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Fabrication of Free-standing Layer-by-layer Films of Layered Double Hydroxide Nanosheets and Polyelectrolytes

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Free-standing films of layered double hydroxide nanosheets and polyelectrolytes were fabricated via layer-by-layer self-assembly techniques and further substrate erosion methods. The obtained films were ultrathin and showed excellent flexibility, good transparency, and high thermal stability.

Layered double hydroxides (LDHs), also known as hydrotalcites or anionic clays, have attracted much attention because of their potential applications in areas such as catalysis, separation, sensors, biology, and medicine.[1] Recently, LDHs have been successfully exfoliated into single or several layers.[2] These thin LDH nanosheets (LDHNS) exhibit novel physical and chemical properties and have been used as building blocks for the construction of various functional nanocomposite films by layer-by-layer (LbL) self-assembly techniques.[3] However, these LbL-assembled LDH composite films are all deposited on solid substrates which provide firm support but can meanwhile influence their properties.

The preparation of LbL-assembled free-standing composite films which exist without solid substrates is meaningful.[4] These free-standing LbL structures not only have the same advantages as traditional LbL films but exhibit additional properties facilitating their potential use as nanomechanical films,[5a] thermal sensors,[5b] diffusion barriers,[5c] nanoreactors and nanoactuators. Recently self-supporting LDH films were prepared by the solvent evaporation of LDH nanoparticles[6a] or water-swellable LDH hybrids,[6b] and they could be anion exchanged with inorganic and organic anions in the film state. However, the thickness of the obtained self-supporting LDH films was above 10 μm, and somewhat they were brittle after ion-exchange process in solvent. Therefore, free-standing ultrathin LDH films with good properties are strongly demanded for the application of LDHs in micro- and nanodevices.

Herein, we firstly fabricated the free-standing LbL LDHNS and polyelectrolytes composite films. By the substrate erosion method, the LDHNS and polyelectrolyte composite films fabricated via LbL self-assembly could be released from the substrates. The resulting free-standing films were ultrathin and showed excellent flexibility, good transparency, and high thermal stability.

Mg–Al LDHNS, as an example, was chosen for the preparation of free-standing LDH composite film. Mg–Al–NO_3 LDHs were synthesized and delaminated according to methods reported previously.[2,7] The detailed experimental procedures and the characterization of products are given in Supporting Information.[8] The preparation of LDHNS and polyelectrolyte composite films by the LbL assembly technique was carried out as follows: The cleaned substrates (see Supporting Information[8]) such as glass wafers and quartz slides were precoated with polyethylenimine (PEI) by immersing into an aqueous solution of PEI ($1.0\,g\,L^{-1}$, pH 8) for 20 min to obtain a positively charged surface. Then a deposition cycle of four sequential immersion steps was conducted. Firstly, the PEI-primed substrates were immersed in a solution of poly(acrylic acid) (PAA, $1.0\,g\,L^{-1}$, pH adjusted to 6 with NaOH), followed by an immersion in PEI solution ($1.0\,g\,L^{-1}$, pH 8), then the substrates were immersed into PAA solution again, followed by an immersion in a colloidal suspension of Mg–Al LDHNS ($1.0\,g\,L^{-1}$, pH 7). These operations were repeated n times to obtain multilayer films of PEI/(PAA/PEI/PAA/LDHNS)$_n$, or more briefly, (P/L)$_n$. In this paper, (P/L)$_{10}$ free-standing films were chosen for typical discussions. All deposition time was 20 min. Before each layer deposition, the substrates were thoroughly washed with doubly distilled water. But drying was omitted until the end of the self-assembly.

In order to produce a tight network of matrix among LDHNS and polymeric species, the resulting films were heated at 120 °C overnight, followed by immersion into an aqueous solution of glutaraldehyde (0.5 wt %, pH 7) for 1 h at room temperature.[5a] The films were thoroughly rinsed with doubly distilled water. The free-standing films were released from the substrates by immersion into 0.2 wt % aqueous hydrofluoric acid (pH adjusted to 5 with NaOH) for 30 min. The resulting films were transferred in doubly distilled water where they could be picked up with a 60 meshed sieve and were finally dried in vacuum at room temperature.

The morphology of the (P/L)$_{10}$ free-standing film is shown in Figure 1. As indicated in the photograph (Figures 1a), the (P/L)$_{10}$ free-standing film was planar with a typical size of about 5 cm × 1.5 cm similar to that of the substrate, which is different from draped pure polyelectrolyte free-standing multilayer film.[5d] This may be attributed to the introduction of inorganic LDHNS

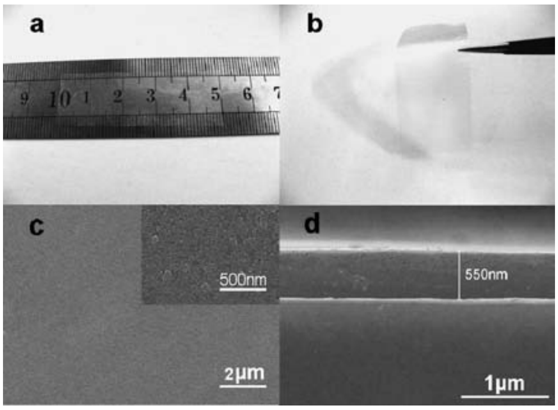

Figure 1. Morphology of the (P/L)$_{10}$ free-standing film: (a) and (b) camera picture, (c) top view SEM, (d) cross-sectional SEM.

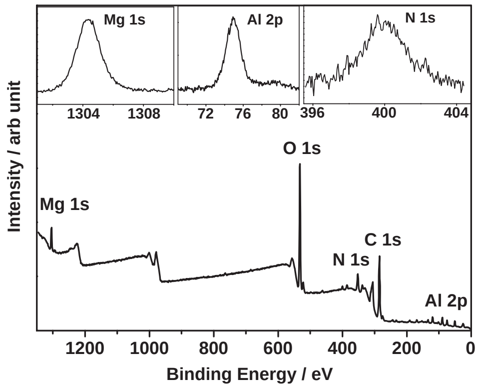

Figure 2. XPS spectra of the $(P/L)_{10}$ free-standing film. The insert figures are spectrum of Mg1s, Al2p, and N1s.

resulting in increase of the rigidity of the free-standing multilayer film. The $(P/L)_{10}$ free-standing film was also highly transparent. The transmittance of the film was about 80% over the entire visible region and essentially independent of wavelength, as shown in Figure S5.[8] Moreover, the $(P/L)_{10}$ free-standing film was flexible (Figure 1b). It could be easily handled with tweezers or transferred onto other substrates such as Si wafers, ITO substrates or TEM copper grids. More importantly, the free-standing film was stable in solvent such as water, ethanol, or acetone. The scanning electron microscopy (SEM) of the $(P/L)_{10}$ free-standing film was characterized by transferring the film onto a glass slide. The top view SEM image (Figure 1c) showed a flat and smooth surface, and a rigid structure could be observed at a high magnification. The corresponding cross-sectional SEM image of Figure 1d showed that the $(P/L)_{10}$ free-standing film had a uniform thickness of 550 nm with standard deviation of 5%. This ultrathin film is useful for the fabrication of micro- or nanodevices,[4] which could not be prepared with the usual methods such as the solvent evaporation method.[6] Moreover, the thickness of the $(P/L)_n$ free-standing films increased linearly with the number of film deposition cycles (see Figure S6),[8] indicating that the thickness of the free-standing films were as well controlled as the conventional LbL films. No cracks and clearly separate layers were observed in the cross section. This indicates that the LDHNS and polyelectrolyte may form the interpenetrating network, which is the reason that the $(P/L)_{10}$ free-standing film is very stable.

Elemental analysis of the $(P/L)_{10}$ free-standing film was carried out by X-ray photoelectron spectroscopy (XPS). The XPS spectra (Figure 2) showed the characteristic peaks of carbon (C1s 284.6 eV), oxygen (O1s 532.0 eV), nitrogen (N1s 399.1 eV), magnesium (Mg1s 1303.9 eV), and aluminum (Al2p 74.4 eV), which is consistent with the elements of PAA, PEI, and LDHNS.[3c]

FT-IR spectra of the $(P/L)_{10}$ film before and after the release of the film from the substrate were recorded (See Figure S7).[8] No obvious changes were observed, indicating that the structure of the free-standing film was retained during the releasing process. The M–O and O–M–O vibration band of LDHNS (M = Mg and Al) appeared between 400–800 cm^{-1}.[9] Characteristic amide bonds were observed at 1641 cm^{-1},[5] indicating a partial covalent cross linking of PAA-PEI.

Thermal properties of the $(P/L)_{10}$ free-standing film were characterized by thermal gravimetric–differential thermal analysis (TG-DTA) (See Figure S8a).[8] For comparison, TGA–DTA response of a pure polyelectrolyte free-standing film with the same number of layers was also conducted (See Figure S8b).[8] The decomposition temperature of PAA in the $(P/L)_{10}$ free-standing film increased by 30 °C over that of PAA in the pure polyelectrolyte film. Moreover, the total weight loss of the $(P/L)_{10}$ free-standing film was lower than that of the pure polyelectrolyte film. These indicated the enhanced thermal stability of the composite free-standing film. This improvement was attributed to the incorporation of inorganic LDHNS in the film, which acted as a protective barrier against the thermal degradation of organic species.

In summary, we have prepared a free-standing LbL LDHNS/polyelectrolyte film. The film combined often incompatible properties of large scale, ultrathin thickness, good transparency, flexibility, and thermal stability. This method provides a convenient and useful route for fabrication of free-standing LDH films from LbL LDH multilayer films, which can widen the applications of LDHs, especially for micro- and nanodevices.

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References and Notes

1 D. G. Evans, X. Duan, *Chem. Commun.* **2006**, 485.
2 L. Li, R. Ma, Y. Ebina, N. Iyi, T. Sasaki, *Chem. Mater.* **2005**, *17*, 4386.
3 a) Z. Liu, R. Ma, M. Osada, N. Iyi, Y. Ebina, K. Takada, T. Sasaki, *J. Am. Chem. Soc.* **2006**, *128*, 4872. b) L. Li, R. Ma, Y. Ebina, K. Fukuda, K. Takada, T. Sasaki, *J. Am. Chem. Soc.* **2007**, *129*, 8000. c) X. Zhang, Y. Wang, X. Chen, W. Yang, *Mater. Lett.* **2008**, *62*, 1613.
4 C. Jiang, V. V. Tsukruk, *Adv. Mater.* **2006**, *18*, 829.
5 a) A. A. Mamedov, N. A. Kotov, M. Prato, D. M. Guldi, J. P. Wicksted, A. Hirsch, *Nat. Mater.* **2002**, *1*, 190. b) C. Jiang, S. Markutsya, Y. Pikus, V. V. Tsukruk, *Nat. Mater.* **2004**, *3*, 721. c) M. Nolte, B. Schoeler, C. S. Peyratout, D. G. Kurth, A. Fery, *Adv. Mater.* **2005**, *17*, 1665. d) Y. Ma, J. Sun, J. Shen, *Chem. Mater.* **2007**, *19*, 5058.
6 a) L. Wang, C. Li, M. Liu, D. G. Evans, X. Duan, *Chem. Commun.* **2007**, 123. b) N. Iyi, Y. Ebina, T. Sasaki, *Langmuir* **2008**, *24*, 5591.
7 Y. Zhao, F. Li, R. Zhang, D. G. Evans, X. Duan, *Chem. Mater.* **2002**, *14*, 4286.
8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.
9 J. J. Harris, P. M. DeRose, M. L. Bruening, *J. Am. Chem. Soc.* **1999**, *121*, 1978.