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Template synthesis of SiO_2 nanostructures

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The preparation of nanofibers of different materials has recently attracted wide attention in view of potential future applications in areas such as photocatalysis, electrochemistry, battery research and enzyme immobilization. There are different concepts of using the pores in nanoporous membranes as templates for preparing nanomaterials [1, 2]. This general template synthesis is an elegant approach for the chemical or electrochemical fabrication of nanostructures, particularly in view of its flexibility to produce nanowires of a variety of compositions. The prepared tubules and fibrils can be composed of conductive polymers [3], semiconductors [4] carbon [5] or other materials. Ceramic nanotubes and nanofibrils have been prepared by electrochemical deposition [6] and by sol–gel chemistry. Lakshmi *et al.* [7] showed the possibility of preparing nanofibrile or tubule TiO_2-, ZnO- and WO_3- arrays by sol–gel processing for future applications such as photocatalysis, electrochemistry and enzyme immobilization.

The sol–gel process is characterized by the hydrolysis and condensation of silicon alkoxides to obtain a sol [8]. Further condensation reactions lead to a three-dimensional network and gelation of the system. The gelation rate normally depends on the molar ratio of silicon alkoxide to water, the silicon alkoxide structure, pH and temperature. In this study, the versatile silica-based system and the dip- and spin-coating technique were used to prepare nanostructured SiO_2 samples by the template method.

Commercial porous alumina membranes with three different pore sizes (nominally with diameters of 0.2 μm, 0.1 μm and 0.02 μm) were used as a template material (Whatman-Anodisk 47). We used sol–gel systems with a relatively fast gelation rate for the pore-filling procedure. In the first step, tetraethoxysilane (TEOS, Aldrich, 98% purity), ethanol, water and HCl were mixed in three different molar ratios (Table I) and stirred for 3 h at room temperature. The systems were adjusted to pH 5.8 using 0.05 M NaOH.

TABLE I Molar ratio of used sol systems

Sol type	TEOS	C_2H_5OH	H_2O	HCl
A	1	10	25	0.004
B	1	8	8	0.004
C	1	4	5	0.004

The pores of the alumina membranes were filled using both spin- and dip-coating procedures. The resulting samples were first dried in air at room temperature, subsequently heated in air at 60 °C for 8 h, then immersed in 1.25 M NaOH for 10–15 min to dissolve the alumina template and finally rinsed in water. Characterization involved infrared (IR) spectroscopy (Nicolet 510 Fourier transformation infrared spectrometer using pressed KBr pellets), scanning electron microscopy (SEM; Jeol 840 A microscope using gold sputtered samples) and ^{29}Si nuclear magnetic resonance (NMR) spectroscopy.

The ^{29}Si MAS NMR spectra of the dried silica gels were recorded on a Bruker MSL 300 at 75.470 MHz using a 7 mm BB MAS-probehead (rotation frequency 5 kHz). For the deconvolution of the spectrum, the Linesim program was used.

Three different sol–gel systems (A, B and C) were studied showing different gel times, defined as the period between pH adjustment and solidification of the sol. The gel times were 180 min for system A (large excess of water and ethanol), 68 min for system B and 33 min for system C (highest concentration of TEOS). It follows that the kinetics of hydrolysis and condensation reactions are different for the systems used.

Both spin- and dip-coating of the sol resulted in homogeneous gel layers on the alumina substrates. After dissolution of the alumina template, the structure of the remaining silica was similar for systems A, B and C.

Fig. 1 shows a SEM image of an uncoated alumina membrane with a pore diameter of about

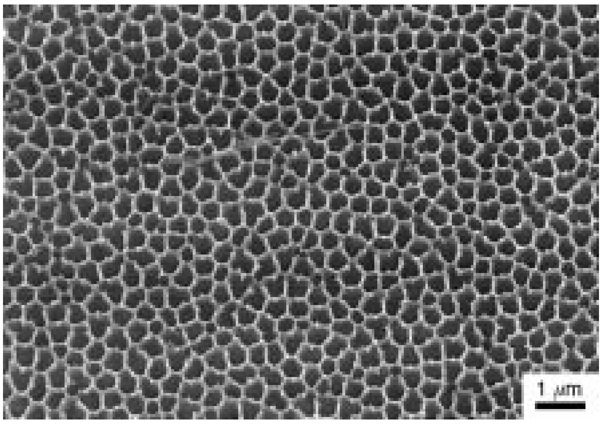

Figure 1 Uncoated alumina membrane (0.1 μm pore diameter).

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0.1 μm. After a partial removal of the alumina (5 min in NaOH) from the coated membrane, an array of closed SiO_2 tubules was observed (Fig. 2, system A).

On the other hand, the complete removal of the membrane (10 min in NaOH) leads to an array of open SiO_2 nanotubules (Fig. 3). In contrast to the tubular structure resulting from the spin technique, the samples prepared by dipping showed a fibril structure comparable with the results reached by Lakshmi *et al.* [7].

IR spectroscopy of the silica sample showed characteristic absorption bands at 788, 954 and 1032 cm^{-1} [9]. The bands at 788 cm^{-1} are attributed to the ring structure of the SiO_4 tetrahedra and the 1032 cm^{-1} band to the Si−O−Si stretching vibration [10]. The 954 cm^{-1} band and the shoulder by 580 cm^{-1} are assigned to SiO^- groups (Fig. 4).

C−H stretching vibrations between 2800 and 3000 cm^{-1} and deformation vibrations (1400–1500 cm^{-1}) are hardly detectable. This points to a small concentration of ethoxy groups in the final gel. The $Si-O^-$ vibration detected at 580 cm^{-1} is probably due to silanol groups. The vibration at 1650 cm^{-1} is attributed to the H−O−H deformation and indicates the presence of incorporated water in the SiO_2 network. OH groups of water and silanol are detectable at 3437 cm^{-1}.

NMR spectroscopy was used to obtain qualitative and quantitative information about the chemical environment of the silicon atoms in the gel, based on characteristic chemical shifts and peak areas (Fig. 5).

The Q^n notation represents silicon atoms bonded to n neighbor silicon atoms via Si−O−Si bonds. Most of the silicon atoms are fully condensed. Only a small number of silanol groups exist in this gel structure in the form of Q^2 and Q^3 groups (Fig. 5). The line-width of the signals is related to the structural uniformity of the corresponding molecular entities, with increasing line-widths indicating more disordered structures. In comparison to glass, the investigated gel structure shows smaller line-widths [11] and therefore greater order.

The combined results of IR and NMR spectroscopy demonstrate that the nanostructures produced by TEOS-based sol–gel techniques within alumina membranes are predominantly composed of SiO_2.

In conclusion, it has been shown that the sol impregnation of submicron-sized alumina membranes followed by gelation of the sol and chemical dissolution of the membrane template can be used to fabricate nanostructured silica.

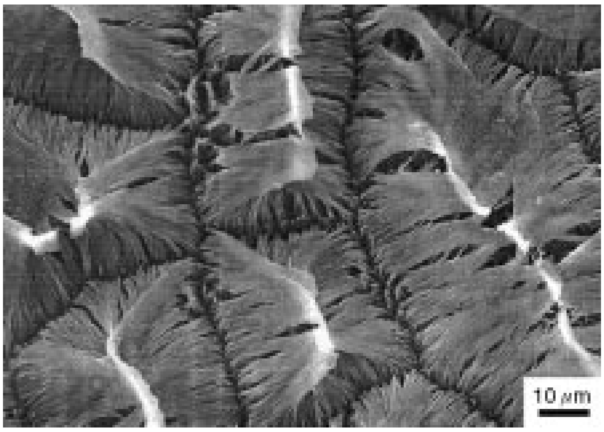

Figure 2 Tubule SiO_2 structure after selective removal of membrane (0.2 μm pore diameter).

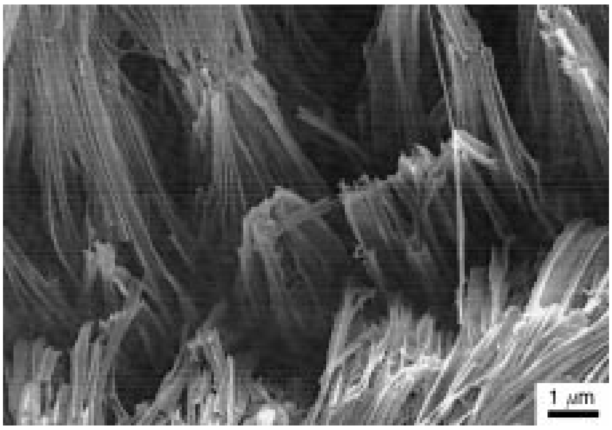

Figure 3 Tubule SiO_2 structure after complete removal of membrane (0.2 μm pore diameter).

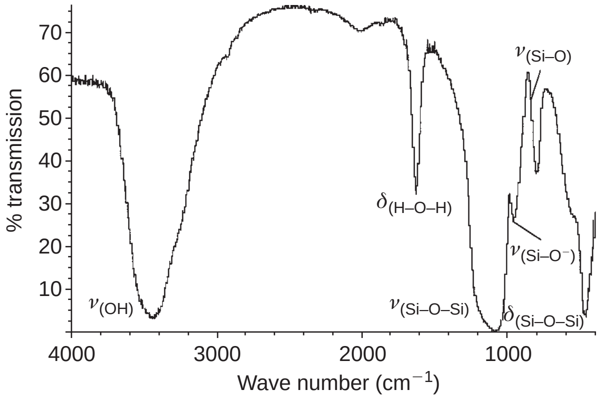

Figure 4 FTIR spectrum of a SiO_2 gel.

	Q^2	Q^3	Q^4
line-width	206 Hz	354 Hz	459 Hz
area	5%	30%	65%

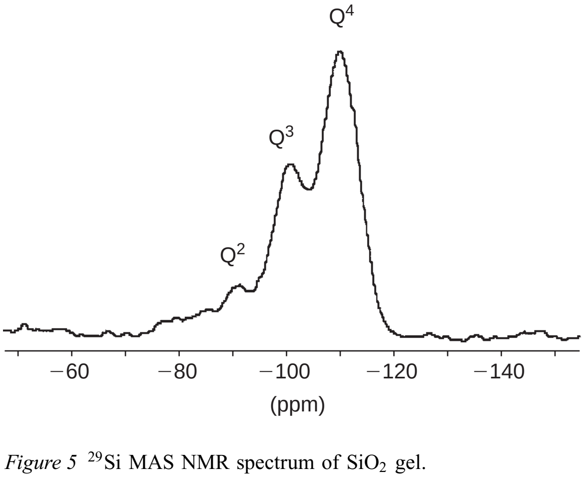

Figure 5 ^{29}Si MAS NMR spectrum of SiO_2 gel.

Acknowledgment

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