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Characterization of self-assembled films of NiGa layered double hydroxide nanosheets and their electrochemical properties

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ABSTRACT

In this study, we have demonstrated the synthesis and delamination of a rarely studied NiGa layered double hydroxide (LDH) system. Hydrothermal treatment under agitation conditions at 200 °C for 4 h resulted in the formation of highly crystalline NiGa LDHs in a shorter time than those synthesized without agitation. The LDH was delaminated into the individual nanosheets in formamide. The most significant finding in this study is the electrochemical behavior of interlayer ferricyanide anions intercalated with the layer-by-layer (LBL) assembly method. The morphology of LBL film with one layer is also monitored with atomic force microscopy. The cyclic voltammogram is similar to potassium metal hexacyanoferrate systems with its unique two-peak wave. Raman spectrum of the film revealed that the metal center of the interlayer cyano complex is in interaction with the Ni^{2+} of the host layer. It was concluded that the two-peak cyclic voltammogram of the film is a result of two different forms of the hexacyanoferrate in the interlayer.

1. Introduction

Layered double hydroxides (LDHs) have a general formula of $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}$ $[A^{n-}_{x/n}\cdot mH_2O]$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively and A is n-valent interlayer guest anion, such as OH^-, CO_3^{2-}, Cl^- or NO_3^-. Positive charge of the layer is generated by the replacement of a portion of divalent metal cation of brucite-like layer with a trivalent cation and is compensated for by the interlayer anions. Divalent cations may be chosen from Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}, where trivalent cations may be Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+} and Ga^{3+} [1–5]. The combinations of these metal cations were largely studied for possible LDH structures. There are, however, only few reports on the NiGa LDH system of which structure and hydrolization behavior was recently revealed by Defontaine et al. [6–8]. Similar Ni^{2+}-based LDH systems were widely studied especially for their electrochemical properties. It was revealed that Ni^{2+} in the host layer is electrochemically active. In addition, Ni^{2+}-containing LDHs have been reported as an alternative electrode material for nickel batteries [9–18]. Electroactivity of Ni^{2+}-based LDH host layers is an attractive property for possible electrochemical applications of these types of LDH nanostructures as thin films.

Most of the layered materials can be delaminated into their individual building units. The unique properties of nanosheets of layered metal oxides were discovered in recent years. In our laboratory, we have reported some distinctive electrochemical, photoelectrochemical and photoluminescent properties of single nanosheets of layered metal oxides [19–22]. As a source of positively charged nanosheets, the delamination of LDHs into the building units of individual nanosheets was just achieved by using various methods [23–31]. Hibino and Jones [26] and Hibino [27] explained the delamination mechanism of glycine-exchanged LDHs in formamide in detail.

In this study, we have studied a NiGa LDH system. Ga^{3+} is known to a have very similar hydrolytic behavior to Al^{3+}. There are several reports on the synthesis of a similar NiAl LDH system with hydrothermal method but the desired level of crystallization could be obtained at long reaction periods [31]. We have replaced Al^{3+} with Ga^{3+} and synthesized the LDH in a short time under agitated hydrothermal conditions. In addition, ion exchange and delamination behaviors of the LDH were researched.

In our previous publications, we have reported that layer-by-layer (LBL) method is a successful and easy way to intercalate various molecules into the interlayer of layered metal oxides [19–21,32]. As oppositely charged nanosheets, exfoliated LDHs can be an alternative or a counterpart for the layered metal oxides, and are worth investigating for their properties in order to understand the applicability as building blocks for functional films. Although there are many reports on the electrochemical behavior of LDH-modified films in various solutions or the electrochemical activity of ion-exchanged interlayer molecules [9–18,33–43], the electrochemical behavior of the thin films of LDH nanosheets intercalated with a complex molecule has not

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been reported yet. Thus, we have investigated the electrochemical behavior of thin multilayer LDH films intercalated with ferricyanide by LBL method. This article is the first report on the electrochemistry of such LDH films.

2. Experimental section

2.1. Synthesis

Hydrothermal method was used for the preparation of NiGa LDHs in this study. $Ni(NO_3)_2 \cdot 6H_2O$ (Wako, Ltd.), $Ga(NO_3)_3 \cdot xH_2O$ ($x = 7.7$ according to the inductively coupled plasma (ICP) spectrometry result) (Aldrich, Ltd.) and hexamethylenetetramine (HMT) (Wako, Ltd.) were used as starting materials for the synthesis of NiGa LDHs. The reaction was performed in a stainless-steel reactor (SUS 316) (Akico Co., Japan) mounted with a shaker. After filling the reactor, it was fixed into the shaker unit of the heating device and temperature was set to 200 °C. The unit was shaken at a rate of 60 rpm for 4 h. The reaction took place under autogenous pressure. The Ni:Ga:HMT molar ratio in the starting solution was adjusted to 2:1:2.5. The aqueous mixture of $Ni(NO_3)_2 \cdot 6H_2O$ and $Ga(NO_3)_3 \cdot 7.7H_2O$ was added to an aqueous solution of HMT so that the final molar ratios would be equal to 0.2, 0.1 and 0.25 M, respectively. Freshly decarbonated Milli-Q water ($R > 18\,M\Omega\,cm$ and TOC = 12 ppb) was used throughout the experiments. After the reaction was completed, the product was removed from the reactor chamber, filtered and washed with a substantial amount of double distilled water and dried overnight at 50 °C.

2.2. Ion-exchange reactions

The salt-acid treatment [44] was carried out to remove the carbonate anions from the interlayer domain of LDHs with using a solution containing 1.5 M NaCl and 4 mM HCl. 0.1 g of LDH powder was stirred in the salt-acid solution for 24 h and recovered by filtering. The ion-exchanged LDH was rinsed with a copious amount of water and dried in an oven at 50 °C overnight.

Potassium ferrocyanide (Takayama Chemicals), potassium ferricyanide (Wako) and glycine (Wako) were used as received. Ten miligrams of Cl^--exchanged NiGa LDH was added into 20 mL of 0.2 M aqueous solution of a corresponding anion. After the solution was stirred for 24 h, LDH powder was washed with double distilled water for three times and dried in an oven at 50 °C.

2.3. Delamination and deposition of thin films

For delamination, 10 mg of glycine-exchanged LDH was shaken in 20 mL formamide for 24 h. Supernatant solution was taken as a delamination solution after centrifuging the solution at 2000 rpm for 20 min. Thin films of delaminated LDHs were deposited on a Pt substrate by LBL method [19–21]. Clean Pt substrates were negatively charged with poly(acrylic acid) (PAA) in 0.1 M PAA solution (pH = 7) for 20 min. Primed substrates were initially immersed into the LDH delamination solution to deposit LDH nanosheets on the substrate. As a second step, the film was dipped into 0.1 M ferricyanide solution for the adsorption of ferricyanide complex on the first LDH layer. The sequence was completed by immersing the modified substrate into the delamination solution again. The process was repeated n times to deposit multi-LDH/ferricyanide layers on a substrate. Each immersion time was 20 min and the film was rinsed with water and dried under N_2 gas after each step.

2.4. Characterization

The crystal structure and the orientation were analyzed from XRD patterns (using Cu $K\alpha$ radiation, Rigaku RINT-2500VHF) of LDH powders. The morphology was examined with a scanning electron microscopy (SEM, JEOL). The compositions were analyzed with ICP spectrometry (Seiko Instruments, SPS7800) and CHN analysis. The ICP analyses were made after dissolving a known amount of LDH powder in a HNO_3 solution. Infrared spectra of the LDH powders before and after ion-exchange reactions were obtained by Fourier-transform infrared spectrometer (FTIR, Perkin Elmer). Raman spectra of the films were taken with JASCO, NRS-3100 Raman spectrometer with the 532.13 nm radiation. Atomic force microscopy (AFM) (Nanoscope, Digital Instruments) was used to obtain AFM images of surface topography of LDH nanosheets and LBL film with one layer on a Mica substrate. A fresh surface of Mica substrate was obtained by removing outer layers. The substrate was dipped into a delamination solution of LDH and hold for 10 min. Then, it was rinsed with a copious amount of water and dried under N_2 gas stream. The process was repeated to obtain one layer LBL film using ferricyanide and delamination solution, respectively. UV–vis absorption spectra of the deposited LDH films were measured using an UV–vis spectrometer (Jasco V-550).

2.5. Electrochemical experiments

The NiGa LDH film intercalated with ferricyanide complex by LBL method was used as the working electrode. All electrochemical experiments were carried out in a conventional three-electrode electrochemical cell with a Pt counter electrode and a saturated Ag/AgCl reference electrode. The working electrode potentials were referred to this reference electrode. Cyclic voltammograms were measured under the potential sweep rate of 20 mV/s. 0.1 M Na_2SO_4 and 0.1 M K_2SO_4 solutions were used as an electrolyte with a pH of around 6.0. N_2 saturation was made in the electrolytes for 40 min before the electrochemical measurements.

3. Results and discussion

3.1. Synthesis and characterization

The present hydrothermal process with agitation for the synthesis of the LDH yielded a product with high crystallinity and regularly arranged crystal sizes in as short as 4 h at 200 °C in contrast to other studies reporting long-time hydrothermal treatment for similar systems performed without agitation [31]. Fig. 1 shows the XRD patterns of the prepared NiGa LDH, chloride, glycine, ferricyanide and ferrocyanide-intercalated NiGa LDHs. The XRD pattern of the prepared NiGa LDH represents the characteristic pattern of sharp and symmetric peaks at lower 2θ angles and weaker ones at higher 2θ angles. The pattern is typical of LDHs crystallized in 3R1 polytype [45]. The unit cell parameters $a = 3.06$ Å and $c = 22.98$ Å for the LDH are in good agreement with the structural parameters given in the literature. SEM micrograph in Fig. 2 shows the morphology of the LDH crystals. Each LDH slab has a lateral size of around 1 μm with oval shapes. The final composition of the LDH was estimated as $Ni_{0.69}Ga_{0.31}(OH)_2(CO_3)_{0.15} \cdot 0.52H_2O$ according to ICP, CHN and TG/DTA analyses.

According to the result of the elemental analyses, the final Ni/Ga ratio is close to the initial ratio in the mixture placed in the reactor, which means that almost all cations are incorporated into the LDH structure. Initial pH value of the reaction solution prior to