

# Synthesis of Mesoporous Silica in Helical Fibers, Vesicle-Like, Film Morphologies by Using Ternary Surfactant System as Organic Template

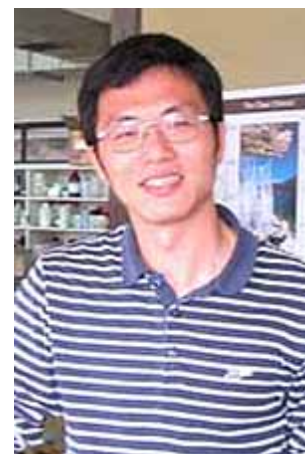
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In nature, numerous spectacular architectures result from the self-assembly of small organic and inorganic building blocks at low concentration into larger macromolecular structures. Recently, much effort has been devoted to synthesize organic-inorganic hybrids with amazing morphologies in order to design and control on the selective preparation of complicated chemical architectures. To mimic silicification in diatoms, using surfactant systems with properties similar to those of phospholipids and highly diluted silica solution as inorganic precursors are desired. Based on the surfactant chemistry, mixture of oppositely charged single-tailed cationic and anionic surfactants produce a very rich variety of aggregate microstructures (e.g., rodlike micelles, vesicles and lamellar) even at high dilution, which can serve both as model biological membranes and as novel organic templates of the mesostructured silica in different remarkable morphologies. Because the surfactant-silica assembly is a form of self-assembly with covalent modification, the morphology is particularly dependent on factors related to reaction kinetics and template behavior, such as the reaction temperature, water content, and pH value of the silica solution. With a well control on the silica condensation rate and surfactant composition, tailoring on the morphology of the mesoporous silica could be achieved.



It is well known that the mesostructural behavior and charge density of cationic and anionic surfactants is dependent on the anionic/cationic surfactant ratio. As the ratio increases to 1.0, phase transformation from rod micelles → vesicles → lamellar phase gradually occurs. These mesostructural surfactants can be used as template or co-template to generate the mesoporous silica in desired form.

At SDS/C<sub>16</sub>TMAB (C<sub>16</sub>TMAB: cetyltrimethylammonium bromide; SDS: sodium dodecylsulfate) weight ratio of 0.135, mesoporous silica helical fibers were obtained from slow silicification of C<sub>16</sub>TMAB-SDS binary-surfactant mixture in a highly-diluted silica solution at pH ≈ 1.5. From low-magnification SEM images, it is clear that the yield of the mesoporous silica helical fiber is high (> 95 %) and the length ranges from tens to few hundred of micrometers (Figure 1). When observing at higher magnification, we can clearly see that the shapes of the helical mesoporous silicas are different including single-helix fibers, double-helix fibers, and triple-helix fibers. The pore size distributions of these samples are sharp and centered at about 3.0–4.0 nm. The BET surface area is around 700–800 m<sup>2</sup> g<sup>-1</sup>.

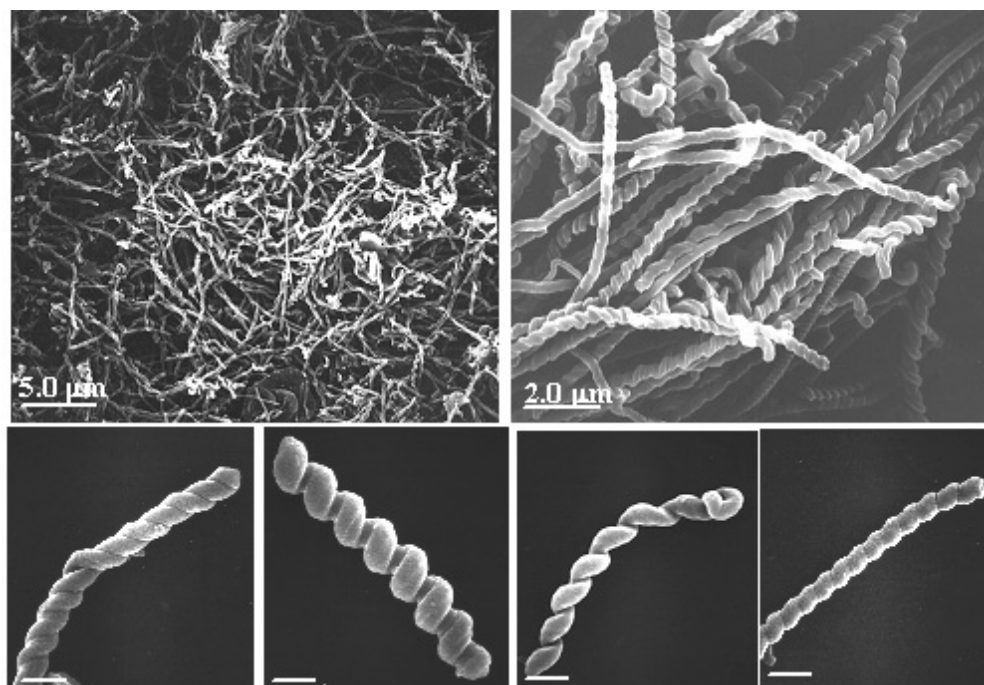


Figure 1. SEM images at different magnifications of various shapes of mesoporous silica helical fibers synthesized with  $C_{16}$ TMAB/SDS template (composition: 1.0 g : 0.135 g in weight ratio) at pH = 1.5.

In addition to acting as mesostructural template, the  $C_{16}$ TMAB-SDS binary-surfactant can also combine with neutral surfactant to form novel template. Hollow silica spheres with mesostructured shells were prepared with a vesicle template of  $C_{16}$ TMAB-SDS-Pluronic P123 ( $EO_{20}PO_{70}EO_{20}$ ) at SDS/ $C_{16}$ TMAB ratio of 0.6–0.8 following a fast silicification in dilute silicate solution at pH  $\approx$  5.0. The mesostructure of the shell is disordered and mesopore size is about 5.5–7.5 nm (Figure 2). A bi-template model, in which the  $C_{16}$ TMA<sup>+</sup>–DS<sup>-</sup> form the stable bilayer vesicle structure and the P123 copolymers anchored on  $C_{16}$ TMA<sup>+</sup>–DS<sup>-</sup> vesicle act as the template for the mesoporous silica, was proposed to explain the formation of the hollow silica spheres with mesostructured shells. This bi-template model can be applied extensively to prepare the hollow silica spheres with mesostructured shells with different diameters and pore sizes by using other  $C_n$ TMA<sup>+</sup>-SDS- $EO_m$ PO<sub>n</sub>EO<sub>n</sub> ternary-surfactant mixtures.

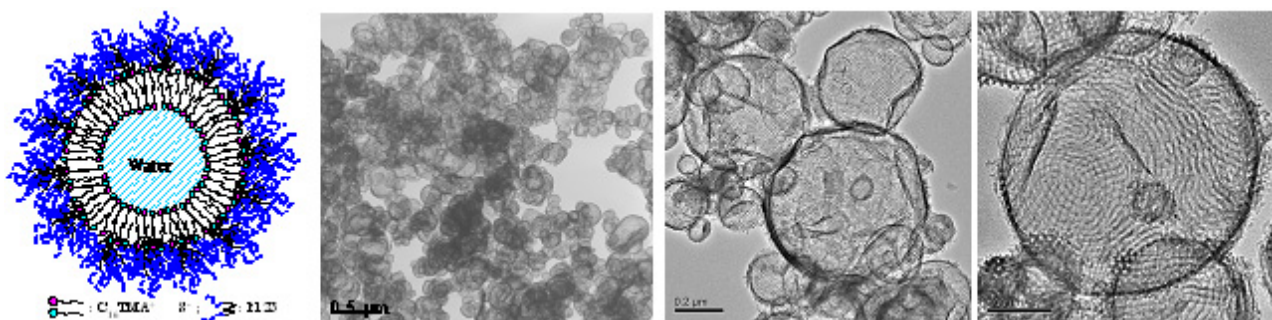


Figure 2. A schematic diagram of the bi-template model for the hollow silica spheres with mesostructured shell. TEM images at different magnifications of the hollow silica spheres with mesostructured shell prepared with P123- $C_{16}$ TMAB-SDS ternary surfactants as template.

At the ionic surfactant ratio of SDS/ $C_{16}$ TMAB  $\approx$  1.67, mesoporous silica film with perpendicular nanochannels can be synthesized by using a ternary surfactant mixture of  $C_{16}$ TMAB, SDS and P123 as

template and silicate solution as inorganic source under neutral condition ( $\text{pH} \approx 6.0$ ). At high-magnification SEM image, one can clearly see that the mesoporous silica film consists of 2D-hexagonally ordered holes facing up (Figure 2). On the edge (upper corner), one can see exposed nanochannels vertical to the film. TEM image reveals clearly the hexagonal-arrayed nanochannels of the film, and the pore size is about 7.0 nm. We proposed a ternary-surfactant template, somewhat idealized, for the formation of the mesostructured film( $\perp$ ) as depicted in Figure 3. Because of the strong specific interaction between  $\text{C}_{16}\text{TMAB}$  and SDS, they form bilayer structures and interact only weakly with the other components. However, the hydrophobic interaction between the pseudo-zwitterionic bilayer and P123 is apparently strong enough to let the P123 micelles intercalate between the bilayers. The excess of anionic SDS over cationic surfactant in the composition probably leads to the slightly negatively charged bilayers which would not allow a separate phase of  $\text{C}_{16}\text{TMAB} + \text{SDS}$  from the ternary surfactant mixture. Under the neutral pH condition, the neutral P123 interacts strongly with a condensing sodium silicate mainly by hydrogen-bonding to form a hexagonal mesostructure. The silicate ions are negatively charged and they do not have a tendency to be attracted to the slightly negatively charged bilayer also. Thus, the free standing mesoporous silica film with perpendicular nanochannels was created.

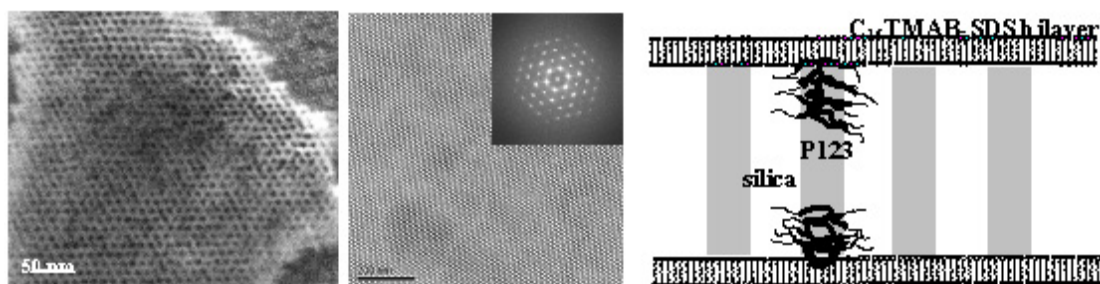


Figure 3 SEM and TEM images of the calcined mesoporous silica film synthesized from  $\text{C}_{16}\text{TMAB}/\text{SDS}/\text{P123} = 0.75/1.0/0.70\text{-H}_2\text{O}$ -sodium silicate at  $\text{pH} \approx 6.0$  and  $T = 40^\circ \text{C}$ . A bi-template model for the formation of mesoporous silica film with vertical nanochannels. The  $\text{C}_{16}\text{TMAB}$ -SDS cationic and anionic surfactants form a bilayer membrane structure and P123/silicate intercalates vertically as a 2D hexagonal structure.

From these works, creating mesoporous silicas in helical, vesicle-like or film morphologies is feasible, and future developments require our combining the knowledge gained from mesostructured silicas and the self-organization of surfactants system. Owing to the large pore size and high porosity, these mesoporous silica could be used as nano-template, the helical morphologies and well-ordered mesostructure are preserved in the resulted carbons. This should open up a new direction for the controlled synthesis and practical use of mesoporous materials for advanced applications such as chiral heterogeneous catalysis, sensors, adsorption, and separation. The ultimate goal is not only to mimic silicification in nature but also to go a step further and be able to preprogram mesoporous materials to produce a specific architecture with defined functionality.