

Experimental

Sample Preparations: Multilayers of PDADMAC ($M_w = 200\text{K}–350\text{K g/mol}$, Aldrich), and PSS ($M_w = 70\,000\text{ g/mol}$, Aldrich) were deposited onto silica colloids (Snowtex, nominal diameter 70–100 nm). 3 g of silica colloid, previously dried for 12 h at 400 °C, was dispersed in 500 mL of a polymer/salt solution, comprised of 0.02 M PDADMAC and 0.1 M NaCl in Millipore Q water. This adsorption solution was left standing for 30 min, then centrifuged at 4300 rpm and the supernatant was removed. 500 mL water was added and the solution was sonicated and centrifuged. The supernatant was then removed to rinse the unadsorbed polyelectrolyte from the colloids. A total of three 500 mL washings were performed after the adsorption of each polymer layer. A small amount (~50 mg) of the coated colloid was then removed for characterization and dried at 65 °C for 12 h prior to measurement. The remaining colloid was then dispersed in 500 mL of a similar solution of the oppositely charged polymer (0.02 M PSS and 0.1 M NaCl), and the adsorption and washing steps repeated, until two layers of PDADMAC and two layers of PSS had been sequentially deposited. An insoluble PEC for reference was prepared by adding 2 mL of 20 wt.-% PDADMAC aqueous solution slowly to 200 mL of a 0.01 M PSS solution, under vigorous stirring. A precipitate formed immediately as a thick milky suspension in solution. This solution was centrifuged, and the supernatant removed by pipette. To remove uncomplexed polyelectrolyte, the complex was then washed with water, agitated to disperse, and centrifuged again as described for the colloids, for a total of three washings.

ζ -Potential Measurements: 30 mg of each dried colloid sample was suspended in 15 mL of 1 mM NaCl solution. The pH of each solution was found to be in the range of 7.4 to 7.7 for the multilayered samples, and 8.2 for the bare silica colloid. Electrophoretic mobilities were measured on a Microelectrophoresis Apparatus Mk II (Rank Brothers, Bottingham) and converted to ζ potentials using the Smoluchowski equation.

NMR Measurements: ^{13}C CP MAS NMR of the carbon spectra were recorded on a Chemagnetics CMX-300 spectrometer for the colloid coated with four layers, the precipitated complex, and both bulk polyelectrolytes. A total suppression of sidebands (TOSS) sequence with background suppression, a spinning speed of 3 kHz, and a contact time of 500 μs were used. Single- and double-quantum ^1H MAS NMR spectra were acquired either on a Bruker ASX500 or DRX700 spectrometer equipped with a 2.5 mm fast MAS probe.

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Silica Nanotubes and Nanofiber Arrays**

By Zhong L. Wang,* Ruiping P. Gao, James L. Gole, and John D. Stout

The synthesis of one-dimensional nanostructures is of fundamental importance to nanotechnology. Nanowires are particularly interesting as they offer the opportunity to investigate electrical and thermal transport processes in size-confined systems, with the possibility of providing a deep understanding of physics at the nano-scale. Silicon and silica nanostructures have attracted considerable attention because of their potential application in mesoscopic research, the development of nanodevices, and the potential use of large surface area structures for catalysis.^[1] Recently Lueber,^[2] Lee,^[3] Yu,^[4] Korgel,^[5] and co-workers have extrapolated on the vapor-liquid-solid (VLS) technique^[6] employing variants of laser ablation and high-pressure synthesis to produce silica-sheathed crystalline silicon nanowires. Lee et al.^[3] have shown that oxides play a dominant role in the nucleation and growth of these semiconductor nanowires by laser ablation, thermal evaporation, and chemical vapor deposition. Lieber et al.^[7] have used catalyst-initiated growth to synthesize silicon-carbon nanotube heterojunctions. Zhu et al. have recently grown silica “nanoflowers”.^[8] We^[9] have applied the techniques of high temperature synthesis to modify the approach of Lee et al.^[3] and generate virtually defect-free SiO_2 -sheathed crystalline silicon nanowires and silica (SiO_2) nanospheres which can be agglomerated to wire-like configurations impregnated with crystalline silicon nanospheres. Side-by-side biaxial nanowires of SiO_2 -SiC have also been synthesized.^[10] In the present report, we demonstrate that this nanoagglomeration can be extended to produce SiO_2 nanowire “bundles” and “brush-like” arrays. The growth appears to be dominated by vapor-phase processes, as the oxides can form a variety of interesting new nanostructures including silica nanobrushes and nanotubes.

The growth of the silica structures initiates from nanofibers composed of tiny amorphous particles. Aligned fiber arrays appear to grow from a single or biaxial nanofiber (Fig. 1a), and have a structure similar to a protozoa and its “flagellum”. The width of the bundle is 300–500 nm. We observe that, after reaching a certain length, the silica fibers in the interior of the bundle cease growth while those in the outer regions continue to grow, forming a cylindrical chamber. Energy dispersive X-ray spectroscopy reveals small crystalline Si nanoparticles

[*] Prof. Z. L. Wang, R. P. Gao
School of Material Science Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332-0245 (USA)
Email: zhong.wang@mse.gatech.edu
Prof. J. L. Gole, J. D. Stout
School of Physics
Georgia Institute of Technology
Atlanta, GA 30332-0430 (USA)
E-mail: james.gole@physics.gatech.edu

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impregnated in the silica cylinder. Further growth of the nanofibers forms a larger silicon (EDS) wire-like structure. The wire-like Si grows along the [110] direction. In some cases, Si nanowires sheathed by a silica layer can be extensive (Fig. 1c) as the growth direction remains [110]. The diameter of the Si core is ~60 nm, and the thickness of the silica sheath is ~20 nm.

We have also observed the surprising growth of silicon nanotubes. The initiation of nanotube growth appears to involve seeding by silicon particles along the growth direction. Figure 2a depicts the growth of the silica nanotubes between silicon particles which may also impregnate the tubes. The image displayed in Figure 2b suggests that a Si particle is located at the area that links the aligned nanofibers and the silica nanotube. The outer diameter of the tube is ~70–80 nm and the wall thickness is ~20 nm. It is possible that the Si particle terminates the growth of the nanofibers located inside the bundle, while the outermost fibers continuously grow forming a continuous shell, which constitutes the nanotube. This process is also suggested by the structure shown in Figure 2c, where the formation of a Si particle at the end of a fiber agglomeration again appears to play a key role in the formation of the nanotube. The silica tubular structure can also appear to be “necklace-like” as shown in Figure 2d, where an internal chain-like structure is apparent. The chain-like structure represents an intermediate between the aligned nanofibers and the continuous nanotube. Figure 2e demonstrates a silica nanotube half-filled by a silicon nanowire.

Silica wires can also be made to form a variety of unique three-dimensional structures. Shown in Figures 3a–d are typical cage structures composed of aligned silica nanofibers. The nanofibers grow into bundles, while paralleling a structure that has cylindrical symmetry. The width of the cage is 0.3–1 μm—much larger than the diameter of the silica nanofibers (ex. ~20 nm). These arrays clearly demonstrate the versatility of the silica nanostructures which can be synthesized. In fact, Figure 3e takes the shape of a “Chinese lantern” structure composed of Si and SiO_x, where an SiO_x tube extends from the top of a silica wire bundle.

The nanostructures demonstrated here are dominated by silica forms. Silicon nanocrystals/nanowires are formed in regions that are densely enclosed by the silica nanofibers. The short segment of the Si wire-like structure in Figure 1a is a typical example. This suggests that the growth may be dominated by vapor phase infiltration. In the regions dominated by silica, the local porous structure would appear to permit the diffusion of oxygen and silicon atoms through the material, resulting in the growth of the silica structure. In the regions densely surrounded by silica, the diffusion of oxygen into the structure may be hindered, thus re-

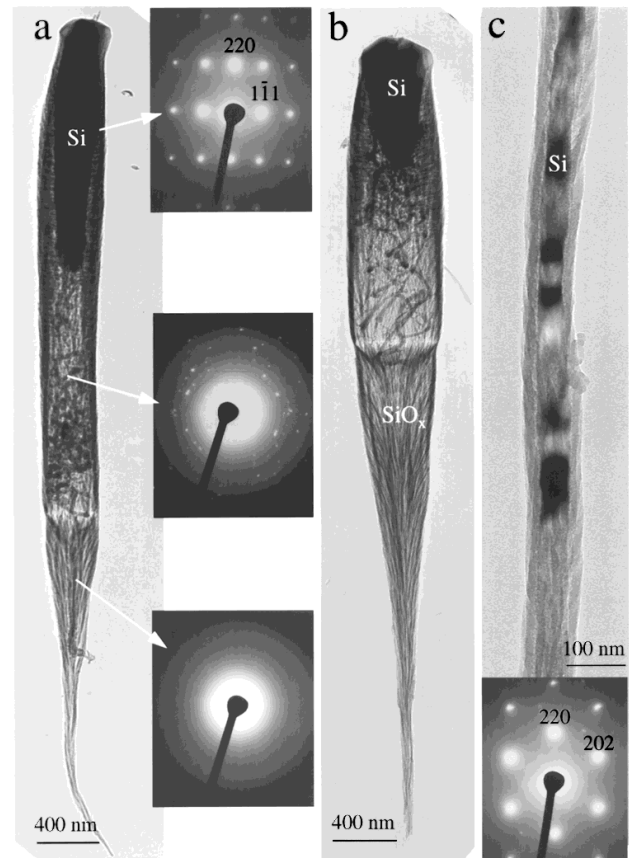


Fig. 1. TEM images of silicon (Si) and silica (SiO₂) nanostructures produced from the pyrolysis of mixed solid Si and SiO₂ powders under nitrogen. Insets are electron diffraction patterns recorded from different segments of the nanostructure, indicating the local crystal structure and growth direction.

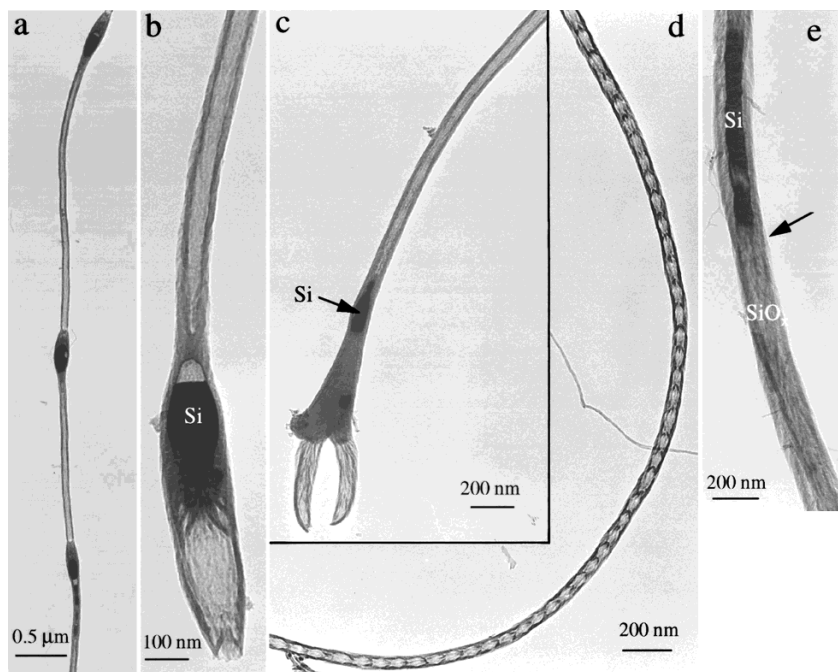


Fig. 2. TEM images of synthesized silica nanotube structures usually formed following the trapping of silicon nanocrystals.

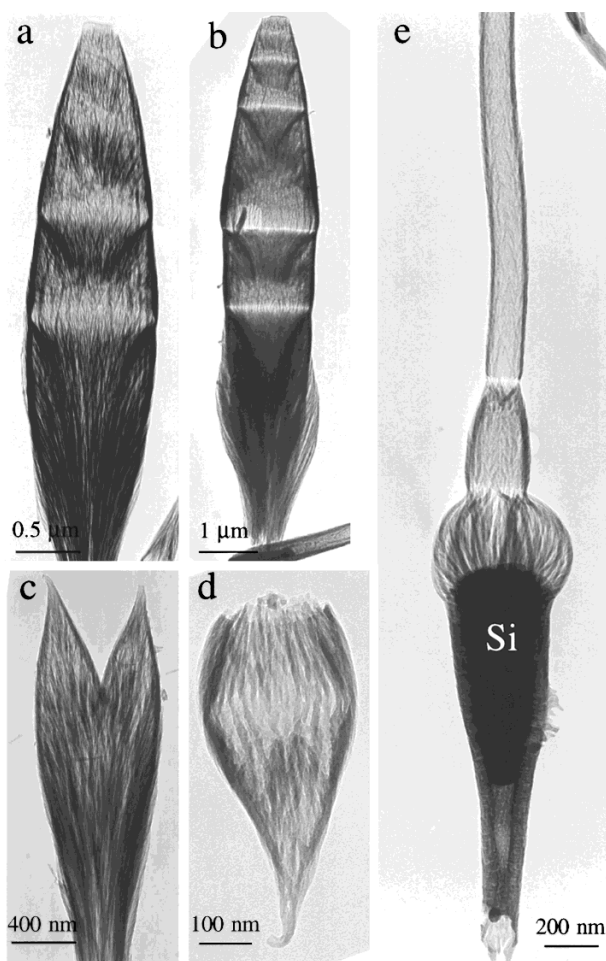


Fig. 3. TEM images of silica “bundled” arrays and cages.

sulting in the accumulation of silicon atoms and the formation of silicon nanostructures. The silicon enclosed by the silica may well be liquid at the synthesis temperature of 1400 °C. An apparent bubble formed next to the silicon particle, as seen in Figure 2b, would suggest this possibility. It seems that the Si particle located at the center may move along the nanotube during the growth, and its trace may result in the formation of the tubular structure.

In summary, a variety of silica nanostructures have been produced by pyrolysis of a mixture of Si and SiO₂. SiO₂ nanowire “bundles” and “brush-like” arrays and silica nanotubes have been synthesized. These structures are unique and they are likely to have applications in catalysis and nanoelectronics.

Experimental

The apparatus used for these experiments has been described elsewhere [9]. Key to the experiments is that the 50/50 Si/SiO₂ equimolar mixture used previously [9] to form crystalline silicon impregnated, wire-like, silica nanosphere agglomerates is heated to a temperature of 1400 °C under a total pressure of nitrogen approaching 950 torr. A double concentric alumina tube (Coors, Vesuvius) combination is heated to the desired temperature in a Lindberg Scientific tube furnace configuration. The inner alumina tube is vacuum sealed by two water-cooled stainless steel end pieces which are attached (Vesuvius–Zyalox Product) to the alumina tube and tightly lock-press fitted against custom viton

o-rings. At one end of the furnace, ultra-high purity (UHP) argon or nitrogen enters through the upstream stainless steel end piece and passes through a matched set of zirconia insulators (Zircar) to the central region of the inner tube oven. Here the entraining argon and/or nitrogen flows over an alumina crucible containing the appropriate Si/SiO₂ mix at a flow rate of 100 sccm controlled by an MKS 2159B flow controller. The total pressure in the inner tube approached 950 torr for both the UHP argon and nitrogen based flows (Barton Differential Pressure Transducer—MKS Instruments Model 220CA-01000A2B Range 1000 torr), controlled by a mechanical pump (Welch 1402) attached to the inner alumina tube through the downstream stainless steel end piece. This end piece is mechanically attached to a “water-cooled” cold plate, whose temperature is adjustable, through a matching set of insulating zirconia blocks. To produce the silicon impregnated silica nanowire “bundles” and “brush-like” arrays the system was operated at a temperature of 1400 °C for 12 h. The parameters controlled in this experiment were 1) gas flow rate, 2) total tube gas pressure, and 3) central region temperature and temperature gradients to the end regions.

Transmission electron microscopy (TEM) analysis was carried out at 200 kV using a Hitachi HT-2000 TEM and 100 kV using a JEOL 100C TEM. The chemical composition of the spectrum was determined by EDS.

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Micromolding in Inverted Polymer Opals (MIPO): Synthesis of Hexagonal Mesoporous Silica Opals**

By San Ming Yang, Neil Coombs, and Geoffrey A. Ozin*

Morphology control of mesoporous silicate materials has stimulated much interest in recent years. Our group, as well as others, have employed different surfactant-templated preparative methods to achieve distinct morphologies of mesoporous silica such as fibers, discs,^[1] hollow helicoids,^[2] toroids,^[3] hollow tubes,^[4] and spheres.^[5] The spherical shape of mesoporous silica inspires special interest in potential applications such as ceramic membranes,^[6] catalyst supports,^[7] and chro-

* Prof. G. A. Ozin, Dr. S. M. Yang, Dr. N. Coombs
Materials Chemistry Research Group
Lash Miller Chemical Laboratories
University of Toronto
80 St. George Street, Ontario, M5S 3H6 (Canada)
E-mail: gozin@alchemy.chem.utoronto.ca

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