Oriented printable layered double hydroxide thin films via facile filtration†

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Highly oriented layered double hydroxide (LDH) thin films are obtained from colloidal dispersion of exfoliated LDH nanosheets in formamide by vacuum filtration. Through filtration, positively charged LDH nanosheets are stacked in interlocking arrangements, which endow LDH thin films with excellent mechanical properties. Consequently, the fresh prepared LDH thin films are printed on different substrates, forming transparent, strong and flexible LDH layers. Utilizing coassembly of positively charged LDH nanosheets with polymeric anions, negatively charged LDH nanohybrids can be obtained. By adding various types of anions into a colloidal dispersion of LDHs and subsequent filtration, LDH thin films with tunable composition and nanostructure can be prepared easily. However, the addition of carbonate or small molecular anionic surfactants leads to aggregation of LDH nanosheets. This facile filtration method will facilitate the fabrication of functional LDH thin films.

Introduction

Inorganic thin films or paper-like materials are playing important roles in current science and technology. They can act as protective layers, chemical filters or adsorbents, electrical barriers, components of optical devices and so on. Recently, a biologically inspired strategy has been used in the fabrication of thin films with excellent mechanical properties, based on nano-scale components such as exfoliated clay,1 graphene nanosheets2 or carbon nanotubes.3 Inspired by natural seashell nacre, which is well known for its high strength and stiffness, exfoliated nanosheets are stacked with each other in the form of unique interlocking arrangements under an external driving force. Layered double hydroxides (LDHs) form a class of anionic clay with layered structure, represented by the general formula $\text{[M}^{\text{I}}_{\text{n}}, \text{M}^{\text{II}}_{\text{n}}(\text{OH})_{\text{m}}][\text{A}^{\text{n-}}_{\text{x}}\text{H}_{\text{y}}\text{O}]^{\text{n-}}$. Positively charged LDH nanosheets build ordered and stable layered structures for various functional anions or polymers. As a result, functional organic–inorganic hybrid materials can be prepared with marvelous properties, such as drug delivery and release,4–7 adsorption,8 photocatalysis,9 polarized photoluminescence,10 photocurrent generation,11 thermochromism,12 etc.

Generally, strategies for fabrication of functional thin films containing LDH nanosheets can be summarized into three routes. Route one is to cast a colloidal dispersion of LDH crystals directly which usually leads to transparent self-supporting LDH films.13–16 The key point is to fabricate LDH thin films in nano-size to minimize the “edge-to-face” interactions.14 An SNAS (Separate Nucleation and Aging Steps) method17 was developed to synthesize LDHs with uniform crystal size in tens of nanometres. Xu18,19 and Gursky20 also reported methods to prepare LDH nanoparticles. Route two is layer-by-layer (LBL) assembly using delaminated LDH nanosheets and other functional components.11,21–23 The total delamination24 of LDHs enables the fabrication of organic–inorganic hybrids with more complicated nanostructure, where exfoliated LDH nanosheets act as building blocks. Route three is a so-called “orientation-controlled immobilization” method. Jung et al.25–27 successfully immobilized LDH crystals on an Si substrate in monolayer assembly. The monolayer of LDHs could undergo ion-exchange reactions, even LBL with different types of LDH crystals.

Ultra-strong graphene bulky paper, which was prepared by simple vacuum filtration of a colloidal dispersion of graphene nanosheets, has attracted most research interest recently.2,28,29 In graphene paper, flexible graphene nanosheets are orderly stacked and attached to each other. In this study, we utilize this facile filtration strategy to fabricate LDH thin films. Two types of LDHs were employed, Co$_2$Al-LDH with lateral size of 6 µm and Ni$_2$Al-LDH with lateral size of 500 nm, to examine the influence of lateral size of LDH nanosheets on the structure and morphology of LDH films. It is interesting to discover that
freshly prepared LDH thin films were able to print on most substrates. Characterized by several techniques, the formation procedures and consequent nanostructure of LDH films were proposed and discussed. Coassembly of LDH nanosheets with various anions was also studied. It is possible to fabricate functional LDH thin films via this facile filtration approach by adding diverse functional polymeric anions into LDH colloids.

**Experimental**

**Materials**

Polyethylene oxide (PEO, $M_w = 300 000$) was purchased from Alfa Aesar. Anionic polyacrylamide (APAM) was synthesized according to the procedures described in the literature. The following analytical grade reagents were purchased from Sinopharm Co. and used as received: CoCl$_2$·6H$_2$O, AlCl$_3$·6H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, urea, NaCl, NaNO$_3$, 37% HCl and sodium dodecylbenzene sulfonate (SDBS).

**Preparation of exfoliated CoAl and NiAl-LDH nanosheets**

Highly crystalline particles of CoAl-CO$_3$-LDH and NiAl-CO$_3$-LDH were synthesized according to a previous report. Typically, an aqueous solution of CoCl$_2$ (10 mM), AlCl$_3$ (5 mM) and urea (35 mM) was allowed to react in a 100 mL Teflon-lined autoclave at 100 °C for 24 h. For the synthesis of NiAl-CO$_3$-LDH, a mixed solution containing Ni(NO$_3$)$_2$ (0.1 M), Al(NO$_3$)$_3$ (0.05 M) and urea (0.15 M) was hydrothermally treated at 190 °C for 48 h. The resulting precipitates were collected by filtration and washed with deionized water and anhydrous ethanol several times.

The delamination procedures were carried out as follows. 0.5 g as-prepared carbonated LDHs were dispersed in a NaCl–HCl mixed solution (1 M NaCl and 3.3 mM HCl in 500 mL deionized water) and stirred under nitrogen atmosphere for 24 h. Then, the obtained Cl⁻-LDHs were converted into their nitrate form by a conventional anion exchange process with 0.1 M NaNO$_3$. Finally, 0.1 g NO$_3$⁻-LDHs were mixed with 100 mL formamide and stirred under nitrogen for 2 days. The resulting transparent suspension was then centrifuged at 8000 rpm for 5 min to remove the unexfoliated particles.

**Fabrication of highly oriented LDH films**

Specific surface treatments were firstly employed to enhance substrate adhesion of LDH films. Aluminium sheet (0.1 mm thickness, 2N grade) was immersed in 0.5% aqueous NaOH solution for 1 min followed by ultrasonic treatment in deionized water and in ethanol for 10 min. Glass slides were cleaned in a “piranha” solution (3 : 1 H$_2$SO$_4$ : H$_2$O$_2$) and ultrasonically treated for 30 min. Poly(ethylene terephthalate) (PET) plastic films were cleaned in ethanol/acetone mixed solution (1 : 1 ethanol : acetone).

Colloidal dispersion of LDH nanosheets in formamide at a concentration of 0.5 mg mL$^{-1}$ was vacuum filtered through a polyamide membrane filter (220 nm pore size, Shanghai Xinya). The membrane with captured LDHs was wetted with a few drops of formamide and then pressed against the substrate surface with LDH side in contact with the substrate. The LDH film was adhered to the substrate under 1 kg pressure at room temperature for 1 h. Subsequently, the membrane filter was torn off and the LDH film was dried under vacuum at room temperature (Scheme 1). It was discovered that the adhesion of LDH thin films is sufficiently strong to prevent delamination during processing.

**Coassembly of LDH nanosheets in formamide**

Anion salts (Na$_2$CO$_3$, NaCl, NaNO$_3$, and SDBS) were dissolved in a small amount of deionized water. Then they were diluted with formamide to an indicated anion concentration of 0.1 M (water/formamide volume ratio of 1/3), 10 mL of such a 0.1 M solution was added dropwise to 10 mL 1 mg mL$^{-1}$ colloidal suspension of LDHs with continuous stirring. APAM and PEO were directly dissolved in formamide at a concentration of 5 wt %. 10 mL APAM or PEO solution was added into 10 mL 1 mg mL$^{-1}$ colloidal suspension of LDHs.

**Characterization**

X-ray diffraction (XRD) patterns of the samples were recorded using an X’Pert X-ray diffractometer with Cu-Kα radiation ($\lambda = 0.1548$ nm). Fourier transform infrared (FT-IR) spectra were recorded in the range of 4000 to 400 cm$^{-1}$ with 4 cm$^{-1}$ resolution on a Nicolet Nexus 470 spectrometer equipped with a DTGS detector by signal-averaging 64 scans. Scanning electron microscopy (SEM) images of LDHs were obtained using a Tescan 5166 MM SEM at 20 kV while the morphology of LDH films was observed by a JEOL JSM-6700 field emission scanning electron microscope (FESEM) under an accelerated voltage of 5.0 kV. Atomic force microscopy (AFM) images were acquired in tapping mode by using a Nanoscope IV from Digital Instruments. For AFM observations, the samples were prepared by casting and drying the solution on freshly cleaved mica at room temperature. Zeta potential of LDH colloids were measured using a Malvern Zetasizer Nano instrument. Before the measurement, water in LDH colloids was removed by rotary evaporation at room temperature.
Results and discussion

Exfoliation of LDHs

In most cases, highly oriented LDH films were fabricated by solvent evaporation method using colloids of LDH nanoparticles,12-15,32,33 i.e. LDH crystal size in tens of nanometres. In the present study, however, exfoliated LDH nanosheets are used to fabricate LDH films whatever the lateral size of LDH crystals is. In order to examine the influence of lateral size of LDH nanosheets on the morphology and structure of LDH thin films, highly crystallized Co$_2$Al-LDH (lateral size in micrometres) and Ni$_2$Al-LDH (lateral size in hundreds of nanometres) were chosen here. Fig. 1 shows SEM images of typical Co$_2$Al-CO$_3$-LDH (Fig. 1a) and Ni$_2$Al-CO$_3$-LDH (Fig. 1b) prepared by hydrothermal treatment. The combination of urea hydrolysis method and hydrothermal treatment ensures that LDHs are well crystallized into regular and large-sized hexagonal platelets. As can be seen, Co$_2$Al-CO$_3$-LDH is uniform in size with an average platelet size of about 6\,\mu m while Ni$_2$Al-CO$_3$-LDH has a relatively wider size distribution and smaller particle size of about 500 nm.

The XRD patterns of Co$_2$Al-CO$_3$-LDH, Ni$_2$Al-CO$_3$-LDH and their anion-exchanged samples are shown in Fig. 2. All diffraction peaks are sharp and narrow, indicating the highly crystalline nature of both types of LDHs. The (003) and (006) diffraction peaks of Co$_2$Al-CO$_3$-LDH and Ni$_2$Al-CO$_3$-LDH appear at 2\theta angles of 11.8° and 23.7°, respectively, while their (110) diffraction peaks are at about 61.4°. According to the Bragg equation, it is estimated that the d-spacing values of both carbonated LDHs are about 0.75 nm. The crystal lattice parameters a and c, which are calculated based on the diffraction peaks of (110) and (003) planes, are 0.3064 and 2.225 nm, respectively. After decarbonation and anion exchange with Cl$^-$ and NO$_3^-$, the basal spacings of CoAl- and NiAl-LDH samples increase from 0.75 nm to 0.78 nm and 0.89 nm, respectively. FTIR spectra (see ESI, Fig. S1†) also confirm the complete decarbonation and consequent anion exchange. The strong absorption peak at 1356 cm$^{-1}$ which belongs to the v3 vibration of CO$_3^{2-}$ of carbonated LDHs disappears after decarbonation. During decarbonation and anion exchange processes, only small border areas of LDH crystals are dissolved or cracked. Both CoAl- and NiAl-LDH preserve hexagonal platelets (see ESI, Fig. S2 and Fig. S3†).

In order to obtain positively charged unilamellar LDH nanosheets, delamination is thought to be effective in the presence of formamide.24 The delamination is achieved by starting from nitrate LDHs and undergoes two separate processes: rapid “osmotic swelling” and subsequent slow exfoliation.21 Transparent dispersions of LDHs were obtained after stirring the NO$_3^-$-LDHs and formamide mixture for 2 days, as shown in Fig. 3a and 3d. The morphology and size of exfoliated LDH nanosheets were examined by AFM. Tapping mode AFM images (Fig. 3b and 3e) showed that the two-dimensional structure of unilamellar LDH nanosheets was maintained, although some small fragments could also be observed. For both CoAl- and NiAl-LDH nanosheets, the height of an individual platelet is about 0.8 nm, which is believed to be the sum of the thickness of unilamellar LDH nanosheets and that of the adsorbed layer of formamide molecules. The lateral size is about 4 \ \mu m and 500 nm for CoAl- and NiAl-LDH nanosheets, respectively.

Fabrication of highly oriented LDH films

Inspired by ultrastrong and stiff natural materials, innovative techniques have been used to fabricate artificial composites by...
mimicking the nanostructures of natural materials, using inorganic nano-platelets as building blocks.\textsuperscript{1,34,35} Positively charged LDH nanosheets are often used in LBL assembly\textsuperscript{21,23,36} while colloidal dispersions of LDH nanoparticles can even form self-supported strong films. Through filtration of exfoliated LDH nanosheets in formamide, oriented LDH films with packed interlocking structure can also be obtained. In our study, the fabrication of highly oriented LDH films requires five steps, as shown in Scheme 1.

After exfoliation of LDHs in formamide, colloids of LDH nanosheets were filtered with a membrane filter. In the presence of vacuum pressure, positively charged LDH nanosheets were deposited on the membrane filter with preferential plane orientation. Due to the strong affinity of LDH nanosheets with formamide molecules, the filtered LDH thin films usually take up small amounts of formamide, which will act as ink solvent during the print process. The wetted LDH film on the filter membrane was pressed against the substrate surface. After holding at an appropriate pressure for 1 h, the membrane filter was torn off, thus leaving an oriented, transparent, strong and flexible LDH thin film adhering to the substrate. Several representative substrates, e.g. Al foil, glass slide and PET plastic film, proved to be suitable to support LDH films (with appropriate film thickness less than 10 μm) during the printing process, as shown in Fig. 5. The interactions between LDH nanosheets and polar surfaces of these substrates may be a combination of electrostatic and van der Waals interactions. In some cases, hydrogen bonding is also a factor which enhances the interfacial interactions. Substrates with non-polar surfaces such as polyethylene and polystyrene films can also support LDH films, indicating the presence of sufficiently strong van der Waals interactions between LDHs and non-polar surfaces. However, the brittle nature of LDHs limits the thickness of printable LDH films. When the thickness of filtered LDH film exceeds 10 μm, the subsequently printed film is poor in quality with cracks or irregular stacks of LDHs. A film with a thickness as large as 1 μm is more suitable for printing. SEM images of CoAl- and NiAl-LDH films printed on Al sheets are shown in Fig. 5. CoAl-LDH film has a surprisingly flat surface from the top view under both low (Fig. 5a) and high (Fig. 5b) magnification observations. NiAl-LDH film also shows a flat surface at low magnification (Fig. 5d). However, the SEM observation at high magnification (Fig. 5e) reveals that individual NiAl-LDH platelets, with lateral size of about 400 nm, are densely packed to form a continuous film. The cross-section observations of both CoAl-LDH (Fig. 5c) and NiAl-LDH (Fig. 5f) films by SEM show highly anisotropic structural features. Fig. 6 shows XRD patterns of CoAl- and NiAl-LDH films printed on Al sheets. Combining the XRD patterns and the SEM observations on the cross-section of LDH films, it can be concluded that the printed LDH films are highly oriented. For CoAl-LDH film, an intense diffraction peak is observed at 2θ = 7.8° (i.e. d-spacing = 1.13 nm, approximately corresponding to a thickness of two packed LDH nanosheets), indicating a staggered packed structure. The XRD pattern of freshly prepared CoAl-LDH wet film also confirms this structure (see Fig. S4†). For the occurrence of multiple diffraction peaks in NiAl-LDH film, it is proposed that exfoliated NiAl-LDH nanosheets are more inclined to restore their original layered structure (Scheme 2).

In order to investigate the coassembly and stacking behavior of LDH nanosheets in formamide, various types of anions were added into the colloidal dispersion of LDH/formamide.

**Coassembly and stacking behavior of LDH nanosheets in formamide**

The colloid of LDH nanosheets is not stable in water,\textsuperscript{37} but it is also shown that exfoliated LDH nanosheets are tolerant of water in formamide (e.g. 1 : 1 water/formamide mixture).\textsuperscript{38} In order to minimize the influence of water on restacking of LDHs, anion salts were dissolved and diluted in 1 : 3 water/formamide mixed solvent. After mixing with 10 mL LDH/formamide colloid, the water content is about 12.5% in volume. Therefore, the influence of water on restacking of LDHs can be eliminated.

When 0.1 M Na$_2$CO$_3$ or SDBS water/formamide mixture was added to LDH/formamide colloids, LDH nanosheets were gradually aggregated into flocculent precipitates. However, the addition of NaCl, NaNO$_3$, APAM or PEO had no influence on exfoliation of LDH nanosheets (as shown in Fig. S5†). It is noticed that carbonate or carboxyl groups will coordinate with cobalt in CoAl-LDH, which leads to a slight color change from pale red to purple. After removing water from the mixture, the zeta potential of dispersed LDH nanosheets was measured using a Malvern Zetasizer Nano. For the samples with addition of Na$_2$CO$_3$ or SDBS, supernatant liquid was collected and measured. Table 1 lists the zeta potential data of the samples, which are in good agreement with the observed phenomena. Obviously, the introduction of Na$_2$CO$_3$ and SDBS severely reduces the zeta potential to around 0 mV, indicating extremely unstable suspensions. In the case of APAM/LDH colloid, the zeta potential changes from 28.2 to −34.0 mV for CoAl-LDH, and 35.1 to −43.0 mV for NiAl-LDH. For the other colloids, the zeta potential changes slightly. We believe that in the presence of sufficient concentration of APAM molecules, coassembly of positively charged LDH nanosheets with APAM will convert the surface property of LDHs from positive to negative.\textsuperscript{39} The same case is for the SDBS/CoAl-LDH sample. Due to hydrophobic interactions between alkyl chains, a bilayer arrangement\textsuperscript{39} of SDBS molecules may be formed, which results in negatively charged surfaces, i.e. zeta potential of −5.6 mV. Considering the extensive applications of negatively charged nanosheets, it is a promising route to fabricate negatively charged LDH nano-hybrids by adding polymeric anions or surfactants.

XRD patterns of CoAl- and NiAl-LDH thin films prepared by vacuum filtration of LDH colloids are shown in Fig. 7. The precipitates in Na$_2$CO$_3$ or SDBS/LDH mixture were also collected and characterized. The XRD patterns of carbonate

![Fig. 4](image-url) Photos of CoAl-LDH thin films printed on Al foil (a), glass slide (b) and PET plastic film (c).
LDH precipitate show two diffraction peaks at 2θ angles of 11.8° and 23.7° for both CoAl- and NiAl-LDH, indicating that the layered structure of carbonated LDHs was restored. The appearance of a series of diffraction peaks in XRD pattern of SDBS/NiAl-LDH sample also indicates the restacking of NiAl-LDH with SDBS as interlayer anions. However, no diffraction peak could be observed for SDBS/CoAl-LDH sample, indicating an irregular aggregation. Considering the zeta potential data of 5.6 mV, the aggregation of SDBS/CoAl-LDH may be induced by hydrophobic interactions among the adsorbed SDBS molecules rather than electrostatic attraction. Moreover, it is believed that in order to restore the original layered structure, LDH nanosheets should have comparable lateral size to match with each other. The lateral size of CoAl-LDH nanosheets in micrometres may be too large to conduct the structural restoration.

Due to different stacking modes of CoAl- and NiAl-LDH films, the influence of anions on nanostructures of LDH films are discussed separately. For CoAl-LDH, the addition of NaCl, NaNO₃, PEO and APAM enlarges the basal spacing from 1.13 nm to 1.50, 1.56, 1.28 and 2.59 nm, respectively, which is due to the incorporation of large quantities of anions or polymers into the stacked interlayer spaces. For the NiAl-LDH films, the diffraction peaks exactly match with the XRD patterns of NiAl–Cl-LDH, NiAl-NO₃-LDH, NiAl-APAM-LDH and NiAl-PEO-LDH. Therefore, it seems that the exfoliated NiAl-LDH nanosheets are apt to restore the layered structure upon filtration whatever anions are added. It is noticed that PEO incorporated CoAl- and NiAl-LDH films both have smaller basal distances than those of APAM incorporated LDH films. The interactions between PEO molecules and LDH nanosheets are mostly

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**Fig. 5** SEM plane view of LDH films at (a, d) low and (b, e) high magnifications, (c, f) cross-section view. a, b, c: CoAl-LDH film; d, e, f: NiAl-LDH film.

**Fig. 6** XRD patterns of CoAl and NiAl-LDH thin film printed on Al substrate (*, diffraction peaks belong to Al substrate; ●, diffraction peak of CoAl-LDH film; ◆, diffraction peaks of NiAl-LDH film).

**Scheme 2** A schematic illustration of LDH nanosheets stacking into LDH films.
hydrogen bonding, which are weaker than electrostatic attractions between LDHs and anions. As a result, fewer PEO than APAM molecules are adsorbed on LDH nanosheets. Moreover, it is interesting to note that with the presence of PEO, the interlayer distance of restored NiAl-LDH increased from 0.82 nm to 1.08 nm. The contents of adsorbed PEO and APAM molecules were estimated by TGA to be 10 wt % and 64 wt %, respectively (Fig. S6†). Adsorption models are proposed as shown in Scheme 3. The morphology of LDH-PEO hybrid films is the same as that of neat LDH films (Fig. S7†).

Utilizing coassembly of functional anions and exfoliated LDH nanosheets, LDH thin films with diverse properties can find many practical applications. Sulforhodamine 101 (Fig. S8a†) is a red fluorescent dye, which is widely used in analysis and detection of biological systems. By coassembly of sulforhodamine 101 with CoAl-LDH nanosheets, CoAl-sulforhodamine-LDH thin films with well-defined red fluorescence can be obtained (Fig. S8b,c†). It is reported that the multilayer assemblies of CoAl-LDH nanosheets exhibit a significant magneto-optical response in the ultraviolet-visible region.21 Thus, CoAl-sulforhodamine-LDH thin films have potential applications in optical and magnetic devices. LDH films can also be used as protective coatings in electro-insulation and anti-corrosion. When LDH films are coated on metal substrates, LDH films serve as barriers isolating external aggressive ions. SEM images of the samples before and after immersion in 3.5% aqueous NaCl solution are shown in Fig. S9.† No sign of corrosion can be seen on the surface of the NiAl-LDH coated Al sheet, indicating good anti-corrosion properties.

In general, we are able to fabricate highly oriented LDH films with tunable composition and nanostructure through coassembly of LDH nanosheets with anions or polymers. Oriented NiAl-LDH thin films consist of restored NiAl-LDH crystals with designed interlayer anions, while large-sized CoAl-LDH nanosheets can adsorb anions to form highly smoothed CoAl-LDH thin film with designed composition and nanostructure.

**Conclusions**

Highly oriented LDH thin films have been prepared via facile filtration of LDH/formamide colloids and printed on different substrates where neat LDH films can act as protective layers. The morphology and nanostructures of CoAl- and NiAl-LDH films are investigated. It is shown that LDH films consist of packed interlocking arrangements of LDH nanosheets, endowing LDH films with excellent mechanical performance to sustain their printability. Utilizing the coassembly and restacking behavior of LDH nanosheets with anions or polymers, LDH thin films with tunable and controllable compositions and nanostructures could be achieved. Moreover, surface charges of LDH nanosheets

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**Table 1** Zeta potential of CoAl and NiAl-LDH colloids with various anions or polymers

<table>
<thead>
<tr>
<th>Z potential (mV)</th>
<th>CoAl +CO$_3^{2-}$</th>
<th>+Cl$^-$</th>
<th>+NO$_3^{-}$</th>
<th>+DBS$^-$</th>
<th>+APAM</th>
<th>+PEO</th>
</tr>
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<tbody>
<tr>
<td>Z potential (mV)</td>
<td>28.2</td>
<td>43.1</td>
<td>14.8</td>
<td>24.9</td>
<td>-5.6</td>
<td>+APAM</td>
</tr>
<tr>
<td></td>
<td>35.1</td>
<td>4.5</td>
<td>41.7</td>
<td>48.2</td>
<td>0.1</td>
<td>-43.0</td>
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**Fig. 7** XRD patterns of LDH samples obtained by adding various anions into LDH colloids. (a) CoAl-LDH samples; (b) NiAl-LDH samples.
could be converted from positive to negative by coassembly of positively charged LDHs with anionic polyacrylamide. This filtration method will facilitate the fabrication of functional LDH thin films.

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Notes and references