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

Jing Bin Han,[a] Jun Lu,[a] Min Wei,*[a] Zhong Lin Wang*[b] and Xue Duan[a]

Received (in Cambridge, UK) 2nd May 2008, Accepted 25th July 2008
First published as an Advance Article on the web 12th September 2008
DOI: 10.1039/b807479h

Transparent heterogeneous ultrathin films of exfoliated layered double hydroxide (LDHs) nanosheets, fabricated alternately with polyanion, have been obtained *via* a layer-by-layer electrostatic self-assembly which yields a series of novel LDH films with potential multifunctionality.

Layered double hydroxides (LDHs), also well-known as hydrotalcite-like compounds or anionic clays, are generally expressed as $[M^{II}_{1-x}M^{II}_{x}(OH)_2](A^{n-})_{x/n}\cdot mH_2O$ (M^{II} divalent and M^{III} trivalent metals, respectively, A^{n-} n-valent anion).[1] Their structure is based on brucite-like layers, where divalent metal cations locate in the center of oxygen octahedra and two-dimensional infinite layers are formed by edge-sharing of $[M(OH)_6]$ octahedra.[2] Partial substitution of trivalent cations by divalent ones results in positively charged hydroxide layers, which is balanced by exchangeable interlayer anions.[3] Recently, LDHs have received considerable attention due to their potential applications as catalysts,[4] acid absorbents,[5] molecular container,[6] flame retardants,[7] pharmaceutically and biologically active materials,[8] electrical and optical functional materials,[9] and so on. However, their applications in practical devices are limited because of the challenge to obtain stable and transparent thin or ultrathin films, either substrate supported or free-standing.

Recently, using exfoliated LDHs nanosheets as building blocks, Sasaki *et al.* obtained LDHs ultrathin films under mild conditions by a layer-by-layer (LBL) self-assembly,[10] one advantage of which is its ability to form ultrathin films with nanometer-level control. Furthermore, the technique has gained high interest because of its simplicity and low-cost equipment used in film preparation, as well as the independence of film deposition from substrate type, size and morphology. Nevertheless, all the multilayer ultrathin LDHs films they reported are based on one kind of LDH nanosheets, which can be considered as homogeneous LDH films, such as (CoAl-LDHs/PSS)$_n$ films.[10b]

In this work, we report the preparation of transparent ultrathin films of various exfoliated LDH nanosheets assembled alternately with polyanion, poly(sodium styrene 4-sulfonate) ($[CH_2CH(C_6H_4)SO_3Na]_m$, PSS). (CoAl-LDH/PSS/MgAl-LDH/PSS)$_{n/2}$, (MgAl-LDH/PSS/NiAl-LDH/PSS)$_{n/2}$, and (CoAl-LDH/PSS/NiAl-LDH/PSS)$_{n/2}$ films were fabricated, which can be defined as heterogeneous LDH films, where n refers to the number of LDH/PSS bilayers, yielding a novel and versatile ultrathin film formed by several kinds of LDHs. Compared with the homogenous ultrathin films with one type of LDH, heterogeneous LDH films possess a tunable function due to their structural diversity and combined functionality. Furthermore, it is advantageous to extend the LBL technique to prepare ultrathin films consisting of various transition-metal-bearing LDHs, since they have been reported to exhibit superior or unique catalytic and electrochemical performance.[11] To the best of our knowledge, this is the first report of multilayer ultrathin films fabricated from heterogeneous exfoliated LDHs.

Heterogeneous ultrathin LDH films were fabricated by the following sequential procedures: synthesis of highly crystalline monodispersive M(□)Al–NO$_3$ LDH (M = Co, Ni, Mg); delamination of these NO$_3$ LDHs in formamide; and finally fabrication of multilayer ultrathin films by assembling different types of positively charged LDH nanosheets alternately with negatively charged PSS onto quartz glass substrates.

Firstly, highly crystalline monodispersive M(□)Al–CO$_3$ LDH (M = Co, Mg) samples were prepared by precipitation through urea hydrolysis, as described in the ESI.† The powder X-ray diffraction (XRD) patterns (Fig. S1†) and FT-IR absorption spectra (Fig. S2†) clearly indicate the high purity of the product. The morphology of M(□)Al-CO$_3$ LDH (M = Co, Mg) was characterized using scanning electron microscopy (SEM) (Fig. S3†), which reveals monodispersive hexagonal plate crystals with a mean lateral dimension of *ca.* 4 μm for CoAl–CO$_3$ LDH, and 2 ~ 4 μm for MgAl–CO$_3$ LDH.

The interlayer CO_3^{2-} must be converted to other ions such as NO_3^- or bipolar ion in order to enable their delamination,[12,13] because of the high affinity of the carbonate to the LDHs layer sheets. In the case of the preparation of CoAl–NO$_3$ and MgAl–NO$_3$ LDH, an effective method based on acid-salt treatment[14] was used to exchange interlayer CO_3^{2-} into NO_3^-. Whereas the NiAl–NO$_3$ LDH with high crystallinity was prepared directly by the urea method under hydrothermal treatment. The experimental details can be found in the ESI.†

Fig. 1 shows the XRD patterns of the M(□)Al–NO$_3$ LDH (M = Co, Ni, Mg) samples, all of which can be indexed as a rhombohedral structure with the d_{003} basal spacings of 9.01, 8.84 and 8.98 Å for CoAl-, NiAl- and MgAl–NO$_3$ LDH, respectively. No other crystalline phase was detected, indicating the high purity of the product. Moreover, the FT-IR spectra (Fig. S4†) of the M(□)Al–NO$_3$ LDH also provide evidence about the

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[a] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, 100029, PR China. E-mail: weimin@mail.buct.edu.cn; Fax: +86-10-64425385; Tel: +86-10-64412131
[b] Center for Nanoscience and Nanotechnology, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA. E-mail: zhong.wang@mse.gatech.edu; Fax: +1-404-8949140; Tel: +1-404-8948008

† Electronic supplementary information (ESI) available: Preparation and characterization of M(□)Al-LDH and (LDH/PSS)$_n$ heterogeneous ultrathin films, XRD patterns, FT-IR spectra and SEM images of M(□)Al-LDH, tapping-mode AFM images of the exfoliated CoAl- and MgAl-LDH nanosheets, UV absorption spectra of (CoAl-LDH/PSS/MgAl-LDH/PSS)$_{n/2}$ and (MgAl-LDH/PSS/NiAl-LDH/PSS)$_{n/2}$ films. See DOI: 10.1039/b807479h

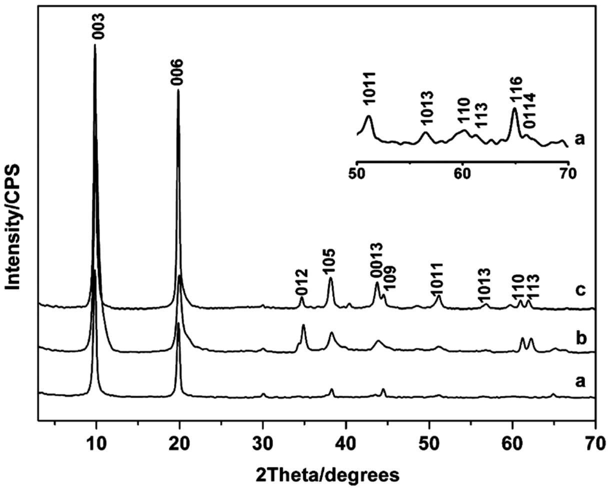


Fig. 1 XRD patterns of (a) CoAl–NO_3 LDH, (b) NiAl–NO_3 LDH, (c) MgAl–NO_3 LDH. For the sake of clarity, the pattern (a) was enlarged 10 times in the inset at $2\theta = 50 \sim 70°$.

presence of NO_3^- (band at 1384 cm^{-1}) and absence of CO_3^{2-} in the interlayer space.[15] Elemental analysis of the M($\square$)Al–NO_3 LDH shows that the molar ratio of M($\square$) : Al is close to 2 : 1 and the Al : N close to 1 : 1. The chemical formulae of LDH precursors are listed in the ESI (Table S1†). The above results unambiguously indicate a complete replacement of interlayer CO_3^{2-} by NO_3^-. The SEM images (Fig. S5†) reveal monodispersive plate crystals, hexagonal in shape with a mean lateral dimension of *ca.* 4 μm for CoAl–NO_3 LDH and 2 ∼ 4 μm for MgAl–NO_3 LDH. The NiAl–NO_3 LDH sample was also crystallized into monodispersive, uniform plate crystals with the platelets size of *ca.* 200 ∼ 400 nm, which is smaller than of that Co- and Mg-containing NO_3 LDH.

Delamination is thought to be a useful and versatile method to obtain unilamellar, positively charged LDH nanosheets, and formamide has been demonstrated to be the most effective reagent to exfoliate LDH through a direct reaction without any heating or refluxing treatment. The reason why we synthesized uniform, highly crystalline, monodispersive M($\square$)Al–NO_3 LDH was based on facilitating the succeeding delamination process. The delamination process was described in the ESI.† Fig. 2 displays the tapping-mode AFM image of the exfoliated NiAl-LDH nanosheets deposited on a cleaned Si wafer substrate, with the height profile along the marked white line. A thin layer of morphologically irregular NiAl-LDH nanosheets with lateral sizes of 200 ∼ 400 nm was observed although smaller fragments and partial overlapped nanosheets coexisted. For CoAl- and MgAl-LDH nanosheets, the lateral size ranges from 2 to 4 μm (Fig. S6†), corresponding to their large-sized particles of LDH precursors. The height profile measurements indicated that the average thickness of the nanosheets was *ca.* 0.8 nm, which is consistent with previous observations reported elsewhere.[10,13]

Due to the positively charged character of LDHs nanosheet, an anionic polyelectrolyte could be assembled with LDH nanosheets layer-by-layer through an electrostatic force. Transparent and heterogeneous multilayered composite films were prepared by sequential deposition of PSS and the two-dimensional platelets of LDH by LBL technique. Before LBL deposition, the substrates such as Si wafer or quartz glass slide were cleaned as reported in literature.[10a] The heterogeneous LBL deposition process of (CoAl-LDH/PSS/NiAl-LDH/PSS)$_{n/2}$ ultrathin film is illuminated in Scheme 1 and described in details in the ESI.†

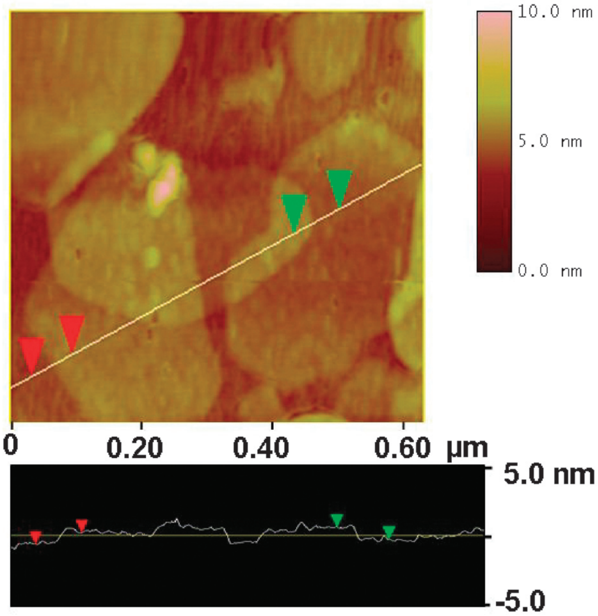
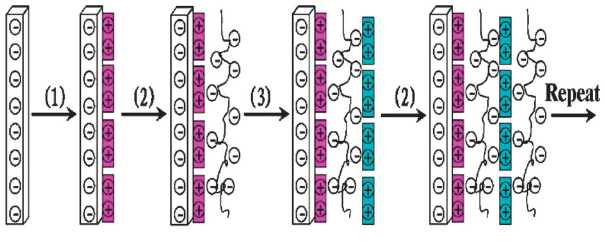


Fig. 2 Tapping-mode AFM image of the exfoliated NiAl-LDH nanosheets deposited on a Si wafer substrate, with a height profile along the marked white line.

The subsequent growth of a multilayer film was monitored by UV-Vis absorption spectroscopy after each deposition of PSS as depicted in Fig. 3. The absorption bands centered at 193 and 225 nm are characteristic of PSS. From the inset of Fig. 3, an exponential increase in absorbance at 193 nm was observed with increasing the number of bilayers. Similar results were obtained in both (CoAl-LDH/PSS/MgAl-LDH/PSS)$_{n/2}$ and (MgAl-LDH/PSS/NiAl-LDH/PSS)$_{n/2}$ films, indicating successful LBL growth (Fig. S7†). The exponential increase should be ascribed as a gradual increase of the roughness of the film surface during the deposition process, which is very similar to that reported elsewhere.[16] There is no absorption band in the visible light region and the films are still highly transparent when *n* reaches 50 (Fig. S8†). Furthermore, ultrathin films containing all of these three types of LDH nanosheets and PSS were also prepared successfully (not shown). Our research indicates that CoAl-, NiAl- and MgAl-LDH nanosheets can be used to fabricate heterogeneous (LDH/PSS)$_n$ films by any sequence of LDH.

The XRD patterns (Fig. 4) for the obtained (CoAl-LDH/PSS/NiAl-LDH/PSS)$_{n/2}$ ultrathin films exhibit a Bragg peak at



Scheme 1 Schematic representation of the process for the fabrication of (CoAl-LDH/PSS/NiAl-LDH/PSS)$_{n/2}$ film: (1) CoAl-LDH nanosheets; (2) PSS; (3) NiAl-LDH nanosheets.

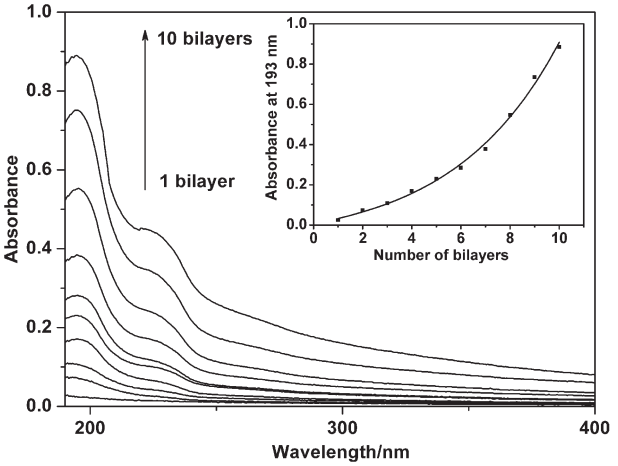


Fig. 3 UV absorption spectra of (CoAl-LDH/PSS/NiAl-LDH/PSS)$_{n/2}$ films. The number of bilayers is 1 to 10 from the bottom to the top (An LDH nanosheet/PSS layer is defined as one bilayer).

$2\theta = 4.12°$ and both its intensity and symmetry increase successively upon increasing deposition cycles. This diffraction feature can be attributed to a so-called superlattice reflection of the inorganic/organic periodic nanostructure.[10b] The average repeating distance is *ca.* 2.14 nm, which is larger than that of homogenous LDH films (~2.0 nm) ever reported.[10a,b] The little expansion is possibly related to the heterogeneous LDH nanosheets as building blocks in this work.

In summary, unilamellar, positively charged LDH nanosheets were obtained by delaminating highly crystalline M(□)Al–NO_3 LDH (M = Co, Ni, Mg). By using these LDH nanosheets as building blocks, the electrostatic LBL procedure was expanded to prepare ultrathin films composed of two or three kinds of LDH nanosheets, yielding a series of transparent heterogeneous ultrathin films. Based on the results, it is expected that a wide variety of LDH ultrathin films can be fabricated in a similar manner by the LBL technique. Moreover, due to the positive charge of the exfoliated LDH nanosheets, a range of functional polyanions (such as bioactive, photoresponsive, conductive, electroluminescent polymer, *etc.*) can be utilized as the counterpart for the LBL assembly of functional ultrathin films. By virtue of the highly tunable compositions both for inorganic and organic parts as well as the interactions and cooperations between them, these heterogeneous films can be potentially applied in industry as catalysts, sensors and photovoltaic devices.

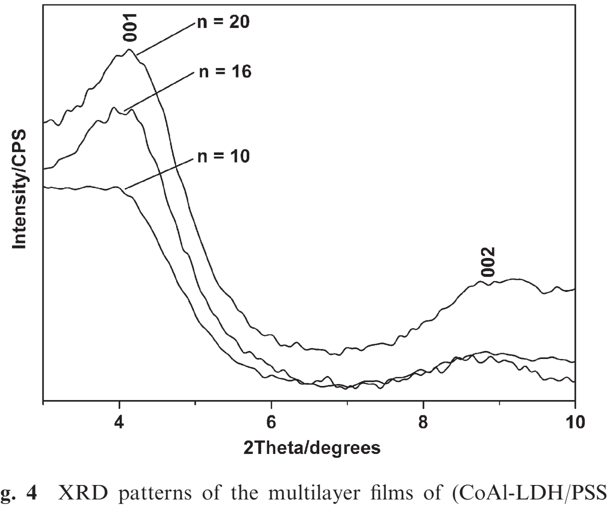


Fig. 4 XRD patterns of the multilayer films of (CoAl-LDH/PSS/NiAl-LDH/PSS)$_{n/2}$ deposited on quartz glass substrate ("*n*" denotes the number of bilayers).

This work was supported by the National Natural Science Foundation of China, the Program for New Century Excellent Talents at University (Grant No.: NCET-05-121), 973 Program (Grant No.: 2009CB939802), and the Program for Changjiang Scholars and Innovative Research Team at University (Grant No.: IRT0406).

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