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Solution phase synthesis of magnesium hydroxide sulfate hydrate nanoribbons

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Abstract
Magnesium hydroxide sulfate hydrate nanoribbons have been synthesized by a solution-phase approach, which is based on the treatment of freshly precipitated magnesium hydroxide in an alcohol–water solution containing high concentrations of magnesium sulfate. These nanoribbons had typical lengths up to the micrometre range, widths of 60–300 nm, and thicknesses of 16–50 nm.

1. Introduction

In the past decade, one-dimensional (1D) nanostructures such as tubes, wires, rods, and belts (or ribbons) have attracted considerable scientific interest due to their unusual morphology and potential applications in nanotechnology [1–4]. A number of 1D materials have been successfully fabricated using various methods [1–12]. Many of these methods have focused on high-temperature techniques and template-directed processes [1–9]. Furthermore, low-temperature approaches to fabricating 1D nanomaterials without using any templates or catalysts have also been developed in recent years [10–12]. Xia and co-workers have demonstrated a solution-phase technique to synthesize nanowires of Se and Ag [10, 11]. Through hydrothermal methods, Li's group have fabricated Bi nanotubes and $Mg(OH)_2$ nanorods [12]. More recently, we have succeeded in the synthesis of nickel hydroxide nanoribbons by treating freshly precipitated nickel hydroxide with high concentrations of nickel sulfate [13]. Since the low-temperature approaches have the advantages of relatively low cost, high purity, and potential for scaling up, exploring these methods appears quite important.

We here describe a solution-phase approach to synthesize nanoribbons of magnesium hydroxide sulfate hydrate (MHSH). This method is based on the treatment of freshly precipitated magnesium hydroxide in an alcohol–water solution containing high concentrations of magnesium sulfate.

According to the references, some 1D MHSH structures such as fibres are very suitable as an additive for the filter medium, resin, filler, and reinforcement of polymers and plastics [14]. To date, however, only a few studies have been reported of the preparation of 1D MHSH structures [14c, 15]. The synthesis of MHSH nanoribbons may provide a promising possibility to enhance the performance of MHSH.

2. Experimental details

In a typical synthesis, 32.0 g (0.130 mol) of $MgSO_4 \cdot 7H_2O$ were dissolved in 130 ml deionized water and mixed with 40 ml of 0.4 M NaOH ethanol solution at room temperature. The reaction mixture including freshly precipitated magnesium hydroxide was then poured into a Teflon-lined stainless steel autoclave. The autoclave was sealed, and maintained at 100 °C for 24 h. After heating, the white precipitates were filtered and rinsed with distilled water several times to remove the byproducts. The final products were further dried under vacuum for 24 h.

3. Results and discussion

The crystal structure of the products was characterized by powder x-ray diffraction (XRD, Rigaku D_{max} 2000,

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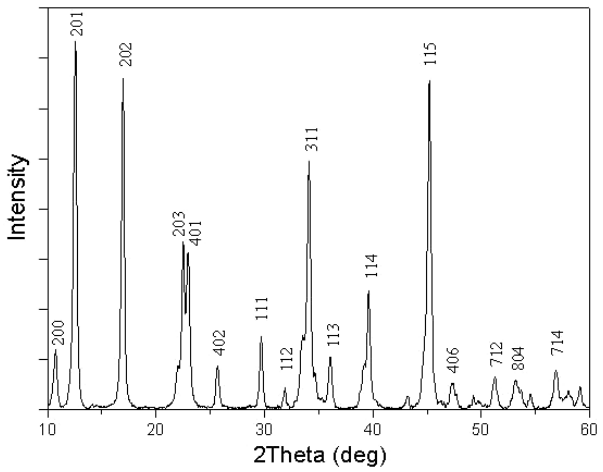

Figure 1. XRD pattern of the MHSH nanoribbons. The numbers above the peaks correspond to the (*hkl*) values of the orthorhombic structure.

Cu Kα). The XRD pattern is shown in figure 1 with all diffraction peaks indexed to the orthorhombic structure $5Mg(OH)_2{\cdot}MgSO_4{\cdot}3H_2O$ [15, 16]. Using PowderX [17], the lattice parameters were calculated to be $a = 15.94$ Å, $b = 3.10$ Å, $c = 13.37$ Å, which match well to the references [15, 16].

The transmission electron microscopy (TEM) image at low magnification revealed that the products possessed ribbon-like geometries (figure 2(A)). These nanoribbons had typical lengths up to the micrometre range, and widths of 60–300 nm. The thickness of the MHSH nanoribbon varies with its width, and typically in the range of 16–50 nm, as examined by atomic force microscopy (AFM, Digital Instrument, Nanoscope III, USA) using tapping mode. The width-to-thickness ratio of the nanoribbon is about 4–10.

High-resolution transmission electron microscopy (HRTEM) provided further insight into the structure of these products. Figure 2(B) displays a lattice-resolved HRTEM image of an individual MHSH nanoribbon. This image clearly reveals $(2\bar{1}4)$ and (214) atomic planes with spacings of 0.21 and 0.21 nm, respectively. The $(2\bar{1}4)$ plane and the (214) plane meet at an angle of about 89.4°, which is consistent with the ideal value of 89.7°. The inset shows the fast Fourier transform (FFT) of the HRTEM image. Based on our TEM and HRTEM observations, the MHSH nanoribbons were single crystals with a preferential [010] growth direction along their long axes and were enclosed by top surfaces (301) and side surfaces (102).

In order to verify the composition of the nanoribbons, we performed energy-dispersive x-ray spectroscopy (EDX). The EDX pattern (figure 3) shows characteristic magnesium, oxygen, and sulfur peaks (the Cu and C signal come from the copper TEM grid). The combination of x-ray fluorescence spectroscopy (XRF) and chemical analyses provided more quantitative data. The composition of the nanoribbons can be represented by the formulae of $4.96Mg(OH)_2{\cdot}MgSO_4{\cdot}2.8H_2O$, which is close to the standard data [16].

The processes of formation of MHSH nanoribbons are proposed as follows. When the freshly precipitated magnesium hydroxide is treated with high concentrations of magnesium sulfate at 100 °C, some seeds of MHSH have been formed. At high concentration, magnesium sulfate as

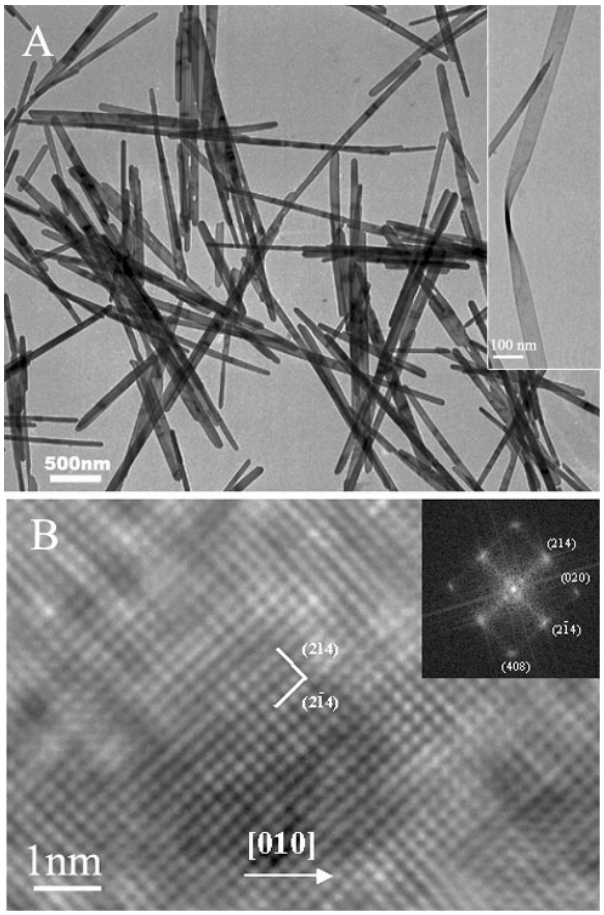

Figure 2. (A) TEM image of the MHSH nanoribbons; the inset shows the ribbon-like structure. (B) HRTEM image of an individual MHSH nanoribbon; the inset shows the corresponding FFT of the image.

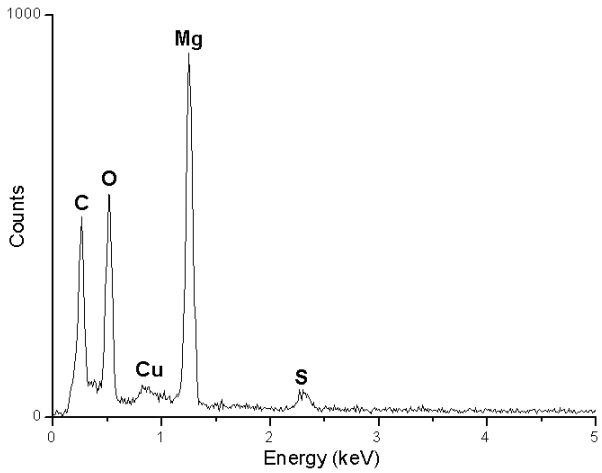

Figure 3. Typical EDX pattern taken on the MHSH nanoribbons.

a solute could be absorbed on the (301) and (102) faces of the seeds and form two-dimensional absorbed layers, which could inhibit the growth rate of these two faces [18]. The role of high concentrations of magnesium sulfate is not only to stimulate the formation of the MHSH seeds but also leads to the oriented growth of MHSH. It is found that when the concentration of magnesium sulfate is below 0.09 mol l^{-1}

in the treatment process, most final products are magnesium hydroxide particles.

To investigate the function of ethanol, we replaced NaOH ethanol solution by NaOH aqueous solution with all the other conditions remaining the same. Few nanoribbons were observed. The results suggest that the addition of ethanol decreases the solubility of magnesium sulfate and results in the formation of an absorbed layer. Increasing the concentration of magnesium sulfate can also achieve this purpose. For example, when 0.2 mol of $MgSO_4 \cdot 7H_2O$ is mixed with 50 ml of 0.4 M NaOH aqueous solution and treated through the typical procedure, the final products exhibit a ribbon-like structure.

4. Conclusions

We report a simple approach to synthesize MHSH nanoribbons. This method is based on the treatment of freshly precipitated magnesium hydroxide in an alcohol–water solution containing high concentrations of magnesium sulfate. It is evident that the high concentration of magnesium sulfate plays a key role in the formation of nanoribbons. This solution-phase approach can be developed to synthesize other 1D nanomaterials.

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