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One-step synthesis of layered yttrium hydroxides in immiscible liquid–liquid systems: Intercalation of sterically-bulky hydrophobic organic anions and doping of europium ions

Mebae Watanabe, Shinobu Fujihara*

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

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ABSTRACT

Inorganic–organic layered rare-earth compounds were synthesized on the basis of a biphasic liquid–liquid system in one pot. Layered yttrium hydroxides (LYHs) were chosen as a host material for the intercalation of hydrophobic organic guest anions such as benzoate, sebacate, or laurate. In a typical synthesis, an organic phase dissolving carboxylic acid was placed in contact with an equal amount of an aqueous phase dissolving yttrium nitrate *n*-hydrate and urea. At elevated temperatures up to 80 °C, urea was hydrolyzed to release hydroxyl anions which were used to form yttrium hydroxide layers. LYHs were then precipitated with the intercalation of carboxylate anions delivered from the organic phase under the distribution law. The structure and the morphology of the LYHs could be modulated by the intercalated anions. Doped with Eu^{3+} ions, the LYHs exhibited red photoluminescence which was enhanced by the intercalated anions due to the antenna effect.

1. Introduction

Inorganic–organic hybrid materials have attracted considerable attention for their novel or enhanced properties such as adsorption capacity [1], optical activity [2], and fire retardancy [3]. Among various types of inorganic–organic hybrid materials, layered materials have been studied for many years because they are basically derived from natural clays. In addition to silicate clay minerals [4], functional layered materials are synthesized from molybdenum disulfide [5], layered protonic titanates [6], or layered hydroxides. Layered metal hydroxide compounds having a characteristic brucite-like structure are recognized as host materials that are suitable for incorporating various types of organic guests. They can be classified into two types depending on the structure and composition. One is well-known layered double hydroxides (LDHs) with a general formula of $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}A^{n-}_{x/n}\cdot mH_2O$. M^{2+} and M^{3+} are different kinds of divalent and trivalent metal ions, respectively, which are located in the octahedral site of brucite-type hydroxide layers. A^{n-} represents interlayered anions to keep a whole charge balance of compounds [7,8]. The other is layered basic metal salts (LBMSs) with a general formula of $[M^{2+}(OH)_{2-x}]^{x+}A^{n-}_{x/n}\cdot mH_2O$, which contains only one kind of a metal ion. Because of their lamellar structure, layered compounds have found practical or potential applications for anion exchange [9], intercalation [10], catalysis [11], two-dimensionally confined reaction space [12], and exfoliation to nanosheets [13].

The present study focuses on layered yttrium hydroxides (LYHs), $Y_2(OH)_5A^{n-}_{1/n}\cdot mH_2O$ (A^{n-}=Cl^-, Br^-, I^-, NO_3^-, CO_3^{2-}, CH_3COO^-, etc.) [14,15], because they are expected to offer a new group of hybrid materials in combination with functional rare-earth elements. Moreover, they have an interesting structure consisting of positively charged $[Y_2(OH)_5]^+$ layers. In common layered compounds such as smectite clay minerals [16], dichalcogenides [17], and some layered oxides [18–20], each single layer can be delaminated in proper solvents to produce functional nanosheet materials. Most of these layers are negatively charged and therefore hybridization with organic anions is not possible. In this sense, positively charged nanosheets formed by exfoliation of layered compounds such as LYHs are promising as a building block to obtain a wide variety of functional materials [21–23]. As a part of the objectives of the study, we have been trying to make hybrids of LYHs with sterically-bulky hydrophobic organic anions which can expand the interlayer space.

LYHs intercalated with organic anions consist of both hydrophilic (hydroxy) and hydrophobic (organic) species and require a two-step synthetic approach [9,15,24]. That is, LYHs containing hydrophilic inorganic anions are prepared first through hydrothermal methods, and then interlayer inorganic anions are exchanged with hydrophobic organic anions at ambient temperatures. In this work, on the other hand, we propose a facile synthesis method for LYHs at one step at moderate temperatures utilizing immiscible liquid–liquid biphasic systems. This synthesis

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* Corresponding author. Tel.: +81 45 566 1581; fax: +81 45 566 1551.
E-mail address: shinobu@applc.keio.ac.jp (S. Fujihara).

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method is based on the principle of distribution equilibrium of solutes between organic and aqueous solutions and is potentially applicable to a variety of inorganic–organic hybrid materials. Actually, our group succeeded in synthesizing layered basic zinc carboxylate at one step by this method [25,26]. It was found that the morphology of layered basic zinc carboxylate could be controlled by changing a kind of carboxylate. Thermal decomposition of such the layered basic zinc carboxylate material led to the formation of nanostructured ZnO, which was applied to electrodes in dye-sensitized solar cells [27]. Although the method of using immiscible liquid–liquid interfaces is known for solvent extraction [28], assembly of monolayers of nanoparticles [29], and limited reaction fields distinct from the bulk phase [30,31], our approach is new in that one liquid phase works as a supplier of components that are hard to be dissolved in the other liquid phase.

Biphasic liquid systems of organic solvents and water are introduced here to synthesize LYHs containing several kinds of sterically bulky organic acid anions such as benzoate ($C_6H_5COO^-$), sebacate ($^-OOC(CH_2)_8COO^-$), and laurate ($CH_3(CH_2)_{10}COO^-$), aiming to modulate their structural and physical properties as optically functional materials. Yttrium nitrate was dissolved in an aqueous phase to which urea was added for releasing hydroxide ions by the hydrolysis at elevated temperatures. The organic acid was continuously delivered from the organic to the aqueous solution to form LYHs by getting supersaturated. Thus we could obtain LYHs by the one-step synthesis. A further attempt was then made to synthesize luminescent hybrids by incorporating trivalent europium (Eu^{3+}) ions into inorganic layers. Luminescence could be enhanced by energy transfer from organic anions to Eu^{3+} ions. Our results then demonstrate that organic anions can interact with inorganic hydroxide layers to produce electronically or optically active hybrid materials.

2. Experimental

Yttrium nitrate *n*-hydrate ($Y(NO_3)_3 \cdot nH_2O$, 99.9% purity, Wako Pure Chemical Industries, Ltd., Japan) and urea ($(NH_2)_2CO$, 99.0%, Wako) were dissolved in deionized water with the assistance of ultrasonication at room temperature to obtain an aqueous solution. Separately, organic solutions of organic acids were prepared as follows. Benzoic acid (C_6H_5COOH, 99.5%, Wako) or lauric acid (dodecanoic acid, $CH_3(CH_2)_{10}COOH$, 98.0%, Wako) was dissolved in xylene. Sebacic acid (decanedioic acid, $HOOC(CH_2)_8COOH$, 97.0%, Wako) was dissolved in 1-butanol. A concentration of Y^{3+} and urea in the aqueous solution was fixed at 0.05 and 1 mol/L, respectively. The role of urea is to supply OH^- ions through the hydrolysis at elevated temperatures. While a part of OH^- ions is used for the formation of yttrium hydroxide, they are also consumed by neutralization of organic acids. In addition, the hydrolysis of urea proceeds gradually. Therefore the concentration of urea should be enough high, as compared to that of Y^{3+}. Concentrations of organic acids in the organic solutions were varied between 0.05 and 0.8 mol/L, as summarized in Table 1. Larger amounts of organic acids in the organic solutions are necessary because only a small portion of them is delivered to the aqueous solution under the distribution law [25]. The actual amount of organic acids used in the formation of hybrids depends on an amount of precipitating yttrium hydroxide.

Table 1
The concentration of the organic acids in the organic solutions.

Organic acid	Concentration [mol/L] (Sample name)		
Benzoic acid	0.1 (B1)	0.3 (B2)	0.6 (B3)
Sebacic acid	0.05 (S1)	0.1 (S2)	0.4 (S3)
Lauric acid	0.2 (L1)	0.4 (L2)	0.8 (L3)

The xylene solution or the 1-butanol solution (8 mL) was placed gently on an equal volume of the aqueous solution in a glass container using a syringe, keeping disturbance minimal. The resultant solutions, which were clearly separated into two phases, were maintained at 80 °C for 24 h in a dry block bath without stirring. A solid phase was then precipitated in the aqueous solutions. In some cases, however, solids were also formed at the interface with the organic solutions, depending on the initial concentration of the organic acids used or the kind of the organic solvents. Details are discussed in the following section. For the collection of solid precipitates in the aqueous solutions, the organic as well as the aqueous solutions were removed by using a syringe. Final samples were obtained by drying the remaining precipitates under the ambient condition.

Samples doped with Eu^{3+} ions were prepared by replacing 5% of $Y(NO_3)_3 \cdot nH_2O$ with $Eu(NO_3)_3 \cdot 6H_2O$ (99.95%, Kanto Chemical Co., Inc., Japan) in preparing the aqueous solution. Concentrations of benzoic acid, sebacic acid, and lauric acid were fixed at 0.1, 0.1, and 0.2 mol/L, respectively, according to the results obtained for the Eu^{3+}-free samples. The rest of the procedure is the same as described above.

X-ray diffraction (XRD) patterns of the samples were recorded by a Bruker D8 ADVANCE diffractometer using Cu*K*α radiation to examine their crystal structure. The $\theta - 2\theta$ scan was started from a low diffraction angle of $2\theta = 2^\circ$ to observe the layered structure. Fourier transform infrared (FT-IR) spectra were measured with a Varian FTS-60A/896 spectrometer using a KBr method in the range of 400–4000 cm^{-1} to confirm the presence of the organic species. Thermogravimetry-differential thermal analysis (TG-DTA) was carried out with a Mac Science 2020S analyzer using a heating rate of 3 °C/min in flowing air to clarify the thermal behavior of the samples. The morphology of the samples was observed by field emission scanning electron microscopy (FE-SEM) using a Hitachi S-4700 or an FEI Sirion microscope. The microstructure of the samples was also observed by field-emission transmission electron microscopy (FE-TEM) using an FEI Tecnai Spirit microscope. Photoluminescence (PL) spectra were measured at room temperature with a JASCO FP-6500 spectrofluorophotometer using a xenon lamp (150 W) as a light source. A filter was used to remove a second-order peak of the excitation light in the PL measurement. Diffuse reflectance spectra were recorded with a JASCO V-670 ultraviolet (UV)–visible spectrophotometer using an integrating sphere unit.

3. Results and discussion

3.1. Appearance of precipitation

The precipitation behavior was dependent on the kind of the organic acids and their concentrations adopted in the biphasic systems. Fig. 1 shows the representative appearance of the precipitates in the glass containers after the reaction at 80 °C for 24 h. The liquid–liquid interface can be seen for any of the combination of the organic solvents and the organic acids. A white precipitate (sample B1; see also Table 1 for the sample nomenclature) is obtained in the aqueous phase at the low benzoic acid concentration (0.1 mol/L) of the xylene solution. When the concentration is increased to 0.3 mol/L, precipitates are obtained both in the aqueous phase (sample B2-a) and at the water–xylene interface (sample B2-i). The samples B1 and B2-a were not only precipitated on the bottom of the glass containers but also deposited on their internal wall in the aqueous phase by the heterogeneous nucleation. At the high concentration of benzoic