

Synthesis of Mesoporous Silica Film - Biomimetic Silicification

Diatoms are unicellular algae that are ubiquitously present in almost every water habitat on Earth. They are mainly known for the intricate geometries and spectacular patterns of their silica-based cell wall. In fact, silica formation of many diatoms is a rather rapid process that usually takes an hour or much less at neutral condition ($\text{pH} \sim 5.0 - 7.0$). Moreover, the fast silica deposition occurring on the organic protein surface is so precise that the species-specific patterns are accurately reproduced during each cell division.

Although the growth mechanism of the diatoms is extremely intricate, the functional studies of the protein role in silica precipitation have still been carried out. It has been responsibly speculated that these organic macromolecules are involved in controlling bio-silica formation, and there exists an interaction-matching between the organic template and silica species. This basic concept of the biomineralization has been widely extended to the synthesis of nanostructured materials templated by organic surfactant micelles or macromolecules. Therefore, the artificial silica-based materials, which possess the complexity and hierarchical structure of the biomineralized composites and match the applications in nanotechnology, have been highly desirable to be synthesized under ambient conditions and at near-neutral pH value.

Based on the chemistry of surfactants, various shapes and morphologies of surfactant micelles, vesicles and liquid crystal phases can be facilely discovered in a surfactant mixture. Thus, it is reasonable that the desired organic templates for producing multi-functions mesoporous materials could be properly prepared by using bi- or multi-surfactants mixtures. To imitate the complex silica deposition, we performed a ternary-surfactant mixture of cationic cetyltrimethylammonium bromide (C_{16}TMAB), anionic sodium dodecyl sulfate (SDS), and neutral Pluronic 123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) surfactants as the template to prepare the mesoporous silica films within seconds. It was found that silica deposition has a capability to distinguish the surface properties of the organic templates (i.e. charge nature and density). By tuning the interaction between the silica and C_{16}TMAB -SDS surfactants composites, the nanochannels direction of the mesoporous silica film is changed. This specific interaction-selectivity provides ones a great deal of information for understanding silica condensation in the membrane-like cell wall of the diatoms.

A typical synthetic process to synthesize the mesoporous silica film is as followed: a ternary-surfactant mixture with the chemical composition of (0.60 – 0.75) g C_{16}TMAB : 1.00 g SDS: 0.70 g P123 in weight ratio was mixed in (25.0 – 50.0) g of H_2O under stirring at $40 \sim 50^\circ\text{C}$ to form a cloudy suspension. The mixture was directly poured into a 150 ml dilute solution of sodium silicate, with $[\text{SiO}_2] = (80.0 - 100.0)$ mM, at $\text{pH} \sim 5.0$. A white precipitate was formed in seconds, and the pH value of the gel solution raised to about 6.0-7.0. The as-synthesized products were filtered, washed, dried, and calcined at 560°C for 6 hr to remove the organic templates. The XRD patterns were recorded at Wiggler-17A beamline ($\lambda = 0.1326$ nm) of NSRRC. The micrographs were taken using a JEOL JSM-6700F scanning electron microscopy (SEM) and a Hitachi S-7100 transmission electron microscopy (TEM) operated at accelerating voltage of 10 and 75 keV, respectively.

Figure 1a shows the low-magnification SEM image of the mesoporous silica products prepared with 1.0 C_{16}TMAB /1.60 SDS/P123-silica- H_2O at pH value of about 6.0. It is obvious that the silica products are micro-sized thin films, but the dimension is not uniform. At a higher magnification (Fig. 1b), one can clearly see that the mesoporous silica film consists of the well-ordered nanochannels normal to the film, and the film thickness (i.e. silica channel length) is less than 100 nm. With a careful examination of the high-resolution TEM micrographs (Fig. 1c), we found that the nanochannels are arranged into a hexagonal array, and the pore size is about 7.0 nm. To get the accurate thickness and to further elucidate the orientation of the films, the microtome TEM micrographs show that the silica-nanochannel length is not uniform and disperses within 30 – 100 nm. Accordingly, the length of nanochannels is larger than pore size, and the aspect ratio of the nanochannels (i.e. the channel length/intercannel spacing size) can be varied within a range of 3.0 to 10.0.

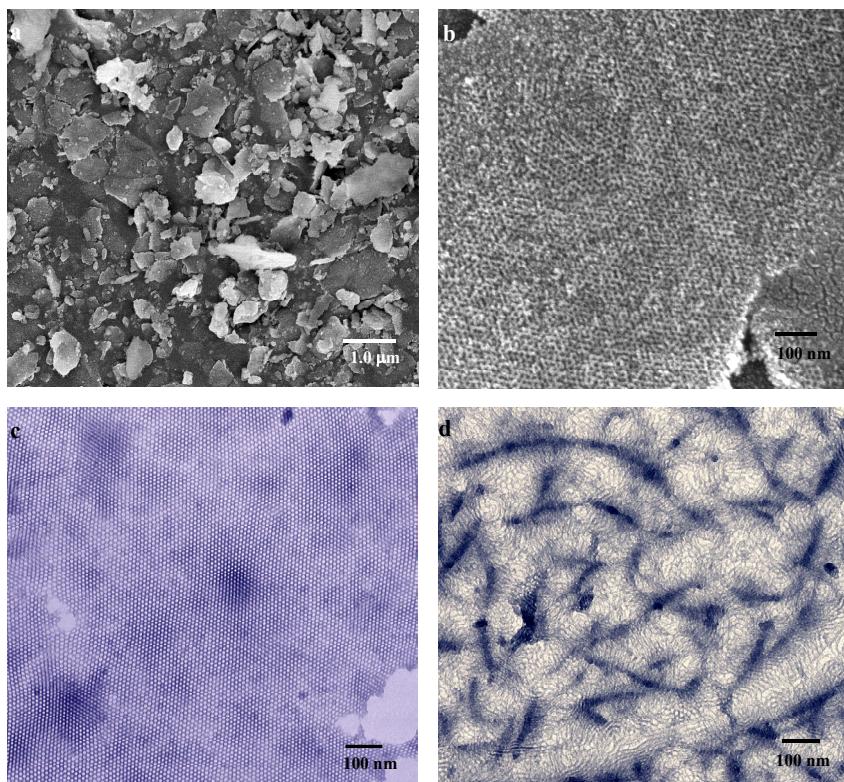


Fig. 1: The SEM and TEM images of the calcined mesoporous silica films (\perp and $//$) synthesized from $C_{16}TMAB/SDS/P123 = 0.75/1.0/0.70$ -H₂O-sodium silica at pH ~ 6.0 and T = 45 °C. **a.** Low-magnification SEM micrograph; **b.** High-resolution SEM image; **c.** TEM micrograph; **d.** TEM image of the calcined mesoporous silica film ($//$).

In comparison, the axial direction of the silica nanochannels of the mesoporous silica films formed at the liquid-vapor or substrate-solution interface via a spin- or dip-coating sol-gel process are parallel to the film. To the best of our knowledge, this is the first time that the mesoporous silica film with nanochannels normal to the surface (denoted as mesoporous silica film (\perp)) can be rapidly synthesized from a diluted silica solution at pH value close to the neutral condition. When the SDS/ $C_{16}TMAB$ molar ratio was reduced to 1.30, the mesoporous silica film was also obtained, but the nanochannels are parallel to the film (Fig. 1d). With a careful examination, one can find that the nanochannels arrangement of the mesoporous silica film ($//$) are disordered.

Figure 2a presents the representative XRD patterns of as-synthesized and calcined mesoporous silica films (\perp and $//$). For the mesoporous silica film (\perp), there are three peaks observed at low angular range of $2\theta \sim 0.6 - 2.5^\circ$, which can be indexed as the (100), (110), and (200) reflection of a well ordered hexagonal mesostructure with a large unit cell ($a_0 \sim 10.0$ nm). However, the mesoporous silica film ($//$) pos-

sesses only two broad peaks. These results are consistent with the observations of the electron microscope. The N₂ adsorption-desorption isotherm of the calcined film (both \perp and $//$) is type IV with an apparent H₁-type hysteresis loop (Fig. 2b). The pore size distribution of these mesoporous films, analyzed by Barrett-Joyner-Halenda, is sharp and centers at about 7.0 nm, and the BET (Brunauer-Emmett-Teller) surface area of these two samples is about 500 m²/g. Combining the data aforementioned, it was reasonably supposed that the nanochannels constructing of the mesoporous film is made up from neutral Pluronic 123 as SBA-15, rather than that of $C_{16}TMAB$ -templated MCM-41.

Here we try to explain these observations by using a schematic diagram in Fig. 3. Due to the effective “neutralization” between the head groups, the cationic-anionic aggregates form in aqueous solution at concentration far below that of the critical micellization concentration of ether pure surfactant. It was logically expected that the negative SDS⁻ would energetically combine with cationic $C_{16}TMA^+$ by the strong electrostatic interaction to form a hydrophobic bilayer phase.

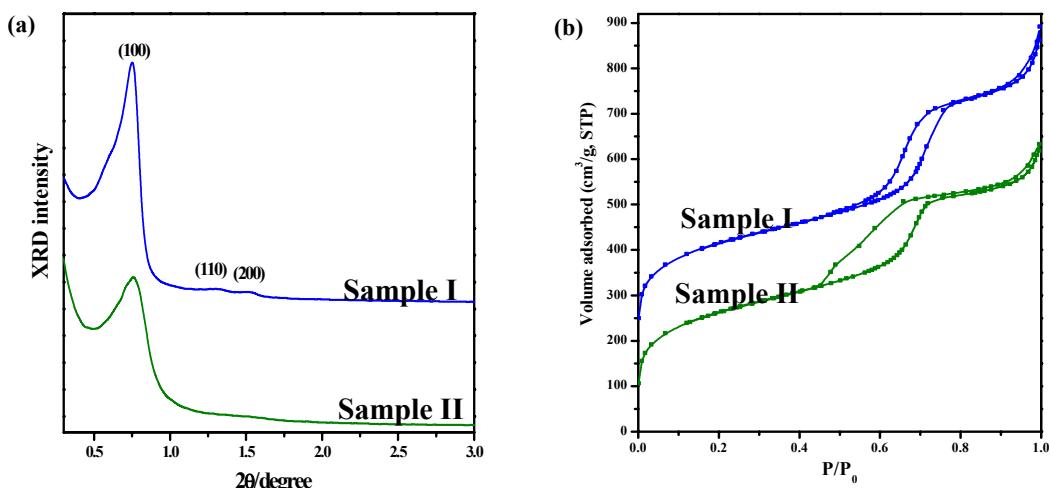


Fig. 2: The XRD patterns (a) and N_2 adsorption-desorption isotherms (b) of the mesoporous silica films with perpendicular and parallel channels. Sample I. Mesoporous silica film (\perp); Sample II. Mesoporous silica film ($/\!/$).

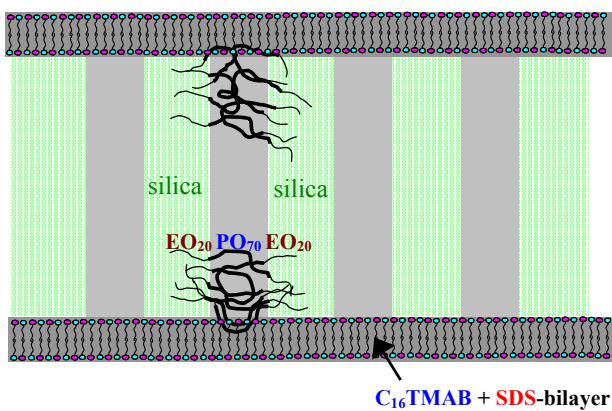


Fig. 3: The schematic diagram for the formation of the mesoporous silica films (\perp). Components are not drawn to scale.

After that, the exceeded amount of SDS would make the $C_{16}\text{TMA}^+ - \text{SDS}^-$ bilayer partially negative, and the added neutral block copolymer Pluronic 123 would coat on that hydrophobic film. Finally, the silica condensation tends to occur on the micelles of Pluronic 123 instead of on $C_{16}\text{TMAB}$ or SDS, and the pore size of mesoporous silica is similar to typical SBA-15 silica. Due to the different SDS- $/C_{16}\text{TMA}^+$ ratio, the surface charge is different. When the ratio is in the range of 1.60, the surface charge of the bilayer must be negative. Because the remaining SDS can not cover the whole hydrophobic surface, Pluronic 123 copolymers fill up the residual part. As the addition of silica solution of pH ~5.0, the silica oligomers condense on the P123. Upon silica condensation, the silica coated P123 micelles become negative-charged (the $pK_a \sim 6.7$ for silica oligomers) that repulse the partially negative

$C_{16}\text{TMA}^+ - \text{SDS}^-$ bilayer. The strong electrostatic repulsion pushes the silica-P123 cylinders to stand on the bilayer, and the mesoporous silica film was formed. As the SDS content decreasing, the negative charge density of the bilayer reduces. The loosely negative-charged bilayer can not prevent the silica-P123 cylinders from lying down on the surface for getting larger orientation freedom, and a disordered mesostructural silica film ($/\!/\!$) was obtained.

In brief, the mesoporous silica film (\perp) can be synthesized with a careful control of chemical components under neutral condition ($\text{pH} \sim 6.0$). This can provide many valuable information of surface nature and charge density to realize the silica deposition process in diatom ($\text{pH} = 5.0 - 7.0$). Moreover, the hierarchically mesoporous silica film (\perp) can be formed from artificial materials to template siliceous structures with such speed and precision under ambient conditions and at near-neutral pH. Thus mesoporous silica film (\perp) should be efficiently prepared to be used in many potential applications for molecular separation, solid mask of the nano-lithograph, direction-controlling solid template and nanoreactors.

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BEAMLINE

17A W20 X-ray Diffraction beamline

EXPERIMENTAL STATION

Powder X-ray Diffraction end station

AUTHORS

H.-P. Lin and Y.-Q. Yeh

Department of Chemistry, National Cheng Kung
University, Tainan, Taiwan

B.-C. Cheng

Department of Chemistry, National Taiwan
University, Taipei, Taiwan

PUBLICATIONS

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CONTACT E-MAIL

hplin@mail.ncku.edu.tw