

Particle–Particle Interactions between Layered Double Hydroxide Nanoparticles

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Reports of layered double hydroxide (LDH) nanoparticles have become common in the past few years.^{1,2} However, nanomaterials are not defined solely by particle size, but rather through the changes in the physical and chemical properties associated with the interface between length scales. Reports regarding the properties of nanosize LDHs include an increase in catalytic activity,³ magnetic properties,⁴ and fire-retardant properties.⁵ Nanoparticles of LDHs are also being studied for applications in the fields of bionanotechnology⁶ and composite materials.⁷ In this paper, we report evidence for a change in particle interactions of LDH nanoparticles. An increase in surface-to-surface interactions is proposed as the driving force for the formation of continuous-oriented films with enhanced adhesion to polar substrates.

The general formula for an LDH is $[M^{2+}_{(1-x)}M^{3+}_x(OH)]A^{n-}_{(x/n)} \cdot mH_2O$, where M^{2+} and M^{3+} are metal cations. If $n = 0$, the layers are neutral and held together by weak van der Waals interactions. Fractional substitution by M^{3+} ($x = 0.33\text{--}0.167$) results in positively charged layers held together by the interlayer anions (A^{n-}), which can be almost any inorganic or organic anion.

When dried, LDHs form stone-like aggregates that do not easily redisperse in water or undergo anion exchange reactions as readily as material that has never been allowed to dry. One characteristic of the LDH aggregates is a house-of-cards structure typical of edge-to-face particle interactions. As illustrated in Figure 1, this type of structure results in interparticle porosity that is characteristic of most clay materials. The net result is that, unlike other materials with structural anisotropy, LDHs cannot be cast as thin films. This has greatly limited their application as membranes and in sensor devices.

Methoxide derivatives of magnesium aluminum LDHs were prepared through coprecipitation methods from magnesium and aluminum chlorides or nitrates dissolved in MeOH in the presence of NaOH. The precipitated methoxide LDH was dispersed in water, leading to complete hydrolysis of the alkoxide ion and the formation of a nearly transparent colloidal suspension (M-LDH(aq)). A variety of M-LDHs with differing layer cations and gallery anions have been synthesized, including: MgAl-LDHs with chloride between the layers ($MgAl-Cl^-$), as well as $MgAl-NO_3^-$, $NiAl-NO_3^-$, $CoAl-Cl^-$, and $ZnAl-NO_3^-$.⁸

An $Mg_3Al(OH)_8Cl$ LDH was synthesized in methanol and analyzed by FTIR and powder diffraction (XRD). A control (water control) was made under the same reaction conditions, using water as the solvent. Infrared spectroscopy of the as-synthesized M-LDH showed bands at 2950 and 1070 cm^{-1} , characteristic of C–H bonds and C–O bonds, respectively. These bands are absent in both the hydrolyzed M-LDH(aq) and the water control.

Powder XRD patterns of the M-LDH, the M-LDH(aq), and the water control were consistent with an LDH. The particle size down the c axis is 80 Å, as calculated using the Scherrer equation.⁹ The particle size in the basal plane can be estimated at 95 nm from the



Figure 1. Schematic of the house-of-cards structure.

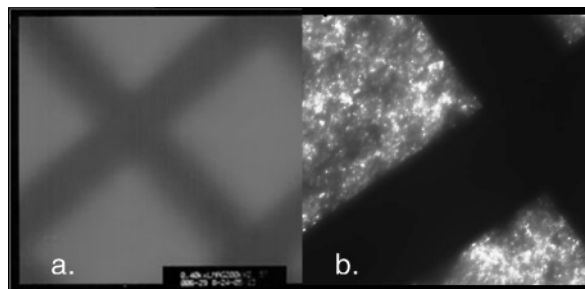


Figure 2. Low magnification TEM micrographs of (a) M-LDH(aq) at 400 \times and (b) water control at 900 \times magnification.

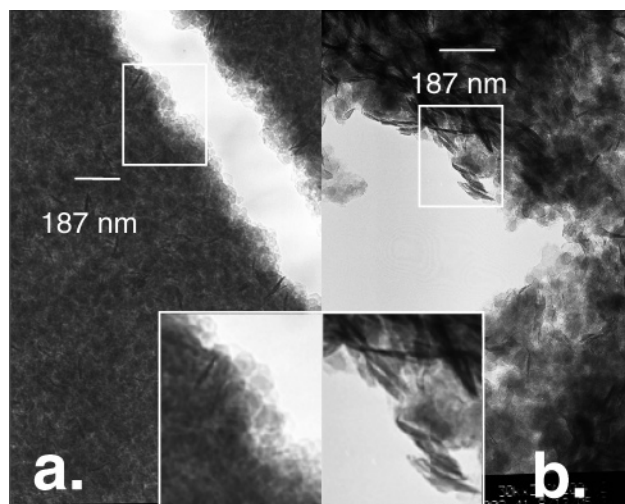


Figure 3. Free-standing films of (a) M-LDH(aq) nanoparticles. (b) Water control.

TEM micrograph in Figure 3 (discussed later). The aspect ratio is 10. Aspect ratios in the literature vary from 5 to nearly 1000.¹⁰

Even with the house-of-cards structure, LDH particles tend to orient in the same direction, enhancing the intensity of the (001) reflections. In films cast from LDH nanoparticles, the particles are so well-oriented that the (110) in-plane reflection at 60° 2 θ is not observed in the XRD pattern. The degree of orientation in the

Table 1. Ratios of Intensities of Oriented vs Unoriented LDH Samples

	$I_{(001)}/I_{(002)}$	$I_{(002)}/I_{(110)}$
oriented film	2.86	399
oriented powder	3.09	25.7
unoriented powder	2.73	4.24

nanoparticle films was determined by comparing the ratios of the intensities of the (001)/(002) reflections to the ratio of the (002)/(110) reflections for an oriented film, a powder, and a randomly oriented powder (mixed with an amorphous material).

The data in Table 1 demonstrates that the ratio between the (001)/(002) reflections remains relatively constant at 3, while the ratio between the (002) and the in-plane reflections of the (110) ranges from 399 to 4.24. The particles in the film are better oriented by 2 orders of magnitude, as compared to that of an unoriented powder.

To determine the factors controlling the orientation of the nanoparticle LDHs, the hydrolyzed LDH and the water control were studied by TEM. The samples were diluted to approximately 0.01 g/mL and 6 μ L were pipetted onto uncoated copper TEM grids and allowed to dry. The low magnification TEM micrographs shown in Figure 2 illustrate the dramatic differences between the continuous M-LDH(aq) film and the water control that tends more toward particle morphology. Only one break in the M-LDH(aq) film was detected while scanning over the grid at low magnification. The film cast from the water control is noncontinuous, even at the low magnification of 900 \times .

At higher magnification, the differences in the morphology of the M-LDH(aq) and the water control are even more striking. The nanoparticles of the M-LDH(aq) still retain the platy hexagonal crystal habit (inset in Figure 3). Particles that are oriented perpendicular to the plane of the film are seen as dark lines. While few of these are present in the M-LDH(aq), they are numerous in the water control. While some of the particles in the water control fall within the nanoscale, the majority of the particles are above 100 nm in size (Figure 3b). In addition to numerous cracks and defects in the film of the water control, there are pores created by the "house of card" structure. The M-LDH(aq) in Figure 3a is continuous even when magnified more than 30 000 times.

The chemical properties of nanomaterials are dominated by surface effects. The preference for face-to-face orientations exhibited by LDH nanoparticles can be attributed to the increase in surface atoms relative to the bulk material. Atoms on the surface and edges are not fully coordinated. In larger particles, the lack of coordination has a greater effect at the edges, as seen in the preponderance of edge-to-surface interactions in the microscale LDH particles. As the particles become smaller, the chemistry is dominated by the surface atoms, as they represent a greater percentage of the total structure. In the case of LDH nanoparticles, the increase in surface-to-surface interactions produces well-oriented films. The increase in surface area also affects the "stickiness" or adhesion properties of the LDH, and the nanoparticle films adhere well to polar substrates such as glass, while self-supporting films can be cast on Teflon.

The only difference in the two films is particle size. While the M-LDH(aq) was synthesized in methanol, hydrolysis in water removes all methoxy groups bound to the LDH particles. The formation of oriented films with enhanced interactions with surfaces will enable the development of new applications for LDH films,

including microchip sensors and reactors, environmental sensors, composite materials with improved barrier properties, and intercellular drug delivery. In theoretical studies, oriented films will enable an ESR investigation of the positioning of the interlayer anions, such as McBride's ESR studies of traditional clays in the 1980s.¹¹

Experimental Methods: MgCl₂·6H₂O, AlCl₃·6H₂O, MgNO₃·6H₂O, AlNO₃·6H₂O, and NaOH were purchased from Sigma-Aldrich and used as received. MeOH was purchased from Univar U.S.A., Inc.

Synthesis of LDHs: A three-neck flask was charged with 100 mL of solvent, and MgCl₂ and AlCl₃ were added in molar ratios of 3:1 for a total of 0.04 mol of metal cations. The solution was heated with stirring to 65 °C. Then 3.6–4.0 g of NaOH in 100 mL in MeOH was slowly added over three minutes. The mixture was digested for 3 days at this temperature with stirring. After cooling, the product was rinsed to a neutral pH. The product was stored under the solvent.

The LDH synthesized in MeOH was hydrolyzed by centrifuging the alcohol suspension and placing the pellet in 400 mL of water.

Film samples were prepared by pipetting the suspended LDH onto cleaned 1" \times 3" microscope slides. Powder samples for XRD analysis were prepared by drying the product at 80 °C overnight.

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