



Large-scale aqueous synthesis of layered double hydroxide single-layer nanosheets



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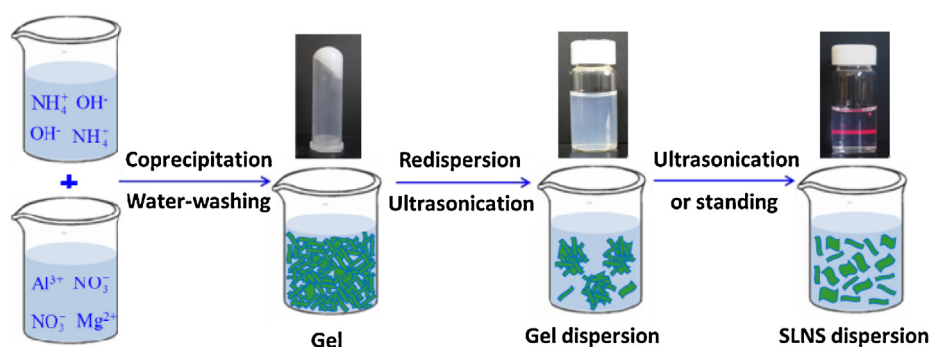
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HIGHLIGHTS

- Layered double hydroxide single-layer nanosheets (SLNSs) were synthesized.
- The synthesis includes three steps: coprecipitation, washing, and redispersion.
- No organic modifiers or organic solvents were used in the synthesis.
- The SLNSs in dispersion remains stable for at least 2 d at room temperature.
- The SLNSs can be directly used as building blocks for functional materials.

GRAPHICAL ABSTRACT



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ABSTRACT

Inorganic layered double hydroxide (LDH) single-layer nanosheets (SLNSs) are traditionally synthesized with the assistance of organic chemicals or in organic solvents, resulting in organic-coated SLNSs or organic dispersions of SLNSs, which may limit their potential applications. Herein, we report, for the first time, a simple aqueous synthetic route to naked (uncoated) LDH SLNSs; this route, which is termed the PWD route for simplicity, includes three steps: aqueous coprecipitation, water-washing, and redispersion in water. The obtained LDH SLNSs were characterized using TEM, AFM, XRD, and dynamic light scattering techniques, and the stability of the LDH SLNS dispersions was determined. Moreover, the co-assemblies of the LDH SLNSs with negatively charged guests, sodium cholate and graphene oxide, were investigated. Results showed that the SLNSs can remain stable (i.e., without layer-by-layer stacking) for a period of time, depending on temperature, and can be directly used as building blocks for functional materials. This new route has many advantages including its simple operation, environmental friendliness, low cost, and ease of large-scale application.

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1. Introduction

The synthesis of ultimate two-dimensional (2D) nanosheets (NSs) of layered solids, such as metal chalcogenides, metal phos-

phates or phosphonates, layered metal oxides, and layered double hydroxides (LDHs), has drawn considerable attention [1–6], this is because the anisotropy of NSs, with thicknesses of around one nanometer and lateral sizes ranging from submicrometer to several tens of micrometers, allows them to serve either as an ideal quantum system for fundamental studies or as a basic building block for functional materials. Among these solids, LDHs are one of the few layered materials with structural positively charged host layers [1].

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LDHs can be represented by the following general formula [1,2]: $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}_{x/n}]^{x-} \cdot mH_2O$. They consist of positively charged Brucite-type metal hydroxide layers and anionic counterions located between the layers. The synthesis of LDH NSs has attracted intense interest [1–4,7–12], owing to that the positively charged NSs have great potential as basic building blocks for constructing functional materials, such as catalysts [13], drug carriers [14], polymer–LDH nanocomposites [15], hydrogels [16], and electromagnetic materials [17], via charge-directed co-assembly with negatively charged basic building blocks. However, it was found that the synthesis of well-dispersed LDH NSs is difficult, due to their high structural charge density and high guest anion content, which leads to strong stacking of the LDH layers [2,4,18,19]. Therefore, inorganic LDH NSs are traditionally synthesized with the assistance of organic chemicals or in organic solvents, such as using delamination of organic intercalated LDHs in appropriate solvents [18–22] direct delamination of LDHs with NO_3^- or ClO_4^- as counter anions in formamide [4,23–27] and microemulsion method [28–31]. As a result, the LDH NSs obtained using these methods are either coated by organic chemicals or dispersed in organic solvents (such as toxic formamide [19]), which may limit their potential applications. From an application, environmental, and cost perspective, there remains an urgent need to develop aqueous direct synthetic methods for naked (i.e., uncoated) LDH SLNSs without using organic chemicals or solvents.

Herein, we report a new route for synthesizing naked Mg_2Al-NO_3 LDH SLNSs. This route, which is called the PWD route for simplicity, comprises the following three steps: Aqueous co-precipitation, water-washing, and redispersion in water. The obtained LDH SLNSs can be directly used as basic building blocks to construct function materials via co-assembly with molecular or layered guests. To the best of our knowledge, there have been no reports on the synthesis of naked LDH SLNSs without using organic solvents or modifiers, although co-precipitation is a general route to get inorganic NSs. Compared with previously reported synthetic methods [7–12,18–31], this new route has many advantages including its simple operation, environmental friendliness, low cost, and ease of large-scale application.

2. Experimental

2.1. Chemicals

Analytical grade $Al(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, and $NH_3 \cdot H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Sodium cholate hydrate (Ch; 99% purity) was purchased from Alfa Aesar. Graphene oxide (GO) was purchased from the Institute of Coal Chemistry, Chinese Academy of Sciences, China. All chemicals were used as received. The water used in the current study was purified using a Hitech-Kflow water-purification system (China).

2.2. Synthesis of LDH SLNSs

Mg_2Al-NO_3 LDH SLNSs were synthesized using the PWD route. In a typical procedure, a $Mg(NO_3)_2/Al(NO_3)_3$ mixed solution with a total salt concentration of 0.3 mol/L and Mg/Al molar ratio of 2 was prepared by dissolving 3.75 g (0.01 mol) of $Al(NO_3)_3 \cdot 9H_2O$ and 5.13 g (0.02 mol) of $Mg(NO_3)_2 \cdot 6H_2O$ in 100 mL of water. An alkali solution (~7 wt%) was prepared by diluting an $NH_3 \cdot H_2O$ solution (25–28 wt%) with water. The mixed salt solution (~100 mL) and alkali solution (~80 mL) were simultaneously added to a beaker within ~10 min under magnetic stirring and N_2 protection, during this process, the pH of the reaction system was held at ~10 by controlling the relative addition rates of the two raw material solutions. After stirring for ~10 min, the resultant precipitate was collected by centrifugation at 12000 rpm and washed thrice with

water via redispersion/centrifugation, yielding the LDH SLNS gel with a solid content (C_s) of ~8.5 wt%. A specific amount of the LDH SLNS gel (~1.2 g) was redispersed in a predetermined amount of water (~49 mL) by ultrasonication to produce an LDH SLNS dispersion ($C_s = 2.0$ g/L).

For comparison, a portion of the LDH SLNS gel was peptized at 80 °C for 24 h to produce a conventional LDH sol sample.

2.3. Co-assembly of LDH SLNSs and organic guests

Co-assemblies of the LDH SLNSs with cholate (Ch) and graphene oxide (GO) were performed to explore the potential of the LDH SLNSs as building blocks for functional materials. Briefly, Ch aqueous solution (50 mL, 0.01 mol/L) or GO dispersion (50 mL, 0.4 g/L) was added to the LDH SLNS dispersion (50 mL, 2.0 g/L) under magnetic stirring at ambient temperature (~25 °C). The suspension was centrifuged at 12000 rpm for 10 min and then washed with water, resulting in LDH nanohybrids intercalated with organic Ch or GO guests, denoted as Ch-LDH or GO-LDH nanohybrids.

2.4. Characterization

X-Ray diffraction (XRD) patterns were recorded on a D8 Advance diffractometer (Bruker, Germany) with Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) at 40 kV and 40 mA. Small-angle X-ray scattering (SAXS) patterns were recorded on a SAXSess system (Anton-Paar, Austria) with Cu $K\alpha$ radiation operating at 50 kV and 40 mA. Transmission electron microscopy (TEM) images were collected on a JEM-1011 microscope (JEOL, Japan) operating at 120 kV. A Nanoscope IIIa Multimode atomic force microscope (AFM, Digital Instruments, USA) was used to examine the morphology of LDH NSs deposited on mica wafers. AFM images were acquired in tapping mode using a Si tip cantilever with a force constant of 40 N m^{-1} . The particle size distribution and zeta potential of the LDH dispersions were determined by dynamic light scattering (DLS) method, using a nano-ZS90 zetasizer analyzer (Malvern, UK). The test dispersions (~0.1 wt%) were prepared by diluting the original samples using water and equilibrated for ~1 h at ambient temperature before DLS measurements. The transmittance (Tr) of the LDH dispersions was measured on an SP-4100 UV–vis spectrometer (Shanghai Spectrum Instruments Co., Ltd., China) at $\lambda = 590$ nm.

3. Results and discussion

3.1. Synthesis of LDH SLNSs

LDH SLNSs were synthesized by a PWD route that includes three steps: Aqueous coprecipitation, water-washing, and redispersion in water. The key to successfully obtaining LDH SLNSs is low (room)-temperature operation, to avoid the layer-by-layer stacking of the SLNSs formed. After co-precipitation and centrifugal water-washing, the obtained LDH SLNS gel had a low C_s of ~8.5 wt%; even using a higher centrifugal speed, the C_s was also difficult to exceed 10 wt%, indicating that the SLNSs have a strong ability to bond (or solidify) water. Most likely, the SLNSs in the gel form a 3D ‘house-of-cards’ aggregate structure [32], the water molecules are hydrogen-bonded to hydroxyl groups of the SLNSs and, simultaneously, coordinated to anions (NO_3^-), forming a 3D hydrogen-bonding network [2,23].

Redispersion of the LDH SLNS gel (such as ~1.2 g) in water (such as ~49 mL) by manual shaking (or ultrasonication for 1 min) resulted in a milk-white dispersion ($C_s = 2$ g/L), as shown in Fig. 1A. Irregular aggregates consisting of curved ultrathin LDH sheets and with a size of ~200–400 nm were observed using TEM in the gel dispersion (Fig. 2A, and Fig. S1A in the Supporting information, SI). After ultrasonication for ~5 min, the milk-white dispersion

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