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Controlled synthesis of $Mg(OH)_2$ nanorods using basic magnesium chloride as precursor

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ABSTRACT

$Mg(OH)_2$ nanorods were successfully prepared by two-step method. The precursor was obtained by hydrolyzed the $MgCl_2$ in $NH_3{\cdot}H_2O$ solution, and then, it transformed into $Mg(OH)_2$ nanorods by a simple solvothermal method without any surfactant or catalyst. The influences of synthesis parameters on the morphological characteristics and sizes of $Mg(OH)_2$ nanoparticles were investigated, such as the proportion of EtOH–H_2O solvent, the reaction temperature, and the treatment time. XRD and FESEM were used to characterize the structure, morphology, and composition of the samples. This method is lower costing, simple and environmentally benign, thus, it should be easy to be scaled up for industrial production.

KEYWORDS
Magnesium hydroxide; nanorods; solvothermal method

Introduction

In recent years, magnesium hydroxide (MH), as a kind of smoking- and toxic-free flame-retardant additive [1, 2], has become one of the most extensive replacements for halogen-based flame retardants, and has been widely added into many materials such as plastic, rubber, and other halogen-free polymeric materials [3, 4]. Compared with other inorganic flame retardants, MH has some advantages such as large heat absorption, strong charring effect, neutralization action and adsorption, and smoke suppression performance [5, 6]. Furthermore, MH could decompose into MgO and H_2O vapor at a relatively higher temperature (300 °C). The H_2O vapor forms a flame-around envelope, which tends to exclude the air and dilute the flammable gases. And the MgO residue forms a thermally inert layer which could create a protective barrier on the polymer substrate [7, 8].

At present, most of the MH flame retardants are amorphous, and have big specific surface area as well as the strong polarity which may induce the aggregation of particles more easily. What's more, the addition amount of MH in plastic, rubber, and other halogen-free polymeric materials should be more than 50 wt% in order to achieve the ideal flame-retardant effect [9, 10]. However, additives can adversely affect the mechanical and physical properties of the composite to some extent, and the tensile strength of

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the composite will also be decreased [11]. As a result, the application of MH flame retardant has been restricted in some fields [12, 13].

Since recent years, one-dimensional (1D) nanomaterials have been the focus of materials synthesis due to their unique physical properties such as extremely small size, large anisotropy, and perfect crystallinity [14]. Based on 1D materials small geometric size and low surface polarity, it can distribute evenly in the composite material without affecting the forming fluidity. In addition, the 1D material has perfect crystallinity that can be widely applicated in functional composites as reinforcing agents [15]. Therefore, as 1D materials, MH nanorods could be good candidates for functional polymeric composites and fiber hybrid materials as reinforcing agents and halogen-free flame-retardants [16], which is beneficial to the application of MH flame retardant.

However, the synthesis of MH nanorods requires critical control during the reaction process. In this article, a controlled solvothermal route in synthesis of well-grown MH nanorods is presented, by the *in situ* disposition basic magnesium chloride precursor in a variety of solvents at a proper temperature and duration time. The effects of synthesis parameters such as reaction temperature, treatment time, and EtOH–H_2O solvent concentration on the size and morphology are investigated. Under optimum condition, the obtained product could meet the requirement of good flame-retardant property due to it has smooth surface, appropriate length-diameter ratio, high homogeneity, and good dispersity. Furthermore, the low cost of the starting reagents and the simplicity of the synthetic route make it a promising method to be scaled up for industrial production.

Experimental

Materials

All chemicals used in this work, such as magnesium chloride ($MgCl_2 \cdot 6H_2O$), sodium hydroxide, ethanol, distilled water, and aqueous ammonia ($NH_3 \cdot H_2O$, 25 wt%) were analytical reagent from the Tianjin GuangFu Chemical Factory, China.

Methods

Field emission scanning electron microanalyzer (FESEM, JSM-6700F, JEOL Lit, Japan) were used to observe the morphology of the MH nanocrystals. The dried MH product was added into distilled water to form a suspension, which was stabilized by a small amount (0.2 wt%) of polyacrylamide (MW = 100,000) for preventing the nanoparticles from agglomerating.

The overall crystallinity and purity of the synthesized sample were examined by X-ray diffraction (XRD) using a Philips X' Pert PRO SUPER apparatus (Nicolet Instrument Co., USA) equipped with graphite monochromatized CuKα radiation ($\lambda = 1.54178$ Å) at a scanning rate of 0.02° s^{-1} in the 2θ range from 5° to 60°.

Thermo gravimetric analysis (TGA) was carried out by a Netsch STA 449F3 thermal gravimetric analyser. Samples were examined under nitrogen flow from 25 °C to 500 °C at a heating rate of 10 °C/min.

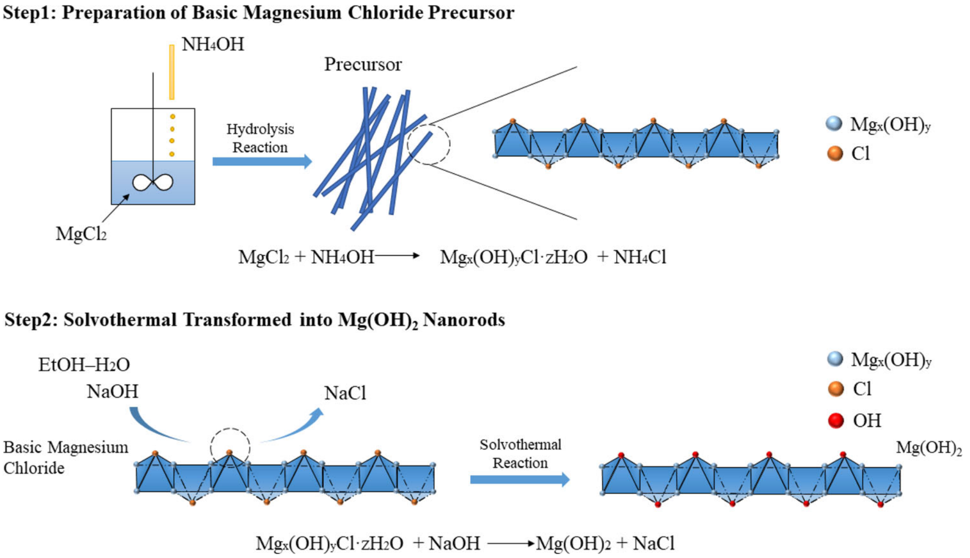


Figure 1. The schematic illustration of the two-step method.

Preparation of the precursor

The basic magnesium chloride precursor was synthesized by a wet chemical process. The procedure which yields precursor has been described in our previous work [17]. In a typical method, 500 mL 4 mol/L^{-1} magnesium chloride solution was prepared from hexahydrate magnesium chloride, and placed in a constant temperature bath at 40 °C. The aqueous ammonia ($NH_3{\cdot}H_2O$, 25 wt%) was added dropwise into magnesium chloride aqueous solution according to the molar ratio of 1:3 while the aqueous solution was stirring. The stirring speed was controlled at 100–150 r/min. The reaction time was 1 h. After the heating and stirring stopped, the solution was left to maintain at room temperature for 24 h. The resulting white precipitate was filtered off and washed with distilled water and ethanol several times. And then freeze dried in Christ Alhpha 1-4 LDplus at −50 °C for 4 h to obtain the basic magnesium chloride precursor.

Preparation of $Mg(OH)_2$ nanorods

The precursor was transformed into $Mg(OH)_2$ nanorods by solvothermal method which analogous to the reported method [18, 19]. In this method, basic magnesium chloride was used as a precursor, NaOH was used as precipitator, different proportions of ethanol and water were used as the reaction solvent.

An appropriate amount of basic magnesium chloride and NaOH was added into a Teflon-lined autoclave of 250 mL capacity. Then, the autoclave was filled with different solvent, such as distilled water (H_2O), EtOH–H_2O (1:3, v/v), EtOH–H_2O (1:1, v/v), EtOH–H_2O (3:1, v/v), and ethanol (EtOH) up to 70% of the total volume. The autoclave was sealed in a stainless-steel tank and maintained at experimental temperature (140 °C, 160 °C,180 °C,200 °C) for a period of time (0.5 h, 1.5 h, 2.5 h, 4 h) without stirring. After cooling to room temperature naturally, the sample was filtered off, washed with distilled water and ethanol. And then freeze dried in Christ Alhpha 1-4 LDplus at −50 °C for 4 h to obtain the MH nanorods.

Results and discussion

Formation of precursor

Figure 2 shows thermogravimetric analysis (TG) of the basic magnesium chloride samples, and there are four obvious weight loss peaks. The first stage started at 35 °C and ended at 100 °C can be assigned to the moisture content and adsorbed water. The second stage started at 100 °C and ended at 210 °C can be assigned to the crystal water removal (Equation (1)). The third stage started at 210 °C and ended at 350 °C can be assigned to the thermal decomposition of basic magnesium chloride to remove hydrogen chloride (Equation (2)). And last stage started at 350 °C and ended at 450 °C corresponded to the decomposition of the $Mg(OH)_2$ (Equation (3)). There are no obvious weight loss peaks exceeded 450 °C, indicating that the basic magnesium chloride has been completely decomposed into magnesium oxide.

$$\mathrm{Mg_x(OH)_yCl \cdot zH_2O \rightarrow Mg_x(OH)_yCl + \ zH_2O} \tag{1}$$

$$\mathrm{Mg_x(OH)_yCl + \ H_2O \rightarrow xMg(OH)_2 + \ HCl} \tag{2}$$

$$\mathrm{Mg(OH)_2 \rightarrow MgO + \ H_2O} \tag{3}$$

According to the three reaction equations of thermal decomposition process, the weight loss ratio is 27.2%, 13.4%, and 20.4%, respectively. The final product of thermal decomposition is MgO, accounting for 46% of the total mass. Considering that the thermal decomposition process does not occur in sequence, the observed mass loss at each stage is slightly different from the calculation. The proportion of each element in basic magnesium chloride can be roughly determined, magnesium accounted for 27.6% and chlorine accounted for 13.5%, inferred that the chemical formula of the precursor is $Mg_3(OH)_5Cl{\cdot}4H_2O$.

Figure 3 shows XRD pattern of the basic magnesium chloride precursor. Most of the diffraction peaks are indexed very well as $Mg_3(OH)_5Cl{\cdot}4H_2O$ according to the standard data (JCPDS 07-0420). And the diffraction peaks at 18.6°, 38.0°, and 50.8° are indexed $Mg(OH)_2$ according to the standard data (JCPDS 07-0239). This indicates that some of the precursors have been converted to magnesium hydroxide.

The SEM images in Fig. 4 shows the basic magnesium chloride precursor consisting entirely of very long rods like nanostructures with diameters in the range of 100–200 nm and lengths in the range of 10–20 μm. At lower magnification (Fig. 4a) it can be verified that nanorods have a relatively uniform width and sharp boundary on this scale. And the high-multiple scanning images (Fig. 4b) show that nanorods with a smooth surface and can be very good dispersion.

The above results show that the basic magnesium chloride prepared under the experimental conditions is a suitable precursor of one-dimensional magnesium hydroxide.

Formation of $Mg(OH)_2$ 1D nanorods

The solvothermal reaction to prepare MH nanorods using basic magnesium chloride as a precursor in a variety of $EtOH–H_2O$ solvent concentration at a proper temperature and treatment time yielded very interesting results. In the whole solvothermal reaction process, to understand the possible mechanism of the formation of MH nanorods,

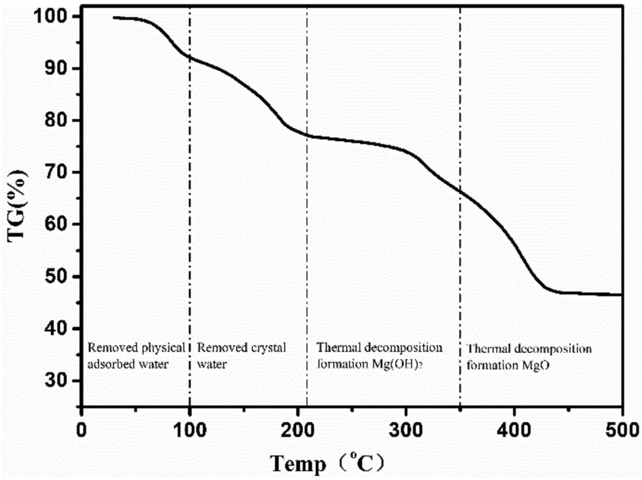


Figure 2. TG curves of basic magnesium chloride precursor.

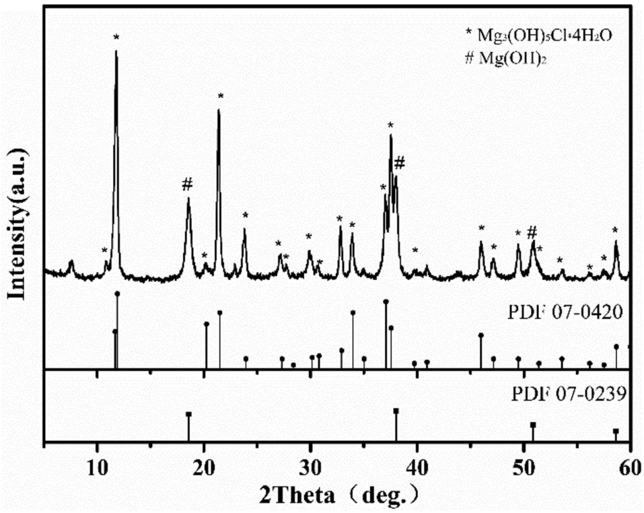


Figure 3. XRD pattern of basic magnesium chloride precursor.

controlled experiments under different conditions were conducted. The detailed conditions and the results of the experiments are listed in Table 1, and all the products are characterized by XRD and SEM.

Effect of reaction solvent

It is well known that solvent plays an important role in determining the crystal morphology. Solvents with different physical and chemical properties can influence the solubility, reactivity, and diffusion behavior of the reactants; in particular, the polarity and coordinating ability of the solvents can influence the crystal morphology of the final product. A series of solvothermal synthetic experiments with $Mg_3(OH)_5Cl{\cdot}4H_2O$ precursors in different solvent, such as distilled water (H_2O), EtOH–H_2O (1:3, v/v),

Table 1. Experimental conditions and results of the experiments.

Sample no.	Solvent	Temp. (°C)	Treatment time (h)	Products phase	Morphology
1	Distilled Water	160	1.5	$Mg(OH)_2$ hexa.	Broken particles and short rods
2	$EtOH–H_2O$ (1:3, v/v)	160	1.5	$Mg(OH)_2$ hexa.	Rods with surface damage
3	$EtOH–H_2O$ (1:1, v/v)	160	1.5	$Mg(OH)_2$ hexa.	Rods
4	$EtOH–H_2O$ (3:1, v/v)	160	1.5	$Mg(OH)_2$ hexa.	Uniform rods
5	Ethanol (EtOH)	160	1.5	$Mg(OH)_2$ hexa. & basic magnesium chloride	Flake
6	$EtOH–H_2O$ (3:1, v/v)	140	1.5	$Mg(OH)_2$ hexa.	Uniform rods
7	$EtOH–H_2O$ (3:1, v/v)	180	1.5	$Mg(OH)_2$ hexa.	Uniform rods
8	$EtOH–H_2O$ (3:1, v/v)	200	1.5	$Mg(OH)_2$ hexa.	Uniform rods
9	$EtOH–H_2O$ (3:1, v/v)	160	0.5	$Mg(OH)_2$ hexa.	Uniform rods
10	$EtOH–H_2O$ (3:1, v/v)	160	2.5	$Mg(OH)_2$ hexa.	Uniform rods
11	$EtOH–H_2O$ (3:1, v/v)	160	4	$Mg(OH)_2$ hexa.	Uniform rods

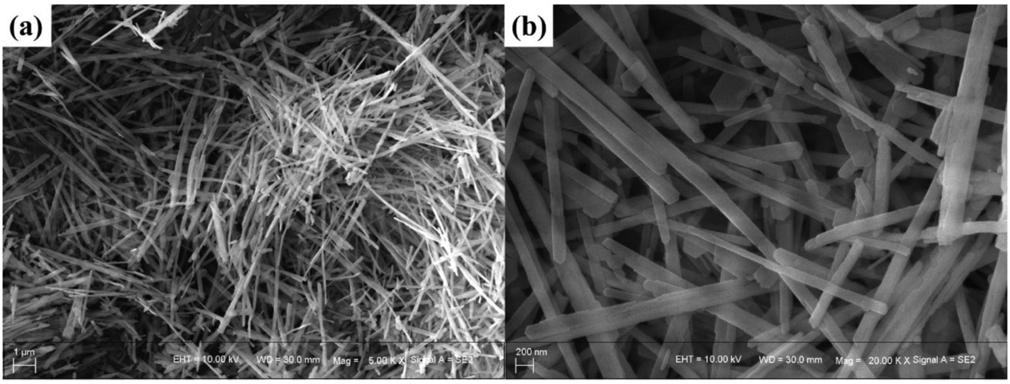


Figure 4. SEM images of basic magnesium chloride precursor in different magnification (a) 5000X; (b) 20000X.

$EtOH–H_2O$ (1:1, v/v), $EtOH–H_2O$ (3:1, v/v), and ethanol (EtOH) were carried out in 160 °C and 1.5 h.

Figure 5 shows the XRD patterns of $Mg(OH)_2$ products prepared in different solvent. It can be observed that there were three strong diffraction peaks at 18.58°, 38.01°, and 50.85°, which indexed very well as hexagonal phase of $Mg(OH)_2$. According to the standard PDF card JCPDS No. 07-0239, these three diffraction peaks, respectively, correspond to (001), (101), and (102) crystal planes of magnesium hydroxide. That means all the products were pure magnesium hydroxide.

Also, it can be seen that the intensity of (001) crystal planes was significantly higher than that of (101) and (102) crystal planes, which indicates that preferred orientations might occur along (001) lattice planes [20].That means the abundance of (001) planes in the anisotropic shape of the 1D nanostructure results in the remarkable increase in the intensity of the 001 reflection [21].

Furthermore, the (101) and (102) crystal planes intensity of the MH products prepared in different solvent was close to each other, but the (001) crystal planes intensity was tremendously different. Comparing I001/I101 ratios, it can be seen that the resultant MH prepared in $EtOH–H_2O$ (3:1, v/v) as the solvent exhibited a highest (001) crystal planes intensity and I001/I101 ratio, which indicated a more pronounced

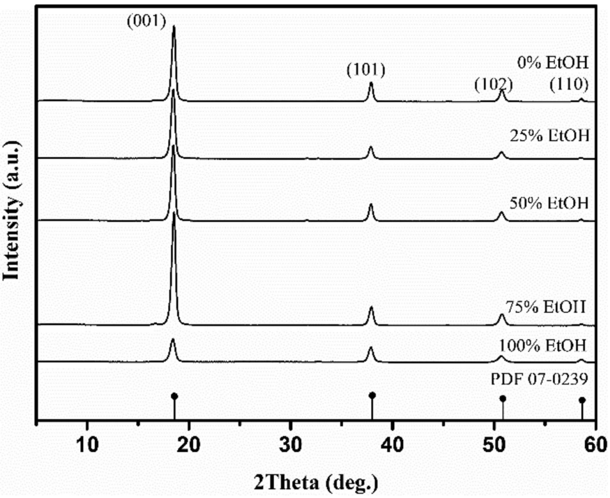
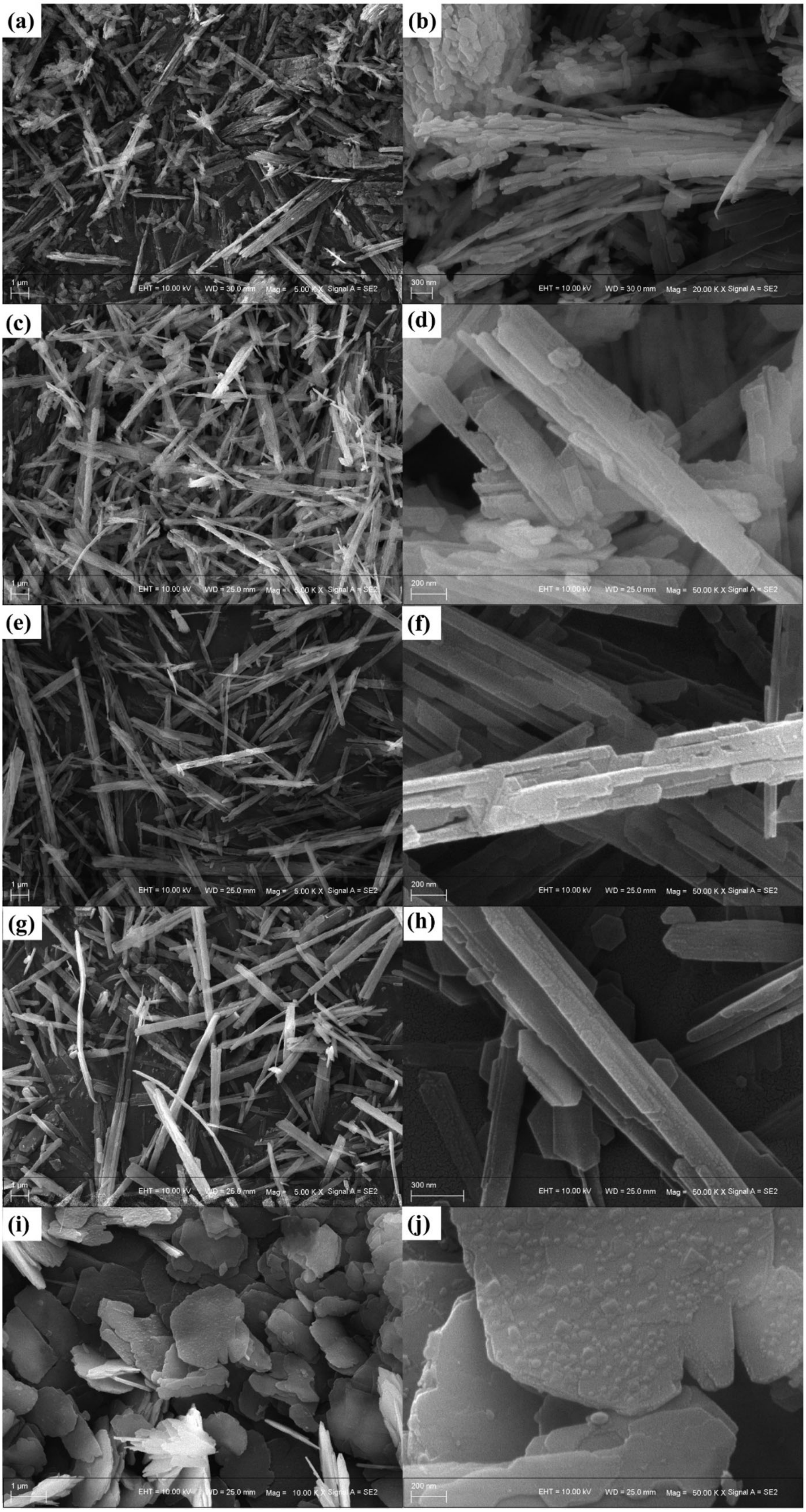


Figure 5. XRD pattern of $Mg(OH)_2$ products prepared in different solvent.

orientation. The evidence shows that the [001] polar property was weaker than [101] polar, which would decrease the internal stress and surface polarity of MH resulting in the more stable structure of MH [22]. And increased exposure of (001) crystal planes would make the MH products have less polar and more dispersible, so the products could be easier to mixed with organic materials [23].

The SEM images of MH were shown in Fig. 6, showing the differences in the morphology under different solvent conditions. It can be seen that in Fig. 6a, MH products prepared in distilled water was nanorods in a disorderly arrangement, and has a serious agglomeration. In the high-multiple scanning images, shown in Fig. 6b, MH has a rough and uneven surface, the particles were scattered and broken. While a small amount of ethanol was added, the polarity of the solvent was changed, and the macroscopic morphology of the product became regular and uniform, with a length of 8–12 μm. However, it could be seen from the high-multiple scanning images, shown in Fig. 6d, that the surface of the rod-shaped structure was damaged, and there were small rectangular flakes peeling off. As the amount of ethanol added increased, the macroscopic morphologies of the MH nanorods obviously improved, the dispersion was better, and the length increased to 12–15 μm. In high-multiple scanning images, shown in Fig. 6f, uneven surfaces of nanorods could be occasionally that is much less serious than MH products prepared in EtOH–H_2O (1:3, v/v). The typical MH nanorods prepared in EtOH–H_2O (3:1, v/v) with a smooth surface can be clearly observed in Fig. 6h, and the dispersion between rods is very good. When 100% ethanol used as the reaction solvent, the products completely lose the one-dimensional structure, exhibits a thin and agglomerated, occasionally “flower” shaped flakes.

Through the experimental, it can be seen that with the increase of the ethanol proportion in solvent, the surface smoothness of the crystal was improved, the L/D ratio was increased, the dispersibility was improved, and the product was easier to filtering and drying.


(a)
1 µm
EHT = 10.00 kV WD = 30.0 mm Mag = 5.00 K X Signal A = SE2
(b)
300 nm
EHT = 10.00 kV WD = 30.0 mm Mag = 20.00 K X Signal A = SE2
(c)
1 µm
EHT = 10.00 kV WD = 25.0 mm Mag = 5.00 K X Signal A = SE2
(d)
200 nm
EHT = 10.00 kV WD = 25.0 mm Mag = 50.00 K X Signal A = SE2
(e)
1 µm
EHT = 10.00 kV WD = 25.0 mm Mag = 5.00 K X Signal A = SE2
(f)
200 nm
EHT = 10.00 kV WD = 25.0 mm Mag = 50.00 K X Signal A = SE2
(g)
1 µm
EHT = 10.00 kV WD = 25.0 mm Mag = 5.00 K X Signal A = SE2
(h)
300 nm
EHT = 10.00 kV WD = 25.0 mm Mag = 50.00 K X Signal A = SE2
(i)
1 µm
EHT = 10.00 kV WD = 25.0 mm Mag = 10.00 K X Signal A = SE2
(j)
200 nm
EHT = 10.00 kV WD = 25.0 mm Mag = 50.00 K X Signal A = SE2

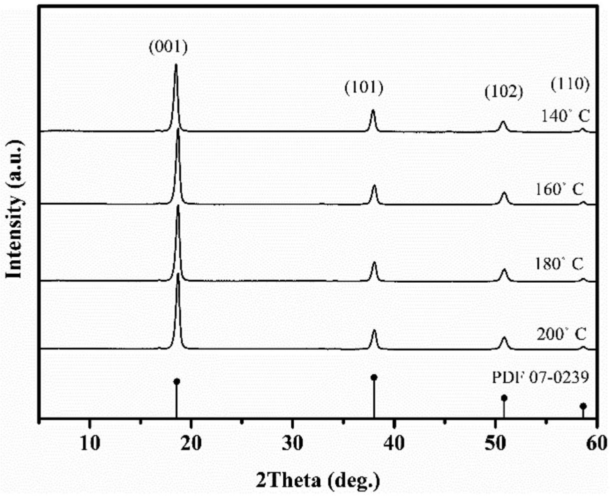


Figure 7. XRD pattern of $Mg(OH)_2$ products prepared in different temperature.

The different morphologies of these whiskers were caused by growth units connecting to each other to form aggregates of different dimensions in different growth conditions, and the stability and growth rate of each aggregate surface of different dimensions were varied, also the ultimate performance in the crystalline morphology is different [24]. The presence of alkoxy group in ethanol can prevent the non-bridging hydroxyl group from damaging the morphology. Meanwhile, the steric hindrance effect of ethanol can also reduce the probability of collision and thus reduce the formation of soft agglomeration, which is conducive to the formation of MH nanorods with better dispersion fibrous structure. Therefore, controlled concentration of ethanol is the key factor for the preparation of 1D MH nanorods.

Effect of reaction temperature

A series of solvothermal synthetic experiments with basic magnesium chloride precursors in different reaction temperature, such as 140 °C, 160 °C, 180 °C, and 200 °C were carried out in $EtOH–H_2O$ (3:1, v/v)and 1.5 h.

Figure 7 displays the XRD patterns of MH synthesized at different reaction temperatures. No impurities have found in the diffraction, which indicated a regular hexagonal phase of $Mg(OH)_2$ (JCPDS No. 07-0239). Along with the increase of temperature, each crystal face growth rate changed and diffraction intensity increased. The sample synthesized at 160 °C exhibited a higher I001/I101 ratio than the sample at 140 °C, which indicated a more pronounced orientation. However, when the reaction temperature higher than 160 °C, the I001/I101 ratio did not change significantly, indicating that the crystal transformation tends to completed.

◀

Figure 6. SEM micrographs of MH products prepared in different solvent (a), (b) distilled water; (c), (d) $EtOH–H_2O$ (1:3, v/v); (e), (f) $EtOH–H_2O$ (1:1, v/v); (g), (h) $EtOH–H_2O$ (3:1, v/v); (i), (j) ethanol (EtOH).

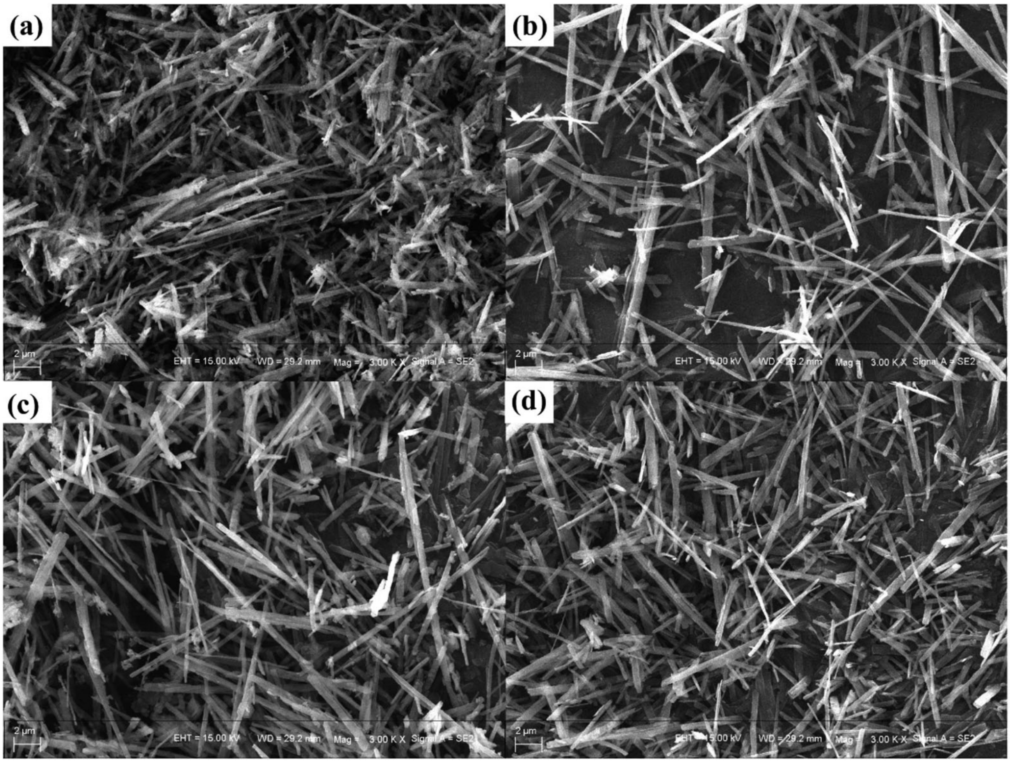


Figure 8. SEM micrographs of MH products prepared in different temperature (a) 140 °C;(b) 160 °C; (c) 180 °C; (d) 200 °C.

SEM investigations show that the reaction products resulting from the 1.5 h solvothermal treatment, with the temperature of EtOH–H_2O (3:1, v/v) solventare140 °C, 160 °C, 180 °C, and 200 °C, consist exclusively of regular one-dimensional nanorods (Fig. 8). The products initially appeared in the form of nanorods of uneven length, as shown in Fig. 8a. When the reaction temperature was elevated to 160 °C, the crystallinity of the as-obtained samples obviously improved, and some isolated nanotubes were observed, as shown in Fig. 8b–d. Considering that when reaction temperature exceeds 160 °C the influence of temperature is not significant, the solvent thermal temperature is preferred as 160 °C.

Effect of reaction treatment time

To investigate the details of the solvothermal process, EtOH–H_2O (3:1, v/v) were employed to investigate the influence of the treatment time on the morphologies of the products with the reaction temperature fixed at 160 °C.

XRD results (Fig. 9) show that the pure magnesium hydroxide was obtained at the four hydrothermal times, and the diffraction peak is completely consistent with hexagonal phase of $Mg(OH)_2$ (JCPDS No. 07-0239). No impurities have been found in the diffraction. With the extension of the hydrothermal time, the crystallinity of the product keeps increasing, as well as theI001/I101 ratio. However, when the treatment time exceed 2.5 h, the I001/I101 ratio changed not significantly.

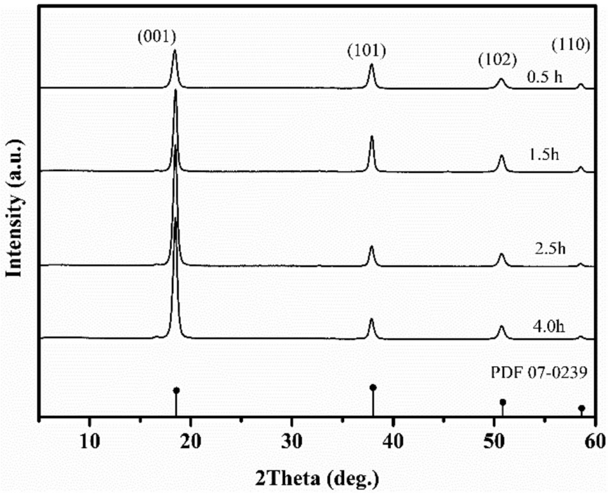


Figure 9. XRD pattern of $Mg(OH)_2$ products prepared in different treatment time.

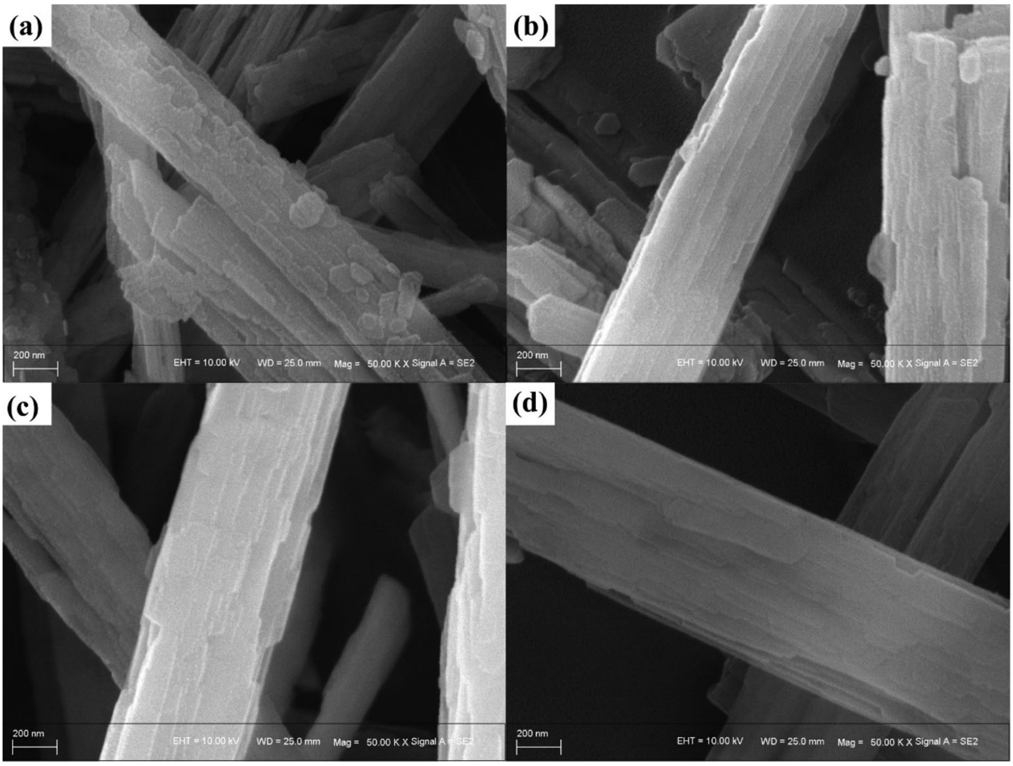


Figure 10. SEM micrographs of MH products prepared in different treatment time(a) 0.5 h;(b) 1.5 h; (c) 2.5 h; (d) 4 h.

Figure 10 shows the SEM photos of magnesium hydroxide prepared under different hydrothermal conditions. It can be seen that when the precursor was treated under solvothermal conditions for 0.5 h, the adhesion of broken particles could be observed on the surface of the product. While the time is extending, the surface smoothness is constantly improved until the surface changes after 2.5 h are not significant, thus, the reaction treatment time is preferred as 2.5 h.

Conclusion

In summary, MH nanorods have been successfully prepared by two-step method using the magnesium chloride and ammonium hydroxide as the raw materials. The proportions of EtOH–H_2O solvent, reaction temperature, and treatment time were studied. The optimal reaction conditions determined by the experiment are as follows: precursor and NaOH are added into a Teflon-lined autoclave, the EtOH–H_2O (3:1, v/v) is used as reaction solvent, then, heated to 160 °C for 2.5 h without stirring.

The MH nanorods showing an obvious one-dimensional structure, and the material surface is smooth. The dispersion properties of the MH products were improved owing to the increase of I001/I101 and the products were loose enough for filtering. In addition, the diameter of nanorods was 400 nm, and the aspect ratio is close to 100. It shows that the process obtained in our work is simple and easy to be scaled up for industrial production.

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