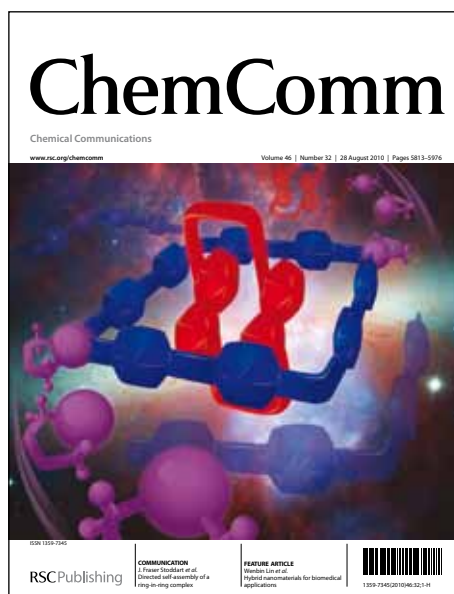


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ARTICLE TYPE

# Formation mechanism and photocatalytic activity of hierarchical NiAl-LDH films on Al substrate prepared under acidic conditions†

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

NiAl-LDH films with hierarchical morphology have been fabricated by immersion of Al substrate in Ni<sup>2+</sup>-containing solutions under strong acidic condition, and the growth processes of the films are discussed in the paper. The as-prepared LDH films exhibit high activity in the photocatalytic degradation of organic contaminants.

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, have attracted considerable attention in recent years because of their potential applications in catalysis, adsorption, bionanotechnology, electrochemistry, separation, sensors and environmental remediation.<sup>1a-b</sup> These compounds can be represented by the general formula  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$  ( $M^{2+}$  divalent and  $M^{3+}$  trivalent cations respectively,  $A^{n-}$  n-valent interlayer anion).<sup>1</sup> For many applications in practical devices, such as heterogeneous catalysts, clay-modified electrodes, sensors, adsorbents and membrane separation, the preparation of nanostructured LDH films with rich morphologies is becoming the inevitable trend for the development of LDH materials.<sup>1a</sup> A variety of films, such as self-supporting NiAl- and ZnAl-LDH films,<sup>2a</sup> MAI-LDH (M = Ni, Zn, Mg) films on porous anodic alumina/aluminium (PAO/Al),<sup>2b-e</sup> metal,<sup>3</sup> glass substrate<sup>4a</sup> or other man-made supports,<sup>4b</sup> hierarchical ZnO/ZnAl-LDH films on metal substrate,<sup>4c</sup> have been obtained using NaOH, urea, ammonia or hexamethylenetetramine as a precipitant.

In the synthetic process, the pH value has an important effect on the formation of LDHs.<sup>5-6</sup> Generally, it is accepted that a basic pH is required for the preparation of LDH powder. According to the literatures,<sup>5a-b,6</sup> the formation process of LDH powder by coprecipitation method can be divided roughly into two stages: initially,  $M^{3+}$  hydroxides or hydrous oxides are usually formed, then further addition of base results in conversion of the  $M^{3+}$  hydr(ous) oxide to LDH with the incorporation of  $M^{2+}$ . The crystallinity of LDH powder synthesized using coprecipitation method usually increased with increasing pH value.<sup>5c-d</sup> As for

LDH film, however, some Al-containing film can be fabricated at near neutral pH. For example, MAI-LDH (M = Ni, Zn) films on PAO/Al or Al has been prepared at pH 6.5 by *in situ* growth method.<sup>2d,3a</sup> Considering that the aluminium hydr(ous) oxide can be formed at pH < 4<sup>5a-b</sup>, if the Al-containing LDH films followed a similar formation process as LDH powder, the fabrication of the films at acidic pH may be feasible. To the best of our knowledge, no exploration has been made to prepare LDH film under strong acidic condition yet.

Inspired by the above speculation, for the first time, we successfully prepared NiAl-LDH films on Al substrate in Ni<sup>2+</sup>-containing solutions with initial pH 2-6 using a simplified *in situ* growth method. The obtained NiAl-LDH films showed high activity in the photocatalytic degradation of methyl orange (MO) and rhodamine B (Rh B), especially the one formed in the solution with initial pH 2. In addition, for better understanding of the nucleation and growth of LDH crystallites on Al substrate, the growth processes of the LDH films under strong acidic conditions were followed by scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDX), powder X-Ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). We hope that the understanding of the formation mechanism of LDH film under acidic condition will be helpful for gaining insight on the synthetic methodology of the material and serve as an important reference for the LDH film to be tailored for specific applications.

In this work, clean Al sheets were immersed in the Ni<sup>2+</sup>-containing solutions with pH value varied from 1 to 6, followed by heating to 80 °C in a water bath for different time as described in ESI†. The white film coating on Al substrate is denoted as NiAlp<sub>xy</sub>, and the precipitate, which was only formed in bulk solutions with initial pH 1 and 2, is denoted as NiAlp<sub>xy</sub>-p (x means the initial pH value of the solution and y means the immersion time (hour) of the Al substrate in solution).

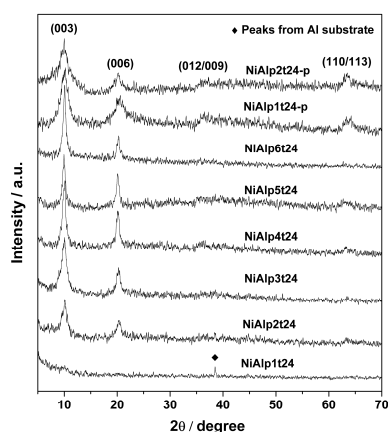
As shown in Fig. 1, XRD patterns of the scraped powders of NiAlp<sub>xt</sub>24 (x = 2-6) and NiAlp<sub>xt</sub>24-p (x = 1, 2) exhibit the characteristic reflections of the LDH structure, showing two strong diffraction peaks corresponding to (003) and (006) planes with a basal spacing of 0.89 nm, which is in good agreement with the values for LDHs with nitrate anions.<sup>3a,4b,5d</sup> At the same time, Fourier transform infrared (FT-IR) spectra of samples (Fig. S1†) also confirm the existence of intercalated nitrate anions. The XRD pattern of NiAlp<sub>1</sub>t24, however, displays no diffraction peak other than that of aluminium metal (PDF No. 85-1327) scraped

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† Electronic Supplementary Information (ESI) available: Preparation and characterization details, XRD, FT-IR, SEM, EDX and XPS patterns, variations of solution's pH, digital photographs of samples.

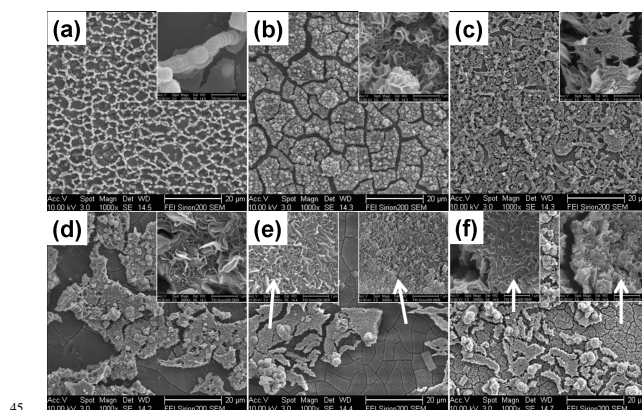


**Fig. 1** XRD patterns of scraped powder of films and precipitates.

from the Al substrate. A comparison of XRD pattern of NiAlp2t24 with that of NiAlp2t72 (Fig. S2(a)† and (b)†) reveals that the crystallinity of LDH increases with increasing immersion time of Al substrate in solution. However, when Zn<sup>2+</sup>, Co<sup>2+</sup> or Mg<sup>2+</sup>-containing solution with initial pH 2 were used in the preparation process, diffraction peaks of LDHs were not detected in the XRD patterns of the as-prepared samples (Fig. S3†).

The morphologies of the prepared NiAlp<sub>x</sub>t<sub>24</sub> were investigated by SEM and the images are shown in Fig. 2. In the case of the film, the images of NiAlp1t24 (Fig. 2(a)) show a network-like morphology formed by the joint of numerous pillar-like protrusions which are essentially amorphous Al(OH)<sub>3</sub> according to the EDX (Fig. S5†) and XRD results (Fig. 1), while LDH platelets are not observed on the surface of the substrate. With the increase of the initial pH value of Ni<sup>2+</sup>-containing solution, LDH films with hierarchical architectures and network-like cracks can be obtained, as shown in Fig. 2(b)-(f). The formation of the cracks can be attributed to the dehydration of the LDH coatings during the drying process.<sup>3c-d</sup> According to Fig. 2(b), the surface of NiAlp2t24 is composed of sphere-like protrusions assembled by LDH crystalline platelets. The platelets are thick but narrow in lateral dimension, connecting tightly to the support. Although there are cracks exist on the surface, no peeling can be observed in the low magnification SEM image. When the pH value increased from 3 to 6, dense LDH films were formed according to the inset SEM images of Fig.2(c)-(f). The LDH platelets are thin but wide in the lateral dimension. The adherence of these films to the support is not as good as NiAlp2t24. Severe peeling of the densely formed films occurred, especially for NiAlp4t24, NiAlp5t24 and NiAlp6t24. At the same time, a new layer of microcrystals began to form on the exposed substrate as revealed by the high magnification SEM images (Fig. 2 insets of (d)-(f)). It should be pointed out that these phenomena were not observed in the fabrication of ZnAl-LDH film on Al substrate by *in situ* growth method using NH<sub>3</sub>·H<sub>2</sub>O-NH<sub>4</sub>NO<sub>3</sub> as buffer (pH 6.5).<sup>3a</sup> Variation of pH value of the solution may be responsible for the unique phenomenon in this work (Fig. S4†). Characterizations of NiAlp<sub>x</sub>t<sub>24</sub> by FT-IR, EDX and XPS were performed and results are present in Fig. S1†, Fig. S5† and Fig. S6†, respectively.

In the case of the precipitates formed in the bulk solution (initial pH 1 and 2), agglomerates of tiny curled LDH platelets can be clearly observed (Fig. S7†). The LDH crystalline platelets



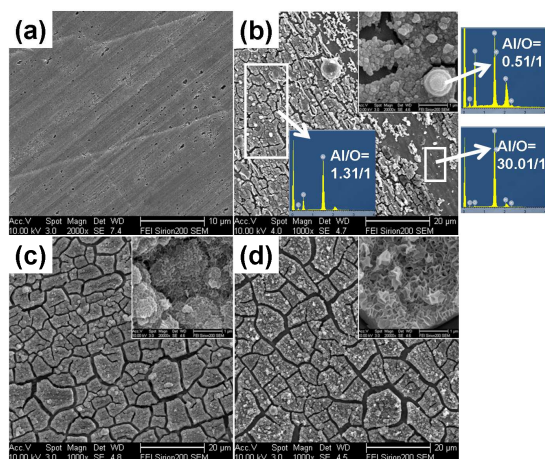
**Fig. 2** SEM images of surface morphology of NiAlp<sub>x</sub>t<sub>24</sub>, x = (a) 1, (b) 2, (c) 3, (d) 4, (e) 5 and (f) 6, at low and high (insets) magnification.

of NiAlp2t24-p are much larger in size than those of NiAlp1t24-p.

Based on the above studies, typical NiAl-LDH film could be fabricated on Al substrate in a Ni<sup>2+</sup>-containing solution with initial pH value as low as 2. A further decrease of the solution's initial pH value to 1 resulted in failure of LDH film formation. For better understanding of the formation mechanism of the film, the growth processes of NiAlp2t24 and NiAlp1t24 films were followed by SEM, respectively (Fig. 3 and Fig. S10†).

As shown in Fig. 3(a) and (b), after the Al substrate was immersed in the Ni<sup>2+</sup>-containing solution (initial pH 2) for 6 h, its smooth surface seemed to be covered by a layer of substance. There are three kinds of typical morphology in Fig. 3(b): uncovered Al substrate, covering layer and sphere-like protrusions on the layer. According to the EDX results shown in the insets of Fig. 3(b), the Al/O ratios of the three areas/spots are 30.01/1, 1.35/1 and 0.51/1, respectively. Signal of Ni was not detected. Considering that the pH value increased from 2 to 3.8 after 6 hours of reaction (see Fig. S4†) accompanied by the release of Al<sup>3+</sup> into the solution, formation of aluminium hydr(ous) oxide layer, such as AlOOH, on Al substrate was expectable.<sup>5a-b</sup> As the immersion time prolonged to 9 h, a layer of microcrystals began to form on the thick aluminium hydr(ous) oxide layer (Fig. 3(c)). Similar interlayer of alumina was also observed in the SEM image of ZnAl-LDH film fabricated under near neutral condition.<sup>3a</sup>

When the immersion time increased to 12 h, the curved sheet-like microcrystals had covered almost the entire substrate surface (Fig. 3(d)). At the same time, a small amount of flocculent precipitate formed in the bulk solution. The XRD patterns of scraped powder of NiAlp2t12 and NiAlp2t12-p are shown in Fig. S2(c)† and (d)†. The broad diffraction peaks of LDH are presented in the XRD pattern of NiAlp2t12-p, whereas no diffraction peak other than that of aluminium metal scraped from the Al substrate can be detected in the XRD pattern of the scraped NiAlp2t12 powder. The difference in crystallinity between these two substances suggests that they are formed separately. We hence infer that the formation of LDH film on the interlayer and precipitate in solution can be explained by heterogeneous and homogenous nucleation mechanism, respectively.<sup>2d</sup> The size of the microcrystal on interlayer gradually increased with increasing crystallization time, and a layer of much larger and thicker LDH crystallites was formed after 24 h (Fig. 2(b)). The XPS spectra of NiAlp2t24 indicated that the formation of Al-O-Ni bonds in



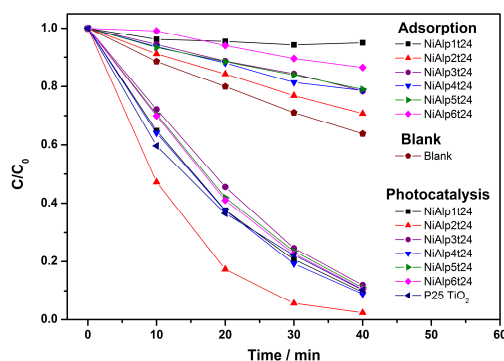
**Fig. 3** SEM images of surface morphology of NiAlp2ty,  $y =$  (a) 0 h, (b) 6 h, (c) 9 h and (d) 12 h, at low magnification. Insets are images at high magnification and the EDX results of corresponding areas and spot.

5 NiAl-LDH lowered the binding energy of Al 2p, compared to that of the Al 2p of NiAlp2t6 (Fig. S8†).

According to our above investigations, a possible formation mechanism of NiAl-LDH film on Al substrate under strong acidic condition can be proposed as follows: (i) dissolution of aluminium by reacting with  $H^+$  to provide  $Al^{3+}$  which are enriched on the surface of the Al substrate; (ii) formation of aluminium hydr(ous) oxide layer on Al substrate under acidic condition (Fig. 3(b)); (iii) nucleation and growth of LDHs on the phase boundary (Fig. 3(c), (d) and Fig. 2(b)). Meanwhile, the formation process of NiAlp1t24 is discussed in ESI (Fig. S9†).

More recently, interest has been focused on the LDHs as they show high activity and good stability in photocatalysis.<sup>7</sup> Moreover, immobilization of LDH on a substrate can not only facilitate the manipulation, but also improve the catalytic activity as the material presents different morphology compared to the powder sample.<sup>8</sup> To evaluate the activity of the LDH films fabricated under acidic conditions, photocatalytic degradations of MO and Rh B were carried out under ultraviolet radiation. Meanwhile, photocatalytic property of Degussa P25  $TiO_2$  was investigated for comparison, and the adsorption properties of MO on NiAlp2t24 are also showed in Fig. 4 and Fig. S10†. Among the six films and  $TiO_2$ , NiAlp2t24 showed the highest activity in photodegradation of MO (Fig. 4), indicating that the morphology and structure should be the main influencing factor on the photocatalytic performance of NiAl-LDH films, which is affected by the initial pH value of  $Ni^{2+}$ -containing solution significantly. As for Rh B, NiAlp2t24 exhibited an approximate photocatalytic performance as P25  $TiO_2$  (Fig. S11†).

In summary, NiAl-LDH films with hierarchical morphology on Al substrate have been fabricated in  $Ni^{2+}$ -containing solution (initial pH 2-6) by *in situ* growth method. The obtained films showed remarkable activity in photocatalytic degradation of organic contaminants. The formation of the film under strong acidic condition was supposed to experience the following steps: dissolution of aluminium, formation of aluminium hydr(ous) oxide layer on Al substrate, nucleation and growth of LDH crystals on the interlayer. The finding of this work is a useful extension of both the preparation conditions and the formation mechanism of the LDH film fabrication using *in situ* growth



**Fig. 4** Photocatalytic degradation of MO under UV-light irradiation and adsorption of MO on NiAlp2t24 in the dark.

method. They may be of great value in designing of LDH materials for the control of environmental pollutants and other various potential applications.

This work was supported by the Project of Shandong Province Higher Educational Science and Technology Program (J13LD13), the Colleges and Universities Outstanding Young Teachers Domestic Visiting Scholars Program of Shandong Province and the Chinese Academy of Sciences (“Hundred Talents Project”).

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