Large continuous, transparent and oriented self-supporting films of layered double hydroxides with tunable chemical composition†

Lianying Wang, Cang Li, Miao Liu, David G. Evans and Xue Duan*

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Highly ordered transparent self-supporting films of layered double hydroxides (LDHs) with a size of the order of cm^2 have been obtained by a simple method; the chemical composition of both the layers and interlayers can be readily tuned, as demonstrated by the preparation of [ZnAl–NO_3] LDH, [NiAl–NO_3] LDH and [Tb(EDTA)]$^-$ intercalated-ZnAl LDH films.

For application in practical devices, inorganic materials must be fabricated into well-oriented continuous supported thin films or self-supporting membranes, and this step can be at least as challenging a problem as the synthesis of the material itself.[1] Furthermore, for many applications in sensing and photocatalysis the films should be optically transparent. Layered double hydroxides (LDHs) have attracted much attention because of their potential applications in areas such as catalysis,[2] separation,[3] sensors,[4] electrochemistry,[5] and bionanotechnology.[6] The composition of LDHs may be expressed by the general formula $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]A^{n-}{}_{x/n}\cdot mH_2O$, where the cations M^{2+} and M^{3+} occupy the octahedral holes in a brucite-like layer and A^{n-} is an anion located in the hydrated galleries between the layers.[7] The range of possible LDH compositions is almost limitless, which is unique among layered materials.

Unlike many other layered materials however, LDHs are notoriously difficult to fabricate into thin films and this has severely constrained development of practical applications. A variety of attempts to prepare LDH films have been previously reported in the literature.[8–13] Those prepared by Langmuir–Blodgett deposition or ultrasonic deposition are not suitable for practical applications owing to their discontinuous nature and poor mechanical properties.[9,10] Exfoliation of LDHs in organic solvents such as formamide gives colloidal LDH particles which may be used as building blocks in the preparation of transparent oriented LDH films by layer-by-layer techniques or by deposition methods,[11,12] but the multi-step exfoliation process is time-consuming and involves toxic organic solvents. More importantly, the type of anion which can be incorporated is severely limited.

Ideally what is required is the ability to cast a film directly from an aqueous suspension of an LDH without any pre-treatment, in a simple process which is applicable to LDHs with a wide range of composition. LDHs prepared by conventional co-precipitation methods are invariably polydisperse,[7b] and when a suspension is cast on a glass slide, the resulting films suffer from random orientation of crystallites and low transparency.[11b,12b,13] We have previously shown[14] that when LDHs are prepared using a method involving separate nucleation and aging steps (SNAS), in which rapid mixing and nucleation in a colloid mill is followed by a separate aging process, the diameter of the resulting LDH platelets is smaller, and the size distribution is considerably more uniform, than that obtained using conventional co-precipitation methods. In this Communication, we show how the resulting monodisperse mixture of LDH nanoparticles may be used as a precursor for fabrication of unprecedented large transparent self-supporting films of LDHs in a simple process which may be employed with LDHs having a wide range of compositions.

Suspensions of [ZnAl–NO_3] and [NiAl–NO_3] LDH nanoparticles were prepared by the SNAS method,[14] as described in the ESI.† The interlayer nitrate anion may be exchanged *in situ* by a wide variety of other functional anions, without any significant variation in crystallite size and size distribution. Therefore, the chemical composition in the interlayers of the colloidal LDH nanoparticles can be readily tuned. For example, Tb^{3+} can be incorporated into the interlayer galleries by anion exchange of its EDTA complex with the [ZnAl–NO_3] precursor, similar to our previous work with other EDTA complexes,[15] as described in the ESI.† On the basis of elemental analysis and TG data, the samples can be formulated as $Zn_2Al(OH)_6(NO_3)\cdot 2.0H_2O$, $Ni_2Al(OH)_6(NO_3)\cdot 2.1H_2O$, and $Zn_2Al(OH)_6[Tb(EDTA)]_{0.44}(NO_3)_{0.56}\cdot 2.2H_2O$, respectively. The analytical and IR spectroscopic data suggest that co-intercalation of carbonate anions is minimal.

The resulting LDH suspensions, after dilution to 2 wt% at near neutral pH, were contained in a glass vessel and dried in air at 60 °C for 4 h. Transparent self-supporting films with large dimensions of up to centimetres can be peeled off from the base and vertical sides of the vessels. The thickness of the film can be controlled from several to hundreds of microns by changing the concentration of the suspension and the drying conditions. The films are mechanically strong enough to be handled with tweezers, if some care is taken. Ultrathin supported LDH films also can be prepared using this method, and silicon, glass and quartz can all be used as the supporting substrate.

Photographs of the self-supporting films are shown in Fig. 1. The films are continuous in length, with a size in the order of centimetres, and have smooth surfaces. The respective light green and light brown colors of the [NiAl–NO_3] and [ZnAl–Tb(EDTA)] LDH films are in accord with the characteristic electronic absorptions of the cations.[16,17] The films are all highly transparent. For example, the transmittance of a [ZnAl–NO_3] LDH film with

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State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, 100029, P. R. China. E-mail: duanx@mail.buct.edu.cn; Fax: +86-10-64425385; Tel: +86-10-64425395

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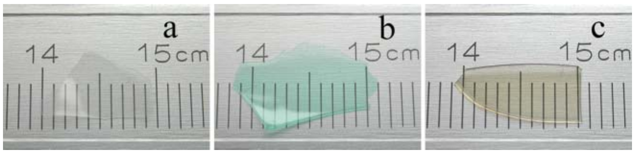

Fig. 1 Photographs of transparent self-supporting LDH films of (a) [ZnAl–NO_3], (b) [NiAl–NO_3], and (c) [ZnAl–Tb(EDTA)]. The ruler with centimetre scale lies behind the films.

thickness 24 μm is above 80% over the entire visible region and essentially independent of wavelength, as shown in the ESI.† In contrast, it has been reported that much thinner supported LDH films prepared by other methods have significantly lower transmittance which is strongly wavelength dependent.[8a] We have recently shown that [NiAl–NO_3] LDH is photochromic,[18] and [ZnAl–Tb(EDTA)] LDH is luminescent by virtue of the presence of the rare earth ion,[17] giving an indication of the way in which different functionality can readily be incorporated into our transparent self-supporting LDH films.

The powder X-ray diffraction (XRD) patterns of the LDH samples as the self-supporting film itself and after grinding into powder form are shown in Fig. 2. In each case, the XRD patterns exhibit the characteristic reflections of the LDH structure with a series of (00*l*) peaks appearing as narrow, symmetric, strong lines at low angle. The basal spacing of [ZnAl–NO_3] and [NiAl–NO_3] powder samples is 0.898 and 0.886 nm, respectively, which is similar to the values reported in the literature for LDHs with NO_3^- anions.[19] The basal spacing expands to 1.403 nm when NO_3^- is replaced by $[Tb(EDTA)]^-$ in an ion-exchange reaction, indicating that the rare earth complex has been successfully intercalated into the interlayer galleries.[15] The thickness of the platelets in the films can be estimated using the Scherrer equation based on the peak widths of the (00*l*) reflections as 13, 6, and 8 nm for [ZnAl–NO_3], [NiAl–NO_3], and [ZnAl–Tb(EDTA)] LDH, respectively. The absence of any non-basal reflections ($h, k \neq 0$) at high angle for the films is as expected for extremely well *c*-oriented assemblies of LDH platelets.[12] In contrast, after grinding to powder form, the materials show additional (10) and (11) reflection peaks indicative of diffuse scattering arising from irregular stacking of LDH host sheets.

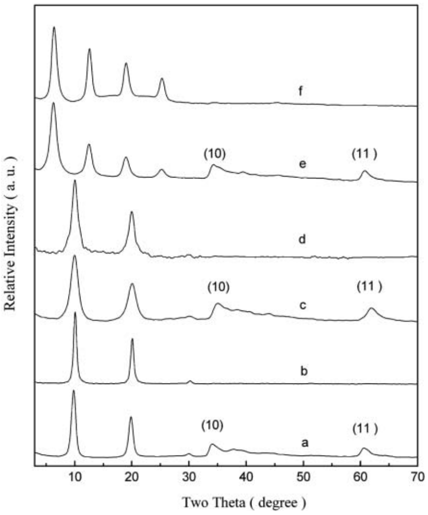

Fig. 2 XRD patterns of (a) [ZnAl–NO_3] LDH powder, (b) [ZnAl–NO_3] LDH self-supporting film, (c) [NiAl–NO_3] LDH powder, (d) [NiAl–NO_3] LDH self-supporting film, (e) [ZnAl–Tb(EDTA)] LDH powder and (f) [ZnAl–Tb(EDTA)] LDH self-supporting film.

SEM images of the [ZnAl–NO_3] LDH film are shown in Fig. 3. The film has a surprisingly flat surface in the top view (Fig. 3a). A high magnification SEM image of the film (Fig. 3b) reveals that the individual [ZnAl–NO_3] platelets, with dimensions of the order of 40 nm, are densely packed in the two-dimensional plane of the film. There is a high degree of *c*-orientation of the LDH platelets with edges of the particles only rarely being seen, consistent with the XRD data in Fig. 2. The edge view image shows the film thickness to be about 24 μm with highly anisotropic structural features discernable in the inset high-resolution image (Fig. 3c). The presence of elongated features in the inset image, longer than the lateral size of [ZnAl–NO_3] LDH platelets, is indicative of edge-to-edge attachment between individual nanoparticles. The transparent [NiAl–NO_3] and [ZnAl–Tb(EDTA)] films also have a similar uniform densely packed *c*-oriented arrangement of platelets (SEM images not shown). The SEM results are consistent with the high degree of transparency and wavelength independence of the transmittance of the films (see the ESI†), since both the pores between the LDHs platelets and the LDHs platelet diameters are much smaller than the wavelength of visible light, such that Mie and Rayleigh scattering are minimized.[20] In contrast, under the same conditions a polydisperse LDH suspension prepared by a conventional co-precipitation method afforded an opaque, rough film composed of randomly oriented polydisperse LDH particles (as shown in Fig. 3d), consistent with previous reports.[12b]

Although LDH particles are platelets and thus have a tendency to rest on their largest faces, formation of the films as a result of settling under gravity alone can be ruled out because the *c*-oriented films can also be formed on the vertical sides of glass vessels. The sharing of surface anions between platelets, specifically face-to-face type aggregation of platelets, has been observed for LDH materials.[21] Recently, Xu *et al.* have shown that the crystal size and crystallinity of an LDH can affect the aggregation of individual platelets.[22] Small platelet crystallites of LDHs have high surface energies and tend to aggregate.[12c] The uniform and small crystal size (∼40 nm) of the LDH platelets prepared by the SNAS method favor not only face-to-face type interactions but also edge-to-edge type interaction between individual LDH platelets, as has been observed for montmorillonite,[23] and is the major factor in the formation of a uniform densely packed *c*-oriented LDH film. For larger polydisperse particles, edge-to-face interactions become more significant[12c] leading to interparticle porosity and reduced optical transparency.

In summary, we have developed a simple and general way to fabricate oriented films of LDHs with large dimensions of the order of cm^2. Unlike other methods reported in the literature, that described here combines the virtues of simplicity, absence of organic solvents, and large production capability and can be extended to a wide range of layer and interlayer compositions. Compared with those produced by other methods reported in the literature, the resulting films are superior in that whilst they are sufficiently thick and mechanically robust to be self supporting, they retain a high degree of optical transparency. The results presented here thus represent a breakthrough in both fundamental and applied studies of LDHs. For example, the orientation of guest anions in oriented films can be studied by measuring the

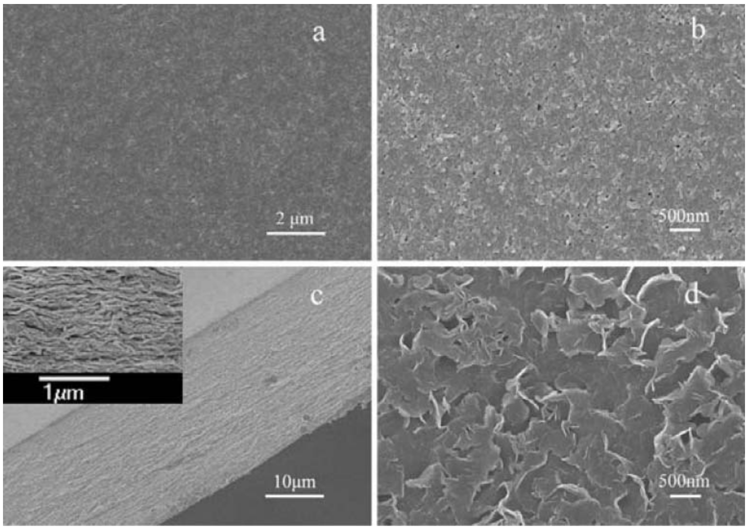

Fig. 3 SEM images of the transparent self-supporting LDH films of [ZnAl–NO_3] prepared by the solvent evaporation method: (a) top view, (b) same as (a) at high magnification, (c) edge view with a high-resolution image of this structure shown in the inset image. Image (d) is the SEM image of the top view of an opaque film of [ZnAl–NO_3] LDH prepared by a conventional coprecipitation method.

dichroic ratio of selected vibrational bands of the guest as has been reported for montmorillonite,[24] allowing more detailed study of host–guest interactions in LDHs. Furthermore, new practical applications of LDHs as separation membranes and hosts for optically and electrically active guest species in sensors are indicated.

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