

## Preparation of Magnesium Hydroxide Chloride Hydrate Nanowires Using Calcined Dolomite

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**Abstract:** Magnesium hydroxide chloride hydrate (MHCH) nanowires are important polymer fillers and precursors for one-dimensional nanostructures. Here a novel method was presented to prepare MHCH nanowires using calcined dolomite as raw materials *via* a hydrothermal approach. XRD, SEM, and FT-IR analyses indicate that the as-prepared MHCH is well crystallized  $\text{Mg}_{10}(\text{OH})_{18}\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  nanowires with diameters of 50–120 nm and length of several tens micrometers. The TG-DTA patterns of MHCH consisted of two steps and MHCH is at endothermic status during the whole heating process. The molar ratio of  $(\text{MgO}+\text{CaO})$  in calcined dolomite to  $\text{MgCl}_2$  ( $R$ ) plays a key role to the structure and morphology of MHCH. The aspect ratio of MHCH nanowires decreases with the increasing of  $R$  and  $\text{Mg}(\text{OH})_2$  will be formed when  $R$  was greater than 0.5. The optimum  $R$  to prepare MHCH is between 0.025 and 0.075. This study will extend the potential applications of dolomite due to the extensive applications of MHCH.

**Key words:** calcined dolomite; magnesium hydroxide chloride hydrate (MHCH); nanowire; magnesium chloride; hydrothermal

Magnesium hydroxide chloride hydrate (MHCH), with general formula of  $\text{Mg}_x(\text{OH})_y\text{Cl}_z \cdot m\text{H}_2\text{O}$  ( $2x-y-z=0$ ,  $0 \leq m \leq 6$ ), is a needle-crystallized inorganic material with various applications. In the cement field, MHCH is the major component of Sorel cement (*i.e.* magnesium oxychloride cement). Compared with traditional Portland cement, this cement has many superior properties such as high fire resistance, low thermal conductivity, high resistance to abrasion, good mechanical and elastic properties<sup>[1]</sup>. In the filler field, MHCH can be used as plastic reinforcement agents, flame retardants, and heat-insulating materials<sup>[2]</sup>. Moreover, one-dimensional (1D) MHCH has an important application as the precursor to prepare 1D  $\text{MgO}$  or  $\text{Mg}(\text{OH})_2$  nanostructures. For instance,  $\text{Mg}(\text{OH})_2$  nanorods can be prepared from 1D MHCH through  $\text{NaOH}$  treatment or solvothermal method<sup>[3-4]</sup>. Fan<sup>[5]</sup> synthesized  $\text{Mg}(\text{OH})_2$  nanotubes using  $\text{Mg}_{10}(\text{OH})_{18}\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  nanowires as precursors *via* a solvothermal method using ethylenediamine as solvent.  $\text{MgO}$  nanorods can be obtained from needle-like MHCH, through  $\text{Mg}(\text{OH})_2$  nanorods as intermediate to preserve the 1D morphology<sup>[6-7]</sup>.

Dolomite, the mineral, is an important resource of Ca

and Mg in the Earth. Ideal dolomite has a crystal lattice consisting of alternating layers of Ca and Mg, separated by layers of  $\text{CO}_3$  and can be typically represented by a stoichiometric chemical composition of  $\text{CaMg}(\text{CO}_3)_2$ <sup>[8]</sup>. After modified, dolomites can be used as effective catalysts, bactericidal material, absorbent for arsenate, acidic gases and heavy metal ions, and so on<sup>[9-13]</sup>. In addition, dolomite can be used as raw material to produce  $\text{MgO}$  powders, magnesium hydroxide, basic magnesium carbonate, calcium carbonate, hydrotalcite, and so on<sup>[14-17]</sup>.

## 1 Experimental

In this study, a novel approach was presented to prepare MHCH nanowires using calcined dolomite as raw material *via* a hydrothermal approach. In a typical procedure, dolomite (obtained from Zhejiang Province, China) which contains 99.0%  $\text{CaMg}(\text{CO}_3)_2$  and 1.0% impurities such as  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$ , was broken into pieces and calcined at 950°C for 5 h. After calcination, dolomite was decomposed to  $\text{MgO}$  and  $\text{CaO}$ . Under continuous stirring, 0.96 g calcined dolomite (containing 0.01 mol  $\text{MgO}$  and 0.01 mol

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CaO) was added into 100 mL 4 mol/L  $\text{MgCl}_2$  solutions. When white floccules appeared in the solution, the stirring stopped and the upper part of the mixture was poured into another beaker. After sealed and left at room temperature for 1 d, the resulting precipitation was added into a Teflon-lined stainless autoclave, sealed and heated at  $160^\circ\text{C}$  for 6 h in a temperature-controlled oven. After cooled to room temperature naturally, the as-obtained product was filtered, washed with deionized water and anhydrous ethanol, and dried at  $60^\circ\text{C}$  for 6 h. Finally, soft and white MHCH powders were obtained.

## 2 Results and discussion

Figure 1 shows the XRD pattern and SEM image of calcined dolomite. Two main components, MgO and CaO, can be identified in the XRD pattern. Some tiny peaks such as at  $2\theta=27^\circ$  and  $60^\circ$  can be ascribed to the impurities such as  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$ . The SEM image of indicate that the calcined dolomite consists of nanoplates with diameters of 50–100 nm. Figure 2 presents the typical XRD pattern and SEM image of MHCH nanowires prepared using calcined dolomite. A set of diffraction peaks in the XRD pattern were recorded as strong characteristic peaks, which can be indexed as monoclinic end-centered  $\text{Mg}_{10}(\text{OH})_{18}\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ . The cell parameters calculated from 2.263 nm, and  $\beta = 102.4^\circ$ , which are close to the reported

these diffraction data are  $a = 0.811$  nm,  $b = 0.314$  nm,  $c =$  data (JCPDF#07-0409). No other phase can be found in this XRD pattern. The sharply shape of the peaks indicates that the as-prepared  $\text{Mg}_{10}(\text{OH})_{18}\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  is well crystal-lized. The corresponding SEM image shows that the as-prepared MHCH nanowires are straight with random arrangement. The diameter and length of a single MHCH nanowire are 50–120 nm and several tens micrometers, respectively. As shown in the inset TEM image, the large nanowires with diameter of greater than 150 nm are composed by several individual smaller nanowires.

The FT-IR and TG-DTA analyses of the as-prepared MHCH nanowires are shown in Fig. 3. The FT-IR spectrum of MHCH is consistent with former researchers, suggesting that the crystal structure of MHCH consists of infinite chains of “ $\text{MgO}_6$ ” octahedral layers,  $\text{OH}^-$  ions, and  $\text{H}_2\text{O}$  molecules<sup>[18]</sup>. The absorption peaks at 3630, 3553, 3433 and  $1637\text{ cm}^{-1}$  can be assigned to the  $\text{OH}^-$  stretching vibrations of crystal  $\text{H}_2\text{O}$  molecules and  $\text{OH}^-$  ions. Bands at 1157 and  $1439\text{ cm}^{-1}$  might be the characteristic vibration peaks of hydrogen bond between  $\text{H}_2\text{O}$  and  $\text{Cl}^-$ . As for the absorption peaks at 661, 599, 511 and  $419\text{ cm}^{-1}$ , they can be assigned to the stretching and bending vibrations of Mg–O bond in “ $\text{MgO}_6$ ” octahedral<sup>[19]</sup>.

The TG-DTA pattern of MHCH shows two major steps.

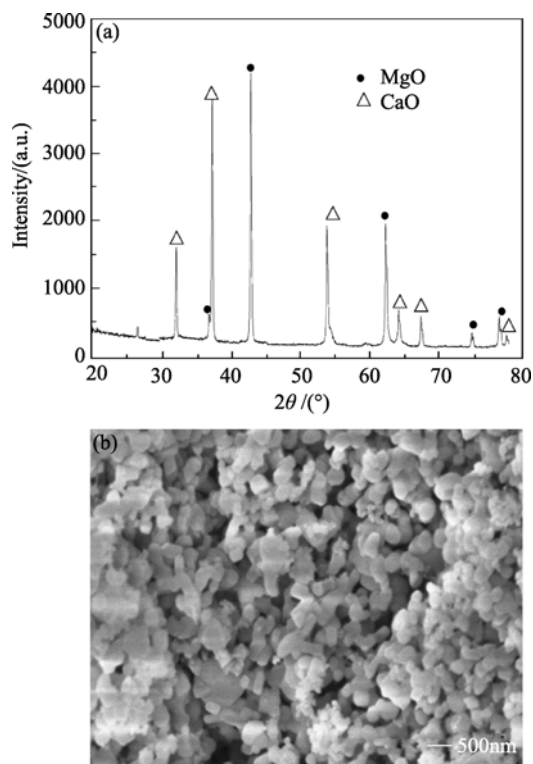


Fig. 1 XRD pattern (a) and SEM image (b) of calcined dolomite after calcined at  $950^\circ\text{C}$  for 5 h

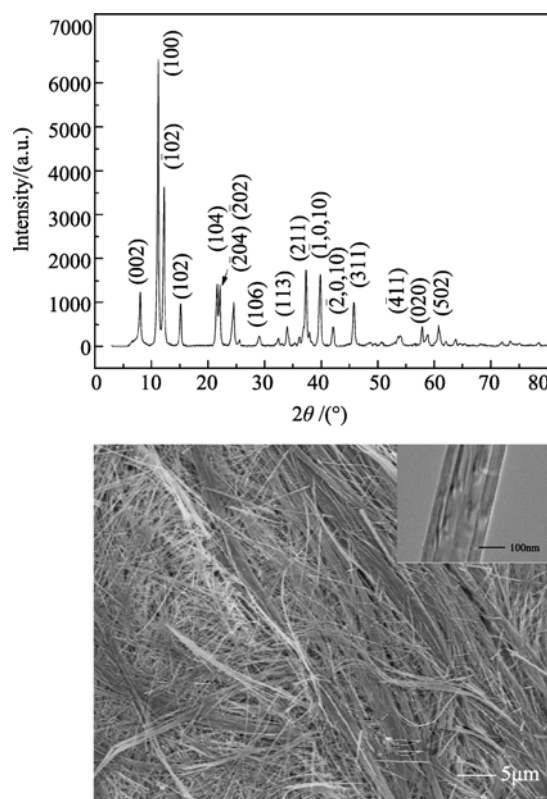


Fig. 2 XRD pattern and corresponding SEM image of MHCH nanowires prepared using calcined dolomite *via* hydrothermal approach at  $160^\circ\text{C}$  for 6 h

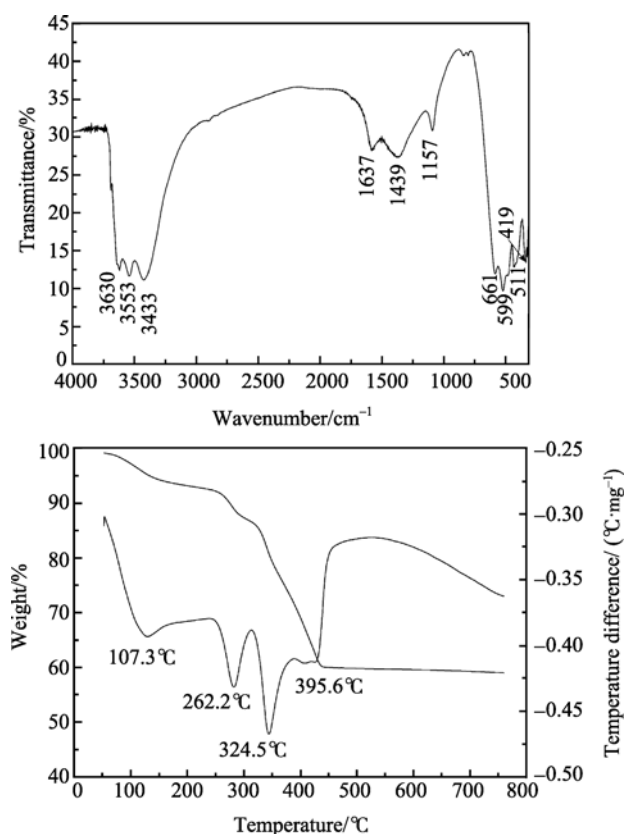


Fig. 3 Typical FT-IR and TG-DTA patterns of as-prepared MHCH nanowires

The first step starts at 50°C, ends at 220°C, and exhibits a weight loss of 7% and an endothermic peak at 107°C. This step is attributed to the dehydration of MHCH. The second step starts at above 230°C and ends at 417°C, resulting a weight loss of 33%. There are three endothermic peaks

(262.2°C, 324.5°C and 395.6°C) in this step, owing to the continuous detaching of H<sub>2</sub>O, OH<sup>-</sup> and HCl. The TG analysis is consistent with the crystal structure of Mg<sub>10</sub>(OH)<sub>18</sub>Cl<sub>2</sub>·5H<sub>2</sub>O. Note that the as-prepared MHCH is at endothermic status during the whole heating process, indicating that MHCH may be applied as flame retardant for plastics.

It is accepted that the minimum MgCl<sub>2</sub> concentration to prepare MHCH is 1.96 mol/L, and the reaction temperature determines the phase of MHCH<sup>[20-21]</sup>. Therefore, we investigated the effect of molar ratio of (MgO+CaO) to MgCl<sub>2</sub> (*R*) on the structure and morphology of MHCH. As shown in Fig. 4, no product was obtained when *R* was 0.025. Only Mg<sub>10</sub>(OH)<sub>18</sub>Cl<sub>2</sub>·5H<sub>2</sub>O can be found when *R* was between 0.075 and 0.2. When *R* was increased to 0.5, however, typical Mg(OH)<sub>2</sub> peaks appears in the XRD pattern. The other faint peaks is the characteristic peaks of Mg<sub>3</sub>(OH)<sub>5</sub>Cl·4H<sub>2</sub>O. Finally when *R* was further increased to 1.0, MHCH phase disappeared and only well crystallized Mg(OH)<sub>2</sub> was prepared. In the corresponding SEM images, all the samples prepared under *R* of 0.075–0.2 exhibit 1D morphologies. The length of MHCH decreases with the increasing of *R*, from 4 μm at 0.075 to 2.5 μm at 0.1, and further to 1.2 μm at 0.2. The diameter of MHCH, however, changes slightly with *R* and maintains at about 75 nm. When *R* was increased to 0.5, the product showed mixture of MHCH whiskers and bulk crystals of Mg(OH)<sub>2</sub>. Finally when *R* was 1.0, MHCH disappeared and only well crystallized Mg(OH)<sub>2</sub> plates with diameters of 300 nm–1 μm could be found. These results are similar to the CaO-MgCl<sub>2</sub>-H<sub>2</sub>O system<sup>[22]</sup> and can be attributed to two reasons. First, the function of MgO and CaO in MgCl<sub>2</sub> solution involves

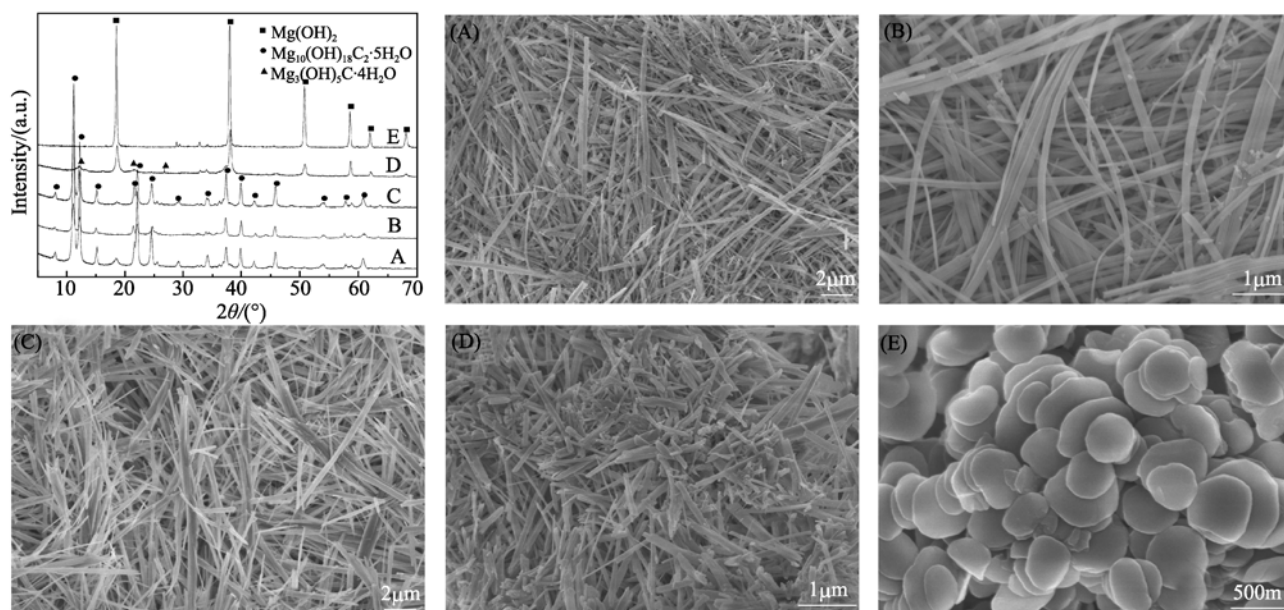


Fig. 4 XRD patterns and SEM images of the samples prepared under different molar ratios of (MgO+CaO) to MgCl<sub>2</sub> (*R*) (A) 0.075, (B) 0.1, (C) 0.2, (D) 0.5, and (E) 1.0. No product was obtained when *R* was 0.025

neutralization and hydration, the supersaturation for the synthesis of MHCH nanowires will be inadequate and hydrate phase  $\text{Mg}(\text{OH})_2$  will be formed when  $\text{MgO}$  and  $\text{CaO}$  are exceeding. Second, the increasing  $R$  leads to the increase amount of crystal nuclei, and thus restrict the growing space for each nucleus and decrease the length of MHCH nanowires.

### 3 Conclusions

In summary, MHCH nanowires were successfully prepared using calcined dolomite as raw material *via* a hydrothermal method. XRD and SEM characterizations indicate that the as-prepared MHCH nanowires is well crystallized  $\text{Mg}_{10}(\text{OH})_{18}\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  with diameter of 50–120 nm and length of several tens micrometers. FT-IR and TG-DTA analyses confirm the crystal structure of MHCH. Because the length of MHCH nanowires decreases with the increasing of  $R$  and  $\text{Mg}(\text{OH})_2$  will be formed when  $R$  is greater than 0.5, the optimum  $R$  to prepare MHCH nanowires is between 0.025 and 0.075. Due to the extensive applications of MHCH, this research will extend the potential applications of dolomite.

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# 白云石锻粉制备碱式氯化镁纳米线的研究

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**摘 要:** 碱式氯化镁(MHCH)纳米线是一种重要的高分子填充剂及一维纳米结构的前驱体. 本文以白云岩锻粉为原料, 利用水热反应制备了 MHCH 纳米线. 通过 XRD、SEM 和 FT-IR 表征表明所制备的 MHCH 是完好结晶的  $\text{Mg}_{10}(\text{OH})_{18}\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  纳米线, 其直径和长度分别为 50~120 nm 和数十微米. TG-DTA 测试表明, MHCH 的热分解分为两步, 在加热过程中 MHCH 始终处于吸热状态. 白云石锻粉中的 MgO 和 CaO 与氯化镁的摩尔比  $R$  对 MHCH 的结构和形貌具有重要的影响: MHCH 的长径比随  $R$  的增大而减小, 而当  $R$  大于 0.5 时, 体系中将出现  $\text{Mg}(\text{OH})_2$ ; 制备 MHCH 的最佳摩尔比  $R$  在 0.025 和 0.075 之间. 由于 MHCH 用途广泛, 本研究将拓宽白云石的潜在应用价值.

**关 键 词:** 白云石锻粉; 碱式氯化镁(MHCH); 纳米线; 氯化镁; 水热

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