

Selective Layer Reaction of Layer-by-Layer Assembled Layered Double-Hydroxide Nanocrystals

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Assembly of nanosized inorganic particles on solid surfaces is important for biomimetic materials chemistry and technological applications.¹ Layered double hydroxides (LDHs) are one of the most useful classes of inorganic layered compounds and have recently received considerable attention in the fields of catalysts, separations, and the immobilization of biological compounds.² Although the stepwise formation of multilayered nanostructural films from macromolecular precursors has been intensively studied,^{3,4} the adsorption of polyelectrolytes has proven problematic because of the difficulty in controlling the interfacial properties, especially in the case of layered compounds with reactive edge sites for topotactic reactions. Although the guests of two-dimensional compounds may be topochemically exchanged depending on their relative affinity to the hosts, it has not so far been possible to control the monitoring of the swelling and blocking of the edge of the crystalline sheets against the incoming guests in the powder samples. However, the development of immobilized layered compounds on solid substrates with a controlled orientation has opened up the possibility of having a predesigned platform to observe the progress of the exchange reaction for separate crystalline sheets.⁵

Herein, we present a novel synthetic strategy to graft the surface of Si substrates using organic acids to produce a layer-by-layer assembly of LDH nanocrystals on their surface. The adsorption of carboxyalkylphosphonic acids on the hydroxyl groups of LDH also drives the on-off control of the entrance of the guest through the broken edge of LDH, which allows for the remarkable expansion of the target layer in multilayer LDH nanocrystals by replacing the carbonate with alkyl dicarboxylate ions in the interlayer space of LDH.

We synthesized well-crystallized $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}]\text{CO}_3 \cdot n\text{H}_2\text{O}$, denoted as MgAl-LDH, using the coprecipitation and hydrothermal treatment method,⁶ which has a diameter of several hundred nanometers and a thickness of about 100 nm. For the preparation of the monolayer (1 L) on Si, the cleaned Si substrates were dipped in MgAl-LDH colloidal solution at room temperature.⁵ The surface of the MgAl-LDH/Si samples was grafted with 10 mM 2-carboxyethylphosphonic acid (denoted as “capo”) in ethanol at room temperature, washed with ethanol, and dried at 200 °C in air. To form the second-layer, the capo-coated MgAl-LDH/Si was treated with MgAl-LDH solution. The repetition of the sequential capo-LDH layering procedure allowed us to produce a multilayer of MgAl-LDH on Si.

The IR spectra confirmed the adsorption of capo on MgAl-LDH (see Supporting Information Figure S1). The capo with its weak acidity was adsorbed on the positively charged surface of MgAl-LDH by the ion-exchange mechanism, because it cannot self-

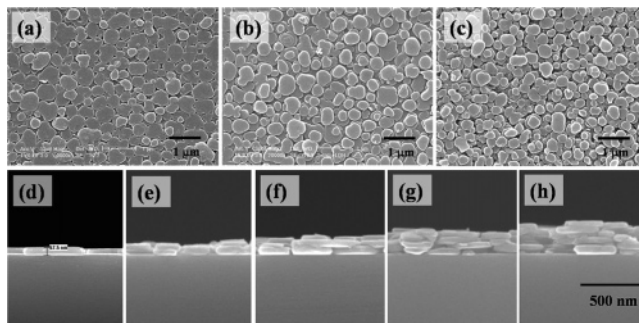


Figure 1. SEM images of the monolayer 1 L (a), 3 L (b), and 5 L MgAl-LDH/Si (c). Cross-sectional views of 1 L (d), 2 L (e), 3 L (f), 4 L (g) and 5 L (h) samples.

condense by the formation of P–O–P bonds under mild conditions, but only react with the surface to form monolayers.⁷

Other acids such as dicarboxylic, phosphoric, and alkylphosphonic acids could also be used for multilayer assembly, but the experimental conditions, for example, the concentration, time, and temperature, required to inhibit anion exchange in the interlayer have narrow ranges (vide infra).

Multilayer as well as monolayer MgAl-LDH/Si has a continuous coverage and ordered orientation, as shown in the SEM images in Figure 1. The assembly of the additional layers of nanoparticles proceeded by face-to-face stacking, and the resulting structure was uniform throughout the entire substrate but less dense than the first layer of nanoparticles. The surface of MgAl-LDH in each layer remained intact to all outward appearances, even after dipping in capo-ethanol solution. The MgAl-LDH does not adhere on the MgAl-LDH/Si without capo grafting, which strongly suggests that the MgAl-LDH is attracted to the capo-grafted surface of 1 L capo-MgAl-LDH. The instant aggregation between the capo treated MgAl-LDH and pristine MgAl-LDH provides evidence for the assembly mechanism (see Supporting Information Figure S2). The preferred orientation of MgAl-LDH was confirmed by the strong enhancement of the (001) peaks in the X-ray diffraction (XRD) patterns of both the 1 L and 5 L samples presented in Figure 2.⁵ In a previous study, solvent evaporation of the colloidal solution gave a random orientation,⁸ and it was difficult to obtain a well-defined multilayer array, as in the present study.

The anion exchange reaction of 1,10-decanedicarboxylic acid was carried out in 1-propanol/toluene (0.5%, v/v) at 120 °C for 24 h to prepare organic diacid-MgAl-LDH nanocomposites (denoted as DC-LDH).⁵ The exchange was successful for the 1 L MgAl-LDH/Si, but not for the 1 L capo-MgAl-LDH/Si, indicating that the capo modification on the edge sites inhibits the dicarboxylates from entering the interlayer gallery.⁹ We applied the solvothermal reaction to MgAl-LDH/(capo-MgAl-LDH)₄/Si possessing one MgAl-LDH top layer and four lower capo-MgAl-LDH layers for

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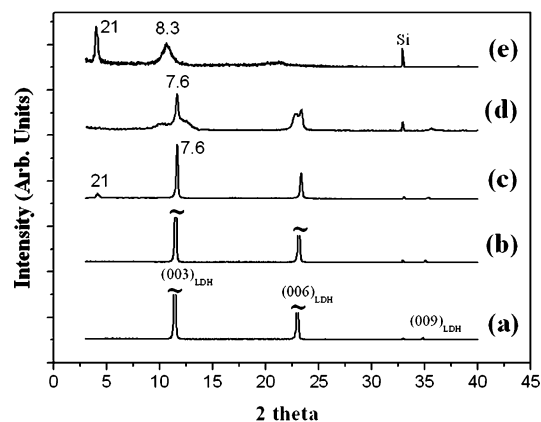


Figure 2. XRD spectra of 1 L (a), 5 L (b), DC-LDH/(capo-MgAl-LDH)₄/Si (c), ethanol/water-washed 5 L (d) and (DC-LDH, capo-MgAl-LDH)₅/Si prepared by post-washing (e). The scale of trace e is multiplied by 10.

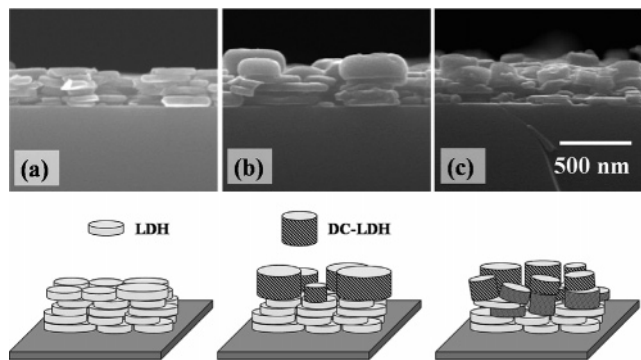


Figure 3. SEM images of 5 L MgAl-LDH/Si (a) top layer exchanged DC-LDH/(capo-MgAl-LDH)₄/Si (b) and further exchanged (DC-LDH, capo-MgAl-LDH)₅/Si (c).

layer-by-layer assembly. The dicarboxylic acids were only prominently exchanged in the gallery space of the top layer MgAl-LDH, and the height of the nanocrystals dramatically increased, as shown in the SEM image of Figure 3b. A thorough inspection under SEM revealed that most of the DC-LDH on the top layer of the 5 L MgAl-LDH/Si kept their lateral positions after the anion exchange, and their horizontal sizes remained constant. This result clearly demonstrates that the capo grafting on the edge side inhibited the dicarboxylates from entering the interlayer space in the four lower capo-coated layers. Although the functionalization of the edge in layered compounds has been accomplished and experimentally studied,⁹ to the best of our knowledge, this is the first experimental observation of the blocking of the edge site against ion exchange. In Figure 2, the XRD spectra for DC-LDH/(capo-MgAl-LDH)₄/Si show two peaks corresponding to DC-LDH (21 Å) and capo-MgAl-LDH (7.6 Å). The basal spacing of 21 Å implies that the interlayer dicarboxylates are oriented vertically.^{5b}

The selectivity of the exchange reaction of the multilayered nanocrystals could be adjusted by leaching the adsorbed capo out of the DC-LDH/(capo-MgAl-LDH)₄/Si with ethanol/water solution at room temperature. The identical solvothermal reaction for the washed samples gave rise to further intercalation into the third and fourth layers of (DC-LDH, capo-MgAl-LDH)₅/Si, as shown in Figure 3c, demonstrating that the adsorbed capo on the open edge of the lower level capo-MgAl-LDH was removed to make way for

the resulting volume expansion. Most of the first and second layers did not expand, presumably because the capo molecules still remained to protect the edge sides, because of the reduced washing efficiency and diffusion rate through the continuously covered layer-by-layer assembly.

These phenomena could not be observed systematically in the randomly oriented powder samples, especially in the house-of-cards structures of LDH.¹⁰ The XRD data for the (DC-LDH, capo-MgAl-LDH)₅/Si showed an intense peak for well-defined DC-LDH (21 Å) and a broad one for the partially swelled MgAl-LDH (8.3 Å). The ethanol/water washing induces crystallographic disordering of the basal spacing, which is ascribed to the swelling of the edge sites,^{9b} which is supported by the observation of several peaks at around 7.6 Å, as shown in Figure 2d. The solvents and grafted capo may be incorporated into the external areas of some of the particles and block the entrance of the guest.

In summary, we demonstrated the layer-by-layer assembly and selective layer expansion of MgAl-LDH on Si using 2-carboxyethylphosphonic acid. By considering the relative affinity for the incorporation and adsorption of guests on the host layers, this edge-grafting mechanism and on-off control of the crystalline edge sites can be extended to the adjustment of the release properties of guest molecules and the catalytic ability of layered composite materials. Multilayer MgAl-LDH nanocomposites can be designed by surface treatment, thus making them useful to fabricate functional nanosensors, catalysts, ion-selective electrodes, optical coatings, and nanosized containers for biomolecules.

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Supporting Information Available: FT-IR spectra, photographs of colloidal solutions, and SEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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