

Electronic Supplementary Information for

Synthesis, characterization and optical properties of ordered macroporous organosilicas

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1. Preparation of OMOS bulks

The PS spheres with size ranging from 0.2 to 1.5 μm were synthesized by using an emulsifier-free emulsion polymerization method as described by Shim and coworkers.¹ The freshly prepared colloidal suspension was transferred into a glass container with a cap and allowed to self assemble for several weeks. Due to gravitation and non-covalent interactions, the spheres self organized themselves into a solid-state, face-centred cubic (fcc) structure on the bottom of the vessel. The liquid phase was removed with a dropper. The solid was then dried slowly at room temperature to obtain a colloidal crystal, namely the template. After annealing at 110 °C for 10 min, the solid colloidal crystal was broken into small segments of ca. 2 mm³ and placed in a petri dish with a filter paper. A silsesquioxane precursor was then added to fully wet the opal and the filter paper (incipient wetness). The silsesquioxane was allowed to hydrolyze and condense in air for 24 h. The infiltration-hydrolysis process was repeated three times to ensure complete infiltration of the template voids. The PS spheres were then dissolved away using toluene and subsequently washed with ethanol. The final solids were dried at 50 °C. Three silsesquioxanes, namely 1,2-bis (triethoxysilyl) methane (BTEM), 1,2-bis (triethoxysilyl) ethane (BTEE), and 1,2-bis (triethoxysilyl) ethylene (BTEY), were used as the organosilica precursors.

2. Preparation of OMOS films

To measure the optical properties, thin films of the OMOSs were prepared as follows. PS colloidal films were first fabricated on a glass slide with a flow-controlled vertical deposition (FCVD) method recently developed in our laboratory.² As the structure of the thin films of PS spheres could be destroyed by the silsesquioxanes, pre-hydrolyzed silsesquioxane sols were used as the infiltration precursors. The sols were prepared as follows. 1 mL a silsesquioxane was added in mixture of 10 mL of ethanol and 1 mL of 0.05 M HCl solution under stirring for 4 h. The sol precursor was allowed to immerse the colloidal crystal films, and then to hydrolyze and condense in air for 24 h. The infiltration-hydrolysis process was repeated several times to ensure complete filling of the voids of the colloidal films. Removal of the PS spheres was conducted in the same way as described above. For comparison purposes, an ordered macroporous silica was also prepared with tetraethyl orthosilicate (TEOS) as the precursor.

3. Characterization techniques

Scanning electronic microscopy (SEM) images were collected on a JEOL JSM-5600LV and JEOL JSM-6700F microscope. Thermogravimetric analysis (TGA) was carried out on a TA Instrument TGA 2050 thermogravimetric analyzer under N₂ flow with a flow rate of 100 mL/min. Fourier transform infrared (FTIR) spectra were collected on a Bio-Rad FTS 135 with a resolution of 4 cm⁻¹ in the wavelength range of 400-4000 cm⁻¹. KBr method was used. Solid-state nuclear magnetic resonance (NMR) spectra were collected on a Bruker DRX400 MHz FT-NMR spectrometer operated at a frequency of 100.6 MHz and 79.5 MHz for ¹³C and ²⁹Si respectively. The magic-angle-spinning (MAS) rate was 8 kHz and a magnet with a rotor size of 4 mm was used. The optical transmission spectra were measured on a Shimadzu UV-3101PC UV-visible-near-infrared spectrophotometer.

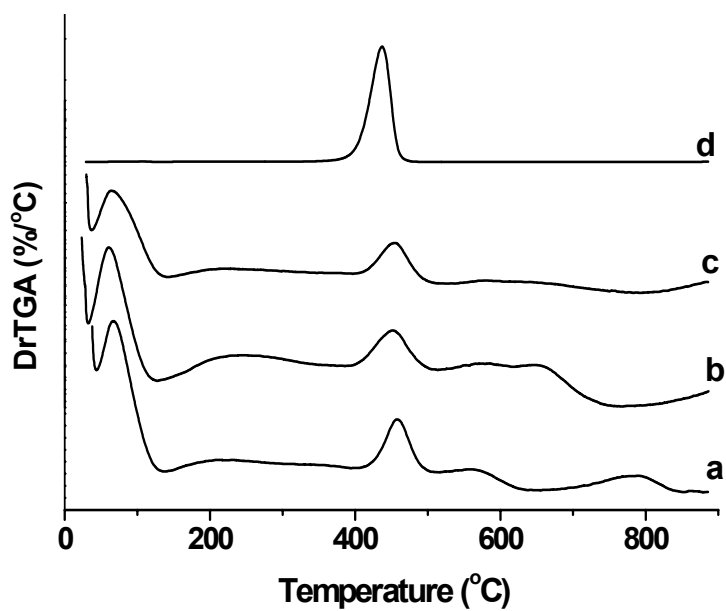


Fig. S1. DrTGA curves of (a) OMOS-BTEM, (b) OMOS-BTEE, (c) OMOS-BTEEY, and (d) PS colloidal crystal.

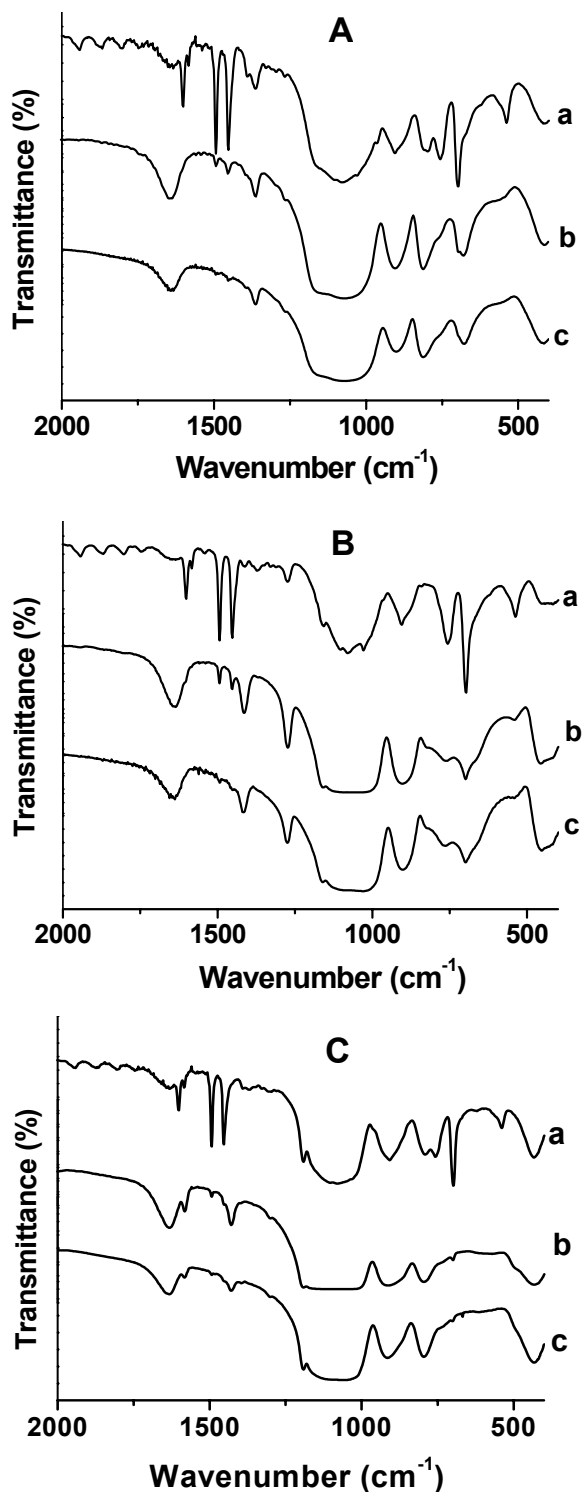


Fig. S2. FTIR spectra of (A) OMOS-BTEM, (B) OMOS-BTEE, and (C) OMOS-BTEEY samples. Spectra **a**, **b**, and **c** represent the samples before solvent extraction, after solvent extraction one time, and after solvent extraction three times, respectively.

Supplementary Material for Chemical Communications

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References:

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- 2 Z. Zhou and X. S. Zhao, *Langmuir*, 2004, **20**, 1524.