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Hiroaki Kosuge [a], Hitoshi Kasai [a], Shuji Okada [a], Hidetoshi Oikawa [a] & Hachiro Nakanishi [a]

[a] Institute for Chemical Reaction Science, Tohoku University, Sendai, 980-8577, Japan

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Preparation of Organic-Inorganic Layered Perovskite Microcrystals

HIROAKI KOSUGE, HITOSHI KASAI, SHUJI OKADA, HIDETOSHI OIKAWA and HACHIRO NAKANISHI

Institute for Chemical Reaction Science, Tohoku University, Sendai 980–8577, Japan

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The self-organized layered perovskite microcrystals could be prepared by the reprecipitation method. In the present hybrid systems, the dissolved states of perovskite in the solvent were found to be of importance, since they have remarkably affected the resulting structure of layered perovskite.

Keywords: Microcrystal; Excitonic absorption; Layered Perovskite

INTRODUCTION

Recently, fine particles including microcrystals have been extensively investigated because of their peculiar optical properties. For example, inorganic microcrystals of semiconductors have been found to show the enhancement of third-order nonlinear optical (NLO) properties originated from quantum confinement effect. On the other hand, we have established the reprecipitation method as a convenient and mild technique to prepare organic microcrystals in disperse system[1], and observed the interesting blue-shift of absorption peak with decreasing crystal size, which is likely to occur by softening crystal lattice, rather than quantum confinement effect[2]. However, organic-inorganic hybrid microcrystals have been scarcely researched so far. In the present study, we have investigated microcrystals of organic-inorganic layered perovskite, *i.e.* $(C_nH_{2n+1}NH_3)_2PbI_4$ where n is 6, 10 or 18 (hereafter, C_nPbI_4 for abbreviation), which are expected to exhibit an excitonic absorption peak and a large third-order NLO susceptibility[3].

EXPERIMENTAL

C_nPbI_4 crystals ware prepared from C_n-alkyl ammonium iodide and lead iodide. They were mixed in two to one molar ratio and then dissolved in acetone. The orange crystals were obtained by slow evaporation of the acetone solution.

C_nPbI_4 microcrystals were prepared by the reprecipitation method: 1 mM acetone solution of C_nPbI_4 (150 μL) was injected into 10 ml of cyclohexane with stirring.

RESULTS AND DISCUSSION

$C_{10}PbI_4$ microcrystal dispersed in cyclohexane exhibited sharp excitonic absorption peak at 506 nm as shown in FIGURE 1. The absorption peak was blue-shifted, compared with the spin-coated $C_{10}PbI_4$ film (λ_{max}=510 nm) at the bulk crystal state ((b) in FIGURE 1). The size of microcrystals were estimated to be about 100 to 300 nm by dynamic light scattering measurement. The blue-shift phenomenon of perovskite microcrystal seems to be caused by lattice softening, as well as other organic microcrystals[2].

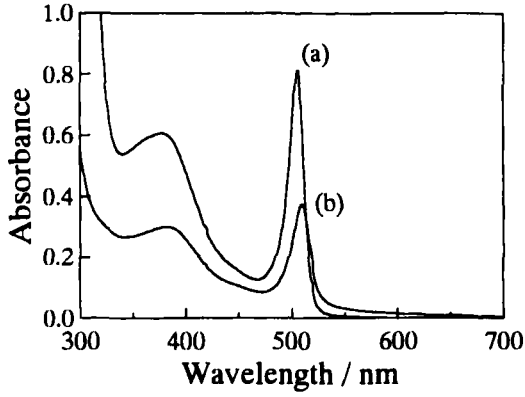

FIGURE 1 UV and visible absorption spectra of (a) $C_{10}PbI_4$ microcrystal dispersed in cyclohexane, (b) spin-coated $C_{10}PbI_4$ film.

The excitonic absorption peak of $C_{10}PbI_4$ microcrystal dispersion, when kept under atmosphere at room temperature, gradually decreased with the elapse of time as shown in FIGURE 2, and disappeared after 17 hours. The perovskite crystal was known to be not so much stable but the decomposition of the layered structure was accelerated by microcrystallization. This may probably be due to the enlarged specific surface area of microcrystals.

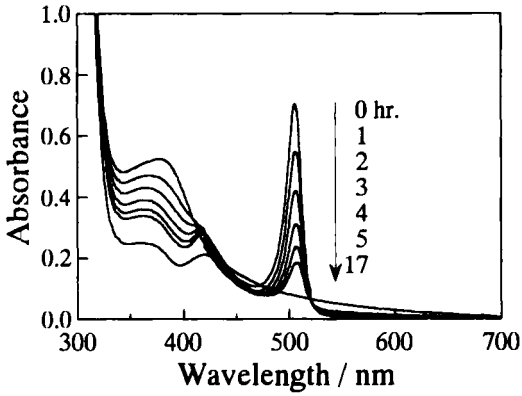

FIGURE 2 UV and visible absorption spectral changes of $C_{10}PbI_4$ microcrystal with the elapse of time.

The $C_{10}PbI_4$ microcrystal with λ_{max}=506 nm shown in FIGURE 1 was prepared by reprecipitation from the fresh acetone solution. However, the peak intensity at λ_{max} reduced with the stored-period of acetone solution as shown in FIGURE 3. In addition, λ_{max} itself was shifted with the stored-period from 506 nm to 520 nm. Ultimately, $C_{10}PbI_4$ microcrystal prepared using acetone solution stored for 12 hours exhibited no excitonic absorption peak, suggesting that layered structure was not formed.

^{1}H NMR spectra indicated that the dissolved states of $C_{10}PbI_4$ in acetone also varied with time between two states. Thus, it is estimated that the difference in the dissolved states is responsible for the changes of spectra of resulting perovskite microcrystals.

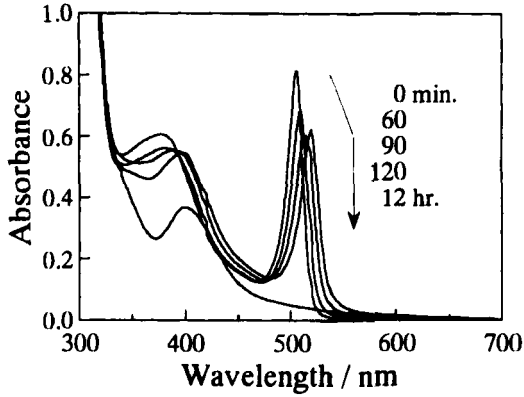

FIGURE 3 UV and visible absorption spectra changes of $C_{10}PbI_4$ microcrystals, depending on the stored-period of the acetone solution.

The absorption spectra of C_6PbI_4 microcrystal also varied with stored-period as well as $C_{10}PbI_4$. In a word, the excitonic absorption peak appeared at 506 nm, and the peak shifted from 506 nm to 520 nm, when prepared using stored solution. In case of $C_{18}PbI_4$, its microcrystal exhibited excitonic absorption peak at 520 nm, when freshly-prepared solution was used.

In conclusion, it has become apparent that the reprecipitation method was capable of preparing the hybrid systems. In the present hybrid systems, the dissolved states of C_nPbI_4 in acetone, which was mainly influenced by the stored-period, has remarkably affected the microcrystal structure of layered perovskite.

Acknowledgments

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