

# The preparation of $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ nanotubes under solvothermal conditions

Junjian Xu · Xuemei Li · Weiwei Zhou · Lei Ding ·  
Zhong Jin · Yan Li

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**Abstract** With magnesium carbonate hydroxide and nanoporous silica as the starting materials, chrysotile ( $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ) nanotubes were prepared by using a solvothermal method at  $400^\circ\text{C}$  within four hours. This new method needs no strong alkali medium and the reaction time is very short. EDX analysis showed a molar ratio of 3Mg:2Si:9O of the product. Selected Area Electron Diffraction (SAED) pattern indicated that the tube axis is along [100] direction. HRTEM image showed the nanotubes were multi-walled and the distance between the two close layers was about 0.75 nm, which is very near to the distance of {001} planes. Thus, combining the results of SAED and HRTEM, we can conclude that the {001} planes of serpentine roll up along the [100] direction to form the tubular structure. The effects of various reaction conditions and the formation mechanism were also discussed.

**Keywords** Nanotube ·  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$  · Solvothermal synthesis

## Introduction

Because of their unusual structure and physical and chemical properties, more and more researches have been contributed in the synthesis and property study of inorganic nanotubes. New types of silicates with tunable pore sizes have been paid much attention because of their great potential applications

in many areas, such as catalysis, molecular sieves, and gas adsorption and separation [1–9].

Serpentine with the chemical composition of  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$  is a kind of magnesium silicate mineral of layered structures [10]. A sheet of Si-O tetrahedrons joins with a sheet of Mg-O octahedrons through the shared apical O atoms to form a layer [11]. When the layers are rolled cylindrically, the tubules will be formed [12]. This kind of serpentine fibrous mineral is normally called chrysotile (asbestos). This incombustible, chemical-resistant, fibrous mineral can be used in fireproofing, electrical insulation, building materials, brake linings, and chemical filters.

More recently, along with the development of nanoscience and technology, the chrysotile nanotubes are attracting new attentions. They have some unusual properties, such as the collective charge excitations found in the infrared spectra [13]. They were also widely used to host some functional materials within their tubes. The materials resident in the tubes often present typical characters of nanomaterials because of the size-restrict effect of the tube channels [14, 15]. And as the chrysotile fibers are transparent, they are favorable hosts for making and directly using optical nanomaterials. For example, Romanov et al. produced three-dimensional arrays of structurally confined InP wire-like nanostructures in channels of a chrysotile asbestos matrix by chemical vapor deposition and studied their luminescence property [14]. Terasakix and co-workers synthesized CdSe in the nanochannels of the transparent fibrous magnesium silicates of chrysotile asbestos and sepiolite. They found that the optical absorption spectra of the CdSe nanofilaments displayed a blue shift and a strong polarization dependence compared with bulk CdSe [15].

As the naturally obtained chrysotile contains many impurities and is not suitable for using in nanoscience and technology, people have been working on the preparation

J. Xu · X. Li · W. Zhou · L. Ding · Z. Jin · Y. Li (✉)  
Key Laboratory for the Physics and Chemistry of Nanodevices,  
College of Chemistry and Molecular Engineering, Peking  
University, Beijing 100871, China  
e-mail: yanli@pku.edu.cn

of  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$  nanotubes. Here we use the chemical formula instead of the name “chrysotile” to show that the synthesized product is pure. In the last few years, there are some reports on the synthesis of tubular  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ . Roveri and co-workers grew tubulate  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$  crystals with the hydrothermal method at  $300^\circ\text{C}$ . They began the reaction with  $\text{MgCl}_2$ ,  $\text{NaOH}$  and mesoporous silica MCM-41 [11]. Gusarov and co-workers prepared  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$  tubes at the temperature of  $300\text{--}400^\circ\text{C}$  and the pressure of  $70\text{--}100\text{ MPa}$  with the treatment duration of  $1\text{--}2$  days [16]. Li and teammates synthesized the tubulate  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$  in a mixed water-ethanol solvent system, in which the treatment duration was two days [17]. Very recently, Foresti et al. synthesized Fe-doped chrysotile nanotubes by hydrothermal pathways similar to [11] at  $300^\circ\text{C}$  for 8 h to 3 days [18].

As stated above, all of the synthesis reported was performed under hydrothermal or solvothermal conditions with water or ethanol-water mixtures as the solvents. The reaction durations were all very long, normally in days. Moreover, they used a strong alkalic condition which is very unfavorable to both the autoclave and the environment. We designed a new solvothermal process, in which  $\text{MgCO}_3\cdot 4\text{Mg}(\text{OH})_2\cdot 6\text{H}_2\text{O}$  and nanoporous silica were used as the starting materials and glycol as the solvent, and no alkalization was needed. In our experiments, single crystalline  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$  nanotubes were obtained within four hours. Compared to the reported research, our experimental process was much easier to be completed.

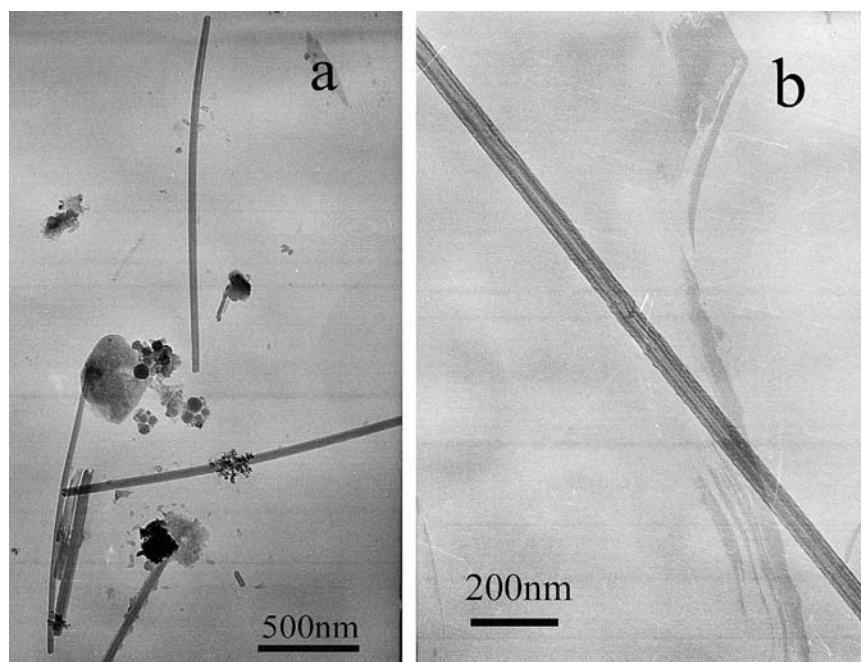
## Experimental

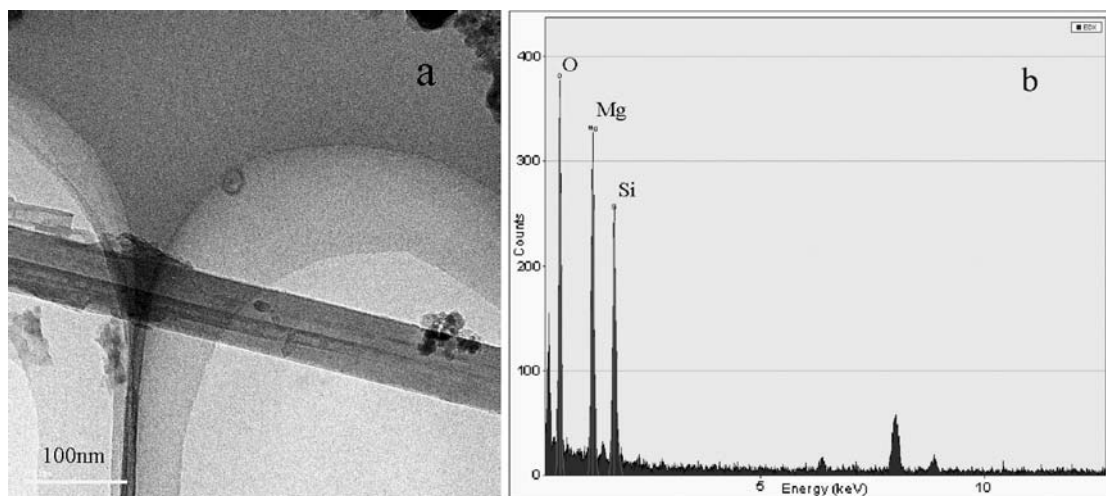
$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$  nanotubes were prepared by a solvothermal method with glycol as the solvent. Typically, 0.10 g Nanoporous Silica Sieve (Jilin University High.Tech Ltd.) with the pore size of  $6\text{--}7\text{ nm}$  and 0.40 g  $\text{MgCO}_3\cdot 4\text{Mg}(\text{OH})_2\cdot 6\text{H}_2\text{O}$  (Beijing Chemical Plant) were put into an stainless steel autoclave with the capacity of 15 ml. Then, 10 ml glycol was added into the autoclave as the solvent. The autoclave was put into a furnace, heated up to  $400^\circ\text{C}$  and maintained for four hours. Then, the autoclave was cooled down in air. The products were washed with water and ethanol for several times. At last, the washed products were characterized by TEM, HRTEM and EDX. The TEM observation and the selected area electron diffraction (SAED) were finished on a Hitachi-8000 transmission microscope operated at 200 kV. The HRTEM images were got on a Hitachi-9000 NAR transmission microscope operated also at 200 kV. And the EDX spectrum of a single nanotube was obtained with an EDAX equipped on a FEI F30 field-emission transmission microscope.

## Results and discussion

The products obtained at the typical condition were observed by TEM, and some tubular materials were found. Figure 1 (a) and (b) showed two typical examples of nanotubes. It was

**Fig. 1** The TEM images of the tubulate products





**Fig. 2** The EDX spectrum of a single tube in the products

found that most of the tubes were straight. The inner diameter is almost uniform with the size of around 7 nm, which is very near to the pore size of the mesoporous silica. However, the outer diameter and the length of the nanotubes were not very uniform. By summarizing many different samples, we found that the diameter of the tubes was around 40 nm to 130 nm, and the length of the nanotubes could be hundreds of nanometers to several microns.

We measured the EDX Spectrum of a single nanotube to determine the chemical composition of the nanotube. Figure 3(a) shows the single tube which was analyzed, and the result was shown in Fig. 3(b). The molar ratio of Mg:Si:O was calculated to be 3:2:9. Combined with the general knowledge of chemistry, we could speculate that the nanotube was composed of  $Mg_3Si_2O_5(OH)_4$ , which is with the same composition as the minerals of serpentine and chrysotile.

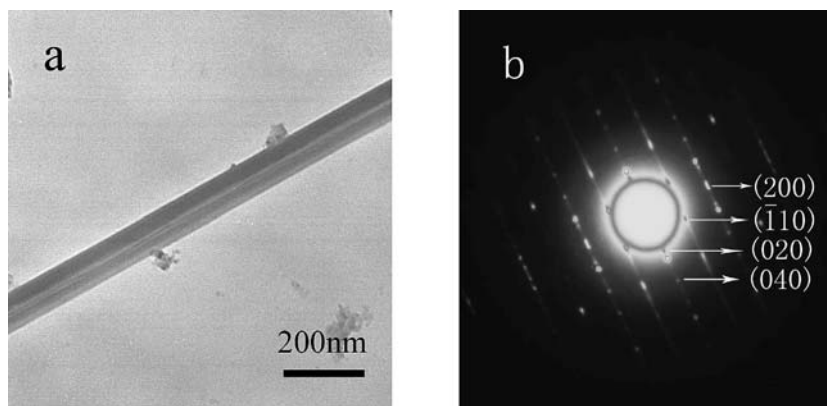
We got the selected area electron diffraction pattern of a single nanotube. The image of Fig. 2(a) was the tube which was tested. The electronic diffraction pattern showed in Fig. 2(b) indicates that the nanotube is a single crystallite. The diffraction spots displayed rectangular symmetry. By referring to the standard X-Ray Diffraction data (JCPDS 73-

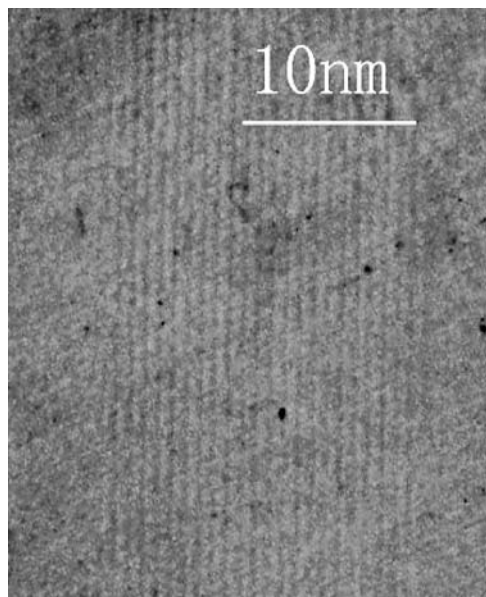
1336), the parameters of unit cell are,  $a = 5.31 \text{ \AA}$ ,  $b = 9.20 \text{ \AA}$ ,  $c = 7.31 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90$ . There are the diffraction spots in Fig. 2(b) with the corresponding  $d$  values of  $4.5 \text{ \AA}$ ,  $4.5 \text{ \AA}$ , and  $2.6 \text{ \AA}$ , which are in good accordance with those of the (020),  $(\bar{1}10)$ , and (200) faces of serpentine. The length direction of the tube is along [100]. And the (002) and (004) faces were observed along the perpendicular direction of the axis [100].

HRTEM was also used to characterize the structure of the tube. Many stripes could be observed in the image of Fig. 4. It can be seen that the wall of the tube is with layered structure. The distance between the two close layers was confirmed to be  $7.4 \text{ \AA}$ . By measuring more samples with different diameter, we could find that the average diameter was  $7.5 \text{ \AA}$ , which was very close to the  $d$  value of the (001) face stands for, i.e.  $7.3 \text{ \AA}$ . So, it seems that the {001} planes of Serpentine roll up along the [100] direction to form the tubules.

We also studied the influence of various reaction conditions on the formation of  $Mg_3Si_2O_5(OH)_4$  nanotubes. We first tried many different magnesium and silicon sources. When the reactant  $MgCO_3 \cdot 4Mg(OH)_2 \cdot 6H_2O$  was replaced by another five kinds of chemicals containing magnesium,

**Fig. 3** The TEM image (a) and electronic diffraction image (b) of a single tube





**Fig. 4** The HRTEM image of a Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> tube

such as magnesium powder, MgO, Mg(NO<sub>3</sub>)<sub>2</sub>, MgCO<sub>3</sub> and MgSO<sub>4</sub>, only very few nanotubes could be found. It seems that the selection of MgCO<sub>3</sub>·4Mg(OH)<sub>2</sub>·6H<sub>2</sub>O as the magnesium source is very important.

Besides the nanoporous silica, we also used Na<sub>2</sub>SiO<sub>3</sub> or tetraethyl orthosilicate as the silicon source, but no nanotubes could be found. And when we used the commercial silica xerogel, the Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> nanotubes could be prepared, but the yield was extremely low. The use of nanoporous silica as the starting material is crucial to get higher yield of Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> nanotubes. It's out of question that the high surface area of the nanoporous silica is favorable to the kinetics of the reaction [11]. And the ordered nanopores with the size of 6–7 nm also take great roles. It has been mentioned that the inner diameter of the nanotubes we got is almost the same as the pore size of the initial nanoporous silica. This indicates that some of the walls of the nanopores may act as the starting spots as well as the templates of the synthesis process. And compared with the strong alkali conditions other researches have used in their synthesis, which will destroy the mesoporous structure of MCM 41 very quickly, the mild reaction condition we used helps to maintain the mesoporous structure of the starting material, and as a result the template effect of the pores was achieved.

We also checked the influence of temperature and the reaction duration. When the reaction time was 4 h, it was found that when the temperature is under 280°C, no tubes could be formed. A few tubes could be found at the temperature of 350°C. 400°C and 450°C are ideal for the synthesis of Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> nanotubes. When the temperature was further increased to 500°C and 600°C, the yield of nanotubes didn't change much. When the reaction time was longer

than 4 h, e.g. 12 or 24 h, the yield of nanotubes wouldn't change much. However, when the reaction time was shorter than 4 h, the yield of nanotubes decreased sharply. Taking all the experiments above, we chose the reaction temperature of 400°C and reaction duration of 4 h as the optimized condition.

## Conclusions

Tubular Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> was prepared under solvothermal condition at 400°C with the reaction duration of 4 h. From the SAED and HRTEM results we knew that the nanotube is a multi-walled single crystal. And the tube extends along the axis of [100]. The distance of the two close layers in the tube walls was about 0.75 nm, which is very similar to the *d* value of {001} planes. This is a new and convenient way to obtain single crystalline Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> nanotubes. The adoption of MgCO<sub>3</sub>·4Mg(OH)<sub>2</sub>·6H<sub>2</sub>O as the magnesium source and nanoporous silica as the silicon source is very important to make the process be carried out at a milder condition and shorter period of time. The nanopores of the nanoporous silica may act as the template for the formation of nanotubes. Because the products were obtained after the treatment of high temperature and pressure, the nanotubulate Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> should be very stable in high temperature and high pressure. And this affords the nanotubes much larger possibility to be used in many fields.

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