



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

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ARTICLE INFO

Article history:

Received 22 May 2008

Received in revised form

17 August 2008

Accepted 19 August 2008

Available online 28 August 2008

Keywords:

Layered double hydroxides

Ion exchange

Delamination

Electrochemistry

Layer-by-layer assembly

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 Ni²⁺ 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.

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1. Introduction

Layered double hydroxides (LDHs) have a general formula of $[M_1^{2+}_x M_2^{3+}_{3-x}(\text{OH})_2]^{x+} [A^{n-}_{x/n} \cdot m\text{H}_2\text{O}]$, where M_1^{2+} and M_2^{3+} are divalent and trivalent metal cations, respectively and A is n-valent interlayer guest anion, such as OH⁻, CO₃²⁻, Cl⁻ or NO₃⁻. 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 Ca²⁺, Mg²⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺ and Zn²⁺, where trivalent cations may be Al³⁺, Cr³⁺, Mn³⁺, Fe³⁺, Co³⁺ and Ga³⁺ [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 hydrolyzation behavior was recently revealed by Defontaine et al. [6–8]. Similar Ni²⁺-based LDH systems were widely studied especially for their electrochemical properties. It was revealed that Ni²⁺ in the host layer is electrochemically active. In addition, Ni²⁺-containing LDHs have been reported as an alternative electrode material for nickel batteries [9–18]. Electroactivity of Ni²⁺-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. Ga³⁺ is known to have very similar hydrolytic behavior to Al³⁺. 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 Al³⁺ with Ga³⁺ 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. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Wako, Ltd.), $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ($x = 7.7$ 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 $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ga}(\text{NO}_3)_3 \cdot 7.7\text{H}_2\text{O}$ 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 ($R > 18 \text{ M}\Omega \text{ cm}$ and $\text{TOC} = 12 \text{ ppb}$) 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 milligrams 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 N₂ 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 HNO₃ 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 N₂ 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 Na₂SO₄ and 0.1 M K₂SO₄ solutions were used as an electrolyte with a pH of around 6.0. N₂ 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 $a = 3.06 \text{ \AA}$ and $c = 22.98 \text{ \AA}$ 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 $\text{Ni}_{0.69}\text{Ga}_{0.31}(\text{OH})_2(\text{CO}_3)_{0.15} \cdot 0.52\text{H}_2\text{O}$ 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

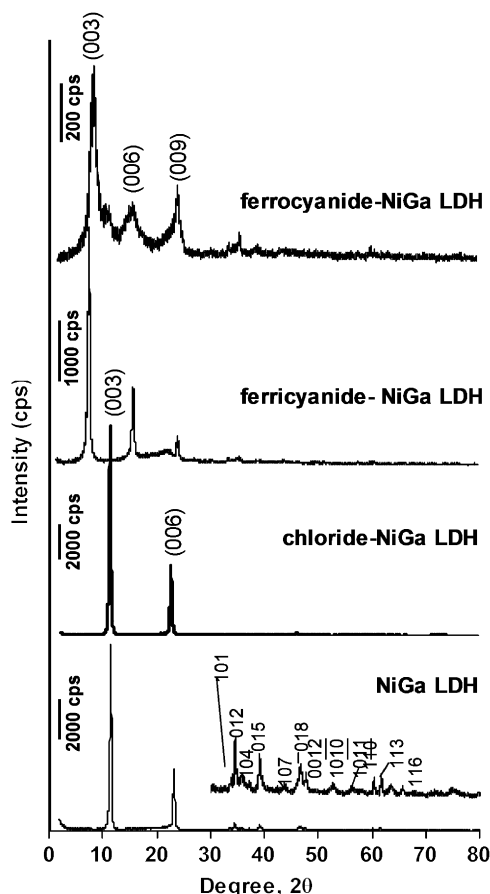


Fig. 1. XRD patterns of prepared NiGa LDH, chloride, glycine, ferricyanide and ferrocyanide-exchanged NiGa LDH.

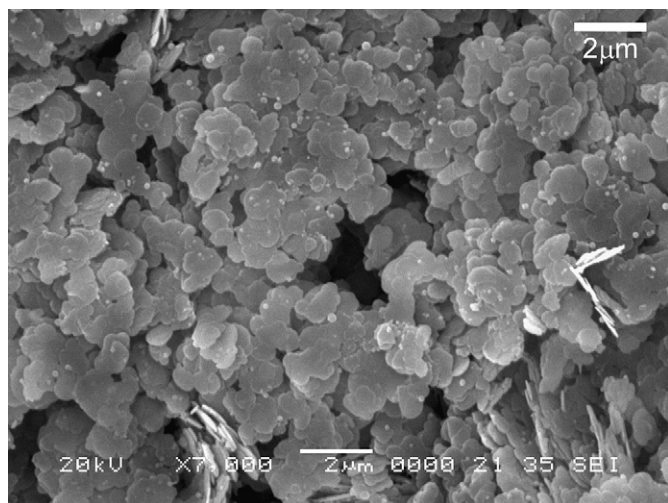


Fig. 2. SEM image of the NiGa LDH.

applying hydrothermal treatment was around 4, which is high enough for the formation of hydroxides species of Ga and Ni as precursors to LDH [7]. The hydrothermal treatment starts crystallization of the LDH from readily available Ga and Ni hydroxides. Increase in the temperature promotes the decomposition of HMT, release of NH_3 , and consequently increase in the pH. This will carry the reaction through the formation of more hydrolyzed species and nucleation of the LDH. The final pH value of 7.5 after

the hydrothermal treatment is in the range that all Ni^{2+} and Ga^{3+} were totally hydrolyzed and can contribute to the formation of LDHs [7,8].

It was discussed in a series of three papers by Defontaine et al. [6–8] that NiGa LDHs are crystallized in the expense of GaOOH species formed in the initial state of hydrolyzation at lower pH values. We have recently showed that a Ga^{3+} LDH system, MgGa LDH, is formed from the initially present GaOOH precursors during the hydrothermal treatment [46]. Thus, it is reasonable to suggest that the crystallization of NiGa LDH starts with the formation of GaOOH precursors initially and Ni^{2+} incorporates into the structure to form single-phase LDHs. In addition, carrying out the hydrothermal reaction in agitation conditions promotes the diffusion of the species, which brings about the crystallization of LDHs in relatively shorter times [46].

3.2. Ion exchange and intercalation

The XRD patterns of the NiGa LDH intercalated with various molecules were given in Fig. 1. The results show that the LDH goes through the intercalation reaction of various molecules. Intercalation reaction with ferricyanide and ferrocyanide carries the basal spacing to 10.98 and 10.71 Å, respectively. There is a slight difference in the basal spacing between LDHs intercalated with two cyano complexes probably because of the structural difference, which might be as a result of the fact that the ferrocyanide ion is known to have a smaller radius (4.33 Å) than that of ferricyanide ion (4.45 Å) [47]. In general, the cyano complexes are oriented in the interlayer with their three-fold axis preferably parallel to the host layer, which would also be the case according to the interlayer distance of the intercalated LDHs [47,48]. FTIR figures (Fig. 3) also confirm the intercalation of the molecules in the interlayer.

Fig. 3(a) shows the FTIR spectra of the prepared LDH, chloride, glycine, ferricyanide and ferrocyanide-intercalated NiGa LDHs. LDHs are known to have high affinity to carbonate anion, which is an obstacle for further processes of LDHs like ion exchange or delamination. Recently, a method was introduced to increase the reactivity of interlayer of LDHs by Iyi et al. [44,49,50] and they have presented that a very high percentage of carbonates can be replaced by Cl^- , NO_3^- or other anions, which are easier to replace with various kinds of molecules. The method involves the ion-exchange reaction of LDHs in an acid-salt mixture of corresponding anion. In our experiments, we have carried out the exchange of interlayer CO_3^{2-} with Cl^- in a mixture of NaCl and HCl. As shown in Fig. 3(a) a significant amount of CO_3^{2-} was removed with this method. There remained a very weak CO_3^{2-} peak on the FTIR diagram of the Cl^- -exchanged LDH. In addition, exchanging carbonates with Cl^- resulted in expansion in the interlayer from 7.66 to 7.89 Å as expected (Fig. 1). As seen in Fig. 3(a), glycine-exchanged LDHs gives CH_2 and COO peaks at 1347 and 1583 cm^{-1} , respectively, which reveals that glycine exists in the interlayer.

Ferro- and ferricyanide-intercalated LDHs gave two identical peaks in the region of 2000–2090 cm^{-1} as given in Fig. 3(b). The C–N stretching mode of ferrocyanide gave peaks at 2030 ± 5 and 2085 ± 3 cm^{-1} for both samples. The peaks at 2035 and 2088 cm^{-1} correspond to the ferrocyanide molecule itself and the cubic structure of the molecule, respectively [48,51]. The FTIR spectrum of ferricyanide-intercalated LDH gave a sharp peak at 2117 cm^{-1} , which was assigned to the intercalated ferricyanide molecule [48]. The appearance of ferrocyanide-related peaks at 2035 and 2088 cm^{-1} on the spectrum of ferricyanide-intercalated sample suggests that both ferrocyanide forms co-exist in the interlayer of the LDH. The existence of ferrocyanide in the ferricyanide-intercalated LDH is a result of the partial reduction of ferricyanide during intercalation. There are several reports on the similar

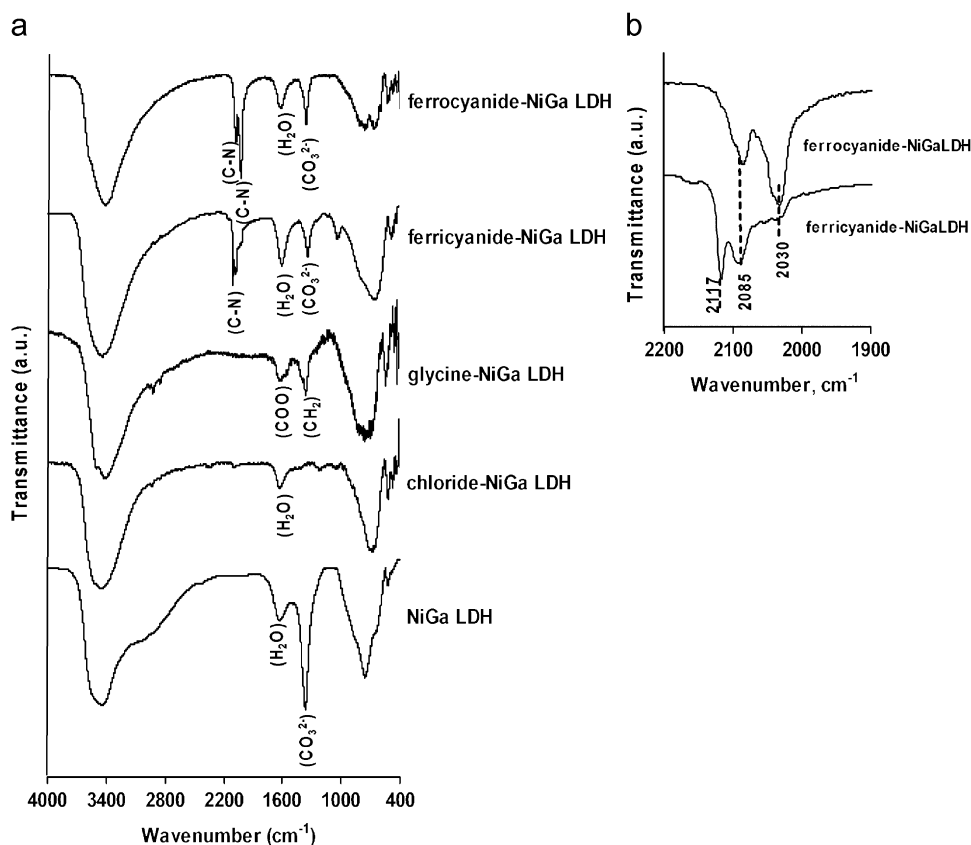


Fig. 3. FTIR spectra of (a) prepared NiGa LDH, chloride, glycine, ferricyanide and ferrocyanide-exchanged NiGa LDHs, and (b) the FTIR spectra of ferricyanide and ferrocyanide-exchanged NiGa LDHs in the region 1900–2200 cm^{-1} .

behavior of ferricyanide anions in the interlayer of LDHs [47,48,51–55]. The interlayer distance of ferricyanide-intercalated LDH is 6.18 Å (the basal spacing is 10.98 Å from Fig. 1 and the theoretical thickness of brucite-like layer is 4.8 Å) which is smaller than the size of ferricyanide along three-fold axis (6.5 Å). This means there is a compression of ferricyanide molecules by the host layer of LDHs resulting in the partial reduction of ferricyanide to ferrocyanide [54,55]. On the FTIR spectra of the intercalated samples in Fig. 3(a), we have also observed a peak of CO_3^{2-} at $\sim 1360 \text{ cm}^{-1}$, which shows that CO_3^{2-} co-exist in the interlayer of the intercalated LDHs. These results show that the NiGa LDH prepared in a very short time in hydrothermal conditions possesses the usual ion-exchange properties like other LDHs.

3.3. Delamination

According to Hibino et al., glycine exchange is necessary to delaminate LDHs as glycine in the interlayer of LDHs attracts a large amount of formamide due to the hydrogen bonding. Delamination of the LDH was carried out according to the procedure followed by Hibino [26,27]. Glycine-intercalated LDH was dispersed in formamide and as explained already, according to the mechanism taking place in the interlayer of LDHs intercalated with glycine, delamination of LDHs could be achieved. AFM picture given in Fig. 4(a) clearly shows that LDH slabs were broken apart into the single nanosheets. These delaminated sheets were distributed on a mica substrate randomly and, there observed some overlapping of the sheets. Height analysis gives an approximate value of 0.71 nm, which is in agreement with the theoretical thickness of a single LDH layer (0.48 nm).

3.4. Electrochemistry of thin films

The thin films in this study were prepared by using a simple LBL method. The two components, which are positively charged LDH nanosheets and ferricyanide complex were assembled by sequential adsorption on Pt substrate. UV–vis spectra of the films represent that films were successfully deposited on a substrate with LBL method by introducing ferricyanide complex into the host layers (not shown). The intensity of absorption in UV–vis spectra increases with the increasing number of layers, which shows that the fabrication of composite complex molecule-LDH thin films is possible with the LBL method. This is the first report for such films composed of individual LDH nanosheets and an inorganic metal complex. Since these kinds of films might have a potential in various applications, we have investigated the electrochemical behavior of these films in aqueous solutions.

The XRD patterns (Fig. 5) of multilayer LBL films of ferricyanide-LDH nanosheets show peaks at a lower 2θ value of 8.3° and 16.6° . The basal spacing of 10.6 Å is consistent with the spacing of ferricyanide-exchanged LDHs as shown in Fig. 1. Intensity of peaks increases with increasing number of layers, which confirms the possible growth of LBL films containing individual LDH nanosheets and ferricyanide molecules. The peak at 11.6° indicates that non-delaminated LDHs exist in the present LBL films. AFM image in Fig. 4(b) shows the morphology of LBL film with one layer. Non-delaminated irregular particles are seen as small particles on the film.

Fig. 6(a) shows the cyclic voltammogram of the ferricyanide-intercalated LBL film with three layers in Na_2SO_4 solution. It gave only one rather broad peak in Na_2SO_4 solution and its formal potential was measured as 0.38 V. This peak can be attributed to the redox reaction of cyanide complex in the interlayer [56].

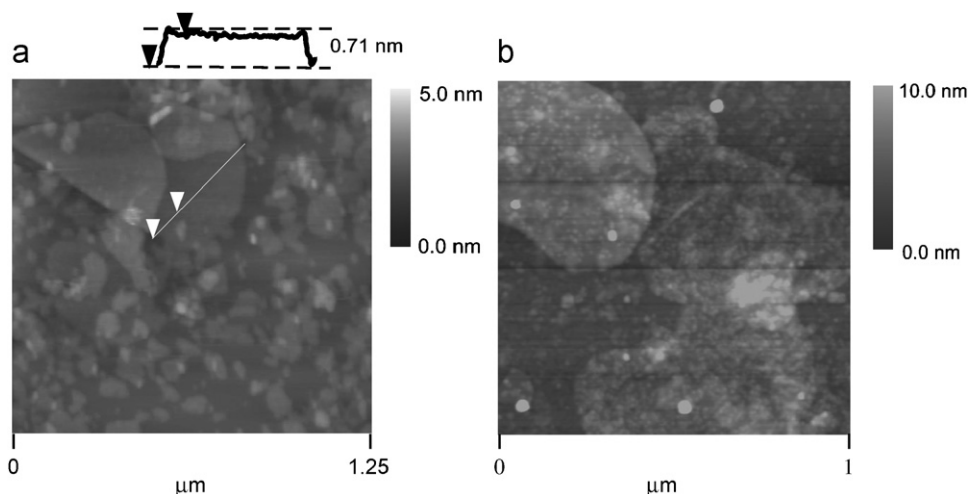


Fig. 4. AFM image of (a) the LDH nanosheets obtained by the delamination of NiGa LDH. The height profile along the line is given above the AFM image (b) LBL film with one layer.

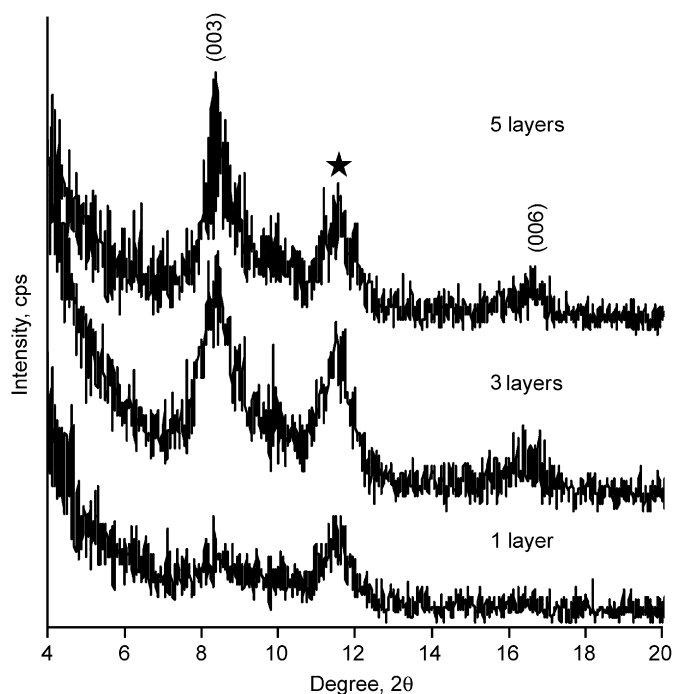
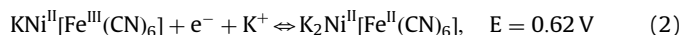
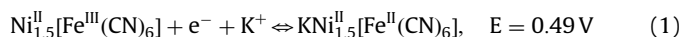


Fig. 5. XRD patterns of LBL film with 1, 3 and 5 layers. The film was prepared by sequential adsorption of the LDH nanosheets and ferricyanide by LBL method. The star represents non-delaminated LDHs.

On the other hand, two redox peaks were observed in K_2SO_4 solution as shown in Fig. 6(b). This figure shows the cyclic voltammograms of the films with 1, 3, and 5 layers prepared by LBL method. Increase in the current with increasing number of layers suggests that LBL is successful for the preparation of such films as mentioned above. The two redox peaks seen in this figure are similar to the electrochemical behavior of the films comprising metal hexacyanoferrate molecules [56–63]. There are, apparently, two forms of the cyano complex in the interlayer and these forms produce a two-peak redox wave with each peak at different formal potentials, i.e. 0.49 and 0.62 V. This feature with given formal potentials is very similar to the behavior of Ni hexacyanoferrate films having Prussian blue-like structure. The redox peak couple was assigned to the K^+ -poor form of the

complex for the peak at more negative value and K^+ -rich form for that at more positive value, and can be represented by the following equations, respectively [35,57–59,62–64]:



Cyclic voltammograms of the Ni hexacyanoferrate films having a Prussian blue-like structure is influenced by the incorporation of the electrolyte cation into the structure [56,60,62,63]. These types of films can go into the intercalation/deintercalation sequence of the electrolyte cation during the cyclic sweep. Thus, the two-peak feature observed for the cyclic voltammograms can be assigned to the two forms of interlayer ferricyanide incorporated with the interlayer K^+ .

The intercalation of K^+ together with the cyano complex was confirmed by the XPS spectra of the film. The K2p XPS spectra given in Fig. 7 shows the presence of K^+ in the film before cyclic sweep.

It was already concluded that the intercalated cyano complex interacts with the Ni^{2+} of the NiAl LDH as it would be the case in this study as well [35,55]. Interlayer complex interacts with the host layer and as a result of this interaction a cubic or cubic-like structure of metal hexacyanoferrate is formed and this structure is capable of intercalation of electrolyte cations during cyclic sweep.

Raman spectra of the films in Fig. 8 were taken in order to observe the possible interaction of the interlayer complex molecules with the host layer after cyclic sweep. Three peaks can be resolved on the Raman spectra of the films. The peak observed at 2139 cm^{-1} together with weaker peaks at 2102 and 2180 cm^{-1} can be ascribed to the stretching mode of Fe–CN bond interacting with the Ni of the host layer [55]. These peaks indicate that ferricyanide intercalated into the LDH by LBL method was partially reduced. This is in accordance with the data observed for the bulk form of the ion-exchanged LDH as given above and similarly, partial reduction in the ferricyanide might be as a result of the stress applied on the molecule by the host layer. In addition, the cyano complexes have such an orientation in the interlayer that cubic or cubic-like structure of these complexes are formed in the interlayer and as a result, Ni^{2+} of the host layer interacts with the metal center of the complex and the observed two-peak redox wave is as a result of the two forms of nickel cyanoferrate compound, which are K^+ -rich and K^+ -poor forms.

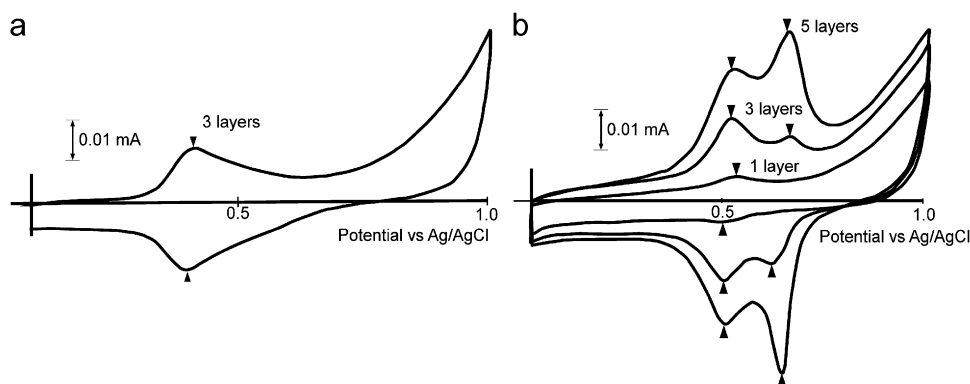


Fig. 6. Cyclic voltammograms of LBL film with (a) three layers in Na_2SO_4 solution and (b) 1, 3 and 5 layers in K_2SO_4 solution.

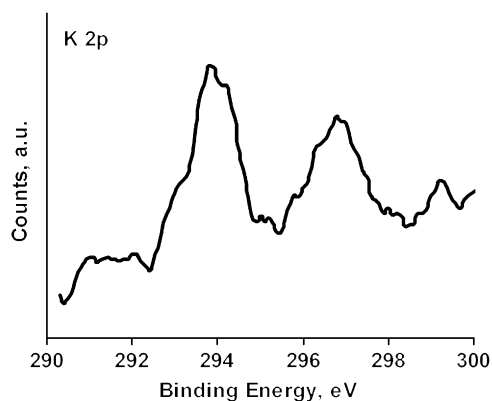


Fig. 7. XPS spectrum of the ferricyanide-intercalated film of the LDH nanosheets prepared by LBL method. The film has three layers.

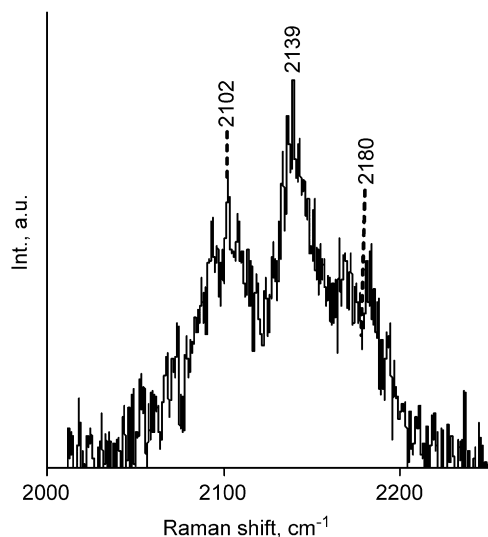


Fig. 8. Narrow range Raman spectrum of the ferricyanide-intercalated film of the LDH nanosheets by LBL method after cyclic sweep. The film has three layers.

4. Conclusions

A NiGa LDH system was prepared by a simple hydrothermal method in a relatively shorter reaction time in comparison with the similar systems. Crystallization of the LDH in such a short reaction time is believed to be due to the agitation conditions applied to the reaction media [46]. The highly crystalline NiGa

LDH could be ion exchanged with various molecules and also delaminated into its individual nanosheets. These nanosheets were used for the preparation of thin films of ferricyanide-LDH particular system by LBL method. The films showed typical electrochemical response of metal hexacyanoferrate, which was believed to be formed in the interlayer as a result of the interaction of interlayer cyano complex with the host layer. This report is the first to show such electrochemical response of these particular LDH thin film systems.

Acknowledgment

This work was supported by The Grant-in-Aid for Japan Society for the Promotion of Science (JSPS) fellows (nos. 1705413 and 19205025).

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