



Effect of layer charges on exfoliation of montmorillonite in aqueous solutions



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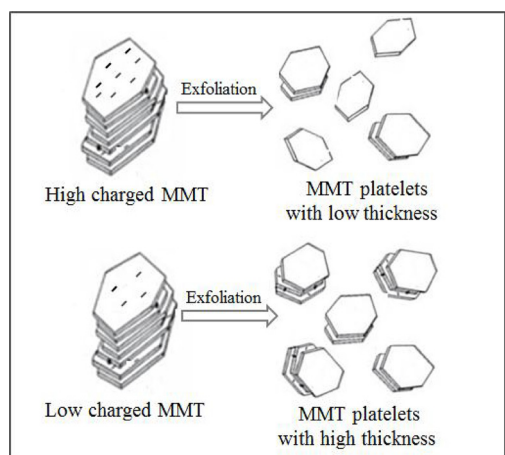
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GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the exfoliation of montmorillonite related with electric charges on the layers in aqueous solutions were investigated through the measurements of zeta potential, turbidity and atomic force microscopy, as well as molecular dynamics simulation. The charge amount on montmorillonite layers was adjusted by blocking or neutralizing the layer charges with tetraethylenepentaminecopper (II) ([Cu(tetren)]²⁺) through cation exchange reaction. The experimental results have shown that the exfoliation closely correlated to the amount of the layer charges. The larger are the charge amount on montmorillonite layers, the more easily the montmorillonite is exfoliated. This observation might be attributed to the repulsive energy (electrostatic and hydration repulsion) was stronger between the high charged montmorillonite layers than low charged ones.

1. Introduction

In recent years, the preparation and application of mono- to few-

layer layered materials have been intensively investigated owing to their exceptional role in a great variety of technological and industrial applications [1–5]. Layered materials, as the name suggests, are solids

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with strong in-plane chemical bonds but weak out-of-plane van der Waals bonds. As a result, these materials can be sheared parallel or expanded to nanometer-thin sheets in-plane direction. The separation of large aggregates (booklets) into smaller platelets is defined as exfoliation [6,7].

As a typical layered material, the exfoliation behaviors of montmorillonite (MMT) in aqueous medium have caused widely public attention for a long time [8–11]. As a smectite type clay mineral, MMT has 2:1 structural units consists of two tetrahedral sheets of silica sandwiching an octahedral sheet of alumina. Its general formula is $(\text{Na})_{0.7}(\text{Al}_{3.3}\text{Mg}_{0.7})\text{Si}_3\text{O}_{20}(\text{OH})_4\cdot n\text{H}_2\text{O}$. Isomorphous substitutions of Mg for Al in the octahedral sheet of alumina and Al for Si in the tetrahedral sheets result in layer charges within MMT layers. MMT layer has cation exchange capacity which is balanced by cations (e.g., Na^+ , Ca^{2+}) within MMT inter-layer space. Since the hydration of these cations, the water molecules can get into the inter-layer space and cause the hydration swelling of MMT. In addition, the interaction force between the MMT layers is weak electrostatic forces and van der Waals forces. Owing to these characteristics, MMT has the ability to exfoliate free-standing nanometer-thin layers [12].

There are a number of methods used for the exfoliation of MMT that involve intercalation, ion exchange, or ultrasonic waves [8,13,14]. When water or polar organic molecules intercalated into the MMT layers attracted by the exchangeable cations, the MMT platelets will expand in a direction vertical to the layers. The exfoliation of MMT will produce a large number of fine particles which have adverse effect on both flotation and comminution [15–17]. In addition, exfoliation can dramatically increase the cation exchange capacity (CEC) and specific surface area values of lamellar MMT. Exfoliated MMT nanosheets can be incorporated into polymer/MMT nanocomposites to form an innovative class of materials that have a great of potential as superabsorbents, drug delivery system, tissue scaffolds, rheological modifier, wound dressing, and biosensors [18,19].

Despite the importance of MMT exfoliation in many industrial processes, very little work has been done to explore the specific effect of layer charge on the exfoliation of MMT. Though some molecular simulations studies were used to study effect of layer charge on the crystalline swelling MMT [20–22], the traditional experimental method is still scarce. In this work, an attempt has been made to study exfoliation of MMT with charge amounts in aqueous solutions. The aim is to explore the relationship between exfoliation and layer charges of MMT particles in aqueous solutions, and get more understandings of the preparation and application of MMT nanosheets.

2. Experimental

2.1. Materials

Crude MMT sample used in this work was obtained from Sanding Technology Co., Ltd, Zhejiang province, China. The purification of grounded MMT was carried out based on a common method described in previous papers [23]. Carbonates were removed by dilute hydrochloric acid ($\text{pH} > 4.5$) carbonates from MMT sample. And sodium citrate, sodium bicarbonate, sodium chloride and sodium dithionate buffering system ($\text{pH} 8.3$) was used to remove iron oxides. H_2O_2 solution was used to oxidize organic material at 70°C . The X-ray diffraction (XRD) pattern of the MMT sample was given in Fig. 1, shows that the MMT have high grade with few impurities. The particle size distribution of the MMT sample was given in Fig. 2, shows that the ranges of particle size of MMT sample are between 0.1 and $3.5\ \mu\text{m}$.

The analytical pure $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, tetraethylenepentamine, NaCl, NaOH and HCl were obtained from the Sinopharm Chemical Reagent Co., Ltd (China). Millipore Milli-Q Direct 8/16 ultrapure water ($18.2\ \text{M}\Omega$) was used in this work.

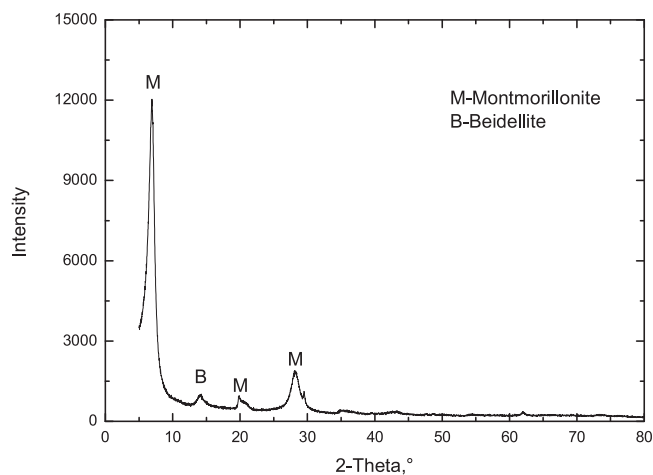


Fig. 1. XRD pattern of the MMT sample.

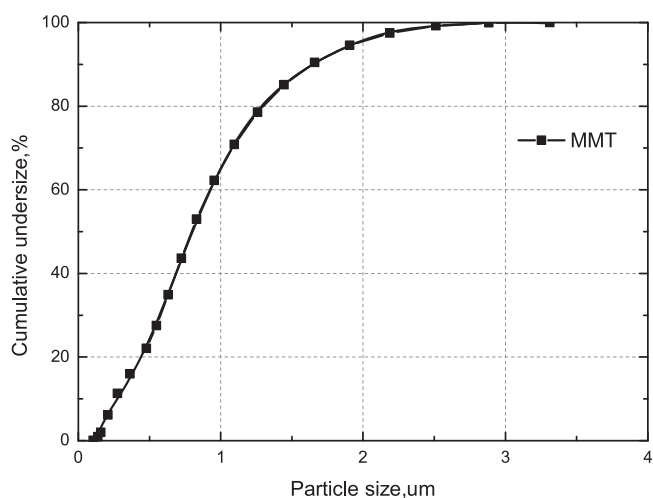


Fig. 2. Particle size distribution of the MMT sample.

2.2. Preparation of MMT with different charge amounts

The MMT with different charge amounts were got according to the method that block or neutralize the layer charges with the cation, tetraethylenepentamincopper(II) ($[\text{Cu}(\text{tetren})]^{2+}$) through cation exchange reaction. $[\text{Cu}(\text{tetren})]^{2+}$ ions have a high affinity for MMT surfaces and can enter the interlayer space blocking or neutralizing the negative layer charges. The more $[\text{Cu}(\text{tetren})]^{2+}$ adsorbed on the MMT surfaces, the less layer charges MMT has. An common process was performed to prepare the $[\text{Cu}(\text{tetren})]^{2+}$ solutions in ultrapure water [24]. A $0.01\ \text{mol/L}$ $[\text{Cu}(\text{tetren})]^{2+}$ solution was prepared by dissolving $0.01\ \text{mol}$ of tetraethylenepentamine and $0.01\ \text{mol}$ of $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ in ultrapure water and filling up to $1\ \text{L}$ ($\text{pH} = 8.4$). $0.1\ \text{g}$ of the natural MMT and $100\ \text{ml}$ of the $[\text{Cu}(\text{tetren})]^{2+}$ solution with different concentration were added to a conical flask. After $12\ \text{h}$ equilibration with magnetic stirring, $[\text{Cu}(\text{tetren})]^{2+}$ was adsorbed onto the MMT sample to block or neutralize the layer charges, and MMT sample with different charge amounts were obtained after centrifugation.

2.3. Measurements

XRD measurement was performed using a Bruker D8 Advance X-ray diffractometer with $\text{CuK}\alpha$ radiation. The diffraction angle of the patterns was recorded from 3° to 80° with a scanning speed of $10^\circ/\text{min}$. The particle size distribution of the MMT samples was obtained by the Malvern Mastersizer 2000. MMT suspension should be dispersed fully

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