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

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Preparation of M(□)Al-CO_3 LDH (M=Co, Mg)

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_3O_4 impurity, a three-neck flask (equipped with a reflux condenser) under a nitrogen flow instead of autoclave was employed. Typically, $CoCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$ 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, $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, 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 mixed solution was placed into a Teflon-lined stainless steel autoclave, sealed, and hydrothermally treated at 110 °C 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 M(□)Al-NO_3 LDH (M=Co, Mg, Ni)

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(□)Al-CO_3 LDH (M=Co, Mg) 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 $Ni(NO_3)_2 \cdot 6H_2O$ (0.10 M), $Al(NO_3)_3 \cdot 9H_2O$ (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-NO_3 LDH (M=Co, Mg, Ni)

The unilamellar, positively charged LDH nanosheets were synthesized by vigorously agitating 0.1 g of M(Ⅱ)Al-NO_3 LDH in 100 cm^3 of formamide at room temperature under a N_2 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

LDH samples	chemical formulae
CoAl-CO_3 LDH	$[Co_{0.66}Al_{0.34}(OH)_2](CO_3^{2-})_{0.17}\cdot 0.49H_2O$
MgAl-CO_3 LDH	$[Mg_{0.68}Al_{0.32}(OH)_2](CO_3^{2-})_{0.16}\cdot 0.52H_2O$
CoAl-NO_3 LDH	$[Co_{0.66}Al_{0.34}(OH)_2](NO_3^{-})_{0.34}\cdot 0.51H_2O$
MgAl-NO_3 LDH	$[Mg_{0.68}Al_{0.32}(OH)_2](NO_3^{-})_{0.32}\cdot 0.52H_2O$
NiAl-NO_3 LDH	$[Ni_{0.67}Al_{0.33}(OH)_2](NO_3^{-})_{0.33}\cdot 0.51H_2O$

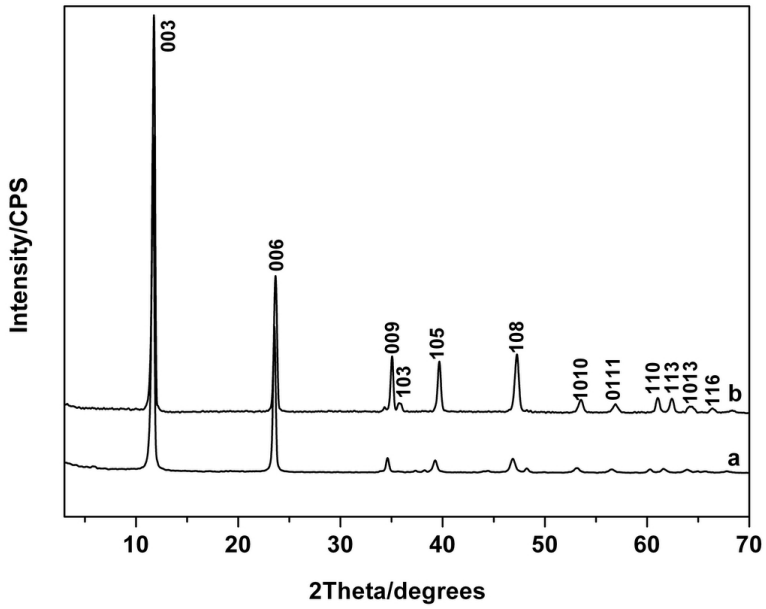

Fig. S1 Powder XRD patterns of the (a) CoAl- and (b) MgAl-CO_3 LDH samples.

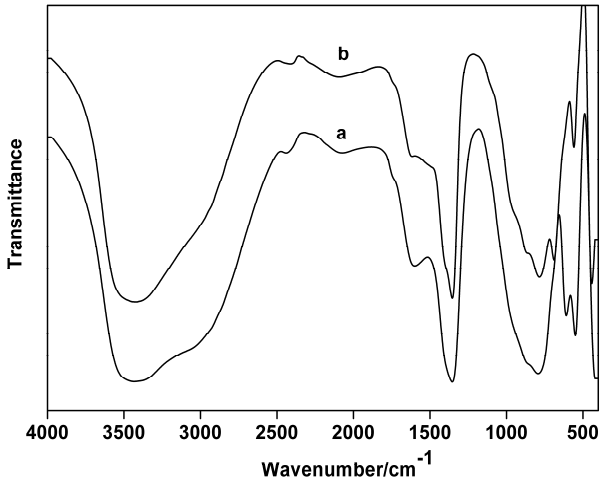

Fig. S2 FT-IR spectra of the (a) CoAl- and (b) MgAl-CO_3 LDH samples.

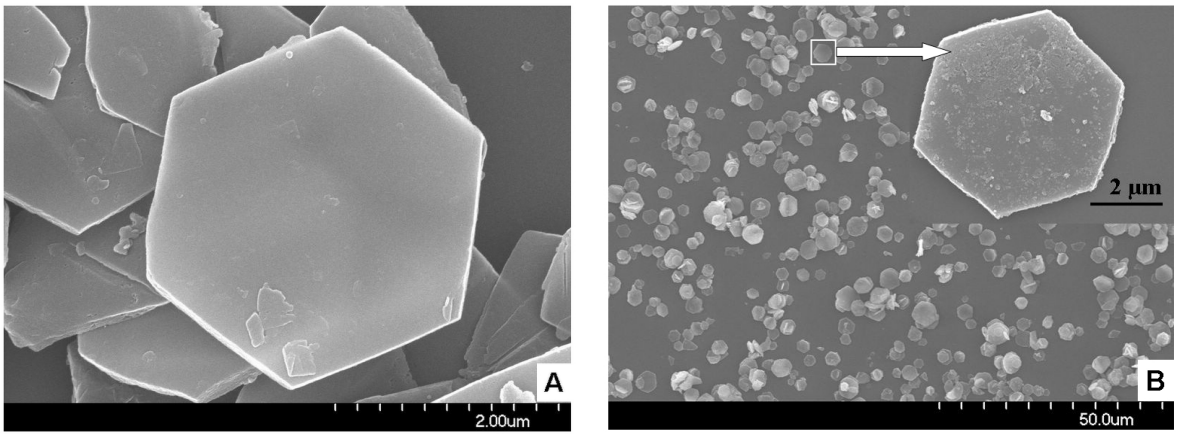

Fig. S3 SEM images of (A) CoAl- and (B) MgAl-CO_3 LDH samples.

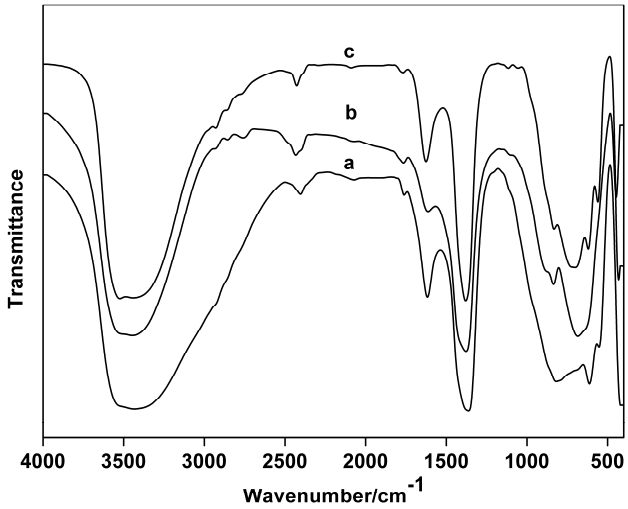

Fig. S4 FT-IR spectra of the (a) CoAl-, (b) MgAl- and (c) NiAl-NO_3 LDH samples.

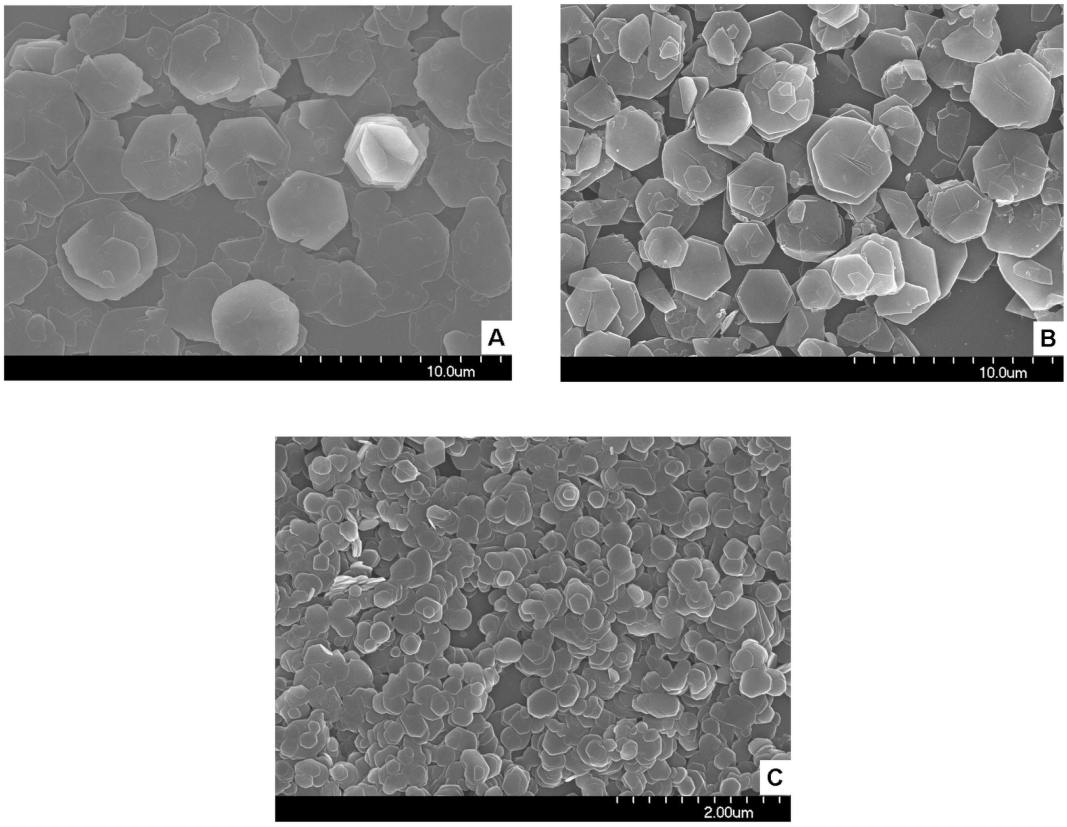

Fig. S5 SEM images of (A) CoAl- (B) MgAl- and (C) NiAl-NO_3 LDH samples.

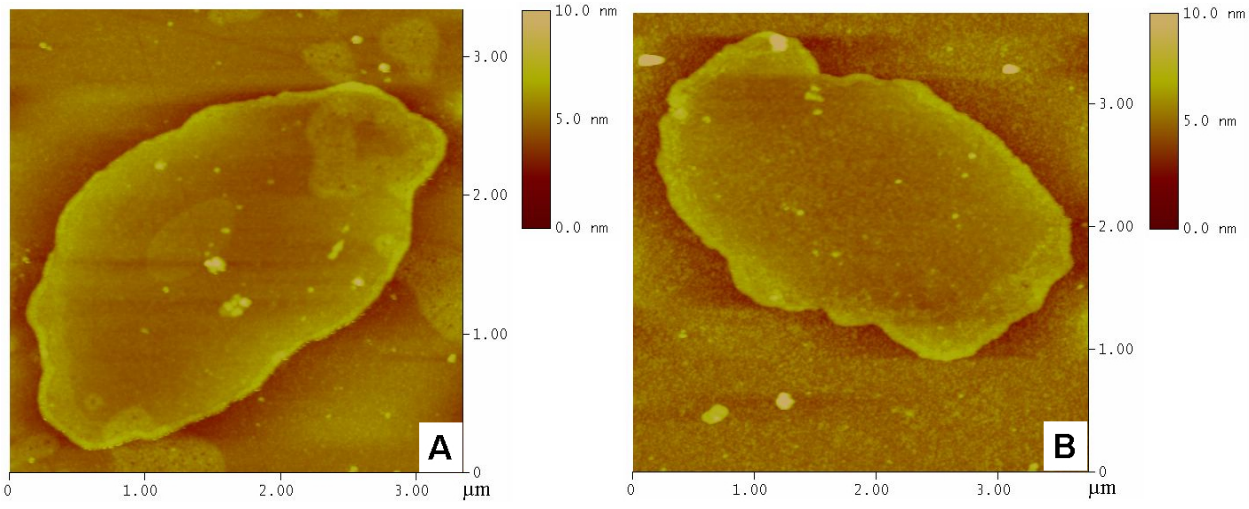

Fig. S6 Tapping-mode AFM images of (A) the exfoliated CoAl- and (B) MgAl-LDH nanosheets deposited on Si wafer substrate.

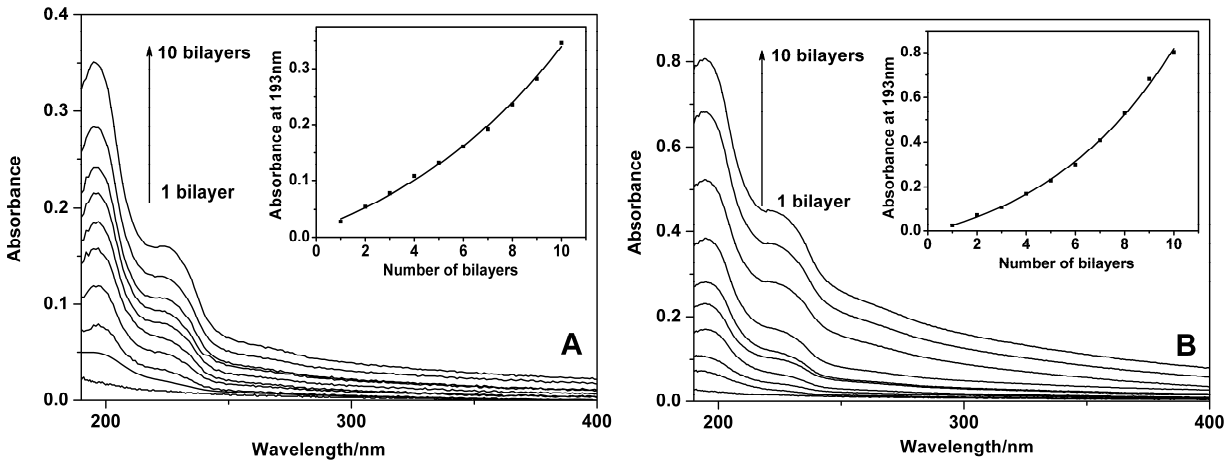

Fig. S7 UV absorption spectra of (A) (CoAl-LDH/PSS/MgAl-LDH/PSS)$_{n/2}$ and (B) (MgAl-LDH/PSS/NiAl-LDH/PSS)$_{n/2}$ films. The numbers of bilayers are 1 to 10 from the bottom to the top (An LDH nanosheet/PSS layer is defined as one bilayer).

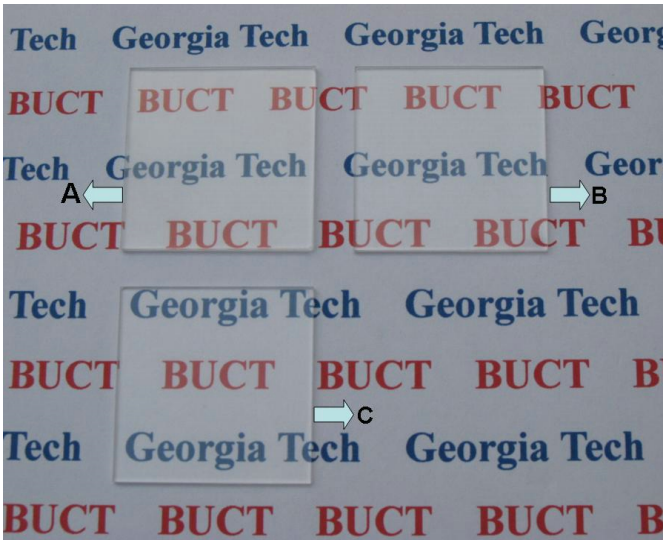

Fig. S8 Photograph of transparent films of (A) (CoAl-LDH/PSS/MgAl-LDH/PSS)$_{n/2}$, (B) (MgAl-LDH/PSS/NiAl-LDH/PSS)$_{n/2}$ and (C) (CoAl-LDH/PSS/NiAl-LDH/PSS)$_{n/2}$ (n=50). The size of the quartz glass substrate is 3.0×3.0 cm.

References:

1 Z. P. Liu, R. Z. Ma, M. Osada, N. Iyi, Y. Ebina, K. Takada and T. Sasaki, *J. Am. Chem. Soc*., 2006, **128**, 4872.

2 N. Iyi, T. Matsumoto, Y. Kaneko and K. Kitamura, *Chem. Mater.*, 2004, **16**, 2926.