Heterogeneous ultrathin films fabricated by alternate assembly of exfoliated layered double hydroxides and polyanion

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Preparation of $\text{M(\:\text{Co, Mg})Al-CO}_3\text{LDH}$

The CoAl-CO$_3$ LDH with high crystallinity and well-defined hexagonal shape was prepared as reported in ref:1 in order to avoid the formation of Co$_3$O$_4$ impurity, a three-neck flask (equipped with a reflux condenser) under a nitrogen flow instead of autoclave was employed. Typically, CoCl$_2$·6H$_2$O, AlCl$_3$·6H$_2$O and urea were dissolved in 800 cm$^3$ deionized water to give the final concentrations of 10, 5.0 and 35 mM, respectively. The solution was then heated at 97 °C under refluxing and continuous stirring for 2 days. In the case of the preparation of MgAl-CO$_3$ LDH, Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, and urea were dissolved in 100 cm$^3$ of deionized water to give the final concentrations of 0.2, 0.1, and 1.0 M, respectively. The solution was then heated at 110 °C under refluxing and continuous stirring for 24 h. The resulting product was filtered, washed with deionized water and anhydrous ethanol for several times, and finally dried at ambient temperature in air.

Preparation of $\text{M(\:\text{Co, Mg, Ni})Al-NO}_3\text{LDH}$

The samples of CoAl- and MgAl-NO$_3$ LDH were synthesized by salt-acid method reported by Iyi et al.2 Typically, 0.5 g of M(\:\text{Co, Mg})Al-CO$_3$ LDH was treated with 500 cm$^3$ of an aqueous salt-acid solution containing NaNO$_3$ (0.75 mol) and HNO$_3$ (0.0025 mol) in a three-neck flask under nitrogen flow and continuous stirring conditions at ambient temperature for 24 h to expel interlayer carbonate ions. Otherwise, highly crystallized NiAl-NO$_3$ LDH was prepared directly by urea method under hydrothermal treatment. The mixed solution of Ni(NO$_3$)$_2$·6H$_2$O (0.10 M), Al(NO$_3$)$_3$·9H$_2$O (0.05 M), and urea (0.15 M) was placed in an autoclave and heated at 190 °C for 48 h. The resulting product
were filtered, washed as before, and finally vacuum-dried.

**Exfoliation of M(Ⅱ)Al-NO₃ LDH (M=Co, Mg, Ni)**

The unilamellar, positively charged LDH nanosheets were synthesized by vigorously agitating 0.1 g of M(Ⅱ)Al-NO₃ LDH in 100 cm³ of formamide at room temperature under a N₂ gas flow for 2 days.

**Fabrication of (CoAl-LDH/PSS/NiAl-LDH/PSS)ₙ/2 heterogeneous film**

The overall process of LBL deposition of heterogeneous ultrathin film of (CoAl-LDH/PSS/NiAl-LDH/PSS)ₙ/2 consists of a cyclic repetition of the following steps: (a) dipping the treated substrate with negatively charged surface into formamide containing exfoliated CoAl-LDH nanosheets for 10 min; (b) rinsing with deionized water thoroughly and then dipping into an aqueous solution of PSS for 15 min; (c) rinsing with deionized water and dipping the substrate into the NiAl-LDH nanosheets colloid for another 10 min; (d) the same procedure as step b. A series of these operations were repeated to obtain multilayer films of (CoAl-LDH/PSS/NiAl-LDH/PSS)ₙ/2. The resulting films were finally rinsed with deionized water and dried at ambient temperature in a vacuum oven.

**Sample characterization**

Powder X-ray diffraction data were recorded by a Shimadzu XRD-6000 power X-ray diffractometer using Cu Kα radiation (λ = 0.154 nm) at 40 kV, 30 mA, a scanning rate of 5° min⁻¹, and a 2θ angle ranging from 3° to 70°. UV absorption spectra were performed on a Shimadzu UV-2501PC spectrometer. The Fourier transform infrared (FT-IR) spectra were recorded using a Vector 22 (Bruker) spectrophotometer using the KBr pellet technique in the range of 4000~400 cm⁻¹ with 2 cm⁻¹ resolution. The morphology of the LDH samples was investigated by using a Hitachi S-4700 scanning electron microscope (SEM) at an acceleration voltage of 20 KV. The surface topography and thickness of LDH nanosheets deposited onto Si wafers were examined using a NanoScope IIIa atomic force microscope (AFM) from Veeco Instruments. The contents of the metals of LDH samples were determined by inductively coupled plasma (ICP) emission spectroscopy on a Shimadzu ICPS-7500 instrument. Carbon, Hydrogen and nitrogen analyses were carried out using a Perkin Elmer Elementarvario elemental analysis instrument. The interlayer water content was evaluated by thermogravimetry and differential thermal analysis using a Hengjiu HCT-2 thermal instrument.
### Table S1. Chemical formulae of the LDH precursors

<table>
<thead>
<tr>
<th>LDH samples</th>
<th>chemical formulae</th>
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<tbody>
<tr>
<td>CoAl-CO$_3$ LDH</td>
<td>$<a href="%5Ctext%7BCO%7D_3%5E%7B2-%7D">\text{Co}<em>{0.66}\text{Al}</em>{0.34}(\text{OH})_2</a>_{0.17} \cdot 0.49\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>MgAl-CO$_3$ LDH</td>
<td>$<a href="%5Ctext%7BCO%7D_3%5E%7B2-%7D">\text{Mg}<em>{0.68}\text{Al}</em>{0.32}(\text{OH})_2</a>_{0.16} \cdot 0.52\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>CoAl-NO$_3$ LDH</td>
<td>$<a href="%5Ctext%7BNO%7D_3%5E-">\text{Co}<em>{0.66}\text{Al}</em>{0.34}(\text{OH})_2</a>_{0.34} \cdot 0.51\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>MgAl-NO$_3$ LDH</td>
<td>$<a href="%5Ctext%7BNO%7D_3%5E-">\text{Mg}<em>{0.68}\text{Al}</em>{0.32}(\text{OH})_2</a>_{0.32} \cdot 0.52\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>NiAl-NO$_3$ LDH</td>
<td>$<a href="%5Ctext%7BNO%7D_3%5E-">\text{Ni}<em>{0.67}\text{Al}</em>{0.33}(\text{OH})_2</a>_{0.33} \cdot 0.51\text{H}_2\text{O}$</td>
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**Fig. S1** Powder XRD patterns of the (a) CoAl- and (b) MgAl-CO$_3$ LDH samples.
Fig. S2 FT-IR spectra of the (a) CoAl- and (b) MgAl-CO$_3$ LDH samples.

Fig. S3 SEM images of (A) CoAl- and (B) MgAl-CO$_3$ LDH samples.

Fig. S4 FT-IR spectra of the (a) CoAl-, (b) MgAl- and (c) NiAl-NO$_3$ LDH samples.
**Fig. S5** SEM images of (A) CoAl- (B) MgAl- and (C) NiAl-NO₃ LDH samples.

**Fig. S6** Tapping-mode AFM images of (A) the exfoliated CoAl- and (B) MgAl-LDH nanosheets deposited on Si wafer substrate.
**Fig. S7** UV absorption spectra of (A) (CoAl-LDH/PSS/MgAl-LDH/PSS)$_n$/2 and (B) (MgAl-LDH/PSS/NiAl-LDH/PSS)$_n$/2 films. The numbers of bilayers are 1 to 10 from the bottom to the top (An LDH nanosheet/PSS layer is defined as one bilayer).

**Fig. S8** Photograph of transparent films of (A) (CoAl-LDH/PSS/MgAl-LDH/PSS)$_n$/2, (B) (MgAl-LDH/PSS/NiAl-LDH/PSS)$_n$/2 and (C) (CoAl-LDH/PSS/NiAl-LDH/PSS)$_n$/2 ($n=50$). The size of the quartz glass substrate is 3.0×3.0 cm.

**References:**
