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Stable Suspension of Layered Double Hydroxide Nanoparticles in Aqueous Solution

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We report a simple but efficient method to prepare stable homogeneous suspensions of monodispersed MgAl-layered double hydroxide (LDH) nanoparticles. This new method involves a fast coprecipitation followed by controlled hydrothermal treatment. In such suspensions, the LDH particle size can be controlled in the range of 50−300 nm with the aspect ratio about 5−10. These LDHs can be incorporated with various metal cations, such as Ni^{2+}, Fe^{2+}, Fe^{3+}, and Gd^{3+}, into the hydroxide layers and intercalated with many inorganic anions, such as Cl^-, CO_3^{2-}, and NO_3^-, into the interlayer spacing, as well as DNA and drug molecules.

Layered double hydroxides (LDHs) are a family of inorganic layered materials and have recently attracted increasing attention because of their potential applications in wide areas, such as catalysis, adsorption, and nanocomposite and drug delivery.[1−6] Most divalent and trivalent cations with suitable anions can form LDHs. Structurally, they consist of cationic brucite-like layers in which divalent ions are partially substituted by trivalent ones and exchangeable anions and water molecules in the interlayer to balance the positive charges.[1,2]

The conventional method for synthesizing LDH materials is coprecipitation at varied or constant pH, followed by aging at a certain temperature,[1−3] resulting in aggregates with size of 1−10 μm that contain hundreds of thousands of sheet-like LDH nanocrystallites in each aggregate, as represented in Figure 1A. To take full advantage of LDH material properties in the applications for cellular drug/gene delivery, polymer/LDH nanobiocomposites, and LDH thin films via spin/dip coating, it is necessary to disperse the LDH aggregates into individual sheet-like nanocrystallites in a stable aqueous suspension (Figure 1C). Recently, there are few reports on the observations of colloidal LDH suspensions;[7,8] however, questions, such as how to disperse and how well dispersed, how stable the suspension is, and more importantly, how the nanosheet size can be controlled, have not been clearly addressed yet. This communication reports a general but useful method to prepare stable homogeneous LDH suspensions with controllable particle sizes in 50−300 nm.

Precipitate MgAl−LDH was prepared by a coprecipitation method in the presence of excess Mg^{2+}.[9] Briefly, to prepare $Mg_2Al(OH)_6Cl{\cdot}xH_2O$, 10 mL of mixed salt solution containing $MgCl_2$ (3.0 mmol) and $AlCl_3$ (1.0 mmol) was added within 5 s into a 40 mL NaOH solution (0.15 M) under vigorous stirring, followed by 10−30 min stirring with the reactor isolated from air. Pure LDH slurry was obtained via centrifuge separation and washing, and then manually dispersed in 40 mL of deionized water and hydrothermally treated in an autoclave at 100 °C for 16 h, resulting in a stable homogeneous suspension. LDH crystallites were collected with a high-speed centrifuge (e.g. 20 000*g*) for characterization with XRD and FTIR. Other samples with different metal cations and compositions were prepared in a similar way.

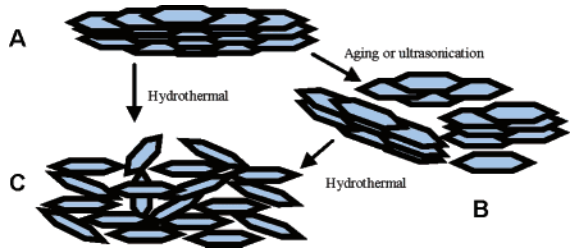

Figure 1. Dispersion of an LDH aggregate (A) into several smaller LDH aggregates (B) via aging process, or both (A and B) into individual LDH nanosheet crystallites (C) via the new hydrothermal treatment method.

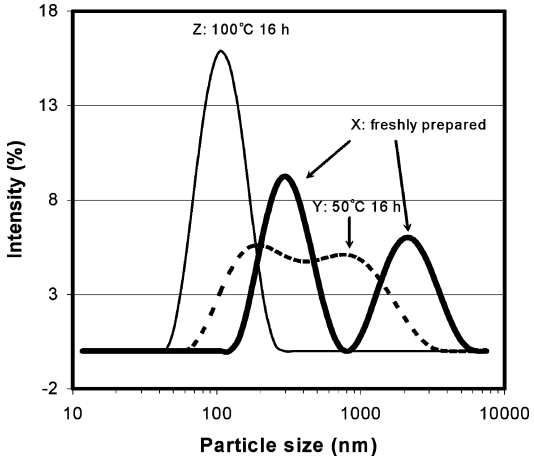

Figure 2. Particle size distribution of Mg_2Al−Cl−LDH samples collected with the photon correlation spectroscopy (PCS): (X) Coprecipitated and stirred for 10 min at room temperature, with two peaks at 320 and 2300 nm; (Y) sample X aged at 50 °C for 16 h, with two broad peaks at 220 and 955 nm; (Z) as-prepared with the new method, with one sharp peak at 114 nm. For seriously aggregated samples X and Y, ultrasonic treatment for 20 min was conducted for dispersion and also for convenience of PCS measurement.

The Mg_2Al−Cl−LDH suspensions made with the above hydrothermal method are stable for 1−6 months, and the LDH nanosheets have controllable lateral dimensions in the range of 50−300 nm. The LDH materials collected from the suspension exhibit the typical layered features from X-ray diffraction patterns (Supporting Information S1) and demonstrate a good crystallinity, with the (*003*) spacing of 0.785 nm.[9] FTIR spectrum (Supporting Information S2) is also typical for Mg_2Al−Cl−LDH.[3,10] Elemental analysis gives the atomic ratio [Mg]/[Al] = 1.8−1.9, slightly less than the designed value (2.0), which is due to more Mg^{2+} leaching than Al^{3+} from the hydroxide layers[9,11] and results in formation of traces of gibbsite (Supporting Information S1).

Moreover, the as-prepared Mg_2Al−Cl−LDH suspension presents a striking contrast to the conventionally prepared suspensions

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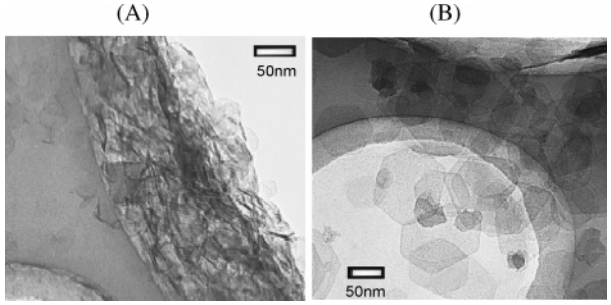

Figure 3. TEM images of $Mg_2Al-Cl-LDH$ (A) aged at 50 °C for 16 h, and dispersed with ultrasonic treatment for 20 min; (B) hydrothermally treated at 100 °C for 16 h.

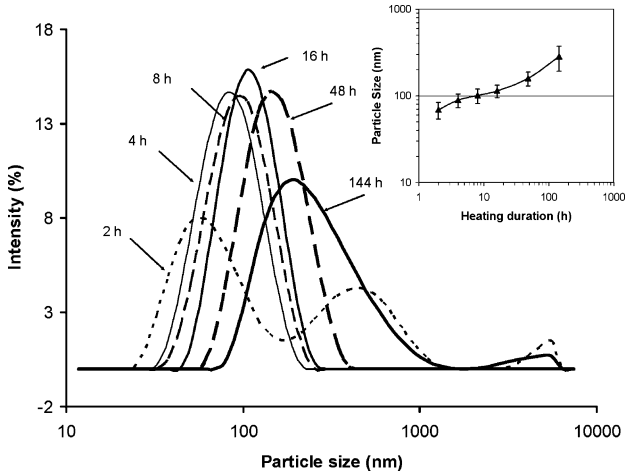

Figure 4. Dispersion of $Mg_2Al-Cl-LDH$ aggregates with heating duration during the hydrothermal treatment at 100 °C, where the distribution curves were obtained with PCS.

(Figure 2). This suspension has a narrow particle size distribution (PSD) with an equivalent hydrodynamic diameter of 114 nm (Figure 2Z). However, the suspension of freshly precipitated $Mg_2Al-Cl-LDH$ consists of a bimodal particle size distribution, with diameters at 320 and 2300 nm, respectively (Figure 2X). After aging at 50 °C overnight, the aggregates decrease in size to 220−955 nm (Figure 2Y). This means that the aggregates are only partially dispersed after aging and ultrasonication. Visually, the well-dispersed suspension looks transparent, while the conventional one is quite turbid. Therefore, the aggregates are completely segregated and well dispersed into much smaller particles after the hydrothermal treatment. We believe that these smaller particles are the primary crystallites of LDH materials, as suggested by TEM images in Figure 3. Figure 3A shows a part of an agglomerated LDH aggregate, which is composed of primary LDH crystallites with a lateral size around 50 nm. In Figure 3B, the LDH crystallites are very well separated, with only casual overlapping. They are also well shaped in hexagonal form with the lateral size in 60−150 nm, just falling within the range, as shown in the Figure 2Z curve, which means that the real lateral dimension from TEM images is very close to the hydrodynamic diameter from PCS, although the aspect ratio is normally 5−10.

The segregation process can be revealed through the change of PSD of LDH suspensions. As can be seen in Figure 4, the LDH particles in the suspensions are very uniform with a narrow PSD after the hydrothermal treatment for a suitable period of time (4−48 h). The 2 or 144 h treatment leads to the PSD bands with much bigger particles (Figure 4), indicating the presence of some degrees of aggregation. It seems that 2 h treatment at 100 °C is not long enough to de-aggregate all aggregates into individual LDH crystallites, while the 144 h treatment produces bigger LDH crystallites that tend to re-aggregate in the later period of hydrothermal treatment. The data in Supporting Information S3 at different temperatures also demonstrate the similar phenomena and reveal that the average primary particle size is doubled when the temperature increases from 80 to 150 °C with 8 or 16 h treatment. Therefore, the LDH particle size can be well controlled by choosing a suitable treatment temperature and duration.

It is worthy noting that the homogeneous LDH suspensions are highly reproducible under the same conditions. This method has been successfully applied to make many other LDH suspensions with various compositions, such as $Mg_2Al-LDH$ with Cl^-, CO_3^{2-}, or NO_3^- as the counteranion, $Mg_3Al-LDH$, and $Mg_4Al-LDH$, as well as Fe^{2+}, Fe^{3+}, Ni^{2+}, and Gd^{3+} containing LDH materials. The LDH concentration can vary from 0.2 to 5% (w/w). All the stable inorganic LDH suspensions we prepared in this research show a positive zeta potential in the range of 30−50 mV.

The major factors in forming LDH aggregates are the sharing of surface anions and edges of different crystallites, and the glue effect of amorphous LDH materials.[12] We think that hydrothermal treatment leads to a more even distribution of cations in hydroxide layers, a more regular crystallite shape, and growth of individual crystallites via cation diffusion and crystallite repining. Therefore, positively charged LDH platelets can escape from the aggregates through Brownian motion and can be stably suspended as colloids. An important prerequisite for complete segregation is to remove extra salts prior to hydrothermal treatment.

In conclusion, stable suspensions of MgAl−LDHs with different inorganic anions and cationic substitutions can be made with controllable particle size in the range of 50−300 nm in the lateral dimension and with the aspect ratio about 5−10. Such LDH suspensions can be used to adsorb dilute drug molecules or DNAs and directly used as the cellular delivery agents. Such LDH suspensions can be also directly used as the nanofillers in polymer nanocomposites. Moreover, stable LDH suspension can be used for LDH thin films for catalysis, gas separation, sensing, and electrochemical materials.

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Supporting Information Available: Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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