

Formation of Artificial Frustule through a Phase Transition

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General Methods. The transmission electron microscopy (TEM) images were obtained using an FEI TecnaiG220. The field emission scanning electron microscopy (FESEM) images were taken on a Hitachi S-4800. Specific surface areas and pore-size distributions were determined by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods using N₂ adsorption isotherms measured with a Micromeritics ASAP 2020M+C instrument. The small angle X-ray diffraction (SAXRD) patterns were recorded on an X' Pert-Pro MPD X-ray diffractometer.

Characterization of amphiphile L-18Val6NBr: FT-IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3423.8 ($\nu_{\text{N-H}}$, amide A), 1636.2 ($\nu_{\text{C=O}}$, amide I), 1545.9 ($\delta_{\text{N-H}}$, amide II). ¹H-NMR (300 MHz, CDCl₃, Me₄Si, 25 °C): δ = 0.86-1.0 (9H, m, CH₃), 1.25-1.46 (41H, m, alkyl and N⁺CH₂CH₃), 1.70 (6H, br, N⁺CH₂CH₂, CONHCH₂CH₂, and NHCOCH₂CH₂), 1.50-1.57 (2H, m, CH₂CH₂CONH), 2.24 (2H, t, J = 6.0 Hz, CH₂CONH), 2.40-2.60 (1H, m, (CH₃)₂CH), 3.10-3.30 (4H, m, N⁺CH₂CH₂ and CONHCH₂), 3.47 (6H, q, J = 7.2 Hz, N⁺CH₂CH₃), 4.22 (1H, m, NHCHCO). Elemental analysis: C₃₃H₇₂BrN₃O₂ (Mw; 646.87), calc. (%): C, 65.0; H, 11.2; N, 6.5. Found: C, 64.0; H, 11.2; N, 6.4.

Synthesis of the mesoporous silica hollow spheres:

Sol-gel polycondensation of tetraethyl orthosilicate (TEOS) was carried out as follows: L-18Val6NBr (0.20 g, 0.32 mmol) was dissolved in deionized water (50 g, 2.8 mmol) with stirring at room temperature. Aqueous NaOH solution (0.35 mL, 2 M) was then added to the solution. The solution was heated to 80 °C, and TEOS (1.0 mL, 4.5 mmol) was added at a stirring rate of 1500 rpm. The mixture was stirred at 80 °C for a further 2 h. The resulting products were collected by filtration and dried at room temperature. The template was then removed by washing with a mixture of 80 mL of methanol and 5.0 mL of 36 wt.% aqueous HCl followed by calcination at 550 °C for 5 h in air. The temperature ramp rate used was 1.0 °Cmin⁻¹. About 200 – 250 mg of silica was obtained.

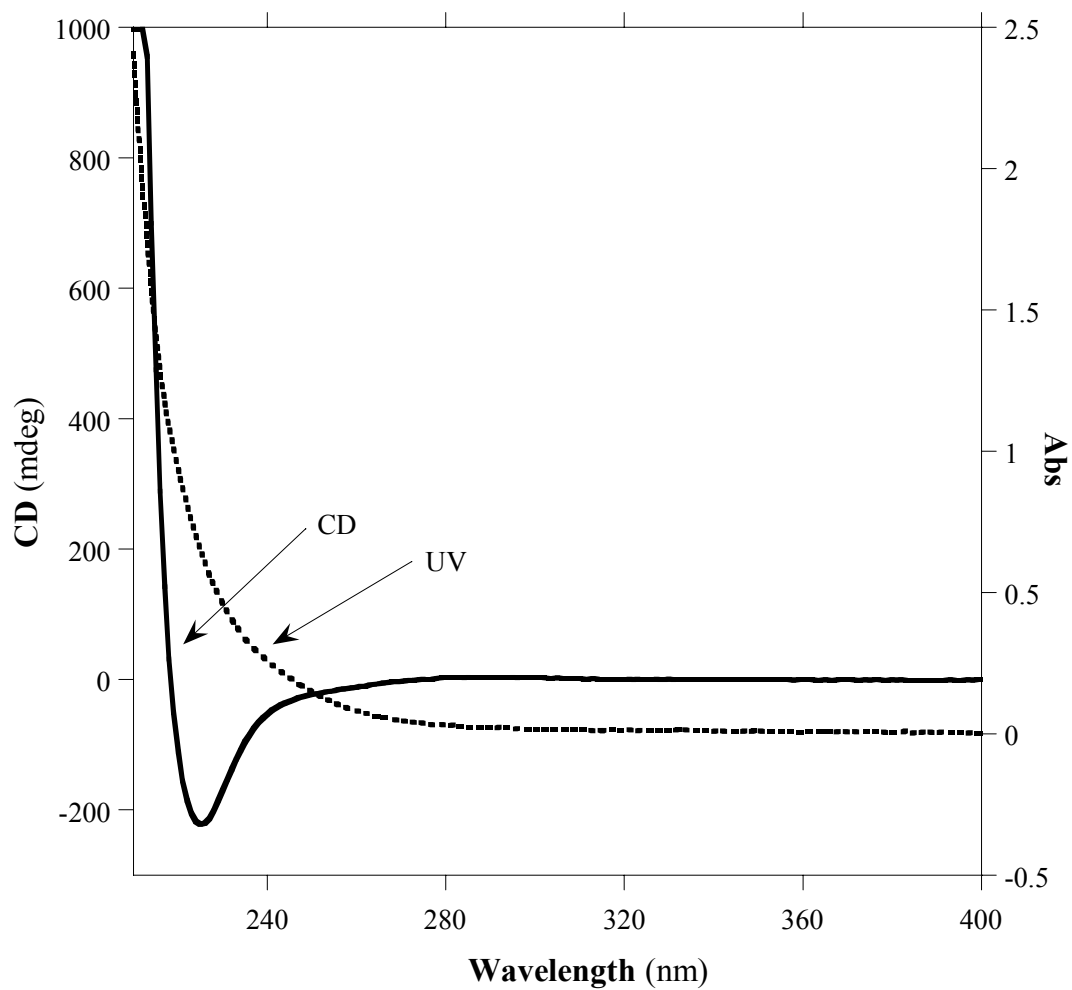


Figure S1. CD and UV spectra of L-18Val6NBr aqueous solution (20.0 mg/mL).

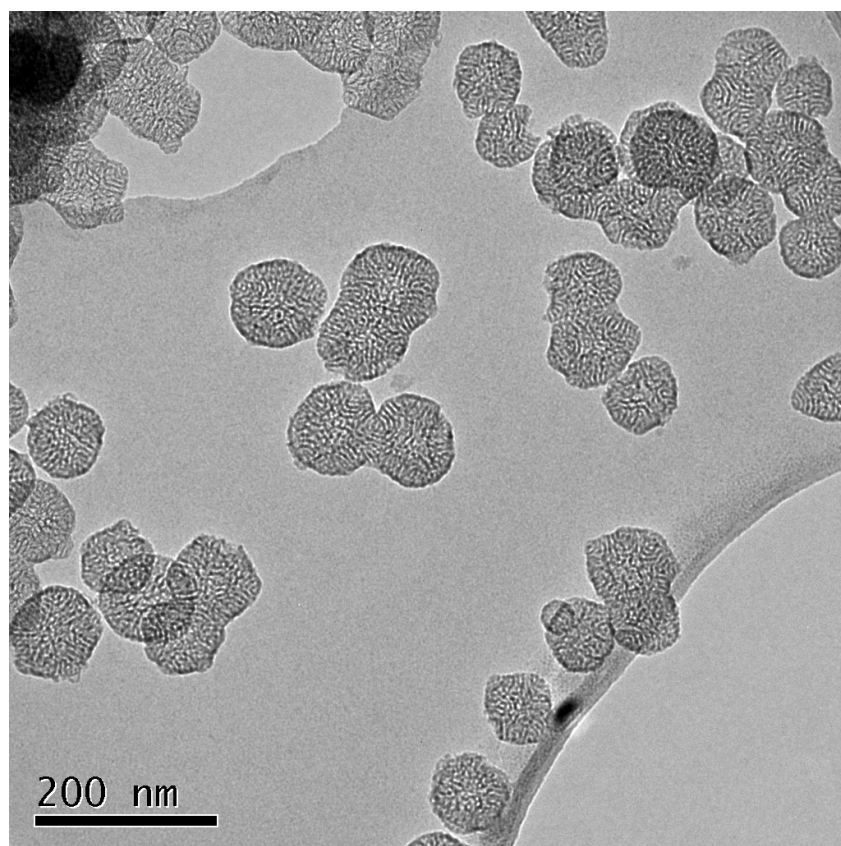


Figure S2. TEM image of the mesoporous silica hollow spheres prepared using the single-templating approach.

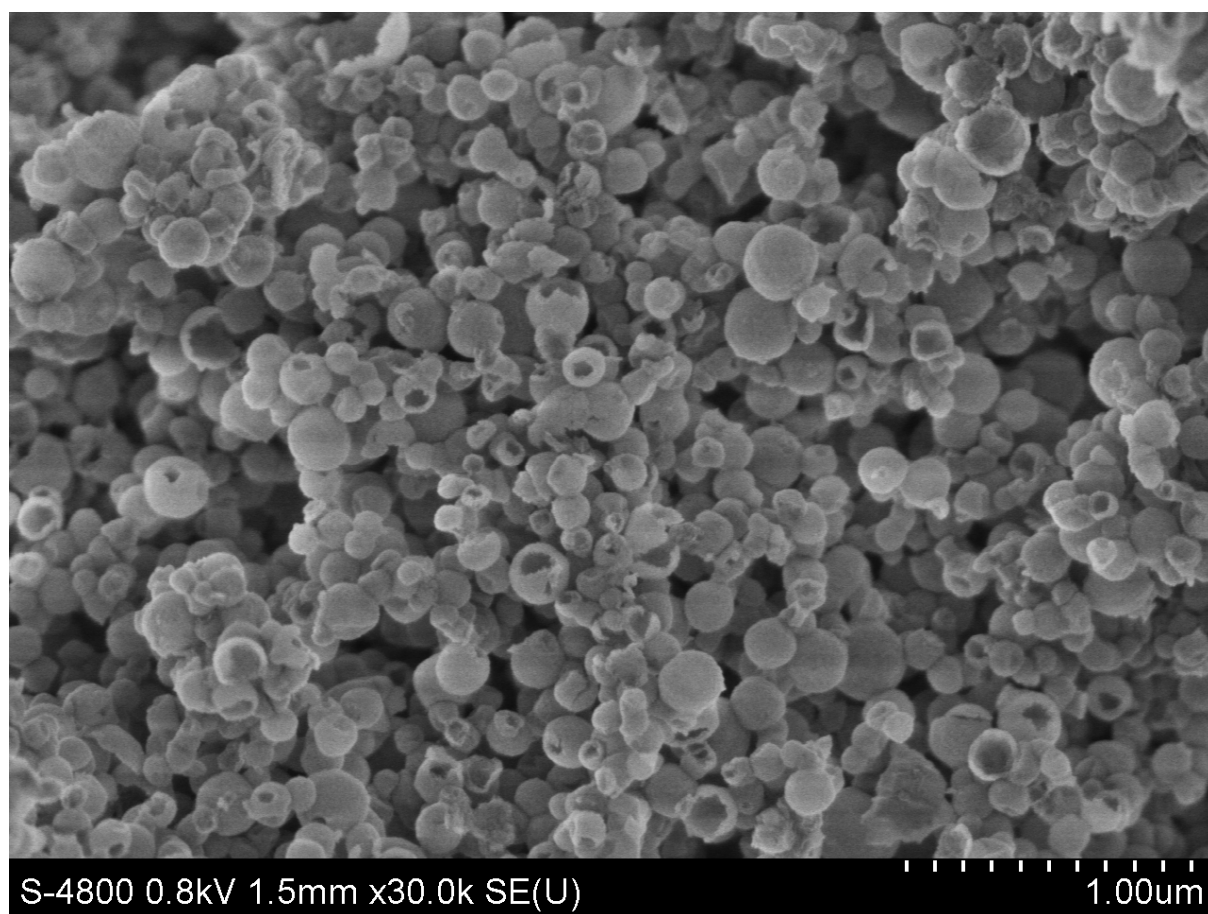


Figure S3. FESEM image of the mesoporous silica hollow spheres prepared using the dual-templating approach.

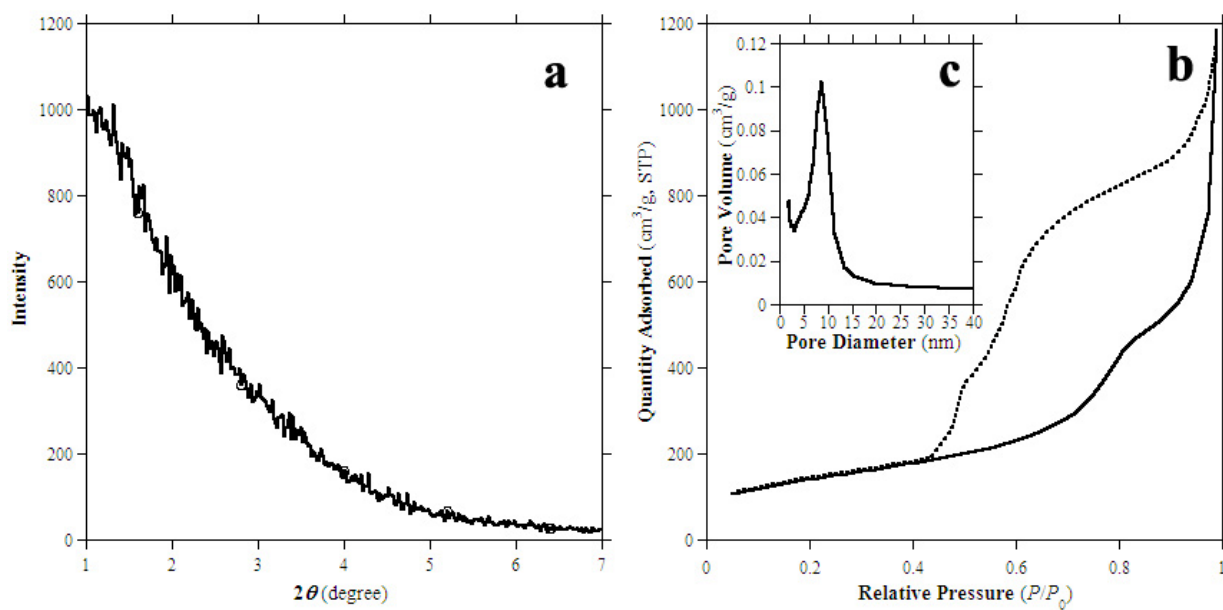


Figure S4. a) SAXRD pattern; (b) Sorption isothermal plots and (c) BIH pore size distribution obtained from the adsorption branch.