Structural Control of Mesoporous Silica Nanowire Arrays in Porous Alumina Membranes

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Progress in the synthesis of size-controlled nanomaterials has enabled a better understanding of the size-dependent electrical, optical, and magnetic properties of individual nanostructures of semiconductors,[1−3] metals,[4,5] and other materials.[6,7] Beyond size control in the preparation of nanomaterials, the greater challenge is to control the assembly of individual nanoparticles (or nanowires, etc.) into hierarchically structured architectures so that their position in a complex matrix is determined. This is especially true in the case of one-dimensional nanomaterials or so-called nanowires/nanorods (particles with lengths much greater than width, i.e., large aspect ratio) so as to avoid complex entangled structural arrangements. It might be imagined that material functionality demands that it is necessary to assemble individual one-dimensional nanomaterials into unidirectional arrays or regular patterns. One simple and promising strategy to achieve this aim is to synthesize a desired material within host materials that possess well-ordered nanospaces, so-called template synthesis.[8] To date, mesoporous silica[9−13] and anodic aluminum oxide, AAO,[14−18] porous membranes are two materials which have been successfully employed as hosts in synthesizing ordered arrays of nanomaterials. In our laboratories it has been shown that highly crystalline and dense arrays of semiconductors, metal, and oxide nanowires can be obtained as bulk materials and thin films[11−13] and that the nanowires formed have low resistance electrical conductivity.[19] Mesoporous silica has smaller pore sizes than AAO and so may offer advantages in terms of quantum size effects and property control. However, AAO is relatively easily prepared to provide pores of well-defined orientation that are relatively easily filled (because of larger sizes) and it might be imagined that it could be more easily integrated into current sensor or electronic devices as progression of current silicon technology.[17] One method of using the advantages of both materials is the combination of AAO with mesoporous silica to form new hierarchical structures. Of particular interest is the formation of composites in which the mesopores of the silica are aligned parallel to the channels of the alumina framework. It is our intention to eventually fill the mesopores with desired materials to form unidirectional nanowire arrays whose density could be up to 10^{12} per cm^2 with a uniform diameter over several nanometers. It is also possible to selectively dissolve the AAO matrix to release ordered mesoporous silica nanowires. These porous silica nanowires are of interest per se because of interest in these materials as light guides, catalysts, and light emitters.[20]

To the best of our knowledge, Yang et al. first reported the filling of mesoporous silica within commercially available porous alumina membrane.[21] Their process involved modification of the alumina pore surface resulting in a concentric circular morphology. Recently, Teramae et al. [22] reported the filling of mesoporous silica (MCM-41) in porous alumina with the silica mesopores oriented parallel to the alumina host pores. However, the well-ordered silica mesopores near the alumina pore wall became less ordered in the interior of the pore. Herein, we report the preparation of highly ordered 1D mesoporous silica nanostructures within porous anodic alumina membranes using a simple sol−gel method that is applicable to large-scale synthesis. The morphology of the 1D mesoporous silica, either nanotubes or nanowires, can be controlled depending on the aging process employed. More importantly, the orientation of the mesopores within the alumina membrane can be controlled by varying the aging environment.

The one-dimensional mesoporous silica nanostructure arrays were prepared via a simple sol−gel and rotary

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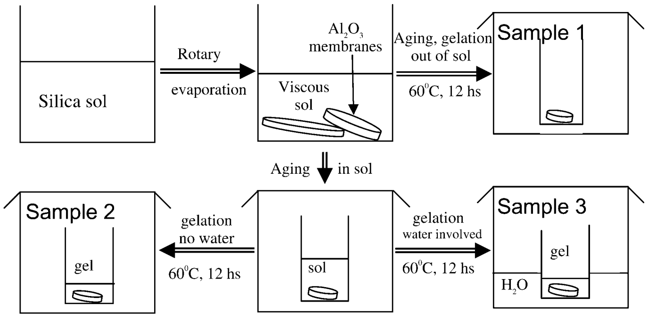
Scheme 1. Preparation Process for Controlled One-Dimensional Mesoporous Silica Nanostructure Arrays within Porous Alumina Membranes



evaporation method by using tetraethoxysilane (TEOS) as a silica source and poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer surfactants (BASF, Pluronic P123) as the structure-directing agent. Commercially available porous anodic alumina membranes (Whatman, Anodisc 25, pore diameter 200 nm, thickness 60 μm) were used as the substrate and they were not treated or modified in any way. In brief, TEOS (10.4 g), absolute ethanol (25 g), and HCl (acid catalysts and primary water source, 1 g of 1 M HCl solution) were mixed together in the presence of P123 (5 g).[23] The resultant mixture was stirred at 37 °C for 10 min to form a clear solution. The alumina membranes were immersed in the as-prepared sol and all of the volatile solvent was removed in vacuo using a rotary evaporator at 40 °C for approximately 25 min (Scheme 1). This was necessary to ensure complete filling of silica sols into the pores of the alumina membrane and to reduce the time needed for gelation. PXRD data were collected on a Panalytical Expert MPD system with an Accelerator detector. A Cu Kα X-ray source at 40 kV and 40 mA was used. Incident and exit Stöller slits were used to maintain parallel beam geometries. Scanning electron microscopy (SEM) data were collected on a JEOL 5500 system at 25 kV beam energy. Transmission electron microscopy data were acquired using a JEOL 2000FX TEMSCAN at 200 kV beam energy. For detailed imaging of the silica nanowires and nanotubes formed in these reactions the AAO membrane was removed using 5 M HCl and the silica materials were collected by filtration.

Aging (i.e., the conditions where hydrolysis and condensation of the TEOS occurred) regimes were explored for their effect on the composite materials and three materials were prepared (see Scheme 1). In the first instance the membranes were placed in the viscous sol formed by partial solvent removal described above for 30 min and then removed. The composite membrane materials so-formed were sealed and aged at 60 °C for 12 h (designated sample **1**). The effect of aging the samples within the sol was also investigated. This was achieved by allowing the membrane to remain in the viscous sol, sealing the container, and aging at 60 °C for 12 h, to yield sample **2**. The water composition in the precursor silica sol was not enough in sample **1** and **2** preparations for the complete hydrolysis of TEOS and, therefore, the effect of water content on the aging process was explored by sealing the viscous sol with alumina membranes in a beaker containing sufficient water for complete hydrolysis and aged at 60 °C for 12 h to yield sample **3**. For all three procedures, the silica-filled alumina composites were subsequently calcined at 500 °C for 6 h.

Figure 1 shows SEM images of the as-prepared samples. Sample **1** (i.e., membranes removed from the sol and then aged) revealed the presence of tubular structures that can be clearly observed from Figure 1a (top view) and c (side view). In contrast, denser structures (at this magnification) with rod or wire-like appearances in Figure 1b (top view) and d (side view) are characteristic of samples aged in the sol (typical data shown here from sample **2**). Space between the alumina pore wall and the silica wire or tube was always observed and can be clearly seen in all images in Figure 1. This indicates that the silica gels within the alumina pores have undergone contraction during the drying and calcination processes. The volume contraction is between 5 and 15% in all cases and consistent with the densification expected for these sol−gel precursors. Teramae et al. stated that contraction of the gels occurred in a direction parallel to the alumina pores.[22] It is clear from our work that shrinkage occurs primarily in a direction perpendicular to the AAO pores with void space being created at the silica−alumina interface and internal to the silica nanotubes. This seems more likely as it might be expected that the sol−gel has some chemical affinity with the pore wall, so preventing large scale shrinkage in the vertical direction. However, the observation of this shrinkage phenomenon suggests that the silica strain energy imparted by reaction and calcination exceed any chemical interaction between the alumina pore walls and the silica gels within them. This does not imply that the silica−alumina interface has no chemical affinity, indeed the results suggest the opposite. In the case of the materials obtained externally, i.e., remote from the mother sol, well-defined tubes are formed. This suggests that during condensation of the silica moieties, shrinkage occurs internally (from pore wall center inward) because of a strong interaction of the densifying sol with the AAO pore walls. Separation from the AAO pore wall is more likely to occur during rapid densification during calcination. This assumption is reached as tube-like entities are not observed from in-sol aging, the obvious conclusion being that capillary forces resulting from shrinking and tube formation fill the void space leading to dense systems. As no sol is present during calcination, the void space around the wire cannot be filled. As a result of these conclusions, it might be implied that the microstructure of the silica gels inside the alumina pores should possess a structure similar to that of the mother gels (i.e., show well-ordered mesoporous structures) as they are “remote” from the pore wall during high-temperature densification (see below).

TEM images of the silica nanomaterials prepared in this way and then removed from the alumina matrix by hydrochloric acid (Figure 2a and b) further confirm the nanotubular and solid nanowire-like structure characteristics for samples aged out of, and in the sol, respectively. It is worth noting the branching observed

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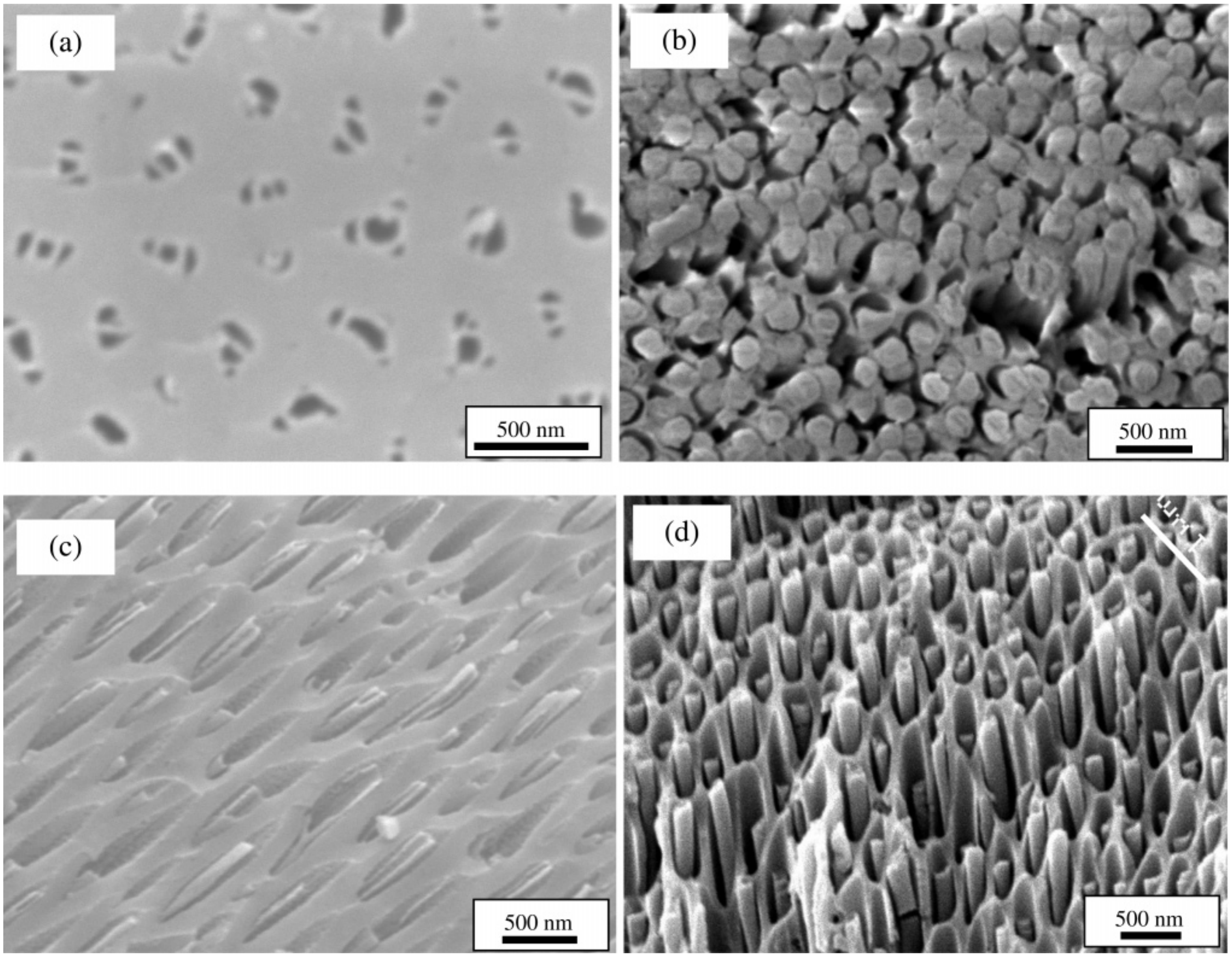

Figure 1. SEM images of one-dimensional mesoporous silica nanostructures within alumina membranes: (a) top view and (c) side view of silica nanotubes from samples aged remote to sol (Scheme 1, sample **1**); (b) top view and (d) side view of silica nanorods from samples aged in sol (Scheme 1, sample **2**).

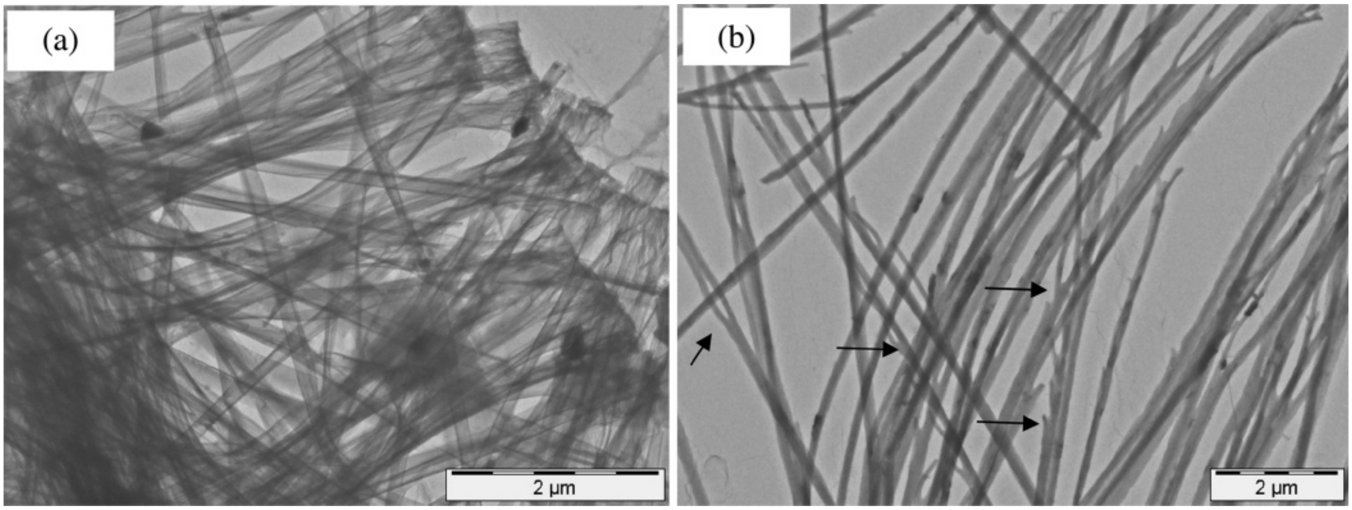

Figure 2. TEM images of (a) silica nanotubes from samples prepared by aging remote to sol (sample **1**), (b) silica nanorods prepared from samples aged in sol (sample **2**). Silica materials removed by AAO dissolution and arrows mark junctions where wires apparently branch.

in some nanowires (see arrows in Figure 2b) which appear to represent “negative” or reverse images of these AAO samples. These data therefore suggest that the methodology employed has ensured full filling of any void space in the alumina membranes.

The nanowires formed by the “in-sol” aging have a well-defined hexagonal arrangement of silica mesopores, evidence for which is provided by powder XRD and TEM. Since it was not possible to obtain PXRD data for the filled alumina membranes, the mother gel was

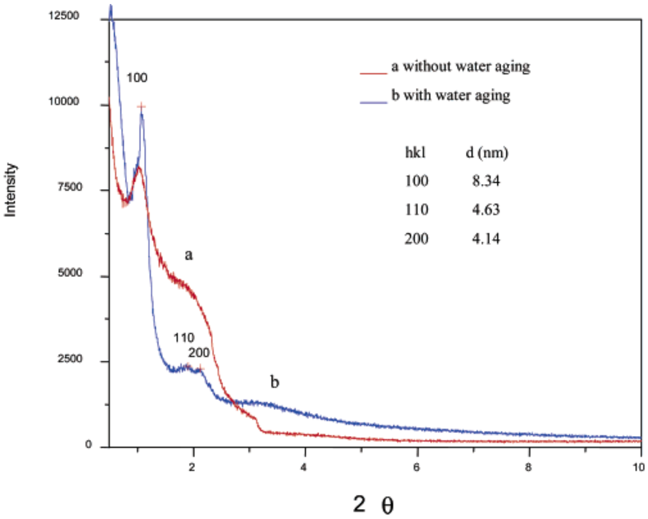

Figure 3. Small-angle XRD patterns of (a) mother gels without water and (b) with water treatment.

analyzed and typical data are shown in Figure 3. For sample **3** (i.e., with the additional water present) good XRD features typical of highly ordered, hexagonally arranged mesoporous silica (SBA-15) can be observed. These are assigned in the figure to the usual (100), (110), and (200) reflections. The (100) *d* spacing is determined at 8.3 nm. In contrast, for sample **2**, with no additional water, only one peak corresponding to the (100) plane of the 2-dimensional hexagonal structure SBA-15 can be identified. The big difference of the XRD results between samples **2** and **3** indicates that additional water treatment during the aging process does affect the structure of the mesoporous silica obtained.

The mesoporous structures are further confirmed by high-magnification TEM and typical data are shown in Figure 4. The images were all obtained by viewing down a direction perpendicular to the longitudinal rod axis. Figure 4a and b relate to sample **2**; only parallel stripes along the longitudinal rod axis can be observed with a periodic spacing of around 8.6 nm (within experimental error this is equal to the PXRD determined (100) *d* spacing of its mother gels). For sample **3** (Figure 4c and d), direct observation through the central part of the wire reveals a parallel pore arrangement with spacing equivalent to the $d_{(100)}$ = 8.6 nm value. At the edges of the wire, the truly hexagonal arrangement of pores can be observed due to the sloping edge of the wire. The pore-to-pore distance of around 10 nm is consistent with a value predicted from the $d_{(100)}$. On the basis of the PXRD and TEM data it is concluded that pore channels of the as-prepared silica nanostructures can be parallel or perpendicular to the longitudinal axis of the AAO pores for samples without and with water involved in the aging procedures.

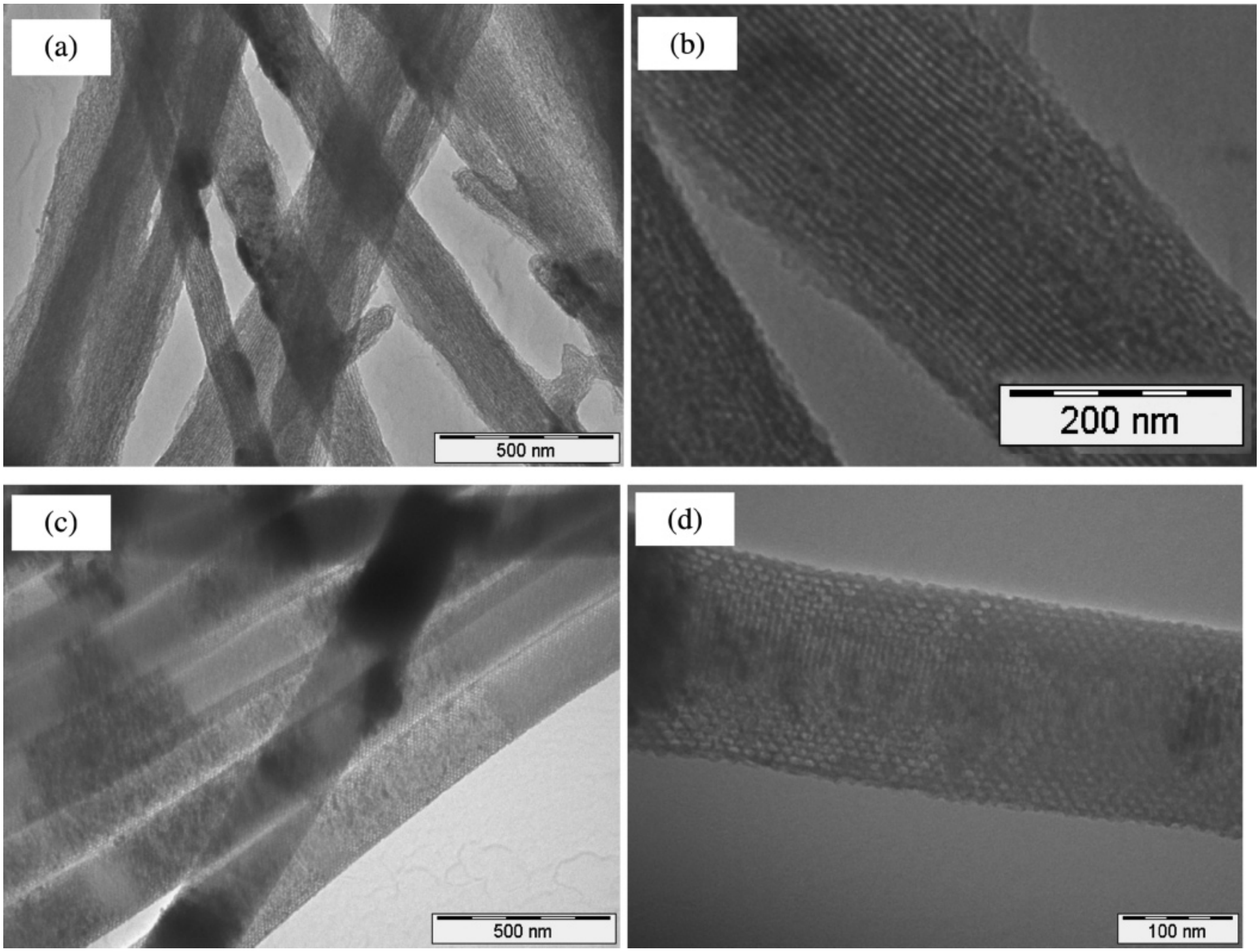

Figure 4. TEM images of mesoporous silica nanorods with mesopores' channel parallel (a and b) and perpendicular (c and d) to the long axes from samples without water (Scheme 1, sample **2**) and with water (Scheme 1, sample **3**) treatment.

Thus, the work here suggests that hydrolysis rates (clearly dependent on water concentration used) have a strong impact on silica mesopore orientation. This is interesting considering work reported by Martin et al. indicates very rapid condensation and gelation take place in the pores of porous alumina for titania sol.[24] However, it is likely that the presence of the surfactant is responsible for this and merits further investigation. SBA-15 rods with pore channels parallel to the longest axis have been successfully synthesized under acidic synthesis condition in free spaces.[25,26] For films, pores are usually parallel to the extended film surface.[27] It thus seems surprising that pores can be observed that preferentially align perpendicular to the long AAO pore direction. Various authors have reported vertical alignment of pores (i.e., perpendicular to the surface) in thin films due to rapid solvent evaporation.[27] On the basis of this argument we tentatively suggest that the gelation rate has a significant bearing on the pore orientation of the mesoporous silica inside of the alumina membranes. The slow gelation process (sample **2**) allows the silica mesopores to align parallel to that of the alumina membranes; while for sample **3,** gelation should be more rapid due to very rapid and complete hydrolysis of TEOS prompted by the additional water treatment. In the latter case the kinetics of the reaction prevent very long range ordering (required by the parallel arrangement of silica mesopores over the whole AAO thickness) and instead local ordering (requiring less mass transport) of pores perpendicular to the AAO pore wall provides an achievable energy minimum.

In summary, controlled one-dimensional mesoporous silica nanotubes and nanowires inside porous alumina membranes can be fabricated via a simple sol−gel rotary evaporation route. The aging environment determines whether nanotubes or nanowires can be obtained. The orientation of the mesopores can be readily controlled so as to produce composites with pores in directions parallel to or perpendicular to the channels of alumina membranes. With such controlled structure characteristics, the as-prepared one-dimensional mesoporous silica nanostructure can be further utilized to incorporate other desired materials within the mesopores with the intention of forming functional and operational nanocomposites. It is emphasized that this is a simple, wet chemical means of producing very well ordered nanostructures. The methods are easily scaleable so as to facilitate mass production of these potentially important materials.

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