

Preparation of Ni²⁺–Fe³⁺ Layered Double Hydroxide Material with High Crystallinity and Well-Defined Hexagonal Shapes

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The synthesis, structure, and properties of layered double hydroxides (LDHs), also well-known as hydrotalcite-like compounds or anionic clays, have been widely studied in recent years because of their potential applications in heterogeneous catalysts, flame retardants, acid absorbents, anion exchangers, electro- and photoactive materials, two-dimensional solid-state nanoreactors, bioactive nanocomposites, and so on.¹ LDHs have a general formula as [M^{II}_{1-x}M^{III}_x(OH)₂][Aⁿ⁻_n]_m·mH₂O (M^{II} divalent and M^{III} trivalent metal ions, Aⁿ⁻ *n*-valent anion), which consist of positively charged brucite-like host layers and hydrated exchangeable anions located in the interlayer gallery for charge balance.² By varying the chemical composition of the brucite-like layers and the interlayer anions, one can obtain a series of LDH materials with different structure and properties.³

Generally, LDH materials can be prepared by direct synthesis, such as precipitation of mixed-metal hydroxide in a solution containing the anion to be located in the interlayer, also by anion exchange, and by the so-called reconstruction method consisting of suspending the solid obtained by mild calcinations of a LDH material in a solution containing the anion to be intercalated.⁴ Recently, well-crystallized LDH crystals with large platelets in micrometer sizes have been obtained by using urea or hexamethylene-

tetramine as hydrolysis agents.⁵ The progressive hydrolysis of urea or hexamethylenetetramine makes the solution alkaline and induces homogeneous nucleation and crystallization of LDH materials. Theoretically, any divalent and trivalent metal ions whose radii are not too different from that of Mg²⁺ can be accommodated in the host layers of LDH materials. However, the obtained LDH materials with high crystallinity and uniform morphology are mainly restricted to Al³⁺-based LDH materials, partly because of the need of utilize the amphoteric nature of Al³⁺, whereas the transition-metal LDH materials such as Ni²⁺–Fe³⁺ LDH material with high crystallinity and well-defined hexagonal shapes have not been obtained through the homogeneous precipitation.^{1d,6} The reason seems to be that Fe³⁺ easily forms gel-like Fe(OH)₃ at very low pH range, which make the formation of well-crystallized Fe³⁺-containing LDHs difficult.^{3,7} Up to now, although there have been some reports on the synthesis of Ni²⁺–Fe³⁺ LDH material, the obtained samples have low crystallinity and irregular shapes. Research results show that the composition and degree of crystallinity, the crystallite size, and its distribution affect the potential applications of LDH materials, thus developing the new synthesis method for Ni²⁺–Fe³⁺ LDH material with high crystallinity and well-defined hexagonal shapes from the viewpoint of probing novel electronic, magnetic, and optical properties.⁸

This communication reports a new synthesis method of Ni²⁺–Fe³⁺ LDH material using urea as hydrolysis agent and trisodium citrate (C₆H₅Na₃O₇·H₂O) (follow abbreviated as TSC) as chelating reagent. Ni²⁺–Fe³⁺ LDH material with high crystallinity and well-defined hexagonal shapes was obtained under a hydrothermal condition at 150 °C for 2 days.

A typical synthetic procedure of Ni²⁺–Fe³⁺ LDH material with high crystallinity and well-defined hexagonal shapes was as followed: Ni(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, and urea were dissolved in 100 cm³ of deionized water to give the final concentrations of 15, 5, and 35 mM, respectively. TSC (0.25 mM) was subsequently introduced into the above aqueous solution under stirring. The obtained mixed solution was then transferred into Teflon-lined stainless steel autoclaves, sealed, and hydrothermally treated at 150 °C for 2 days. After the reaction was completed, the resulting yellow-green solid product was filtered, washed with deionized water and anhydrous ethanol several times, and finally dried at room temperature in air.

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- (1) Liu, Z.; Ma, R.; Osada, M.; Iyi, N.; Ebina, Y.; Takada, K.; Sasaki, T. *J. Am. Chem. Soc.* **2006**, *128*, 4872. (b) Khan, A. I.; O'Hare, D. *J. Mater. Chem.* **2002**, *12*, 3191. (c) Williams, G. R.; O'Hare, D. *J. Mater. Chem.* **2006**, *16*, 3065. (d) Kagunya, W.; Hassan, Z.; Jones, W. *Inorg. Chem.* **1996**, *35*, 5970.
- (2) Costantino, U.; Marmottini, F.; Nocchetti, M.; Vivani, R. *Eur. J. Inorg. Chem.* **1998**, *10*, 1439.
- (3) Liu, Z.; Ma, R.; Ebina, Y.; Iyi, N.; Takada, K.; Sasaki, T. *Langmuir* **2007**, *23*, 861.
- (4) Klopogge, J. T.; Hickey, L.; Trujilano, R.; Holgado, M. J.; San Román, M. S.; Rives, V.; Martens, W. N.; Frost, R. L. *Cryst. Growth Des.* **2006**, *6*, 1533.

- (5) (a) Sileo, E. E.; Jobbágy, M.; Paiva-Santos, C. O.; Regazzoni, A. E. *J. Phys. Chem. B* **2005**, *109*, 10137. (b) Rao, M. M.; Reddy, B. R.; Jayalakshmi, M.; Jaya, V. S.; Sridhar, B. *Mater. Res. Bull.* **2005**, *40*, 347. (c) Iyi, N.; Matsumoto, T.; Kanoko, Y.; Kitamura, K. *Chem. Lett.* **2004**, *33*, 1122.
- (6) (a) Tian, Y.; Wang, G.; Li, F.; Evans, D. G. *Mater. Lett.* **2007**, *61*, 1662. (b) Refait, P.; Abdelmoulab, M.; Simonb, L.; Ge'nin, J.-M. R. *J. Phys. Chem. Solid* **2005**, *66*, 911. (c) Prasanna, S. V.; Kamath, P. V.; Shivakumara, C. *Mater. Res. Bull.* **2007**, *42*, 1028.
- (7) Xu, Y.; Feng, Q.; Kajiyoshi, K.; Yanagisawa, K.; Yang, X.; Makita, Y.; Kasaishi, S.; Ooi, K. *Chem. Mater.* **2002**, *14*, 3844.
- (8) Ma, R.; Liu, Z.; Li, L.; Iyi, N.; Sasaki, T. *J. Mater. Chem.* **2006**, *16*, 3809.

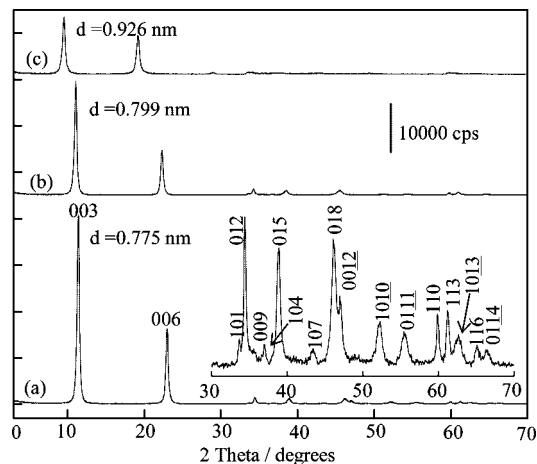


Figure 1. XRD patterns of (a) $\text{Ni}^{2+}\text{-Fe}^{3+}\text{-CO}_3$ LDH material, (b) Cl^- -LDH obtained by treating (a) with a NaCl-HCl mixed solution, and (c) ClO_4^- -LDH obtained by treating (b) with a NaClO_4 solution.

X-ray power diffraction (XRD) analysis of $\text{Ni}^{2+}\text{-Fe}^{3+}$ LDH material was carried out on a D/Max-3c X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), using an operation voltage and current of 40 kV and 40 mA, respectively. All the diffraction peaks of as-prepared $\text{Ni}^{2+}\text{-Fe}^{3+}\text{-CO}_3$ LDH could be indexed as a rhombohedral structure with the refined lattice parameters of $a = 0.3081(5) \text{ nm}$ and $c = 2.3272(6) \text{ nm}$, which are consistent with those of well-known LDH material in CO_3^{2-} form.⁹ The standard deviations for the refined lattice parameters a and c of $\text{Ni}^{2+}\text{-Fe}^{3+}\text{-CO}_3$ LDH synthesized by our new method are 0.0021 and 0.0026, respectively. No other crystalline phases have been detected, indicating the high purity of the product. The diffraction peaks of the obtained product using the new method are not only sharp but also symmetric, distinctly differing from those of $\text{Ni}^{2+}\text{-Fe}^{3+}$ LDH materials prepared using other methods,¹⁰ indicating that $\text{Ni}^{2+}\text{-Fe}^{3+}\text{-CO}_3$ LDH material synthesized has higher crystallinity (Figure 1a). The $\text{Ni}^{2+}\text{-Fe}^{3+}\text{-CO}_3$ LDH material could be converted to Cl^- -LDH when it was treated with an aqueous solution containing 1 M NaCl and 4 mM HCl for 1 day according to the method reported by the Iyi group (Figure 1b).¹¹ After Cl^- -type $\text{Ni}^{2+}\text{-Fe}^{3+}$ LDH was exchanged in a 2.5 M NaClO_4 solution, it was translated to ClO_4^- -type $\text{Ni}^{2+}\text{-Fe}^{3+}$ LDHs with an interlayer spacing of 0.926 nm (Figure 1c), which is very similar to the reported data of 0.924 nm.¹² Meanwhile, the changes in the FT-IR spectra of samples with different anions (see the Supporting Information S1) also provide an evidence for the presence of the incorporated different anions in the interlayer. The noncarbonated $\text{Ni}^{2+}\text{-Fe}^{3+}$ LDHs still maintain high crystallinity, indicating that the $\text{Ni}^{2+}\text{-Fe}^{3+}$ LDHs intercalated with a variety of anions with high crystallinity can further be prepared by an ion-exchange process. These results suggest that the obtained

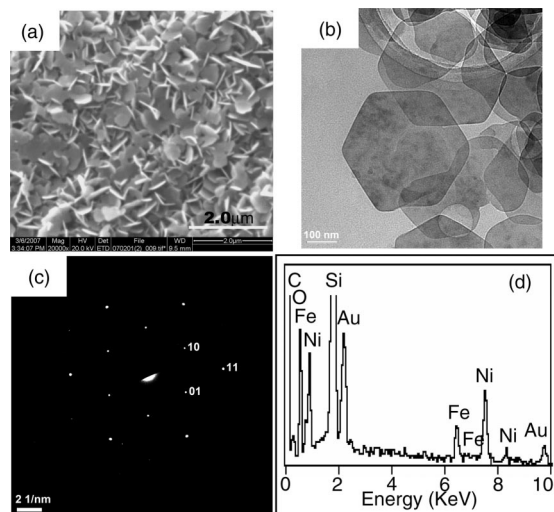


Figure 2. (a) SEM image, (b) TEM image, (c) electron diffraction, and (d) EDS spectrum of $\text{Ni}^{2+}\text{-Fe}^{3+}$ LDH material.

$\text{Ni}^{2+}\text{-Fe}^{3+}$ LDHs materials are indeed bimetallic hydroxides and not Ni(OH)_2 with some amorphous Fe(OH)_3 .

The Ni and Fe contents of $\text{Ni}^{2+}\text{-Fe}^{3+}\text{-CO}_3$ LDH material were determined by atomic absorption spectroscopy using the solutions prepared by dissolving the samples in a dilute HCl solution. On the basis of the results of both the elemental analysis and thermogravimetric measurement (see the Supporting Information S2), the chemical composition of the obtained product is estimated to be $[\text{Ni}_{0.75}\text{Fe}_{0.25}(\text{OH})_2] [(\text{CO}_3)_{0.125} \cdot 0.5\text{H}_2\text{O}]$, with a Ni/Fe molar ratio of 3 and empirical formula weight of 108.5 (Anal. Calcd: Ni, 40.6; Fe, 12.9; C, 1.38; ignition loss, 30.0%. Found: Ni, 40.5; Fe, 12.8; C, 1.41; ignition loss, 31.3%). The composition of individual platelets of the as-prepared $\text{Ni}^{2+}\text{-Fe}^{3+}$ LDH was also characterized by EDS (Figure 2d). The Ni/Fe molar ratio is determined to be about 3 by EDS, which agrees well with the chemical analysis results.

The morphology of $\text{Ni}^{2+}\text{-Fe}^{3+}$ LDH material was characterized with scanning electronic microscopy (SEM) and transmission electron microscopy (TEM). Uniform and thin hexagonal platelets with a mean lateral size of 300 nm and a thickness of 30 nm are observed using SEM (Figure 2a). Evidently, the prepared product is of high quality in terms of morphology, size, uniformity, and crystallinity, which are much superior to those of the sample prepared by the other methods.¹⁰ A typical TEM image (Figure 2b) shows thin hexagonal nanoplates with similar lateral dimensions as those detected by SEM observations. The hexagonal nanoplates have very faint but homogeneous contrast, reflecting their thin nature and uniform thickness. The structure of $\text{Ni}^{2+}\text{-Fe}^{3+}$ LDH material was further characterized by selected area electron diffraction (SAED). The pattern of individual nanoplates of $\text{Ni}^{2+}\text{-Fe}^{3+}$ LDH material exhibits hexagonally arranged spots, confirming their single-crystal nature (Figure 2c). The hexagonal lattice with $a = 0.308 \text{ nm}$ is compatible with the in-plane structural parameter of $\text{Ni}^{2+}\text{-Fe}^{3+}$ LDH crystal determined from the XRD characterization. The hexagonal morphology of $\text{Ni}^{2+}\text{-Fe}^{3+}$ LDH material is thought to be developed naturally as a result of the crystallographic habit of LDH material, and their

(9) Vaccari, A. *Appl. Clay Sci.* **1999**, *14*, 161.

(10) (a) Sato, T.; Fujita, H.; Endo, T.; Shimada, M. *React. Solids* **1988**, *5*, 219. (b) Kagunya, M.; Hassan, Z.; Jones, W. *Inorg. Chem.* **1996**, *35*, 5970.

(11) Iyi, N.; Matsumoto, T.; Kaneko, Y.; Kitamura, K. *Chem. Mater.* **2004**, *16*, 2926.

(12) Ma, R.; Liu, Z.; Takada, K.; Iyi, N.; Bando, Y.; Sasaki, T. *J. Am. Chem. Soc.* **2007**, *129*, 5257.

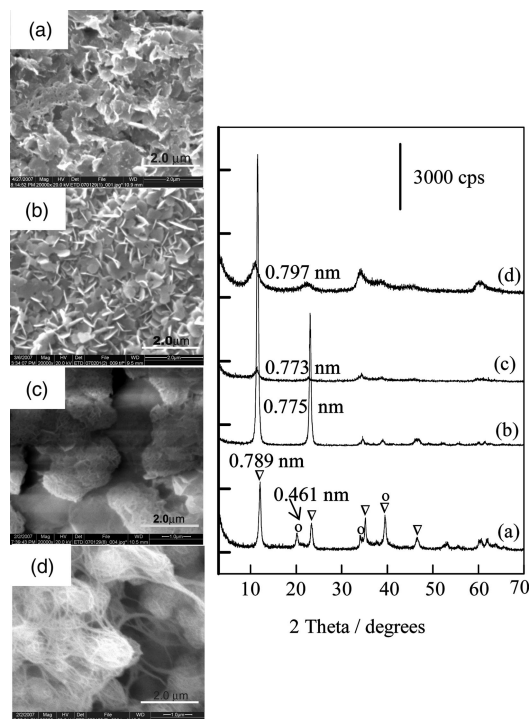
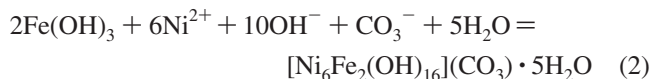


Figure 3. SEM photographs and XRD pattern diffractions of the obtained products in various TSC amounts: (a) TSC = 0.0 mM (∇ , Ni^{2+} - Fe^{3+} LDH; \circ , β - $\text{Ni}(\text{OH})_2$); (b) TSC = 0.5 mM; (c) TSC = 1.5 mM, and (d) TSC = 2.5 mM.

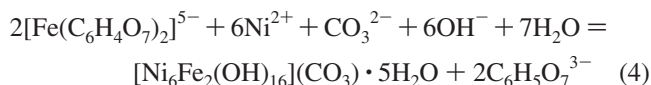
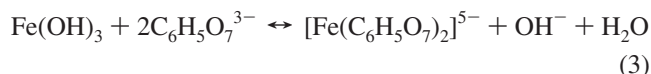
uniformity and high crystallinity could be attributed to a slow and homogeneous nucleation process because of the slow hydrolysis of urea and the chelating function of trisodium citrate.

The effect of chelating agent TSC on the structure and morphology of Ni^{2+} - Fe^{3+} LDH material was further investigated. The change in the crystal phase and the crystal morphology are clearly observed in the obtained products with the addition of different TSC amounts (Figure 3). When no TSC is added, a layered structure with a basal spacing of 0.789 nm and a low crystallinity is obtained accompanied with an impurity phase of β - $\text{Ni}(\text{OH})_2$. The morphology of the obtained product shows a layered structure characterization with small particles (Figure 3a). When the TSC amount added gradually increases to 0.5 mM, Ni^{2+} - Fe^{3+} LDH material with high crystallinity and well-defined hexagonal shapes can be formed (Figure 3b), which is very similar to that of Ni^{2+} - Fe^{3+} LDH material at TSC = 0.25 mM (Figure 1a and Figure 2a). When the TSC amount is further increased to 1.5 and 2.5 mM, respectively, the crystallinity of the obtained samples obviously decreases. In addition, a morphology transformation from well-defined hexagonal shape to a nanowire one can be clearly observed with the increase in the TSC amount (images c and d in Figure 3). Chemical analyses results show that the $\text{Ni}^{2+}/\text{Fe}^{3+}$ molar ratios of the obtained samples are a little lower than 3, indicating that part of Ni^{2+} ions in the solution can not be incorporated in the product (see the Supporting Information S3). The above results clearly reveal that Ni^{2+} - Fe^{3+} LDH material with high crystallinity and well-defined hexagonal shapes can only be formed when a suitable TSC amount is added, and TSC probably plays the critical role in the formation of Ni^{2+} - Fe^{3+} LDH material with high crystallinity hexagonal.

We think TSC plays a functional role in the different periods of the reaction. According to a dissolution/precipitation mechanism already reported for the precipitation of synthetic hydroxalite during the variable pH method,¹³ the formation of Ni^{2+} - Fe^{3+} LDH is proceeds in absence of TSC as follows



Usually, amorphous $\text{Fe}(\text{OH})_3$ is first formed. Further addition of the base results in the conversion of $\text{Fe}(\text{OH})_3$ to Ni^{2+} - Fe^{3+} LDH. The very low solubility of $\text{Fe}(\text{OH})_3$ likely makes the transformation pH value from $\text{Fe}(\text{OH})_3$ to Ni^{2+} - Fe^{3+} LDH close to that of Ni^{2+} ion deposition in the solution, which causes the formation of a little β - $\text{Ni}(\text{OH})_2$ as an impurity phase in the hydrothermal process. On the other hand, an addition of TSC makes the pH deposition range of $\text{Fe}(\text{OH})_3$ in the solution raise because Fe^{3+} ions are chelated by TSC. Meanwhile, the added TSC mainly exists as $\text{C}_6\text{H}_5\text{O}_7^{3-}$ ions because of the OH^- ions liberated by the urea hydrolysis. $\text{C}_6\text{H}_5\text{O}_7^{3-}$ ions induce Fe^{3+} ions in the solution to form the metal-ligand $[\text{Fe}(\text{C}_6\text{H}_4\text{O}_7)_2]^{5-}$.¹⁴ At this condition, the direct conversion of $\text{Fe}(\text{OH})_3$ to Ni^{2+} - Fe^{3+} LDH is probably replaced by the following two reactions



In the favorable concentration of Ni^{2+} and OH^- ions, Ni^{2+} - Fe^{3+} LDH material with high crystallinity can then be formed.

In principle, a crystal growth process consists of nucleation and growth, which are affected by the intrinsic crystal structure and the external conditions.¹⁵ Because the crystal structure of LDHs is hexagonal in nature, the well-defined hexagonal shapes of Ni^{2+} - Fe^{3+} LDH can be formed in a favorable condition. With the increase in the TSC amount added, Ni^{2+} can also be chelated by TSC and form the negative metal ligand of $\text{Ni}(\text{II})$. The negative metal ligands of $\text{Fe}(\text{III})$ and $\text{Ni}(\text{II})$ are preferably adsorbed on the (0001) plane through the Coulombic force, which probably causes the formation of Ni^{2+} - Fe^{3+} LDH with nanowire morphologies. The above explanation about the formation of the Ni^{2+} - Fe^{3+} LDH material with high crystallinity is somewhat conjectural and phenomenological, and research on the detailed mechanism is in progress.

In conclusion, a new synthesis method for Ni^{2+} - Fe^{3+} LDH material with high crystallinity and well-defined hexagonal shapes is developed using urea as hydrolysis agent

(13) Boclair, J. W.; Braterman, P. S. *Chem. Mater.* **1999**, *11*, 298.

(14) Matzapetakis, M.; Raptopoulou, C. P.; Tsohos, A.; Papaefthymiou, V.; Moon, N.; Salifoglou, A. *J. Am. Chem. Soc.* **1998**, *120*, 13266.

(15) (a) Lee, S. M.; Cha, S. N.; Cheon, J. W. *Adv. Mater.* **2003**, *15*, 441. Wu, J.; Zhang, H.; Du, N.; Ma, X.; Yang, D. *J. Phys. Chem. B* **2006**, *110*, 11196.

and trisodium citrate as chelating reagent, which offers a new synthesis pathway for the LDH materials that can not be prepared by the standard homogeneous precipitation method or the coprecipitation method.

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Supporting Information Available: FT-IR spectra, TG-DSC curves, and component analysis of Ni²⁺-Fe³⁺ LDH material (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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