

# Hydrogel route to nanotubes of metal oxides and sulfates

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A tripodal cholamide-based hydrogel has been employed as a template to synthesize inorganic nanotubes. Besides nanotubes of oxides such as SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, WO<sub>3</sub> and ZnO, nanotubes of sulfates such as the water-soluble ZnSO<sub>4</sub> as well as of BaSO<sub>4</sub> have been obtained using this method. An advantage of the use of the hydrogel is that metal alkoxides are not required for the synthesis of the oxide nanotubes. The nanotubes have been characterized by X-ray diffraction and transmission electron microscopy.

## Introduction

Nanotubes of metal oxides have been synthesized by employing different strategies.<sup>1</sup> Sol-gel chemistry has been used by a few workers in the synthesis of nanotubes of metal oxides such as silica<sup>2</sup> and titania.<sup>3</sup> Oxide gels in the presence of surfactants or suitable templates form nanotubes. For example, by coating carbon nanotubes (CNTs) with oxide gels and then burning off the carbon nanotubes, one obtains nanotubes and nanowires of metal oxides such as ZrO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, IrO<sub>2</sub>, RuO<sub>2</sub>, WO<sub>3</sub> and MoO<sub>3</sub>.<sup>4-6</sup> Sol-gel synthesis of oxide nanotubes has also been accomplished in the pores of alumina membranes.<sup>7</sup>

One of the novel methods for the synthesis of metal oxide nanotubes employs gels derived from low molecular weight organic compounds. Organogelators gel solvents at low concentrations due to the formation of a three-dimensional network based on fibrous aggregates in organic fluids.<sup>8,9</sup> The self-assembled organogelators act as templates in the sol-gel polymerization process.<sup>10</sup> The gel fibers are coated with oxidic materials followed by the dissolution of the gel in a suitable solvent and by calcination. This strategy has been employed to synthesize silica nanotubes.<sup>11,12</sup> Shinkai and co-workers have shown that certain cholesterol derivatives can gelate tetraethyl orthosilicate (TEOS), causing silica polymerization,<sup>11,13-16</sup> giving rise to hollow lamellar,<sup>13,14</sup> helical<sup>12</sup>, linear fiber<sup>8,15</sup> or chiral spiral<sup>16,17</sup> structures. Hollow silica tubes have also been synthesized using organic gelators based on chiral diamino-cyclohexane derivatives,<sup>18</sup> 2,3-di-n-decycloxyanthracene,<sup>19</sup> cyclohexane<sup>20</sup> and sugar-appended porphyrin.<sup>21</sup> Jung *et al.*<sup>22</sup> have thus prepared ultrastable mesoporous silica using a phenanthroline-appended cholesterol organogelator as the template. TiO<sub>2</sub> hollow fibers have been obtained by Kobayashi *et al.*<sup>23</sup> using titanium alkoxide as the precursor along with the supramolecular assemblies of *trans*-(1*R*,2*R*)-1,2-cyclohexanedi(11-aminocarbonylundecylpyridinium) hexafluorophosphate as templates. Helical ribbon and double-layered TiO<sub>2</sub> nanotubes have been prepared using a cholesterol based gelator.<sup>24</sup> Nanotubes of transition metal (Ta, V) oxides have also been prepared by this templating method.<sup>25</sup> The above nanotube syntheses have generally made use of organogels as templates.

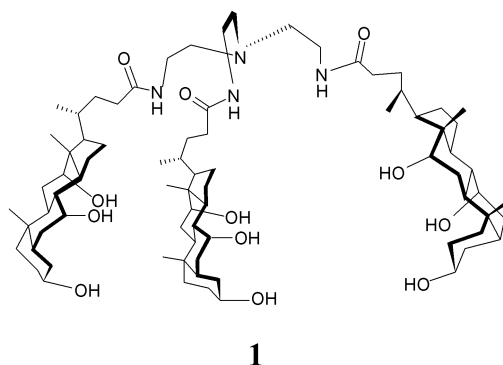
In all the syntheses listed above, organogelators have been used as templates due to which metal alkoxides become the necessary inorganic precursors. Due to the difficulties in synthesizing as well as handling metal alkoxides, most of them

being moisture sensitive, the number of metal oxides that can be synthesized using organogels gets limited. In order to use simple metal salts as precursors, the reactions have to be carried out in an aqueous medium in which these salts are soluble. This prompted us to use hydrogels instead of organogels as templates. Gelation of aqueous fluids is different from that in organic solvents in that the aggregation process in aqueous environments is predominantly driven by the hydrophobic effect. It had been previously reported that a tripodal cholamide (**1**) having hydrophobic surfaces (coming from the  $\beta$ -face of the bile acid backbone) spontaneously aggregates into gel fibers in predominantly aqueous media.<sup>26</sup>

We considered that it might be of value to use this hydrogelator to synthesize nanotubes of metal oxides. It has been possible to prepare nanotubes of SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, ZnO and WO<sub>3</sub> as well as of ZnSO<sub>4</sub> and BaSO<sub>4</sub> by employing this hydrogel.

## Experimental

The gelator **1** was synthesized by the procedure reported elsewhere.<sup>26</sup> In a typical reaction for the synthesis of silica nanotubes, 20 mg (0.03 mmol) of the gelator was dissolved in 0.4 ml CH<sub>3</sub>COOH and 1.6 ml H<sub>2</sub>O was added to induce gelation. This was thoroughly mixed by shaking and warmed slightly to form a sol. To this sol, 0.1 ml (0.45 mmol) of tetraethyl orthosilicate (TEOS, Merck, >98%) was added and the mixture allowed to stand at room temperature. Gel fibers soon formed, simultaneously accompanied by the hydrolysis of TEOS around them. The gel was dried after 24 h in vacuum to

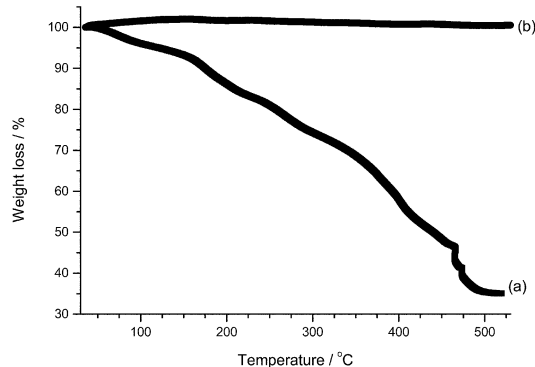


obtain gel fibers coated with silica. In order to prepare titania nanotubes, tetrabutyl orthotitanate (TBOT, Fluka) was used as the starting material. 0.1 ml (0.29 mmol) of TBOT was added to 0.5 ml of distilled  $C_2H_5OH$  and 0.1 ml  $CH_3COOH$  to obtain a gel. This was added to a sol containing 20 mg gelator with 0.3 ml  $CH_3COOH$  and 1.6 ml  $H_2O$  to obtain a white gel. The gel was allowed to stand for a day at room temperature and then dried under vacuum. We thus obtained gel fibers coated with titania. For the synthesis of zirconia nanotubes, 50 mg  $ZrOCl_2$  (0.16 mmol, S. D. Fine, >96%) was dissolved in 1 ml  $H_2O$  and a drop of  $NH_3$  was added to form a gel. This was mixed with a solution containing 20 mg gelator with 0.4 ml  $CH_3COOH$  and 0.6 ml  $H_2O$ . A white gel was obtained, which on drying gave gel fibers coated with zirconia.  $ZrOCl_2$  was chosen as the source of Zr since it is possible to control the rate of hydrolysis of this as compared to other sources of Zr such as zirconium isopropoxide, which are difficult to handle due to their extremely fast hydrolysis in aqueous media.

In order to prepare ZnO nanotubes, a gel was formed initially by taking 35 mg zinc acetate (0.16 mmol, Merck, 98%) in ethanol and mixing with 10 mg KOH in 1 ml ethanol. This was added to a sol containing 20 mg gelator with 1.6 ml  $H_2O$  and 0.4 ml  $CH_3COOH$ . A white gel was obtained that was allowed to stand for a day at ambient temperature and then dried in vacuum. For the synthesis of  $WO_3$  nanotubes, tungstic acid prepared by passing sodium tungstate (S. D. Fine, 99%) through a cation exchange column was used. 2 ml of the above solution was added to a solution containing 20 mg gelator and 0.4 ml  $CH_3COOH$  to obtain a gel. This was allowed to stand for a day at room temperature and then dried in vacuum.

Nanotubes of  $ZnSO_4$  were prepared by starting from an ammonical solution of  $ZnSO_4$  (30 mg  $ZnSO_4$  (0.19 mmol, Qualigens, 99%) in 1.6 ml  $H_2O$  with a drop of  $NH_3$ ) to which a solution containing 20 mg gelator in 0.4 ml  $CH_3COOH$  was added. A white gel was obtained immediately which was dried in vacuum. In order to synthesize nanotubes of  $BaSO_4$ , 55 mg of  $BaCl_2$  (0.23 mmol, Aldrich, 99%) taken in 0.5 ml water was added to a solution containing 20 mg gelator in 0.1 ml  $CH_3COOH$  to form a gel. To this gel, a solution containing 30 mg ammonium sulfate in 0.5 ml water was added to obtain  $BaSO_4$ . This was further dried in vacuum.

Thermogravimetric analysis (TGA) of the samples was carried out on a Mettler-Toledo-TG-850 instrument to verify the removal of the gelator. In Fig. 1, we show a representative TGA curve for the as-synthesized and calcined  $ZrO_2$  nanotubes. In the as-synthesized sample, there is a weight loss of 64% corresponding to the removal of the gelator, which is completely done at a temperature of 475 °C. There was no weight loss in the calcined samples indicating the complete removal of the gelator. In order to remove the template, the samples were generally washed 2–3 times with 10 ml distilled ethanol and then heated to 500 °C for 1 h ( $1\text{ }^\circ\text{C min}^{-1}$ ) in flowing  $O_2$  gas.



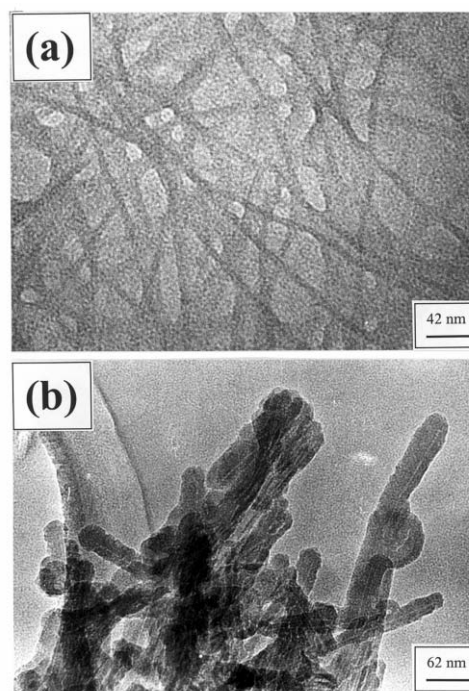
**Fig. 1** TGA curves for the  $ZrO_2$  nanotubes (a) as-synthesized and (b) after removal of the gel by calcination.

After obtaining the gel fibers coated with the inorganic precursors, they were observed by transmission electron microscopy (TEM) using a JEOL JEM 3010 microscope, operating with an accelerating voltage of 300 kV. Samples for TEM studies were prepared by dispersing the nanotubes by sonication in  $CCl_4$ . A drop of the suspension was put on a holey carbon coated Cu grid and allowed to evaporate slowly. Scanning electron microscopy (SEM) images were obtained on a LEICA S440i scanning electron microscope. Powder X-ray diffraction (XRD) patterns were recorded using  $CuK\alpha$  radiation on a Rich-Siefert, XRD-3000-TT diffractometer. XRD patterns revealed the samples to be amorphous before removal of the template. Photoluminescence (PL) measurements were carried out at room temperature with a Perkin-Elmer model LS50B luminescence spectrometer using 325 nm as the excitation wavelength ( $\lambda_{ex}$ ).

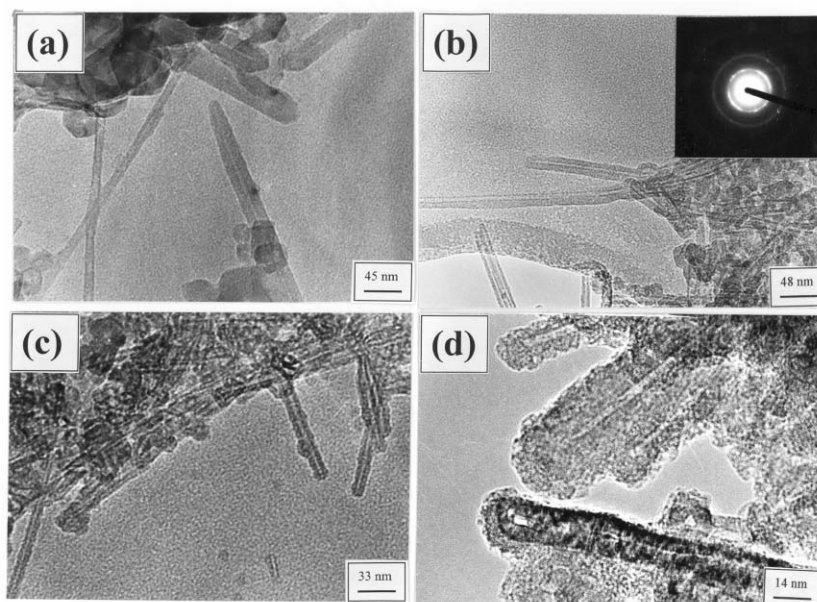
## Results and discussion

The hydrogel contains well-defined fibers with diameters between 8 and 10 nm and lengths extending to a few hundred nanometers as revealed by the TEM images in Fig. 2a. In Fig. 2b, we show a TEM image of the silica nanotubes obtained after removal of the gel template. The image clearly indicates the hollow nature of the tubes, which have an outer diameter of 30–40 nm and an inner diameter of 4–5 nm. The nanotubes have lengths extending to a few hundred nanometers. Although silica shrinks to some extent during the calcination, the size of the nanotubes is comparable with that of the gelator fibers (8–10 nm). The distribution of the diameters is quite narrow as evidenced from Fig. 2b. The  $SiO_2$  nanotubes were X-ray amorphous.

We could obtain good yields of the  $TiO_2$  nanotubes by the hydrogel method. In Fig. 3a, we show a low magnification TEM image of the titania coated gel fibers. After removal of the template with ethanol, followed by calcination, we obtained hollow  $TiO_2$  nanotubes as shown in Figs. 3b–d. These have inner diameters between 4 and 7 nm and an outer diameter between 10 and 20 nm with a narrow size distribution. The lengths go up to a few hundred nanometers. The XRD pattern

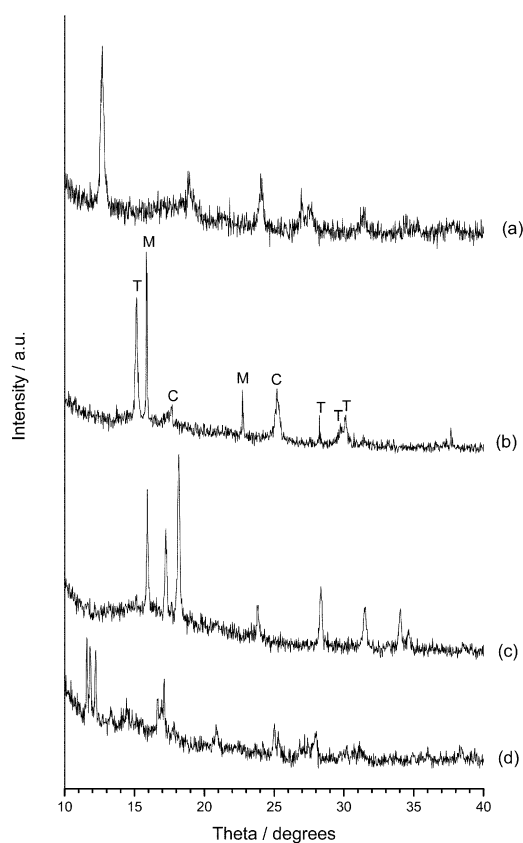


**Fig. 2** Low magnification TEM images of (a) the hydrogel fibers and (b) the silica nanotubes obtained after removal of the gel fibers.



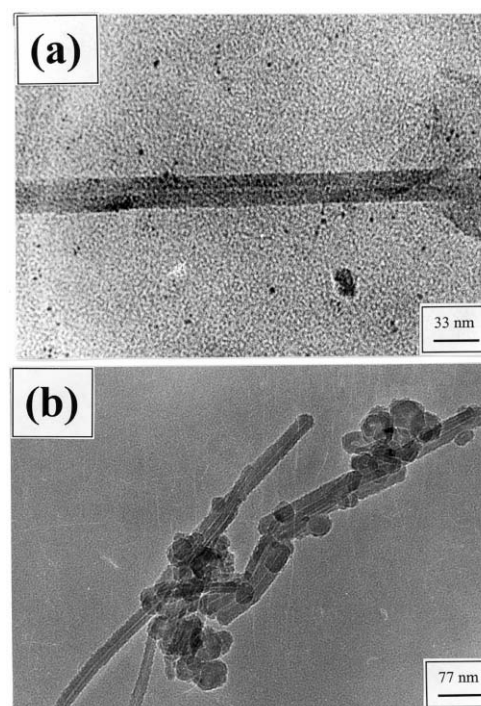
**Fig. 3** TEM images of the titania nanotubes (a) as-synthesized and (b)–(d) after removal of the gel fibers. Inset shows the SAED pattern taken on a single nanotube.

of the  $\text{TiO}_2$  nanotubes (Fig. 4a) showed them to be in the anatase phase (JCPDS file: 21–1272), as also confirmed by the selected area electron diffraction (SAED) pattern (see inset of Fig. 3b). The  $\text{TiO}_2$  nanotubes obtained by using organogelators are reported to have diameters in the range of 150 to 600 nm. The nanotubes obtained by us in the present study are therefore considerably thinner and may be useful for carrying out photocatalytic reactions and other purposes.

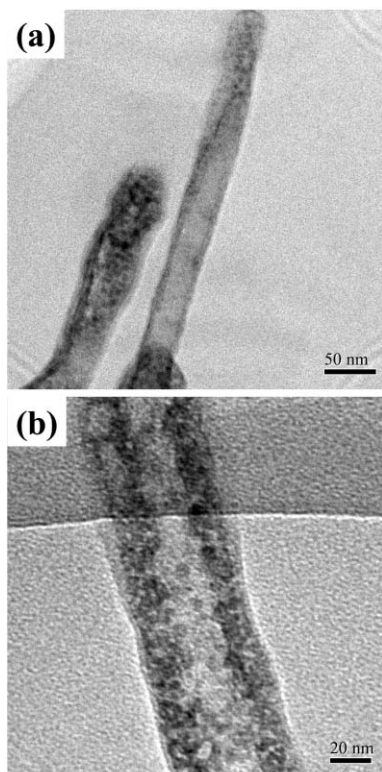


**Fig. 4** XRD patterns of (a)  $\text{TiO}_2$ , (b)  $\text{ZrO}_2$  (where C, M and T denote the cubic, monoclinic and tetragonal phases respectively), (c)  $\text{ZnO}$  and (d)  $\text{WO}_3$  nanotubes.

There have been no reports on the synthesis of zirconia nanotubes using gelators as templates and in Fig. 5, we show TEM images of the zirconia nanotubes synthesized. These have outer diameters of  $\sim 25$  nm and inner diameters between 4 and 7 nm. The length extends to a few hundreds of nanometers. Fig. 5a shows a nanotube with smooth walls. Also seen in Fig. 5b are sphere-like particles along with the nanotubes. These may be formed when the hydrolysis of the inorganic species occurs at a faster rate than the formation of the gel fibers from the gelator. As a result, the inorganic species encapsulate a part of the gelator that leads to hollow, spherical particles after heat treatment. The XRD pattern of the calcined sample (Fig. 4b) shows the nanotubes to be composed of a mixture of the stable monoclinic phase (JCPDS file: 37–1484) with the



**Fig. 5** Low magnification TEM images of the zirconia nanotubes obtained after removal of the gel fibers.



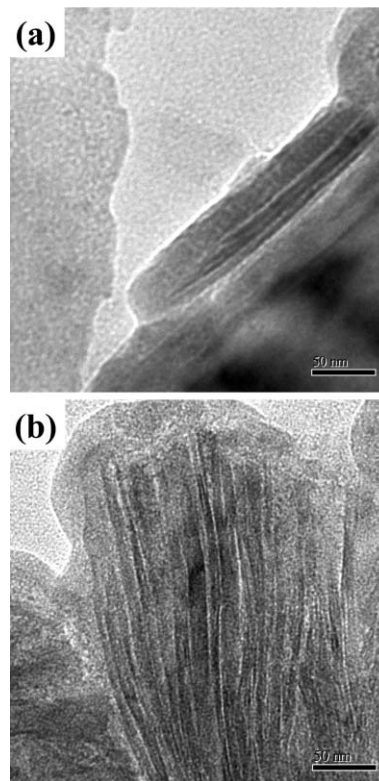
**Fig. 6** Low magnification TEM images of ZnO nanotubes obtained after removal of the gel fibers.

metastable cubic and tetragonal phases (JCPDS files: 27–0997 and 42–1164 respectively).

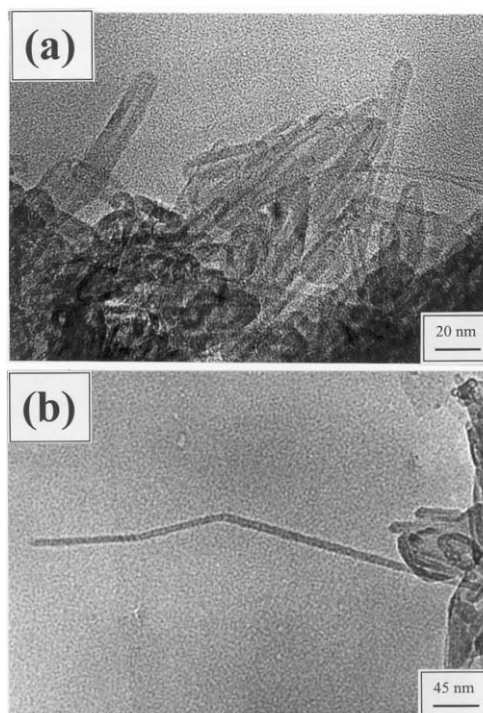
We have been successful in preparing ZnO nanotubes as shown in the electron microscope images in Fig. 6. The yields of the nanotubes were excellent. The nanotubes have outer diameters in the range of 30–60 nm and inner diameters of ~20 nm, with lengths extending into several hundred nanometers. The XRD pattern, shown in Fig. 4c, could be indexed on the basis of the hexagonal structure of ZnO (JCPDS file: 36–1451). ZnO is a wide bandgap (3.37 eV) semiconductor and has been extensively investigated as a short-wavelength light-emitting, transparent conducting and piezoelectric material. There are several reports on the synthesis of ZnO nanowires<sup>27,28</sup> and nanorods<sup>29</sup> but just one on the synthesis of ZnO nanotubes<sup>30</sup> synthesized hydrothermally. These nanotubes had inner diameters in the range of 250 nm. The nanotubes obtained by us are much thinner in diameters, therefore, we considered it worthwhile to investigate the photoluminescence. The photoluminescence spectrum of the ZnO nanotubes obtained by us shows peaks around 385 nm and 440 nm, the former being the major one corresponding to the near band-edge emission of ZnO. The origin of the 440 nm band is not clear.<sup>31</sup> We do not see the PL band around 520 nm due to the single ionized oxygen vacancy in ZnO.

In Fig. 7, we show TEM images of the WO<sub>3</sub> nanotubes obtained after removal of the gel fibers. Shown in Fig. 7a is a single nanotube having an outer diameter of ~40 nm and an inner diameter of ~5 nm. The nanotubes have lengths that go to a few hundred nanometers. A bundle of the WO<sub>3</sub> nanotubes is shown in Fig. 7b. The XRD pattern shown in Fig. 4d, confirms the monoclinic structure of WO<sub>3</sub> (JCPDS file: 43–1035).

We could obtain good yields of ZnSO<sub>4</sub> nanotubes as evidenced from the TEM image shown in Fig. 8a. The nanotubes have an inner diameter of ~4 nm and an outer diameter in the 10–12 nm range. Most of the nanotubes were 200–300 nm long, but a few had lengths going up to several hundreds of nanometers (Fig. 8b). The XRD pattern of the



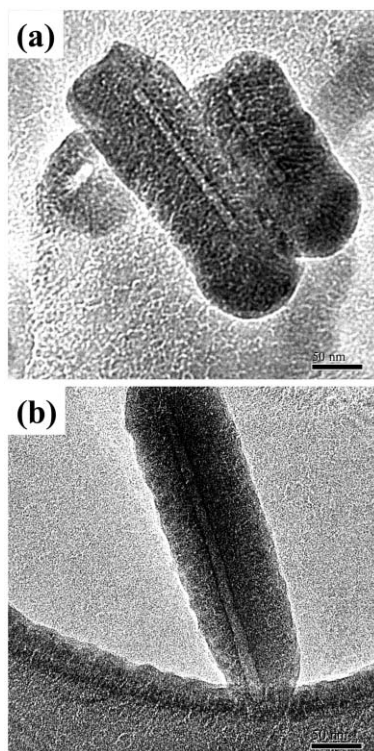
**Fig. 7** Low magnification TEM images of WO<sub>3</sub> nanotubes: (a) a single nanotube and (b) a bundle of nanotubes.



**Fig. 8** Low magnification TEM images of the ZnSO<sub>4</sub> nanotubes obtained after removal of the gel fibers.

nanotubes confirmed the orthorhombic structure (JCPDS file: 080491). These nanotubes are readily soluble in water.

The BaSO<sub>4</sub> nanotubes obtained by us are shown in the low magnification TEM images in Fig. 9. The nanotubes have small aspect ratios, with the outer diameters being in the range of 100 nm and length between 250 and 350 nm. The nanotubes have an inner diameter of ~9 nm indicating that the gel fibers indeed act as templates. The rate at which BaSO<sub>4</sub> precipitated



**Fig. 9** Low magnification TEM images of the BaSO<sub>4</sub> nanotubes obtained after removal of the gel fibers.

was fast compared to the rate of formation of the gel fibers, resulting in the small aspect ratios.

## Conclusions

In conclusion, by using a hydrogelator (**1**), we have successfully prepared a wide range of nanotubes of oxides, which includes SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, ZnO and WO<sub>3</sub> as well as of metal sulfates such as ZnSO<sub>4</sub> and BaSO<sub>4</sub>. The synthesis of the oxide nanotubes is not restricted to the use of inorganic alkoxides as precursors. Nanotubes of a desired diameter can easily be made by a suitable choice of the hydrogelator or by slightly modifying the conditions of gelation. This opens up new avenues to synthesize nanotubes that were previously difficult to synthesize using traditional methods. The surface areas of the nanotubes prepared by us are likely to be appreciable, although we have not actually carried out the measurements. It would be useful to pursue such studies.

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