



Research paper

In situ growth of layered double hydroxide on disordered platelets of montmorillonite



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ABSTRACT

Layered double hydroxide (LDH) was in situ grown on the disordered platelets of montmorillonite (Mt), and a self-assembled sheet-on-sheet nanohybrid was obtained. To obtain a nanohybrid of cationic/anionic clay with exfoliated Mt platelets, NaMt (sodium-montmorillonite) was fractionated and subsequently treated by ultrasonication in a solution of aluminum nitrate and magnesium nitrate to ensure good dispersion of the NaMt and cation adsorption. Subsequently, the precursors were reacted with ammonia under hydrothermal conditions. The phase compositions of the as-prepared samples were analyzed by X-ray diffraction and Fourier transform infrared spectroscopy. Field-emission scanning electron microscopy and high-resolution transmission electron microscopy investigations revealed the typical sheet-on-sheet and exfoliated Mt structures. The results demonstrated that the LDH grown on the disordered platelets of montmorillonite was successfully synthesized by a simple in situ growth route. A possible formation mechanism for the sheet-on-sheet architecture has been suggested. Using ultrasonically pre-exfoliated disordered Mt platelets as matrixes provided an essential substrate for the nucleation and in situ growth of LDH crystallites. The ammonia solution provided hydroxyl moieties for LDH growth and split the Mt platelets via a breaker effect. It is suggested that the in situ-grown LDH crystals, as spacers, played a crucial role in preventing the reaggregation of the disordered Mt platelets. This study can offer some new insights into developing a nanohybrid of cationic/anionic clay with a unique sheet-on-sheet structure.

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1. Introduction

Layered clay minerals, which are considered to be a class of two-dimensional nanomaterials, have been studied and applied widely because they are abundant, inexpensive, environmentally friendly, and possess unique physico-chemical properties (Bergaya et al., 2011). Montmorillonite (Mt) is a typical layered clay mineral that belongs to the class of cationic clay. Layered double hydroxides (LDH) are referred to as anionic clay because their physical and chemical properties are surprisingly similar to those of clay minerals, but their ion-exchanged properties are anionic. Both of these lamellar materials are important for various applications in catalysts or catalyst carriers (Roefsaers et al., 2006; Zhou, 2011), biological materials (Kishimoto et al., 2013), and adsorption materials (Zhu et al., 2014).

It is well-known that Mt, an important layered aluminosilicate, carries a permanent negative charge. The negative layer charge is balanced by the interlayer space, which contains cations, such as Na

and Ca. Unlike Mt, the layered structure of LDH includes permanent positive charges, which are compensated by the exchangeable anions in the interlayer space.

The exfoliation of layered clays with strong chemical bonds within the silicate layers but weak interlayer bonds has attracted much attention because of their remarkable chemical and physical properties (Nicolosi et al., 2013) and their wide applicability in polymer reinforcement (Kawasumi et al., 1997), emulsion stabilization (Abend et al., 1998), flame retardancy (Wang et al., 2002) and film preparation (Liu et al., 2006). The exfoliation of clays in water and organic solvent to prepare stable colloidal dispersions has been well documented (Lagaly and Malberg, 1990; Norrish, 1954). However, exfoliated clay platelets in liquid are easily restacked and reaggregated by flocculation, and as a result, these exfoliated platelets cannot be retained as the dispersed medium is removed. The stability of exfoliated surfactant-intercalated Mt in alcohols has been studied by Venugopal et al. (2006), who found that most of the exfoliated platelets only lasted for a few hours. Although exfoliated clay platelets in the solid state have been obtained by mechanical grinding, they exhibited very small grain sizes because of comminution (Christidis et al., 2004; Dellisanti and Valdré, 2005). Therefore, it is highly desirable to develop an effective route to obtain stable exfoliated Mt platelets.

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Interstratified minerals such as illite–smectite can be found in nature and exhibit both random and regular ordered, layer-to-layer assemblages (Zhou and Keeling, 2013). At present, only a few attempts have been made to assemble layered composites by different layered materials. Very recently, composites involving cationic LDH platelets and anionic Mt platelets have been reported (Chalasan et al., 2013; Yi et al., 2013). These composite materials of Mt and LDH platelets were assembled via a regular mode, and both of the crystal structures were well preserved with different basal spacing. This work is interesting and valuable, and the high stability of the LDH and Mt composites in non-polar solvent offers us new possibilities to prepare stable interstratified materials. However, it should be noted that this method requires appropriate ionic surfactants and a non-polar solvent, as well as a complicated multi-step process. Thus, the feasibility of directly assembling stable composites of LDH and Mt without any additive through a facile one-pot method remains unknown.

To explore these possibilities, we introduce herein the precursors of LDH into the interlayer space of Mt platelets by electrostatic attraction. The as-formed LDH plays a crucial role in the formation of stable disordered Mt platelets by not only preventing the reaggregation of Mt platelets by the spacer effect, but also forming an LDH/Mt nanohybrid with a sheet-on-sheet structure via a facile hydrothermal method. This study may shed light on the formation of a nanohybrid of cationic/anionic clays with a unique sheet-on-sheet structure.

2. Experimental section

2.1. Materials

Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, and ammonia solution were used to synthesize LDH. The three chemicals were of analytical grade and were purchased from Shantou Xilong Chemical Factory (Guangdong, PRC). All chemicals were used without further purification. Ca-montmorillonite (cation exchange capacity (CEC) = 110.5 meq/100 g) was obtained from Inner Mongolia, PRC. The chemical compositions (wt.%) of the Ca-montmorillonite were as follows: SiO₂ 58.16%, Al₂O₃ 16.95%, Fe₂O₃ 5.26%, MgO 3.57%, CaO 2.29%, TiO₂ 0.20%, Na₂O 0.19%, K₂O 0.15%, MnO 0.03%, and P₂O₅ 0.08%, and the ignition loss was 13.12%. The raw sample was further purified by repeated sedimentation to remove the impurities, and the <2 μm fraction was collected and used for the following experiments. The Na₂CO₃ used for sodium modification was also supplied by Shantou Xilong Chemical Factory.

2.2. Synthesis

Sodium-modified montmorillonite (hereafter referred to as NaMt) was prepared by modifying natural Ca-montmorillonite by exchanging calcium ions for sodium ions using the sodium-modification reagent, Na₂CO₃. A mixture of 10 g of Ca-montmorillonite and 0.6 g of Na₂CO₃ was added to 90 mL of deionized water and stirred at 353 K for 2 h. After the cationic exchange reaction, the sediment was removed by sedimentation, and the upper dispersion product was separated and subjected to centrifugation and washing with deionized water 5 times. Subsequently, it was dried overnight in an oven at 353 K. The dried product was ground in an agate mortar to pass through a 200-mesh sieve and stored in a dryer until further use.

The self-assembled nanohybrid of Mt and LDH was prepared as follows: 2.5 g of as-prepared NaMt was stirred with 97.5 mL of deionized water in an oil bath at 363 K for 2 h to obtain the NaMt liquid. Then, the undispersed solid was separated from the NaMt liquid by centrifugation at 4000 rpm, and the upper colloidal dispersion was obtained. Next, 4.1 g of Mg(NO₃)₂·6H₂O and 3.0 g of Al(NO₃)₃·9H₂O were added to the 60-mL colloidal dispersion at a Mg:Al molar ratio of 2:1, followed by stirring for 10 min at room temperature. Then, the mixture was placed into a closed container under a nitrogen blanket. The closed container was ultrasonically treated in an ultrasonic bath

(KS-180EI, 40 kHz, Ningbo Haishu Kesheng Ultrasonic Equipment Co., Ltd, Ningbo, PRC) for 4 h at room temperature. Subsequently, the as-prepared suspension was adjusted to pH 9.5 using ammonia solution, and then, the mixture was transferred into an autoclave pressure vessel and maintained at 413 K for 15 h. When the autoclave pressure vessel had cooled to room temperature, the resulting sample was collected by centrifugation at 4000 rpm. Finally, the obtained sample was washed 5 times with deionized water and dried in an oven at 353 K to a constant weight. The final product, which was composed of different clay platelets, is a nanohybrid, where “nano” refers to the magnitude of the thickness. It is denoted as LDH/Mt hereafter. To investigate the influence of LDH on the nanohybrid structure and morphology, a contrastive experiment in which the other process parameters were maintained was carried out in the synthesis of pure LDH.

2.3. Characterization methods

X-ray diffraction (XRD), using a PANalytical X'pert PRO powder diffractometer equipped with a Cu Kα radiation source (λ = 0.15405 nm) was employed to determine the phase compositions and structures of the samples at 40 kV and 40 mA. Fourier transform infrared spectrometer (FTIR) was performed with a Thermo Nexus 470 infrared spectrometer to study the structure of the materials by analyzing the vibrational frequencies of chemical bonds. Field emission scanning electron microscopy (FESEM; S-4800) and transmission electron microscopy (TEM; JEM-2100F) were used to characterize the microstructure of the samples. For TEM observation, specimens were prepared by dispersion in deionized water and ultrasonic treatment for 15 min. A drop of the resulting dispersion was placed on a holey carbon film supported by a copper grid, after which the deionized water was evaporated. SEM specimens were treated on a conductive adhesive using the same method and then coated in gold.

3. Results and discussion

3.1. XRD results

In the XRD pattern of NaMt (Fig. 1a), the basal spacing of the NaMt is 1.26 nm, which was calculated from the basal reflection (001) using the Bragg equation. This value indicates the successful modification of the Ca-montmorillonite (1.56 nm) (JCPDS No. 13-0135) (Ohtsuka, 1997).

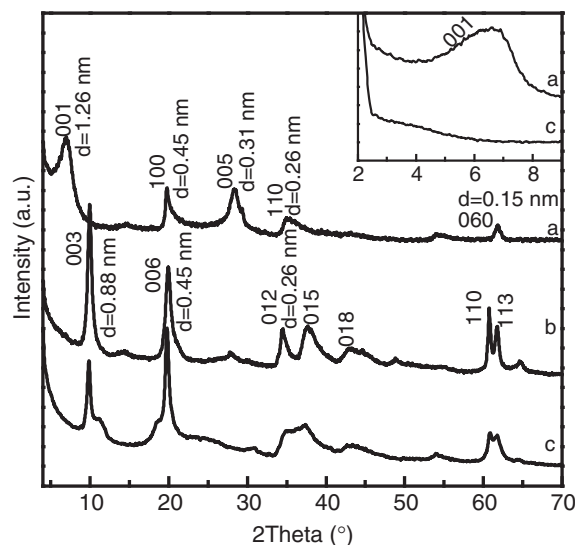


Fig. 1. XRD patterns of samples. (a) NaMt: sodium-modified montmorillonite. (b) LDH: MgAl-layered double hydroxide with a Mg:Al molar ratio of 2:1. (c) LDH/Mt: self-assembled nanohybrid of Mt platelets and LDH platelets. The inset shows the small-angle XRD patterns of (a) and (c) for comparison.

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