

# Mesostructured Silica Tubes and Rods by Templating Porous Membranes

Zhijian Liang\*<sup>[a, b]</sup> and Andrei S. Susa<sup>[a]</sup>

**Abstract:** Mesostructured silica tubes and rods were prepared by deposition of a prehydrolysed silica sol with surfactant onto the cylindrical pores of a polycarbonate (PC) membrane template, followed by calcination to remove the surfactant and membrane template. The tubular and rodlike mor-

phologies of mesostructured silica were demonstrated by scanning electron microscopy (SEM) and transmission elec-

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tron microscopy (TEM) measurements. The tubes and rods show ordered hexagonal mesostructures, which were demonstrated by small angle X-ray diffraction (XRD) patterns and TEM measurements.

## Introduction

One-dimensional nanostructured materials have attracted intensive scientific interest, because of their potential applications in optical, electronic, and magnetic devices. One-dimensional nanostructured materials with various compositions have been prepared from the vapor or solution phase, one-dimensional growth from a seed, or membrane template-directed syntheses.<sup>[1]</sup> Membranes used for templating, for example, alumina and polycarbonate (PC), contain tubular pores through the entire thickness of the membranes. By depositing the desired materials on the walls of cylindrical pores of the membranes, tubes and fibers of metal,<sup>[2]</sup> inorganic oxide,<sup>[3]</sup> semiconductor,<sup>[4]</sup> polymer,<sup>[5]</sup> and carbon<sup>[6]</sup> have been produced by a number of methods, including electroless metal deposition,<sup>[2a,b]</sup> the sol-gel method,<sup>[3]</sup> electrochemical deposition,<sup>[2c-e]</sup> chemical vapor deposition,<sup>[7]</sup> and polymer coating of the membrane pores.<sup>[5,8]</sup> The size and structural properties of the materials prepared by membrane templating are determined by the size, shape, and morphology of the template used.

Mesoporous materials with controllable morphologies are of considerable interest for a variety of practical applica-

tions. Considerable efforts have been made to control the morphologies of mesoporous materials.<sup>[9-11]</sup> One-dimensional mesoporous materials<sup>[12-16]</sup> such as tubes and fibers have received considerable attention due to their potential applications as waveguides,<sup>[12a]</sup> laser materials after doping with dyes,<sup>[12b,d]</sup> and high capacity enzyme immobilization support.<sup>[13b]</sup> A range of methods, such as interfacial growth at a water-oil interface,<sup>[12a,b]</sup> addition of an inorganic salt,<sup>[13a]</sup> one-phase route,<sup>[12f]</sup> spinning,<sup>[15]</sup> and templating one-dimensional materials,<sup>[16]</sup> have been used for the preparation of mesoporous tubes and fibers. Recently, membrane template-directed synthesis has been extended to prepare tubes and fibers of mesostructured silica and silica-titania materials.<sup>[17]</sup> However, until now, PC membrane templates have not been used to construct tubes and rods of mesoporous materials. The main advantages of using PC membranes over alumina membranes<sup>[17]</sup> for preparation of tubes and rods of mesoporous materials are:

- 1) Using alumina membranes can give rise to aluminum-based side reactions during the coating and calcination steps; these reactions are prevented by the use of PC membranes.
- 2) Both PC membrane template and the surfactant can be removed in one step by calcination in this work, but the removal of the alumina membranes usually takes place by dissolving in acidic or alkali solution in a separate step after calcination.

In this paper we report templating polycarbonate (PC) membranes to produce mesostructured silica tubes and rods. The uniformity control of the morphologies is achieved by the template-directed synthesis.

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## Results and Discussion

The preparation procedure (Figure 1) of the tubes involves the following steps:

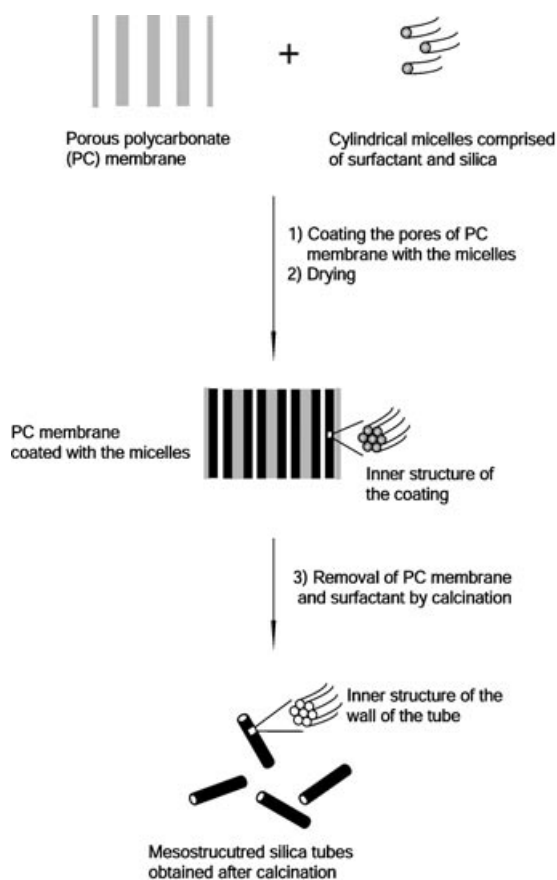


Figure 1. The scheme of the procedure used for preparing mesoporous silica tubes by templating polycarbonate membrane.

- 1) Preparation of silica sol by using nonionic block copolymers as a supramolecular template. The silica sol used for deposition on the cylindrical pore wall surfaces of the PC templates is prepared by the addition of an alcoholic solution of the nonionic surfactant poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>; Pluronic P123) to a prehydrolysed silica sol. The surfactant allows regulation of the porosity and structure of material formed.<sup>[18]</sup> The solution composition and the amount of Pluronic P123 added may be chosen to produce a mesoporous film with the desired phase morphology. Herein hexagonal mesostructures were expected.
- 2) Deposition of the silica sol onto the cylindrical pores of the PC membrane templates by soaking the templates into the sol. The PC membrane used as template in this work contains tubular pores with average diameter of 400 nm and a pore depth of 10 μm. The surface of the membrane is hydrophilic to facilitate the adsorption of the silica sol.<sup>[19]</sup>

- 3) The silica sol adsorbed onto top and bottom surfaces of membrane was removed by adsorption onto filter paper, and the sol was also partly removed from the pores in this case.
- 4) Gelation of the deposited sol on the membrane to form a mesoporous silica film on the pore wall surface of the membrane.
- 5) Calcination to remove the PC membrane templates and the block copolymer species and increase cross-linking of the inorganic framework, which results in the formation of mesoporous silica tubes.

Rods are formed by using silica sol with lower amount of ethanol relative to that used in the preparation of tubes and omitting the silica sol extraction step, which results in fully filling of the pores.

Figure 2a and b show SEM images of mesoporous silica tubes and rods, respectively, prepared in PC membranes with a pore diameter of 400 nm and pore depth of 10 μm.

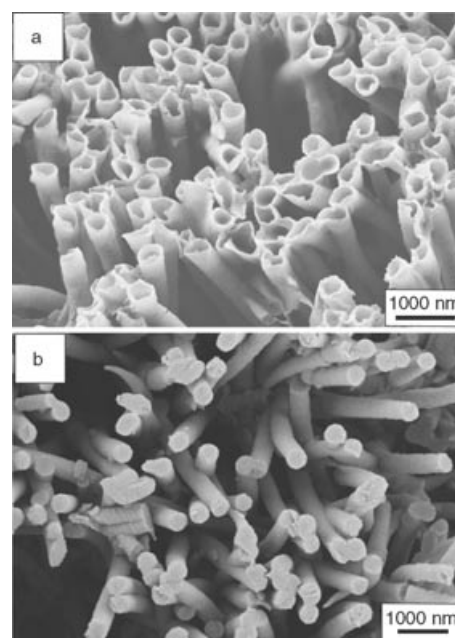


Figure 2. SEM images of mesoporous silica tubes (a) and rods (b) obtained by templating polycarbonate membranes.

The samples show tubular and rodlike morphologies. The rodlike morphology is further confirmed by observation of broken rods (Figure 2b). The tubes and rods shrink by about 15% in length after calcination relative to the thickness of the PC membrane templates. However, shorter tubes and rods are also observed, because some cylindrical pores in the PC membranes do not pass through the whole thickness of the membrane. Alternatively, the tubes and rods may have broken during the process of sample preparation, sonication, or drying stages. The outer diameters of the tubes are around  $350 \pm 65$  nm, thus showing about 15% shrinkage relative to the pore diameters of the PC membranes. The variation in the actual pore diameters of the PC membranes is up to 20%,<sup>[19]</sup> in agreement with our experimentally deter-

mined range. Another reason for deviation in the outer diameters is that individual pores are not uniform in diameter throughout the entire membrane template. This can be visualized by close inspection of the tubes and rods (Figure 2).

Nitrogen sorption isotherms (Figure 3a) of calcined mesoporous silica tubes show type IV behaviour, with type H1 hysteresis loops for a typical mesoporous material with one-

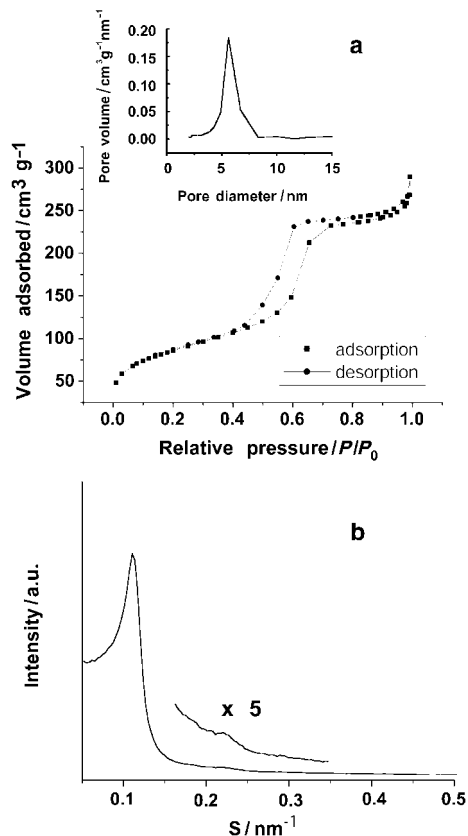


Figure 3. N<sub>2</sub> adsorption and desorption isotherms (a), pore size distribution (inset of a), and small angle X-ray diffraction (XRD) patterns (b) of the mesoporous silica tubes after calcination.

dimensional cylindrical channels. The sample has a pore size of 5.8 nm from the adsorption branch by the Barrett–Joyner–Halenda (BJH) model, a Brunauer–Emmett–Teller (BET) surface area of 311 m<sup>2</sup>g<sup>-1</sup>, and a pore volume of

0.46 cm<sup>3</sup>g<sup>-1</sup>. The surface area is lower than that of hexagonal mesoporous silica materials (SBA-15) prepared by templating the surfactant P123.<sup>[12f]</sup>

The small angle X-ray diffraction (XRD) pattern of mesoporous silica tubes after calcination is shown in Figure 3b. Two peaks are observed in the pattern that can be assigned to the (100) and (200) reflections of the two-dimensional hexagonal space group (*p6mm*), similar to that observed for SBA-15.<sup>[18]</sup> The intense (100) peak reflects a *d* spacing of 8.9 nm, corresponding to a cell parameter *a* of 10.3 nm ( $a = d(100) \times 2\sqrt{3}$ ).

The tubular morphology and mesoporous structure of the calcined tubes were examined by TEM. Figure 4 shows the TEM images of mesoporous silica tubes. The tubular structures are demonstrated by the TEM image of the ends of the tubes (Figure 4a). The TEM images show ordered stripe structures, and “dot” patterns at the edge of the tubes (Figure 4a, b), indicating that the pore channels may run circularly around the longitudinal axis of the tubes. However, the circular channels are not always strictly perpendicular to the longitudinal axis of the tubes in some tubes (pictures not shown). Hollow tubular morphology and circular channels are further confirmed by the microtomed section of the tube (Figure 4c).

Figure 5 shows TEM images of mesoporous silica rods (b and c are images taken on microtomed thin sections of the rods). The TEM image in Figure 5a of the rod clearly shows hexagonal pore arrays. Rodlike morphology is confirmed in the images of the microtomed thin section of the rods, in which ordered stripes perpendicular to the longitudinal axis of the rod are observed. However, “dot” patterns are also observed (Figure 5c); these patterns may be explained by deviation of the orientation of the stripes in some rods or different sections of a rod from the direction perpendicular to the longitudinal axis. Hexagonal pore arrays are observed from the microtomed longitudinal cross-sections parallel to the axis of rods (picture not shown), which is similar to the image shown in Figure 5a. The mesoporous fibers prepared from two- and one-phase routes,<sup>[12]</sup> and templating porous alumina membranes<sup>[17]</sup> have the mesopore channels running circularly around the fiber axis. Similarly in our experiments the mesopore channels of the tubes run circularly around the tube axis. However, the mesopore channels of the rods show different arrangement from that of the tubes, with or-

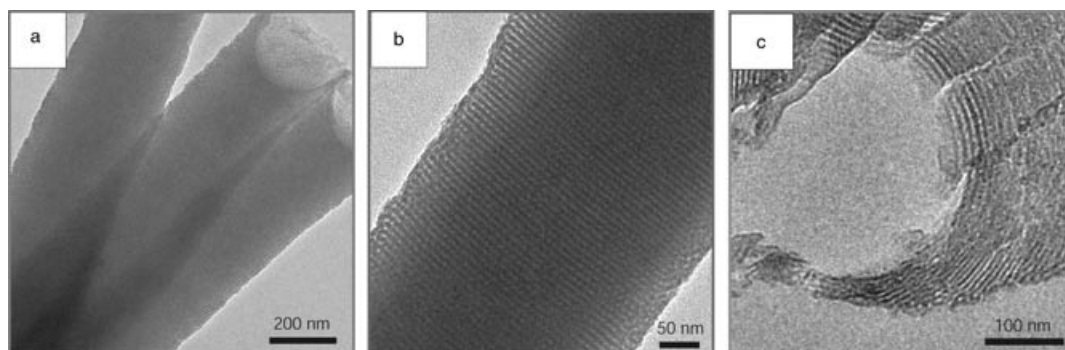


Figure 4. a–c) TEM images of the mesoporous silica tubes; c) microtomed section.

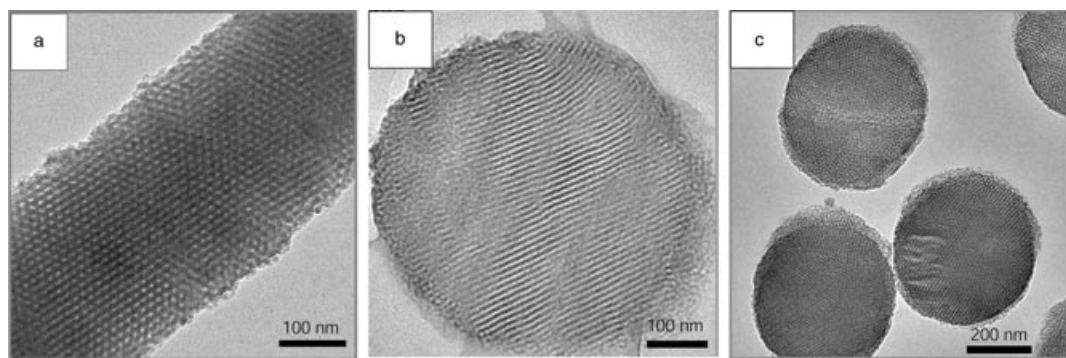


Figure 5. a–c) TEM images of the mesoporous silica rods; b,c) microtomed section.

dered stripes or “dot” patterns found on the microtomed thin sections of the rods.

## Conclusions

In summary, this paper presents an extension of membrane template-directed synthesis to prepare mesostructured silica tubes and rods by deposition of a prehydrolyzed silica sol with surfactant onto the cylindrical pores of polycarbonate (PC) membrane templates, followed by calcination to remove the surfactant and membrane template. The mesopore channels of the tubes are aligned circularly around the longitudinal axis of the tubes. However, the mesopore channels of the rods show different arrangement from that of the tubes, with ordered stripes or “dot” patterns found on the microtomed thin sections of the rods. These tubes and rods might find application in separation processes, drug delivery, and protection of biological active macromolecules. The primary advantage of this approach to mesoporous tubes and rods synthesis is that uniformity control is determined by the templates for which high-quality samples are routinely available. The technique described here can be extended to prepare various oxide mesoporous tubes and rods with controlled size and structural properties. It has shown the possibility to extend the technique to prepare mesoporous titania tubes with ordered pore arrays.

## Experimental Section

**Materials:** PC membranes with a pore diameter of 400 nm and a maximum pore length of 10  $\mu\text{m}$  were obtained from Millipore. The non-ionic surfactant poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$  (Pluronic P123), tetraethyl orthosilicate (98%), hydrochloric acid, and ethanol were obtained from Aldrich. The water used in all experiments was prepared in a three-stage Millipore Milli-Q plus 185 purification system and had a resistivity higher than 18.2  $\text{M}\Omega\text{cm}$ .

**Preparation of silica sol:** The silica sol used for deposition on the cylindrical pore wall surfaces of the PC templates were prepared by the addition of a solution of Pluronic P123 in ethanol to a prehydrolyzed silica sol. First tetraethyl orthosilicate (TEOS) was prehydrolyzed in an acidic water/ethanol solution. Specifically TEOS was mixed with ethanol (EtOH), and then dilute hydrochloric acid was added with stirring at room temperature. The molar ratio of the reaction mixture was TEOS/

$\text{H}_2\text{O}/\text{HCl}/\text{EtOH}$  1:6:0.0089:5.2. After reaction for 30 min, Pluronic P123 dissolved in EtOH was added to the prehydrolyzed silica solution at room temperature. The final molar ratio was  $\text{TEOS}/\text{P123}/\text{H}_2\text{O}/\text{HCl}/\text{EtOH}$  1:9.5  $\times 10^{-3}$ :6:0.0089: $x$  ( $x=15.0$  and 8.7 for preparation of tubes and rods, respectively). The solution was then aged for 3 h before dipping the PC membrane in.

**Preparation of mesostructured silica tubes and rods:** The PC membranes were soaked into the silica sol for 1.5 h. Sonication treatment at the beginning of the soak was used to help the diffusion of the sol into the cylindrical pores. The silica sol was adsorbed onto the whole surface of membrane (including pore walls, top and bottom surfaces of membrane). The sol deposited on the top and bottom surfaces of the membrane was removed by adsorption onto filter paper, and the sol was also partly removed from the pores in this case. Rods were formed by omitting the silica sol extraction step. The samples were stored at room temperature for 4 days to allow for drying and gelation of the sol. Then calcination was carried out by heating at a rate of  $1^\circ\text{Cmin}^{-1}$  to  $550^\circ\text{C}$  and holding for 5 h to remove the PC membrane template and the nonionic surfactants and increase cross-linking of the inorganic framework. After removal of the PC membrane and the nonionic surfactant by calcination, tubes and rods of mesoporous silica were obtained. The samples for scanning electron microscopy and transmission electron microscopy measurements were prepared by redispersing the samples after calcination in ethanol by ultrasonication.

**Characterization:** Scanning electron microscopy (SEM) was recorded with a JEOL (JSEM 6330 F) instrument operated at an acceleration voltage of 5 kV. SEM samples were sputter-coated with Pt. Transmission electron microscopy (TEM) measurements were performed with a Philips CM12 microscope operated at 120 kV. TEM samples were suspended in ethanol by applying ultrasound methods. The suspension was dropped on copper grids with a thin carbon film for TEM measurements. Ultrathin sections of the tubes and the rods (50 nm in thickness) were sliced with a Leica ultracut UCT ultramicrotome after sonicating the samples in ethanol to redisperse the tubes and rods, and drying and setting them in a LR-White resin. The thin sections were placed onto carbon-coated copper grids. The nitrogen adsorption and desorption isotherms at 77 K were measured by using a Micromeritics Gemini II 2375 Surface Area Analyzer. Powder X-ray diffraction pattern were taken on a Nonius CP 120 diffractometer using  $\text{Cu}_{\text{K}\alpha}$  radiation ( $\lambda=1.54 \text{ \AA}$ ).

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