

Synthesis of Oriented Layered Double Hydroxide Thin Films on Sulfonated Polystyrene Substrates

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Oriented dense thin films of LDHs may be grown on sulfonated polystyrene substrates with the (001) direction of the LDH platelets perpendicular to the surface of the substrate.

There has been appreciable recent interest in developing ways of depositing inorganic thin films at low temperature from aqueous solution. Most inorganic films have been deposited on glass or similar supports but there is considerable demand for inorganic coatings on plastics for applications such as sensors or high-density magnetic storage devices¹ and there has been some work on using surface-modified polymers such as sulfonated polystyrene as substrates for ceramics such as (001) oriented calcium carbonate,² (020) oriented goethite (α -FeOOH),³ or titanium dioxide.⁴ The resulting highly oriented films have many potential applications in optical, electrical, and magnetic devices.⁵ Such synthetic processes have been described as biomimetic because of their similarities with the biomineralization of ceramics that occurs in living organisms.¹

Layered double hydroxides (LDHs) have the formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$ and the identities of M^{II} , M^{III} , and A^{n-} together with the value of the coefficient x may be varied over a wide range.^{6,7} LDHs have been attracting considerable attention owing to their potential technological applications including as electrochemical biosensors,⁸ humidity sensors,⁹ modified electrodes,¹⁰ biomimetic catalysts,¹¹ and precursors to magnetic materials.¹² If high-quality oriented LDHs films can be obtained, their enhanced optical, electrical magnetic anisotropy should lead to many potential applications. Unlike many other layered materials, LDHs cannot be easily cast as thin films, which have hindered development of some applications. LDHs films have, however, been prepared from colloidal suspensions deposited on glass¹³ and from Langmuir–Blodgett films deposited on mica.^{14,15} Crystals of LDHs have also been deposited from aqueous suspensions on highly oriented pyrolytic graphite¹⁶ and silicon wafers¹⁷ as substrates. It should be noted that the preparation methods described above are composed of two step-formation of LDH aggregates in aqueous solution as the first step, followed by deposition or coating of the aggregates on inorganic substrates. The resulting films adhere poorly to the surface and low-density films with a large number of defects are formed which are not ideal for application in devices. There have been no reports of LDHs thin films grown on organic substrates. In principle, organic substrates have the advantage of being removable by dissolution in an organic solvent or by oxidation if unsupported ceramic films are required.

Polystyrene surfaces were sulfonated³ by reaction with concentrated sulfuric acid (98% by weight) at room temperature for 24 and 72 h. The peak at about 168.4 eV in XPS patterns is attributed to the binding energy of S2p electrons of sulfonate groups.

The extent of sulfonation increased with time as shown by the values of S/C ratio measured by XPS (0.024 and 0.037, respectively) and the contact angle versus water (38.0 and 13.0°, respectively, compared with 92.5° for the pristine polystyrene). According to the literature,³ a contact angle of 38.0° corresponds to partial sulfonation, whereas one of 13.0° indicates the formation of dense monolayers terminated by sulfonate groups.

LDHs are normally prepared by coprecipitation of solutions of M^{II} and M^{III} salts with alkali. Poorly crystalline samples are generally obtained unless the materials are aged under hydrothermal conditions. Precipitation from homogeneous solutions using the temperature-controlled hydrolysis of urea, which leads to a slow increase in concentration of carbonate ions and pH (the latter associated with the formation of ammonia),^{18,19} results in well-crystallized LDHs with large particle sizes in the range of 2 to 20 μ m. In our experiments, $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ with Mg^{2+}/Al^{3+} molar ratio of 2.00 were dissolved in deionized water (75 mL) to give solutions with a total concentration of metal cations of 0.015 M which were placed in 100-mL polytetrafluoroethylene (PTFE) vessels. Urea ($[urea]/[NO_3^-] = 4$) was dissolved in the above solution. The sulfonated polystyrene substrates were suspended horizontally in the solutions. The containers were sealed and placed in an oven and maintained at 70 °C for 9 days. When the solutions were cooled, the polystyrene substrates were removed and washed well with deionized water, then dried at 40 °C for 6 h. PTFE vessels were used in order to avoid the nucleation expected on glass surfaces. XPS measurements have indicated²⁰ that Fe^{3+} ions are adsorbed on the surface of sulfonate sites of sulfonated polystyrene soon after contact and presumably both Mg^{2+} and Al^{3+} ions are similarly adsorbed. Film formation may proceed by both nucleation on the surface and deposition of colloidal particles precipitated in solution.⁴ In order to minimize the influence of the latter, the transparent films on the underside surfaces of the substrates were examined.

The XRD patterns of film samples are shown in Figure 1. Some sharp diffraction peaks superimposed on the broad feature due to the substrates (Figure 1A), are observed in the case of the LDH films on the sulfonated polystyrene (Figures 1B and 1C). Comparison of the XRD patterns of powder scraped from the films (Figure 1D), the sediment produced by homogeneous precipitation (Figure 1E), and the literature^{18,19} shows that the low-angle peak corresponds to the basal reflection of $MgAl-CO_3^{2-}$ LDH ($d_{003} = 0.763$ nm). The other peaks can be indexed as the (006), (012), (015), and (018) reflections of an LDH phase. The presence of sulfonate groups is necessary for the growth of the films since a sample of unsulfonated polystyrene suspended in the same solution gave an XRD pattern with no reflections corresponding to a LDH phase.

The FT-IR spectrum of the powders scraped from the

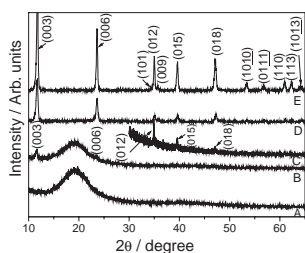


Figure 1. XRD patterns of polystyrene (A), film sample (B, C), powder scraped from films (D) and MgAl-LDH precipitate (E). ((C) is the glancing angle diffraction pattern of the film from 30 to 65°).

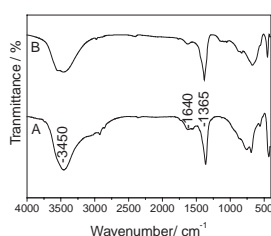


Figure 2. FT-IR spectra powder scraped from film samples (A) and MgAl-LDH precipitation (B).

films (Figure 2A) was identical to that of the LDH sediment (Figure 2B), with a characteristic¹⁹ intense peak due to the inter-layer carbonate ion $[V_3(CO_3)]$ at around 1365 cm^{-1} . Elemental analysis by inductively coupled plasma spectroscopy showed that the Mg^{2+}/Al^{3+} molar ratios in the films (1.61 in the case of the substrate sulfonated for 72 h, in agreement with the XPS measurement) were lower than that in the sediment (about 1.92) and in the precursor solution (2.00). This may indicate that there is some preferential adsorption of Al^{3+} over Mg^{2+} on the surface of the substrate as a consequence of its higher charge. In addition, it is known that Al-rich LDHs can be synthesized by using urea hydrolysis reaction.¹⁹

The scanning electron microscope (SEM) micrographs of films obtained with different substrates are shown in Figure 3. For the unsulfonated polystyrene (Figure 3A) no LDH film is observed, consistent with the XRD results. In the case of the partially sulfonated polystyrene (Figure 3B), the platelets in the LDH film are disordered and some areas of the polymer are not covered by LDH. In contrast, for the highly sulfonated polystyrene (Figure 3C), a dense film with the (001) direction (or *ab* plane) of the LDH crystallites perpendicular to the surface of polystyrene substrates is formed. Interestingly, a similar motif is observed for a related LDH-like compound, $[LiAl_2(OH)_6]^+ [NO_3]^-$, formed on the surface of aluminium alloys by treatment with alkaline lithium salt solutions.²¹ The thickness of the LDH film (Figure 3D) is of the order of μm and may be controlled by varying reaction conditions such as time, temperature and concentration of metal ions.

In summary, we have shown that oriented dense thin films of MgAl-LDH may be grown on surface-sulfonated polystyrene substrates in aqueous solutions. For highly sulfonated substrates, the (001) direction of the MgAl-LDH platelets is perpendicular to the surface. We have also used this method to prepare similar films of other LDHs such as $ZnAl-CO_3^{2-}$ and $NiAl-CO_3^{2-}$.

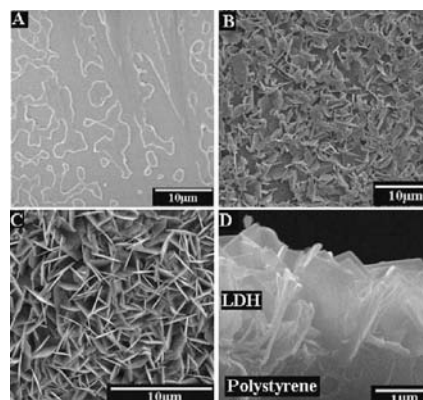


Figure 3. SEM graphs for basal surface of (I) type samples on polystyrene substrates sulfonated for 0 h (A), 24 h (B), and 72 h (C), edge of the samples on substrate sulfonated for 72 h (D).

Further study of the properties of these films and potential applications is underway in our laboratory.

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