

The Morphology of Nano-MgO Particles Induced by Attapulgite

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Abstract—In this paper, a new way to prepare controlled nano-MgO with different morphology facily by using modified attapulgite as hard template was found. The morphology details were investigated by scanning electron microscopy (SEM). It was found that the morphology of nano-MgO particles was induced by the ratio of attapulgite versus Mg^{2+} . The lamella morphology of MgO was converted to sphere particles, then the rod-like and needle-like or fiber-like shape, while the content of attapulgite was raised.

Keywords- nano-MgO; Attapulgite; crystallite

I. INTRODUCTION

Nano magnesium oxide (nano-MgO) is an exceptionally functional materials that have been widely used in catalysts^[1], superconductors^[2], anti-bacterial materials^[3], and so on. Several shapes and sizes nano-MgO particles were synthesized, such as nanosphere, nanocube and nanorod. What the magnesium salts, precipitant were used, and the reaction conditions play an important role on the shapes and sizes of nano-MgO particles. The most conventional method for preparation of nano-MgO is depositing different magnesium salts or magnesium hydroxide at first^[4,5], magnesium precursors and solvents as the reactants, $Mg(OH)_2$ nanocrystallines with rod-, tube-, needle-, or lamella-like morphologies by a hydrothermal reaction were obtained^[6], which was very important for the morphological features of subsequent nano-MgO particles by thermal decomposition.

The physical and chemical properties of Nano-MgO crystallites are directly connected with their sizes, shapes and size dispersion, therefore a new and inexpensive method to synthesize nano-MgO with narrow size distribution, controllable structure and morphology, and large specific surface area is necessary. Generally, one-dimensional nanostructures can be fabricated by template-directed growth methods. Attapulgite(ATP, or palygorskite) clay, a species of hydrated magnesium aluminum silicate mineral with commonly a rod-like or fibrous morphology, is a natural nanostructural material with an ideal formula $Si_3O_{20}(Mg, Al, Fe)_5(OH)_2(OH_2)_4 \cdot 4H_2O$. It is characterized by a porous crystalline structure containing tetrahedral layers alloyed together along longitudinal sideline chains^[7]. Octahedral units of MgO positioned parallel to these corrugations produce open ended (but otherwise enclosed) rectangular channels,

equivalent to about one amphibole unit wide (0.6 nm) and one brucite unit high (0.37 nm)^[8]. Due to its regular structure and large specific surface area, considerable porosity, and thermal stability, ATP has been used as absorbent^[9], catalyst and catalyst support^[10,11]. However, there have few reports published, up to date, with respect to the abrication of oxide nano-structure templated by attapulgite.

To make the synthetic approach more convenient, much effort has been made for nano-structure materials. Anodic alumina membrane^[12] and CNTs or TiO_2 are often used hard template^[13]. Several soft colloidal templates such as anionic sodium dodecylsulphate(SDS) and the cationic cetyltrimethylammonium chloride (CTAC) or bromide(CTAB) also play an important role in controlling the size and shape of inorganic nanocrystals^[14]. In this contribution, we firstly report an efficient method to synthesis nano-MgO with different morphology using natural attapulgite as hard template.

II. EXPERIMENT

The attapulgite was obtained from Jiangsu Jiuchuan Nami Material Technology Co., Ltd with purity more than 90%, and further purified by 3M solution of HCl for 3h under 75°C, washed ATP with distilled water until the chloride was not detected, dried and reserved. All other chemicals used in this work, such as $Mg(NO_3)_2 \cdot 6H_2O$ and urea were A.R. grade reagents.

Nano-MgO particles were prepared by homogeneous precipitation method: firstly the $Mg(NO_3)_2 \cdot 6H_2O$ was dissolved in water at 95°C under vigorous stirring to form a transparent solution. Then urea solution was added dropwise under strong stirring at the mole ratio 1:5 of magnesium ion to urea (Mg^{2+} /urea). The $Mg(OH)_2$ precursor was generated and the resultant suspension was continuously stirred for 3h. After precipitation, the mixture was cooled to room temperature, filtered, ultrasonic washed with deionized water and absolute ethanol several times for an effective removal of NO_3^- ion and the better dispersion of $Mg(OH)_2$ precipitation, which was dried at 80°C for 4 h and calcined at 420°C for 2h.

MgO NPs/ATP were prepared by mixing $Mg(NO_3)_2$ aqueous solution and ATP, Mg^{2+} went into ATP channel by ion exchange, then $Mg(OH)_2$ was deposited homogeneously on the ATP by adding urea. The reactions were as follows:

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$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dispersed in distilled water and stirred in a three necked flask for 5 min, then the ATP were added in the suspension. The mixed solution was kept at 80°C for 3h with stirring, followed by urea adding. The mixture was continually stirred for 20-40 min and then rise the temperature to 95°C for 3 h, filtered, ultrasonic washed with deionized water and absolute ethanol several times, dried and calcined. The ATP can be removed by treating MgO/ATP mixture several times with 2 mol/L NaOH solution at 80°C for 30 min.

Thermal behavior of MgO/ATP mixture was studied on the Thermo Gravimetric Analysis (TGA) PerkinElmer TGA-7). Specimens were put in a platinum crucible and heated at a rate of 10.00 K/ min from 50°C to 800°C in N_2 flow. Morphology and structure were observed on scanning electron microscope (SEM) with Ultra Plus field-emission (Germany Zeiss Co., Ltd) operating at 10 kV.

III. RESULTS

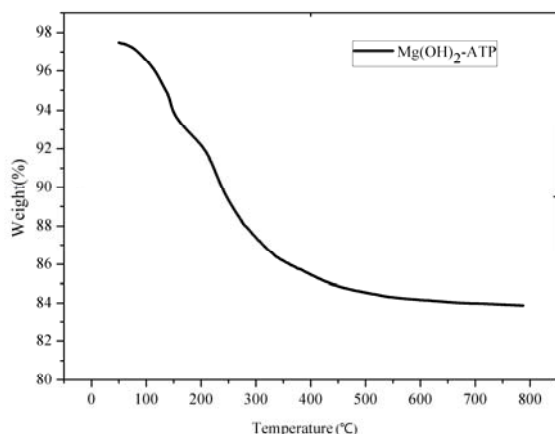


Figure 1. TGA curves obtained in N_2 flow for $\text{Mg}(\text{OH})_2/\text{ATP}$ nanocomposite

The TGA technique was used to analyze the thermal behavior of the MgO/ATP (ATP amount=90%) and thus could provide the necessary data for the following decomposition process. The mass loss curves for MgO/ATP composites are shown in Figure 1. For the MgO/ATP composites, the weight

loss happened mainly below 250°C , which is similar to that of pure ATP, the weight losses below 120°C , and between 120°C and 230°C are the release of free water and adsorbed water of ATP respectively. And the one between 230°C and 330°C can be attributed to the removal of crystal water of ATP. The one from 330°C to 500°C should be the decomposition of $\text{Mg}(\text{OH})_2$ to MgO and the release of the structural water of ATP, which was the basis that we choose 420°C as calcination temperature of the samples, at 420°C , the magnesium hydroxide can decompose completely and the structure of ATP clay can be protected from damage.

Figure 2a shows the homogeneous morphologies of nano- $\text{Mg}(\text{OH})_2$ particles with narrow size distributions and thus was chosen to undergo a subsequent calcination process to obtain MgO nano-crystals. From SEM images (shown in Figure 2a), it can be seen that the $\text{Mg}(\text{OH})_2$ precursors display the lamellar shape, the crystals of precursor was randomly piled up and presented a thin platelet shape, the thickness about 30~40nm and the lateral size about 500nm~1 μm , with a more or less circular contour. Moreover, the $\text{Mg}(\text{OH})_2$ precursor crystallite exhibits a smooth surface morphology (as shown in Figure 2b).

In order to make sure the effects about the amount of ATP on the shapes and sizes of MgO nanoparticles, four ratio of MgO/ATP were chosen to prepare MgO nanoparticles and did some analysis (1) 0wt%; (2) 3wt%; (3) 25wt%; (4) 50wt%. (see Figure 3).

The amount of ATP strongly affected the size and morphological features of the resulting MgO particles. It was found that when the ATP was absent, the MgO powders retained the plate-like features of $\text{Mg}(\text{OH})_2$ precursor, the width of the lamellar powders is about 500~600nm and the thickness of the plate is about 30~40 nm. After it was calcined, the MgO crystallite exhibits a coarse surface compared to its original $\text{Mg}(\text{OH})_2$ precursor (as shown in figure 2b). A higher magnification SEM image (figure 3-1) shows that the coarse morphology platelets are composed of nano-crystals with average crystallite size in 10~15nm connected each other. When the content of ATP is 3%, the MgO crystallite is still lamella morphology but the size of nano-crystals is increased to 20~25nm (as shown in Figure 3-2).

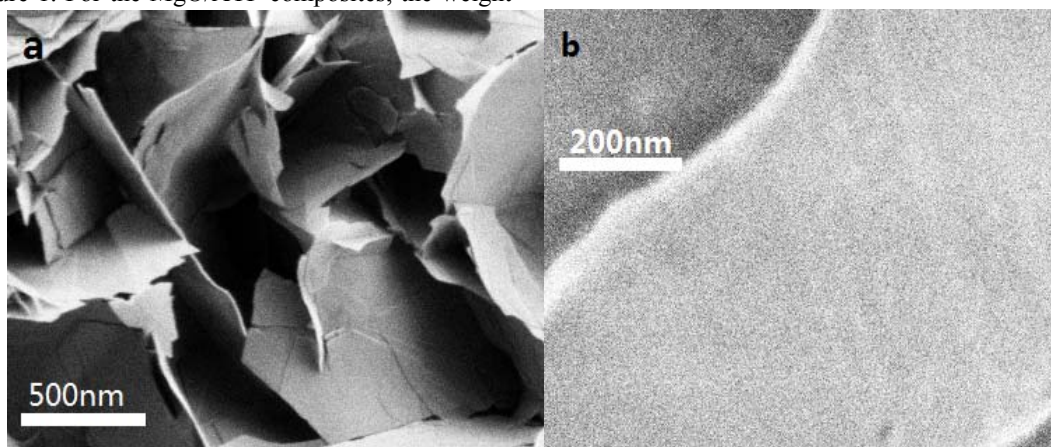


Figure 2. SEM images of the $\text{Mg}(\text{OH})_2$ precursor at a low magnification (a) and at high magnification (b)

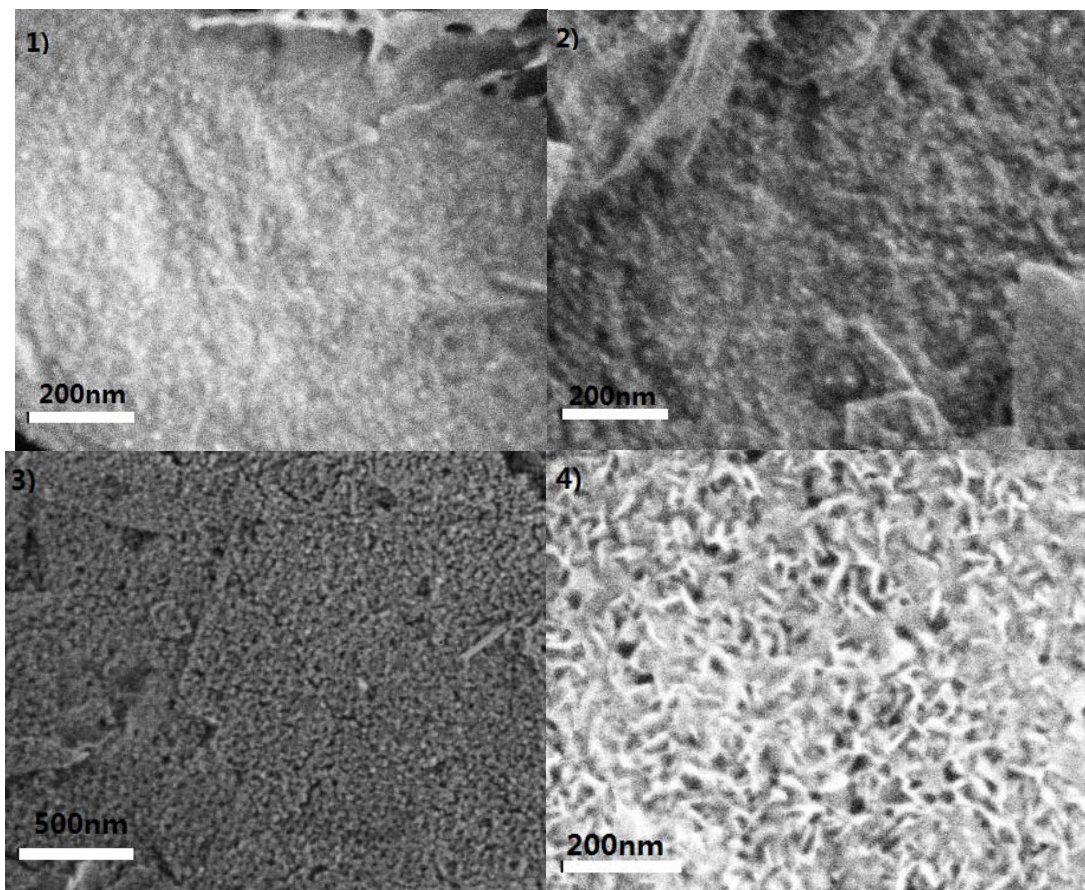


Figure 3. SEM images of MgO nanoparticles, 1) ATP amount=0%; 2) ATP amount=3%; 3) ATP amount=25%; 4) ATP amount=50%

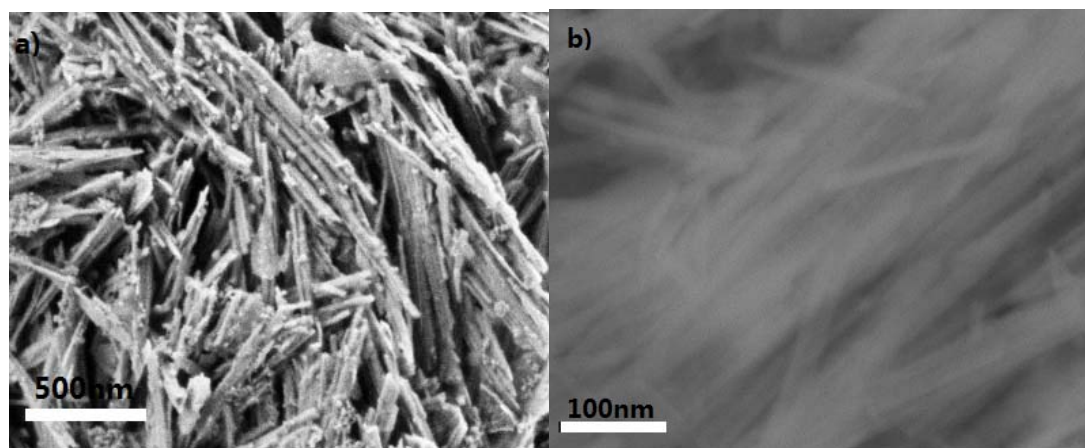


Figure 4. SEM images of MgO/ATP composites, a) ATP amount=25%; b) ATP amount=90%

Furthermore, it was found that the crystallite size of the synthesized MgO particles rises with the increase of the ATP contents. When ATP rise to 25%, the crystal size becomes about 60~70nm, and plate-like particles begin to divide into spherical particles as shown in Figure3-3. When the ATP contents is 50%, the rod-like or needle-like shaped morphology of the MgO particles was formed (Figure3-4). The needle's size was of 80~100nm in length, on an average,

10~15nm in width. The morphological feature and the size of nano-MgO particles have undergone a significant change while ATP content was changed .

The morphology of the pure ATP is a 1-D fibrous shape with a uniform diameter ranging from 20 to 40nm, and the length ranges from 0.5 to 2 μ m. The nano-MgO/ATP specimens were illustrated in Figure 4. As we can see in Figure 4.-a), nano-MgO NPs was uniformly deposited on the surface

of ATP, it is further confirmed that when the content of ATP was about 25%, the morphology of nano-MgO particles were sphere shapes, the template effected seems little. when the ATP content was 90%, As show in Figure 4.-b) crystals of nano-MgO tended to become rod-like or needle-like shape, and grow on the attapulgite fiber very similar with the work about CeO₂ nanotubes facilely via a layer-by-layer deposition approach using modified attapulgite as hard template, a simple and inexpensive way to prepare oxide nanotubes on a large scale by taking advantage of natural clay as sacrificial template^[12]. In this paper, during the process of form of MgO, ATP clay doubtless plays an important role on its size and shape. The formation of MgO consists of two process, one is the thermal decomposition of Mg(OH)₂, another is crystal transformation from Mg(OH)₂ to MgO polycrystalline which is a amorphous process, and attapulgite maybe directly affect the change of crystal. And more, the ATP template effect is getting stronger with the increase of ATP in the form of MgO, but the reason why the morphology of nano-MgO particles are changed from sphere shapes to rod-like or needle-like shapes with the increasing of ATP content is not clear, it needs further research.

IV. CONCLUSION

In this paper, Size and feature controlled nano-MgO were synthesized successfully by using ATP as hard template. The content of ATP affects the shape and the size of nano-MgO crystals. It was a new way to obtain MgO with different morphology. ATP can be used as template to prepare massively nano-MgO crystallites of different size and morphology controlled, which is firstly reported. It needs more research in the aspect of induction mechanism and industrial applications.

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