Controllable Synthesis of Magnesium Oxysulfate Nanowires with Different Morphologies

X. T. Sun · W. T. Shi · L. Xiang · W. C. Zhu

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Abstract One-dimensional magnesium oxysulfate $5\text{Mg(OH)}_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ (abbreviated as $513\text{MOS}$) with high aspect ratio has attracted much attention because of its distinctive properties from those of the conventional bulk materials. $513\text{MOS}$ nanowires with different morphologies were formed by varying the mixing ways of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NH}_4\text{OH}$ solutions at room temperature followed by hydrothermal treatment of the slurries at $150^\circ\text{C}$ for 12 h with or without EDTA. $513\text{MOS}$ nanowires with a length of 20–60 µm and a diameter of 60–300 nm were prepared in the case of double injection (adding $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NH}_4\text{OH}$ solutions simultaneously into water), compared with the $513\text{MOS}$ with a length of 20–30 µm and a diameter of 0.3–1.7 µm in the case of the single injection (adding $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solution into $\text{NH}_4\text{OH}$ solution). The presence of minor amount of EDTA in the single injection method led to the formation of $513\text{MOS}$ nanowires with a length of 100–200 µm, a diameter of 80–200 nm, and an aspect ratio of up to 1000. The analysis of the experimental results indicated that the hydrothermal solutions with a lower supersaturation were favorable for the preferential growth of $513\text{MOS}$ nanowires along b axis.

Keywords Magnesium oxysulfate · Nanowires · Double injection · EDTA · Supersaturation

Introduction

One-dimensional (1D) nanostructured magnesium salts with different morphologies, such as needle [1], rod [2], wire [3], tube [4], and belt [5], have attracted much attention because of their unique properties and potential applications in nanotechnical fields. Up to now much work has been focused on the control of the morphologies of 1D $513\text{MOS}$ since it can be used as the reinforcing agent, the flame retardant, or as the precursor for the fabrication of 1D MgO or Mg(OH)$_2$ [6–8].

It was reported that the $513\text{MOS}$ whisker agglomerates with a length of up to 200 µm and a diameter of 0.8–1.2 µm were formed using MgSO$_4$ and Mg(OH)$_2$ or MgO as the reactants [9, 10]. The sector-like $513\text{MOS}$ whiskers with a length of 20–50 µm and a diameter of 0.2–1.0 µm were synthesized using MgSO$_4$ and NaOH as the raw materials [11–13]. Dispersive 1D $513\text{MOS}$ without agglomerates or the sector-like were formed by employing MgSO$_4$ or the mixture of MgSO$_4$ and MgCl$_2$ as the magnesium source and the weak alkali NH$_4$OH as the precipitation agent [14–16]. But little work has been reported on the control of the sizes (length and diameter) of the 1D $513\text{MOS}$ and it is still a challenge to synthesize 1D $513\text{MOS}$ with high aspect ratio and perfect uniformity.

Generally the solution with a lower supersaturation was favorable for the anisotropic or 1D growth of the crystals, which can be achieved by using dilute reactants or chelating agents. For example, it was reported that the presence of EDTA can control the morphologies and sizes of the corresponding particles owing to the chelating effects of EDTA with Ca$^{2+}$ [17], Zn$^{2+}$ [18], Ce$^{3+}$ [19], Fe$^{3+}$ [20], Co$^{2+}$ [20], and Bi$^{3+}$ [21], which can change the forms of the aqueous ions, producing a solution with less free metal ions to control the crystals growth. The growth
habits of the crystals can also be altered by the capping effect of EDTA on the surfaces of the crystals.

In the present work the 513 MOS nanowires with high aspect ratio were formed by precipitation of MgSO₄ and NH₄OH solutions at room temperature followed by treatment at hydrothermal conditions. The supersaturations of the solutions were controlled at relatively low levels, which were achieved by controlling the mixing ways of the reactants or addition of EDTA. The preferential orientation of 513MOS nanowires was identified and the related process mechanisms were discussed.

**Experimental**

**Synthesis of 513MOS Nanowires**

Commercial reagents (NH₄OH, MgSO₄·7H₂O, and EDTA) with analytical grade provided by Beijing Chemical Regent Factory were used in the experiments.

Three ways were adapted for the formation of the precursor slurries at room temperature: (1) Single injection: 35 mL of 1.0–1.5 mol L⁻¹ MgSO₄ was dropped (3.0 mL min⁻¹) into 20 mL of 5.0–9.0 mol L⁻¹ NH₄OH; (2) Double injection: 35 mL of 1.0–1.5 mol L⁻¹ MgSO₄ and 20 mL 5.0–9.0 mol L⁻¹ NH₄OH were dropped (3.0 mL min⁻¹) simultaneously into 5–10 mL water; (3) Single injection in the presence of EDTA: 35 mL of 1.0–1.5 mol L⁻¹ MgSO₄ mixed with varying amount of EDTA was dropped (3.0 mL min⁻¹) into 20 mL of 5–9 mol L⁻¹ ammonia.

The slurry formed at room temperature was then transferred to a Teflon-lined stainless steel autoclave with an inner volume of 80 cm³, heated (5 °C min⁻¹) to 150 °C and kept under isothermal condition for 8.0–12.0 h. The autoclave was cooled down to room temperature naturally after hydrothermal treatment and the product was filtrated, washed, and dried at 105 °C for 12.0 h.

**Analysis**

The morphology and the microstructure of the samples were examined with the field emission scanning electron microscopy (FESEM, JSM 7401F, JEOL, Japan), the high-resolution transmission electron microscope (HRTEM, JEM-2010, JEOL, Japan) and the selected area electron diffraction (SAED). The crystallization and the composition of the samples were identified by the powder X-ray diffraction (XRD, D/max2500, Rigaku, Japan) using CuKα (λ = 0.154178 nm) radiation. The solution pH was detected by Mettler Toledo Delta 320 pH meter. The concentrations of Mg²⁺ and SO₄²⁻ were analyzed by EDTA titration and barium chromate spectrophotometry (Model 722, Xiaoguang, China), respectively.

**Results and Discussion**

Figure 1 shows the influence of the preparation ways of the precursors on the morphologies of the hydrothermal products. 1D product with a length of 20–30 µm and an ununiform diameter of 0.3–1.7 µm were prepared via the single injection route (Fig. 1a). Uniform nanowires with a length to 20–60 µm and a diameter of 60–300 nm were fabricated in the case of the double injection route (Fig. 1b), which may be connected with the decrease of the supersaturation of 513MOS in the solution due to the dilution of the reactants and will be discussed in detail later.

The influence of EDTA on the morphologies of the hydrothermal products was shown in Fig. 2. 1D products with a length of 30–50 µm and a diameter of 0.2–1 µm were formed at 1.0 × 10⁻³ mol L⁻¹ EDTA (Fig. 1a). The diameter of the product decreased to 80–200 nm (Fig. 2b, c) as the EDTA concentration increased up to 1.0 × 10⁻² mol L⁻¹. The clusters of the products were composed of the twisted nanowires with a length of 100–200 µm and an aspect ratio up to 1,000. The diameter of the product was broadened to 0.15–0.6 µm and the length was about 100 µm in the case of 1.0 × 10⁻¹ mol L⁻¹ EDTA (Fig. 2d).

Figure 3 shows the XRD patterns of the hydrothermal products formed in presence of EDTA. All the diffraction peaks can be indexed as those of the orthorhombic 5Mg(OH)₂·MgSO₄·3H₂O (PDF No. 070415). The gradual increase of the diffraction intensities with the increase of EDTA concentration indicated that the presence of EDTA was favorable for the crystallization of 1D 513 MOS. It was also noticed that most of the XRD peaks were attributed to (h0l) planes, indicating that the 513MOS nanowires may have a preferential growth along b axis owing to its inherent structure.

The HRTEM image and the SAED pattern of the 513MOS nanowires prepared in the presence of EDTA titration and barium chromate spectrophotometry (Model 722, Xiaoguang, China), respectively.
1.0 \times 10^{-2} \text{ mol L}^{-1} \text{ EDTA were shown in Fig. 4. The interplanar distances of the lattice fringes parallel (Fig. 4b, corresponding to the rectangular part of the nanowire in Fig. 4a) and with a 72° angle (Fig. 4c, corresponding to the trigonal part of the nanowire in Fig. 4a) to the growth direction of the whiskers were 5.1 and 2.25 Å, quite similar to the spacing of (202) plane \(d_{(202)} = 5.12\ \text{Å}\) and (114) plane \(d_{(114)} = 2.255\ \text{Å}\), respectively, indicating the preferential orientation of the nanowires along the [010] direction, which was reconfirmed by the SAED analysis in Fig. 4d and also identical with the XRD analysis shown in Fig. 3.

Figure 5 shows the influence of the preparation ways of the Mg(OH)\(_2\) precursors on the variation of [Mg\(^{2+}\)] and the supersaturation of 513MOS with the hydrothermal time. The supersaturation of 513MOS was presented by \([\text{Mg}\(^{2+}\)]^{6}[\text{SO}_4^{2-}][\text{OH}^-]^{10}\) according to the following formation reaction\([13]\):

\[
6\text{Mg}^{2+} + \text{SO}_4^{2-} + 10\text{OH}^- + 3\text{H}_2\text{O} = 5\text{Mg(OH)}_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}
\]

which may be connected with the chelating and/or the capping effects of EDTA. EDTA can form stable chelating complexes with Mg\(^{2+}\). The slow release of Mg\(^{2+}\) from the complexes might be favorable for the 1D growth of 513MOS. The varying binding abilities of EDTA on different planes may also inhibit the radial growth and promote the axial growth of the 513MOS nanowires.

The increase of [Mg\(^{2+}\)] and the supersaturation of 513MOS within initial 8 h of reaction should be attributed mainly to the dissolution of the Mg(OH)\(_2\) precursor, and the decrease of [Mg\(^{2+}\)] and the supersaturation of 513MOS after 6–10 h of reaction may be connected with the formation of 513MOS. The lower supersaturations of 513MOS achieved in either the double injection route or in the presence of minor amount of EDTA were favorable for the formation of 513MOS nanowires with high aspect ratio.

**Conclusion**

513MOS nanowires with a length of 20–60 µm and a diameter of 60–300 nm were synthesized via the double injection-hydrothermal reaction and the uniform 513MOS nanowires with a length of 100–200 µm and a diameter of
80–200 nm were formed via single injection EDTA-assisted hydrothermal reaction route. The lower supersaturations of 513MOS achieved in either the double injection route or in the presence of minor amount of EDTA, were favorable for the preferential growth of 513MOS along b axis, leading to the formation of 513MOS nanowires with high aspect ratios.

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