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Single-step synthesis of layered double hydroxides ultrathin nanosheets

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ABSTRACT

A novel single-step approach was developed to prepare large-scale MgAl–LDHs ultrathin nanosheets. The key point of the successful realization was that we employed a high concentration of H_2O_2. Oxygen molecules, derived from in situ decomposition of H_2O_2, were speculated to be the decisive factor leading to complete separation of LDHs layers. The ultrathin nanosheets were characterized by XRD, TEM, AFM, FT-IR, and TG–DSC. The results indicated that the thickness of these nanosheets was about 1.44 nm, which was almost in perfect agreement with the theoretical thickness of two LDHs layers. From the TG–DSC curves, the weight loss of these exfoliated MgAl–LDHs ultrathin nanosheets at 500 °C was 18.5%, which was much smaller compared to the 32.3% weight loss of unexfoliated MgAl–LDHs.

1. Introduction

Ultrathin nanosheets are very attractive materials because of their unique properties (e.g., exceptionally small thickness and possible quantum size effects) and potential applications. Recently, a number of different ultrathin nanosheets materials, including graphene, oxides, sulfides, silicates and layered double hydroxides (LDHs), have been fabricated successfully [1–8]. In 2004, Geim, Novoselov, and their partners discovered graphene, making the synthesis technology of ultrathin nanosheets become a global research hotspot [9]. Moreover, the 2010 Nobel Prize in Physics, awarded jointly to Geim and Novoselov for groundbreaking experiments regarding the two-dimensional material graphene, has inspired the enthusiasm for synthesizing ultrathin nanosheets to a new level [10]. So far, a typical method for preparing nanosheets has been the exfoliation of layered compounds [4–8]. For example, Economopoulos et al. had prepared graphene by sonicating assisted exfoliating graphite in benzylamine under argon atmosphere [11]. Oh et al. had achieved exfoliated $Li[Mn_{1/3}Co_{1/3}Ni_{1/3}]O_2$ nanosheets by the reaction between the protonated precursor and an aqueous tetramethylammonium hydroxide solution for more than 2 weeks [12]. Adachi-Pagano et al. had reported a method to exfoliate ZnAl–LDHs by exchanging chloride ions with dodecyl sulfate anions and subsequently refluxing in butanol at 120 °C [13]. And O'Leary et al. had delaminated ZnAl–LDHs with dodecyl sulfate anions refluxing in acryl monomers at 70 °C [14]. Hibino and Jones had exfoliated glycine-containing MgAl–LDHs in formamide at room temperature [15,16]. Though these approaches can obtain ultrathin nanosheets, they are not suitable to be industrialized for complicated synthetic procedures and harsh reaction conditions. Therefore, it is urgent to design a practical approach to prepare ultrathin nanosheets. Here, by taking layered double hydroxides as an example, we reported a new strategy to synthesize ultrathin nanosheets with the assistance of hydrogen peroxide.

Layered double hydroxides (LDHs), a family of clay minerals, can be described by the following formula: $[M(II)_{1-x}M(III)_x(OH)_2][(A^{n-})_{x/n}\cdot mH_2O]$, where M(II) and M(III) are di- and trivalent metal cations, A^{n-} is the interlayer anion and m is the number of water molecules [17–20]. The positive charges in host layers originate from partial substitution of M(II) by M(III) and can be balanced by exchangeable interlayer anions [30–32]. Recently, great research interest of LDHs has been stimulated owing to their potential application in many fields, such as exchangers, catalysts, drug carriers, and super capacitors, and so on [21–28,20,29]. In order to further expand their applications, considerable efforts have been devoted to exfoliate LDHs to ultrathin nanosheets. However, LDHs exfoliation is difficult due to their high charge densities on layers and strong interlayer electrostatic interactions.

In this article, we demonstrated a single-step method to synthesize large-scale MgAl–LDHs ultrathin nanosheets. To the best of our knowledge, it was the first time to propose this new strategy. The key point of the successful realization was that we employed

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a high concentration of H_2O_2. The whole process was carried out under hydrothermal conditions with $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, urea and H_2O_2 as reactants, and water as solvent. The successful obtaining of LDHs ultrathin nanosheets was speculated that oxygen molecules, derived from in situ decomposition of H_2O_2, positioned in LDHs interlayer. Because of their violent movements, the spacing between layers increased until layers separated completely. In this study, complete exfoliation of LDHs was also clearly evident by various characterization techniques. Furthermore, the exfoliation mechanism was discussed in detail.

2. Experimental section

2.1. Materials

$Mg(NO_3)_2{\cdot}6H_2O$ (Tianjin Hengxing Chemical Reagents Co.), $Al(NO_3)_3{\cdot}9H_2O$ (Tianjin Hengxing Chemical Reagents Co.), and Urea (Tianjin Yaohua Chemical Reagents Co.) were analytical reagent grade and used without further purification. 30% H_2O_2 (30 wt% H_2O_2 and 70 wt% H_2O) was purchased from Tianjin Hengxing Chemical Reagents Co.

2.2. Synthesis of MgAl–LDHs ultrathin nanosheets

Sufficient amounts of $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, and urea were dissolved into 100 mL 30% H_2O_2 to yield a solution containing 0.01 M Mg^{2+}, 0.005 M Al^{3+}, and 0.05 M urea. And then, this solution was loaded into a Teflon tube, sealed, and heated at 150 °C for 24 h. According to a pressure gauge, the pressure in the tube increased gradually as the increase of reaction time and 2.5 h later reached to a stable value of 12.6 MPa. After the reaction was complete, a translucent colloidal suspension was obtained. The translucent colloidal suspension was filtered, washed, and dried under air atmosphere for characterization. In the following article, these as-prepared MgAl–LDHs ultrathin nanosheets were represented by L3.

2.3. Series of controlled experiments

In order to demonstrate the important role of H_2O_2 in synthesis of MgAl–LDHs ultrathin nanosheets, we carried out a series of controlled experiments. With other reaction conditions unchanged, we transformed the content of H_2O_2 in aqueous solution to 0 wt%, 10 wt%, and 20 wt%. In the following article, we used L0, L1, and L2 to represent those products, respectively.

2.4. Characterizations

Powder X-ray diffraction (XRD) patterns of the solid products were obtained in the 2θ range of 5–70° using a Rigaku D/max-IIIB diffractometer with Cu Kα radiation (λ = 1.54178 Å). Morphology was characterized using transmission electron microscopy (TEM, PHILIPS CM 200 FEG, 160 kV). Scanning electron microscope (SEM) was performed on a Philips XL30 instrument at an acceleration voltage of 20–30 kV and a working distance of 17 mm. The thickness was investigated by an atomic force microscopy (AFM, Nanoscope IIIa). Fourier-transform infrared (FT-IR) spectrum was recorded with an AVATAR 360 FT-IR spectrophotometer using a standard KBr pellet technique. TG–DSC was carried out by heating the dry powder samples at a rate of 10 °C/min in NEZSCH STA 409 PC.

3. Results and discussion

In our experiment, MgAl–LDHs were first exfoliated successfully with the help of H_2O_2. In order to demonstrate the important role of H_2O_2 in the whole process, we changed the content of H_2O_2 from 0 wt% to 30 wt%. Fig. 1 is the photograph of the solutions reaction after 24 h under hydrothermal conditions with $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, urea, and H_2O_2 as reactants, and water as solvent. It is determined that with the increasing percentage of H_2O_2, the resultant solution becomes more transparent. A white precipitate was observed with no presence of H_2O_2 (L0). As H_2O_2 increased to 10%, the white precipitate flocculated (L1) and viscous gels began to form at 20% H_2O_2 content (L2). On reaching 30% H_2O_2, a semitransparent colloidal suspension was obtained (L3). After exposing L3 to air for several weeks, no white precipitation had formed, suggesting the semitransparent colloidal suspension was stable.

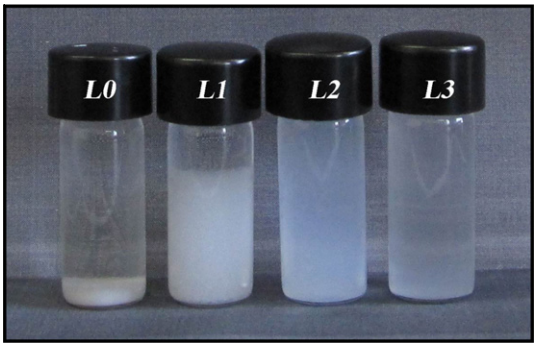

Fig. 1. Photographs of the four resultant solutions obtained in the solution with different content of H_2O_2.

Fig. 2 displays the XRD patterns of the four samples. They represent a typical XRD pattern of MgAl–LDHs. The indexing of the diffraction peaks was carried out using a standard JCPDS file. With increasing content of H_2O_2, there is a tendency to reduce crystallinity. The inset graph on the left indicates that (003) peak shift to low angle when adding H_2O_2 to the solution, suggesting that the interlayer distance of MgAl–LDHs increased. From the inset graph on the right, we can infer that the broadening of peaks has occurred up to L3. It is well-known from literature that (003) diffraction peak is related to the thickness of the brucite-like layer and the interlayer distance. On the other hand, (110) diffraction peak represents the arrangement of ions along the plane of host layer [33–35]. For most LDHs, including L0 and L1, (003) peak is much stronger than (110) peak [36–41]. However, for the exfoliated MgAl–LDHs ultrathin nanosheets (L3) we obtained, the (110) peak is stronger than (003) peak. A relative good growth of lamellate layer is speculated.

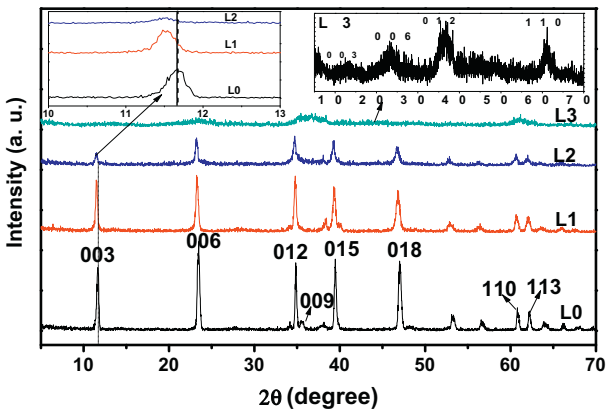

Fig. 2. XRD patterns of L0, L1, L2, and L3. The inset on the left is the enlarged view of (003) peak. The inset on the right is the XRD pattern of L3.