration /wt %	Peak /nm	Intensity	Precursor concentration /wt %	Peak /nm	Intensity
1	523	58.1	3.5	527	14.3
1.5	527	36.9	4	525	11.4
2	525	36.1	6	526	5.7
2.5	526	25.8	8	528	2.7
3	525	18.2	10	524	3.4

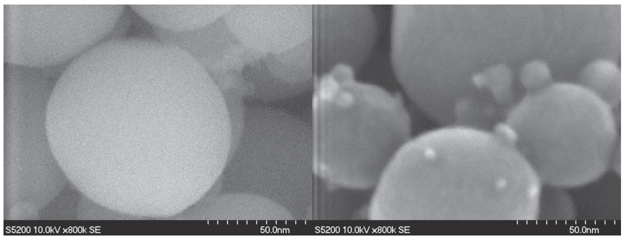

Figure 3. High-resolution SEM images for $CH_3NH_3PbBr_3$ nanoparticles. Left image: bare Al_2O_3 surfaces. Right image: deposited $CH_3NH_3PbBr_3$ crystals prepared with 1 wt % precursor solution.

The crystal size is slightly bigger than the reported Bohr radii.[16] From X-ray diffraction analysis, $Al_2O_3/CH_3NH_3PbBr_3$ film prepared with 10 wt % precursor solutions shows diffraction peaks at 14.87, 21.1, 30.07, 33.71, 43.05, and 45.81°, assigned as (100), (110), (200), (210), (220), and (300) planes, respectively. These diffraction peaks tend to diminish monotonically with dilution of the precursor concentration due to decreased amount of the crystal (see Supporting Information).[20] Nevertheless, the most intense luminescence was observed from pale colored samples. These facts imply that the strong luminescence arises not only from enhanced surface area of $CH_3NH_3PbBr_3$ but also from the formation of quantum size particles. Figure 4 supports this possibility, which shows appearance of illuminant species during the in situ synthesis of $CH_3NH_3PbBr_3$ on the Al_2O_3 film under UV-light irradiation. Intense green luminescence occurs immediately when synthetic reaction starts during spin coating (<30 s).

To examine the effect of mesoporous material on luminescence, Al_2O_3 was replaced with other porous oxides and semiconductors for $CH_3NH_3PbBr_3$ synthesis. TiO_2, SnO_2, and ZrO_2 possess the conduction band levels of −4.0,[17] −4.4,[18] and −2.9 eV[18] vs. vacuum level, respectively. ZrO_2 having an extremely large band gap (5.62 eV) can be regarded as an insulator similar to Al_2O_3.[19] With a mosoporous ZrO_2 film, $CH_3NH_3PbBr_3$ nanoparticle proved to exhibit a strong luminescence similar to Al_2O_3. In contrast, luminescence was virtually absent for both TiO_2 and SnO_2. In our previous study,[10] we determined the conduction band (CB) level of bulk $CH_3NH_3PbBr_3$ to be −3.36 eV (vs. vacuum level). Compared to this CB level, Al_2O_3 and ZrO_2 apparently possess much higher level that inhibits electron injection in terms of sensitization. On the contrary, the CB levels of TiO_2 and SnO_2 are located below that of $CH_3NH_3PbBr_3$, permitting electronic

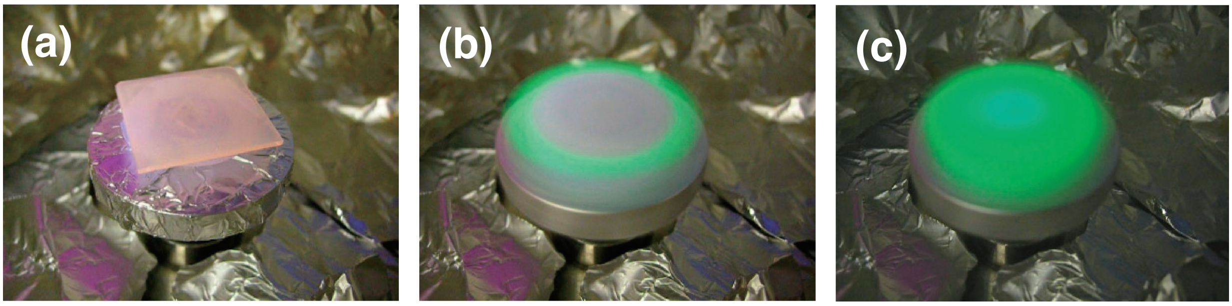

Figure 4. In situ synthesis of illuminant $CH_3NH_3PbBr_3$ nanoparticle by using 1 wt % precursor solution under UV-light irradiation. (a) Colorless $CH_3NH_3PbBr_3$ precursor solution was uniformly dropped onto a mesoporous thin Al_2O_3 film. The Al_2O_3 film is previously heated to dry off the solvent. (b) and (c) Appearance of synthesis reaction. Quick vaporization of organic solvent triggers a nanocrystallization of highly luminous lead bromide perovskite into mesoporous Al_2O_3 structure.

sensitization without causing luminescence. This correlation indicates that intense emission takes place only when the conduction band level of the mesoporous oxide material is located higher (more negative) than that of nanocrystalline $CH_3NH_3PbBr_3$.

In conclusion, we have synthesized luminous lead bromide perovskite nanoparticles by making efficient use of mesoporous media. To the best of our knowledge, this is the first report of photoluminescence using quantum-dot size $CH_3NH_3PbBr_3$. Syntheses of other metal halide perovskites, $CH_3NH_3PbX_3$ (X = Br, I, and Cl), are under way in an attempt to get luminescent function over extended wavelengths. Further, we expect a similar luminescence to be obtained by electronic excitation of the perovskite on the porous surface in junction with a conductive electrode.

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References and Notes

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