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Research Article

Hydrothermal Synthesis of Ni/Al Layered Double Hydroxide Nanorods

Yun Zhao, Fenfei Xiao, and Qingze Jiao

School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, China

Correspondence should be addressed to Yun Zhao, zhaoyun@bit.edu.cn

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Ni/Al layered double hydroxide (LDH) nanorods were successfully synthesized by the hydrothermal reaction. The crystal structure of the products was characterized by X-ray diffraction (XRD). The morphology of the products was observed using transmission electron microscopy (TEM) and field emission scanning electron microscopy (SEM). The influences of reaction time and pH value on the morphology of the Ni/Al LDHs were investigated. The result showed that the well-crystallized nanorods of Ni/Al LDHs could be obtained when the pH value was about 10.0 with a long reaction time (12–18 h) at 180°C.

1. Introduction

Layered double hydroxides (LDHs) or LDH-type compounds belong to a large class of anionic clays. They can be represented by the general formula $[M(II)_{1-x}M(III)_x\cdot(OH)_2]^{x+}[A^{n-}]_{x/n}mH_2O$ [1], where M(II) is a divalent metal cation, such as Mg, Mn, Ni, Zn, and Cu; M(III) is a trivalent metal cation, such as Al, Fe, Co, and Cr; [1] A^{n-} is an exchangeable anion, such as F^-, Cl^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} [2, 3]. The value of x is between 0.2 and 0.34 generally. LDHs are a layered structure with positively charged brucite-like sheets, where M(II) and M(III) are octahedrally coordinated. The excess charge is balanced by anions in the interlayer, together with water molecules. Recently, LDHs have attracted much attention because of their unique applications in many fields. For example, they can be used as catalysts, catalyst supports, ion exchangers, adsorbents, and pigments and also be used in sensor and magnetic technologies [1, 4, 5]. Scotter and ken B, prepared Ni/Al, Mg/Al, Co/Al, Cu/Al LDHs and used them as the catalysts of the steam reforming of methanol to produce hydrogen [6]. Alejandre et al. used Cu/Ni/Al LDHs as precursors of catalysts for the wet air oxidation of phenol aqueous solutions [7]. Most of these advanced functions depend strongly on the composition, size, and morphology. So nanostructures of LDHs will be of particular interest for the applications.

In the last decade, 1-D nanostructures have been paid more attention due to their unique physical and chemical properties and their potential applications in science and engineering. The successful synthesis of nanotubes such as BN, WS_2, and MoS_2 has been reported [8]. Many hydroxide and oxide nanorods or nanotubes have also been prepared [9–15]. However, there is little report relating to LDH nanorods. A variety of Ni-based LDHs such as Ni/Al, Ni/Co, Ni/Fe, and Ni/Mn have been studied as cathode materials and catalysts [16, 17]. If Ni/Al LDHs were fabricated in the form of a one-dimensional (1-D) nanostructure, they would hold promise as highly functionalized materials.

In this paper, Ni/Al LDH nanorods were successfully synthesized by hydrothermal reaction. In particular, the effect factors on the morphology of the LDHs were investigated such as reaction time and pH value.

2. Experimental

A series of Ni/Al LDHs with nominal Ni^{2+}/Al^{3+} atomic ratio of 3/1 were prepared by hydrothermal reaction at 180°C. All of them were prepared as follows: appropriate amounts of $NiSO_4\cdot 6H_2O$ and $Al_2(SO_4)_3\cdot 18H_2O$ (Ni^{2+}/Al^{3+} = 3/1 (molar ratio)) were dissolved in deionized water (40 mL). Then aqueous solution of ammonium hydroxide was added to the above solution drop by drop with vigorous stirring to adjust

Table 1: Chemical formulas and interlayer distances of Ni/Al LDH prepared at different pH values.

pH value	Interlayer distances (nm)	Ni/Al (molar ratio)	Composition of LDHs
5.5	1.0589	1.71	$[Ni_{0.63}Al_{0.37}(OH)_2](SO_4{}^{2-})_{0.19}\cdot 0.88H_2O$
8.5	0.8401	2.86	$[Ni_{0.74}Al_{0.26}(OH)_2](SO_4{}^{2-})_{0.13}(CO_3{}^{2-})_{0.04}\cdot 0.72H_2O$
10.0	0.8708	2.96	$[Ni_{0.75}Al_{0.25}(OH)_2](SO_4{}^{2-})_{0.16}(CO_3{}^{2-})_{0.03}\cdot 0.84H_2O$

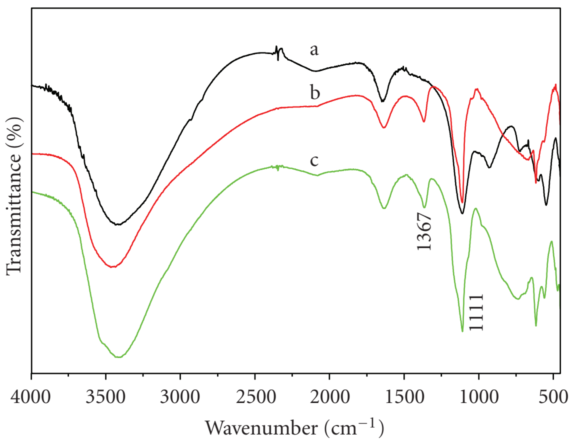


Figure 1: IR spectra of Ni/Al LDHs prepared at different pH values a: 5.5; b: 8.5; c: 10.0.

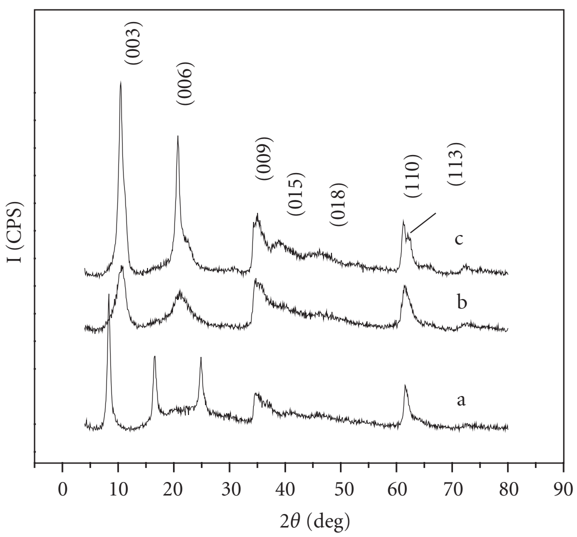


Figure 2: XRD powder patterns of the products prepared at different pH values a: 5.5, b: 8.5, c: 10.0.

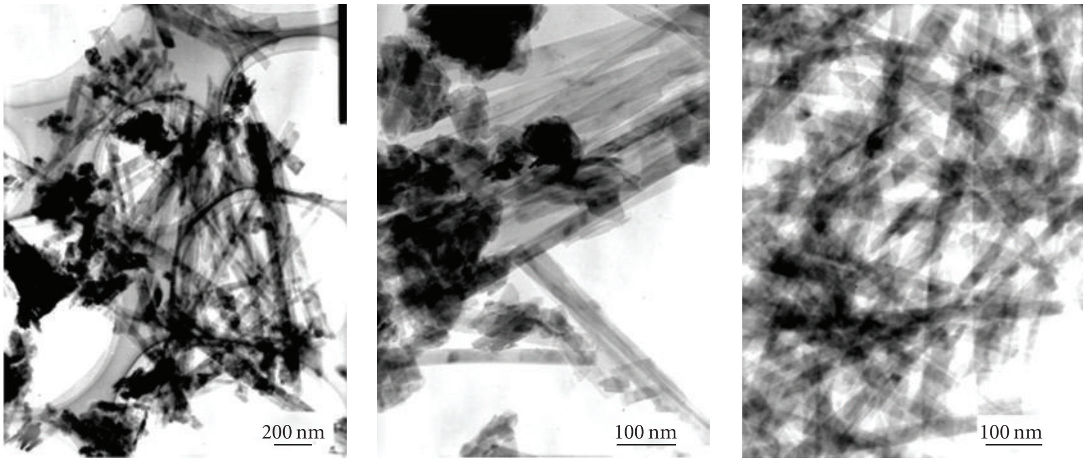
the pH value of the solution. After that, the suspension was transferred into a 50 mL stainless Teflon-lined autoclave and heated at 180°C for appropriate time, then cooled to room temperature naturally. The resulting products were filtrated and washed several times with distilled water and absolute ethanol. The apple-green solid was then collected and dried at room temperature for 12 h.

XRD powder analysis was carried out with a Rigaku D/max-RB12KW X-ray diffractometer using Cu $K_{\alpha 1}$ radiation ($\lambda = 1.5418$ Å) in the 2θ range of 4–80° at room temperature. The TEM micrographs were recorded on a Hitachi H-800 instrument. The SEM images were taken on a Hitachi S4800 field emission scanning electron microscopy. Metals and S analysis was performed on a Perkin-Elmer Optima 3300 DV inductively coupled plasma-atomic emission spectrometer instrument. Microanalysis (% C, H, N) data were collected using a LECO CHN-900 analyzer. IR spectra were recorded on a Bruker Vector 22 spectrometer using KBr pellets.

3. Results and Discussion

3.1. Influence of pH Value on the Structure and the Morphology of LDHs. Chemical formulas for LDHs prepared at different pH are given in Table 1 based on the metals, S analysis, and microanalysis (% C, H, and N) data. A Ni/Al ratio of ~3 for Ni/Al LDHs obtained at pH of 8.5 and 10.0 is consistent with the Ni/Al ratio used in the starting solutions. The Ni/Al ratio of 1.7, however, suggests the incomplete precipitation of Ni^{2+} ions at pH of 5.5. The elemental analyses indicated that the LDH samples prepared at pH of 8.5 and 10.0 contain both sulfate and carbonate anions within the interlayer, however, sulfate anions are the dominant interlayer anion. It can also be confirmed by IR spectrum (Figure 1). The band at 1111 cm^{-1} can be attributed to υ_3 vibration of $SO_4{}^{2-}$, and the band at 1367 cm^{-1} can be assigned to υ_3 vibration of $CO_3{}^{2-}$. The introduction of carbonate can be attributed to the CO_2 in aqueous solution of ammonium hydroxide in the process of preparing LDHs. LDHs prepared at pH = 5.5 contain only sulfate anions in the interlayer due to using the smallest amount of aqueous solution of ammonium hydroxide.

The powder XRD patterns for the Ni/Al LDHs prepared at different pH value are shown in Figure 2. All the XRD patterns exhibit the characteristic reflections of a LDHs material. They show two groups of very close (003), (006), and (009) reflections for LDHs prepared at pH of 8.5 and 10.0 due to containing both sulfate and carbonate anions within the interlayer. No impurity can be detected in the XRD analysis. Therefore pure Ni/Al LDHs must have been obtained at pH of 5.5, 8.5, and 10.0. The lower diffraction intensity for LDHs obtained at pH of 8.5 is observed. This indicates their lower crystallinity. The diffraction peaks of LDHs synthesized at pH of 10.0 are narrow and sharp, which suggest that Ni-Al LDHs prepared at pH = 10.0 are well crystallized. Comparing the positions of 003 and 006 reflections of samples prepared at different pH value, we can see that they shift obviously toward lower 2θ angle with the decrease of pH value. This indicates that when the pH values decreases to 5.5, the distance from the center of one layer to the next for Ni/Al LDHs increases (see Table 1), which is related to the actual Ni/Al molar ratio of the LDHs samples.



(a) (b) (c)

Figure 3: TEM images for Ni/Al LDHs synthesized at different pH values. (a) 5.5; (b) 8.5; (c) 10.0.

Table 2: Chemical formulas of Ni/Al LDH prepared at different reaction times.

Reaction times (h)	Ni/Al (molar ratio)	Composition of LDHs
2	2.57	$[Ni_{0.72}Al_{0.28}(OH)_2](SO_4{}^{2-})_{0.13}(CO_3{}^{2-})_{0.05}\cdot 0.93H_2O$
6	2.70	$[Ni_{0.73}Al_{0.27}(OH)_2](SO_4{}^{2-})_{0.12}(CO_3{}^{2-})_{0.09}\cdot 0.86H_2O$
12	2.96	$[Ni_{0.75}Al_{0.25}(OH)_2](SO_4{}^{2-})_{0.16}(CO_3{}^{2-})_{0.03}\cdot 0.84H_2O$
18	2.93	$[Ni_{0.75}Al_{0.25}(OH)_2](SO_4{}^{2-})_{0.16}(CO_3{}^{2-})_{0.10}\cdot 0.98H_2O$

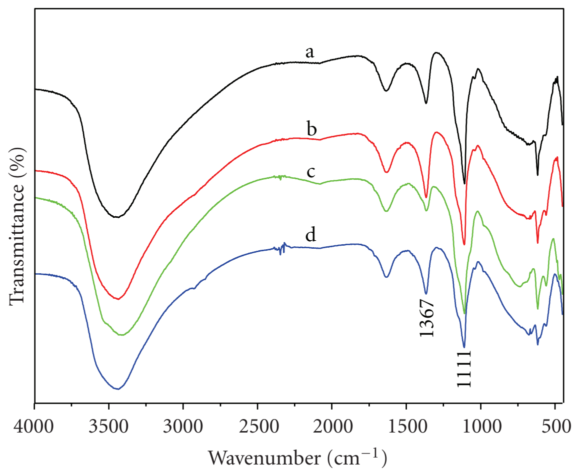


Figure 4: IR spectra of Ni/Al LDHs prepared with different reaction times a: 2 h; b: 6 h; c: 12 h; d: 18 h.

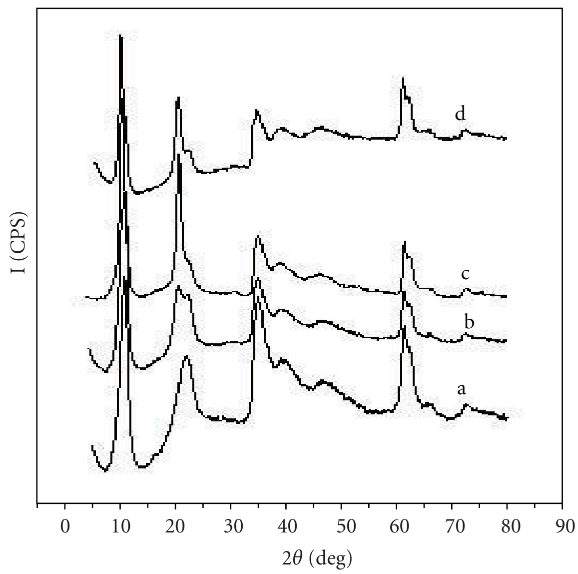


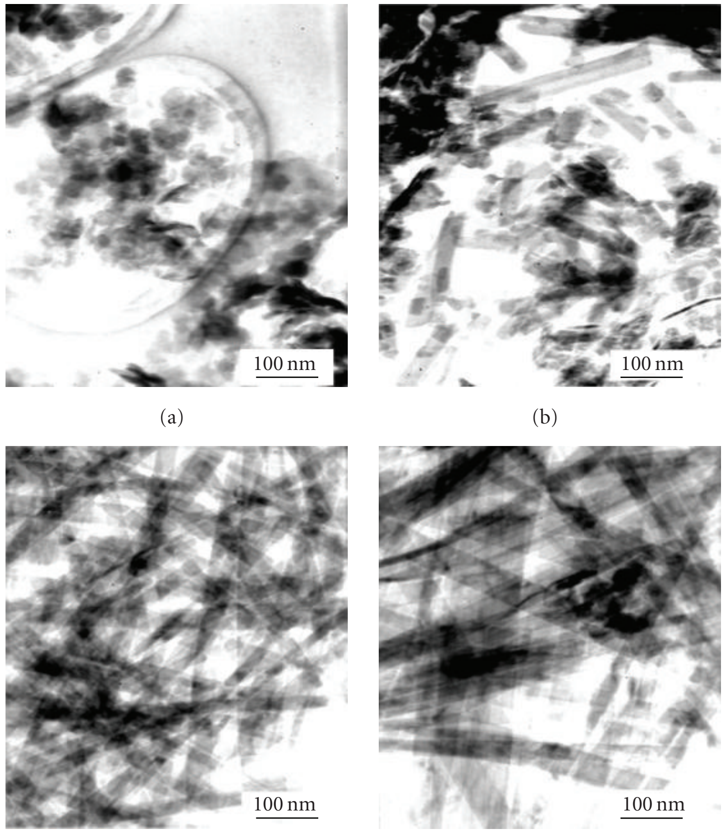
Figure 5: XRD patterns of the products prepared at different reaction times a: 2 h; b: 6 h; c: 12 h; d: 18 h.

As shown in Table 1, the real Ni/Al molar ratio of the LDHs samples decreases with decreasing pH value.

The morphologies of the as-prepared Ni/Al LDHs were examined with transmission electron microscopy (TEM). In Figure 3, the effect of pH value on the morphology of LDHs is demonstrated. It can be seen that nanoparticles and nanorods coexist in Ni/Al LDHs obtained at pH of 5.5 and 8.5. However, only nanorods were formed when the pH value was increased to 10.0. They are 20–40 nm in diameter and 600–1000 nm in length.

It is clear that the pH of 10.0 is suitable for the formation of well crystallized Ni/Al LDH nanorods. So the influence of reaction time on the structure and morphology of Ni/Al LDHs was investigated at pH of 10.0.

3.2. Influence of Reaction Time on the Structure and the Morphology of LDHs. Chemical formulas for LDHs prepared



(c) (d)

Figure 6: TEM images for Ni/Al LDHs with different reaction times, (a) 2 h; (b) 6 h; (c) 12 h; (d) 18 h.

at different times are given in Table 2 based on the metals, S analysis and microanalysis (% C, H, N) data. The elemental analyses, and IR spectrum (Figure 4) yield evidence of the formation of carbonate and sulfate-containing LDHs at different times: 2, 6, 12, and 18 h.

The powder XRD patterns for Ni/Al LDHs synthesized at 180°C for different reaction times (2, 6, 12 and 18 h) are shown in Figure 5. In each case, the XRD patterns exhibit the characteristic reflections of an LDHs material with a basal peak. They also show two groups of very close (003), (006), and (009) reflections for LDHs prepared at different times due to containing both sulfate and carbonate anions within the interlayer. The intensity of the LDH diffraction peaks increases with increasing the reaction time, indicating that, as expected, the crystallinity of the crystallites increase with increasing the reaction time.

From Figure 6, it can be found that the reaction time has a large effect on the morphology of Ni/Al LDHs. When the reaction time was lower than 2 h, only nanoparticles with the size of 15–40 nm were obtained. If the reaction time was up to 6 h, short nanorods were formed and the length was about 50–300 nm. With the increase of the reaction time, nanorods with a high aspect ratio were observed. As can be seen from Figure 4(c), nanorods of Ni/Al LDHs with reaction time of 12 h were 20–40 nm in diameter and 600–1000 nm in length. When the time was prolonged to 18 h, the nanorods increased in length and width. They had a diameter of 30–70 nm and a length of 1–3 μm.

Ni/Al LDHs prepared for 12 h and 18 h were also observed using SEM. As shown in Figure 7, a large amount of Ni/Al LDHs nanorods with much higher aspect ratios were obtained. It confirmed that Ni/Al LDHs nanorods were successfully prepared by hydrothermal reaction at 180°C and pH of 10.0 for a longer reaction time (12–18h).

On the basis of the reports [8, 10, 14], many 1-D nanostructures (nanotubes or nanorods) have been successfully synthesized from layered structures, the so-called 2-D structures such as $Ni(OH)_2$ and $Mg(OH)_2$. Ni/Al LDHs are layered compounds, therefore, we may suppose that the formation of Ni/Al LDHs nanorods might be related to the nature of its lamellar 2-D structures. However the structure of Ni/Al LDHs is different from $Ni(OH)_2$ and $Mg(OH)_2$ with simple layered structures. The structure of Ni/Al layered double hydroxides (LDHs) can be described as containing brucite ($Mg(OH)_2$)-like layers in which some of the divalent cations (Ni^{2+}) have been replaced by trivalent ions (Al^{3+}) giving positively charged sheets. This charge is balanced by intercalation of $CO_3{}^{2-}$ or $SO_4{}^{2-}$ anions in the hydrated interlayer regions. It is obvious that Ni/Al LDHs possess complicated layered structure.

Based on the report [18], highly symmetrical materials, which have hexagonallayered structures, can be grown

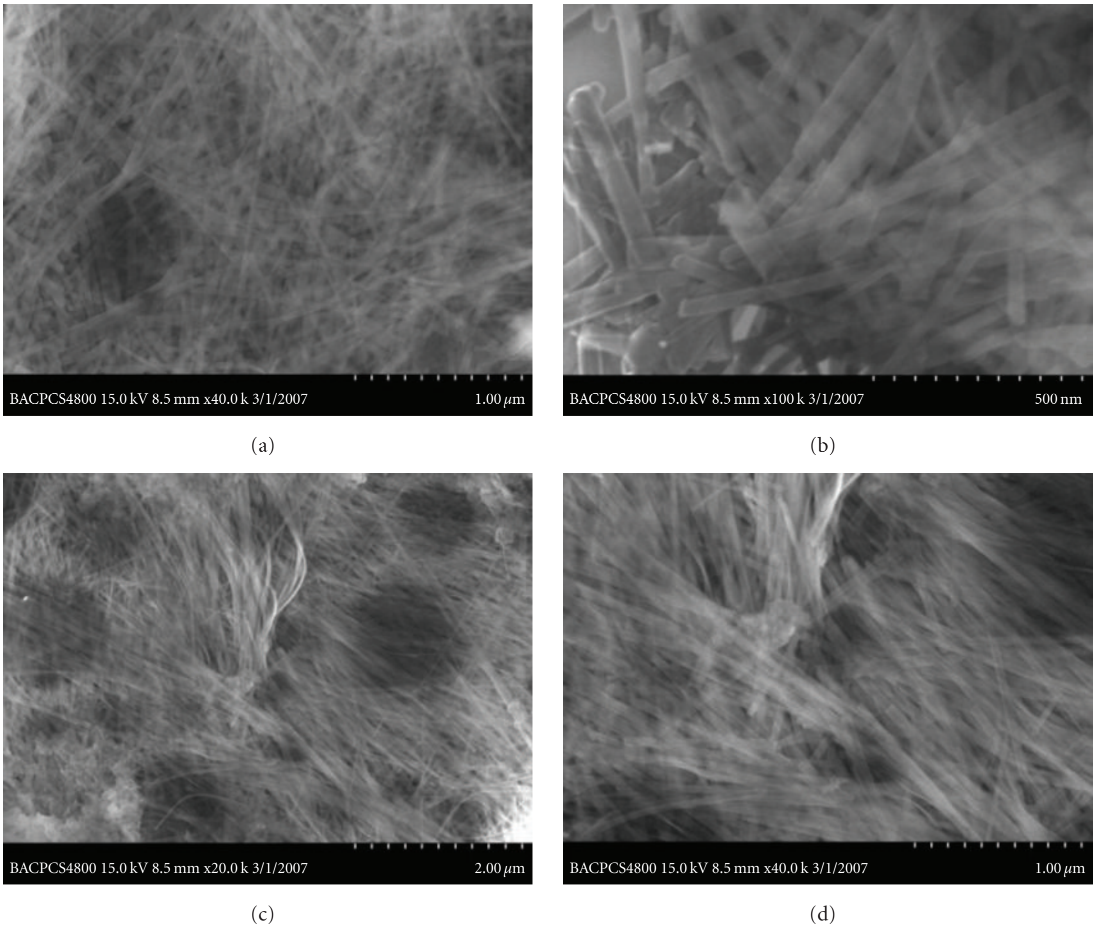


Figure 7: SEM images for Ni/Al LDHs with different reaction times. (a, b) 12 h; (c, d) 18 h.

into low-symmetrical crystallites such as one-dimensional nanorods. LDHs, whose basic layered unit possesses hexagonal symmetry, represent a group of highly symmetrical materials that show peculiar one-dimensional growth anisotropy. Under the present hydrothermal condition, the nucleation of LDHs would occur and there was an intrinsic tendency to grow into rod-like nanoparticles due to its antistropic hexagonal structure. So, formed LDH nanorods are stable geometrical morphologies in the surface chemistry context, because with this shape LDHs have a low system energy [15, 18]. The TEM images with different reaction times showed that the growth of Ni/Al LDH nanorods is forming nanoparticles first, then growing to short nanorods, and finally to long nanorods.

4. Conclusions

In summary, nanoparticles and nanorods of Ni/Al LDHs with size and morphological controls have been synthesized by hydrothermal reaction. The effect factors such as pH value and reaction time on the morphology of the LDHs were investigated. Ni/Al LDH nanorods were successfully prepared by hydrothermal reaction at 180∘C and pH of 10.0 for 12 h–18 h. Ni/Al LDH nanorods with reaction time of 12 h had a diameter of 20–40 nm and a length of 600–1000 nm. When the time prolonged to 18 h, longer and wider nanorods were obtained with a diameter of 30–70 nm and a length of 1–3 μm. The successful growth of nanorods will provide a promising route to low-dimensional nanostructures of other LDHs.

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