Electronic Supporting Information

Dual Templating Synthesis of Hierarchical Porous Silica Materials with Three Orders of Length Scale

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Experimental Details

Materials: *N*-isopropylacrylamide (NIPAM, Fluka) was recrystallized from a toluene/n-hexane mixture. *N,N'*-methylene bisacrylamide (MBAA, Fluka), methacrylic acid (MAA, Merck), perylene (Aldrich) and the fluorescent dye, methacryloxyethyl thiocarbamoyl rhodamine B (MRB, Polysciences, Inc.) were used as received. Potassium persulfate (KPS, Merck), Silicon Oxide (40% in water, colloidal dispersion, 40 nm in diameter, Alfa aesar) and hexane oils were used without further purification. Deionized water was used in all the experiments.

PNIPAM-based microgel particles preparation: The synthesis and characterization of PNIPAM-*co*-MAA microgel particles have been described elsewhere.[1] Typically, 3.0893 g of NIPAM, 0.1075 g of MBAA, 0.1072 g of MAA and 0.0014 g MRB were dissolved into 140 mL of deionized water in a 250 mL two neck reactor fitted with a nitrogen bubbling inlet and outlet, a reflux condenser and stirred with a magnetic stir bar. Then the solution mixture was adjusted to pH 10.88 with sodium hydroxide solution. After stirring the solution for 40 min at 70 °C under nitrogen bubbling, the polymerization was initiated by adding 0.031 g of KPS dissolved in 10 mL of deionized water. The reaction mixture was kept at 70 °C for 7 h. The pH of the dispersion after reaction was 9.27. The resultant microgels were dialyzed for 7 days to remove the unreacted reagents. The final pH of the microgel was ~6.0. The size of the microgel particles was determined by dynamic laser light scattering (LLS) with a diameter of 250 nm.

High Internal Phase Emulsions (HIPEs) Preparation: An oil-in-water emulsion with the internal phase 80 vol% was produced prepared by mixing the particle dispersions (1mL contains 24 wt% silica particles with 40 nm in diameter and 0.8 wt% microgels with 250 nm in diameter) with the hexane oil (4 mL) and then homogenizing the mixture using an Ultra Turrax T25 homogenizer (1 cm head) operating at 13 500 rpm for 30 seconds. The total emulsion volume was kept at 5 mL. In some cases, dye molecule, perylene was added to the oil phase to check the type of the formed emulsions. All the emulsions were stable for at least 6 month.

Freeze and Directly Drying of HIPEs: For freeze drying HIPEs, HIPEs were first immersed in liquid nitrogen to solidify all the HIPEs, and then the solidified HIPEs were dried under a working vacuum pump. For directly drying, HIPEs were directly dried in air at room temperature.

Instrumentation: The appearances the HIPEs stabilized by the silica and microgel particles were taken with a camera (Canon, Digital IXUS 860 IS). The confocal microscopy images were taken on a Nikon Eclipse Ti inverted microscope (Nikon, Japan). Lasers with wavelengths of 543 nm and 408 nm were used to excite the fluorescent microgel particles and perylene molecules, respectively. An oil immersion objective (60x, NA=1.49) was used to view the samples. The HIPEs were placed on the cover slides and a series of x/y layers were scanned. Thermogravimetric analysis (TGA) for the silica/microgel composite porous materials was performed at Hi-Res TGA 2950 Thermogravimetric Analyzer (TA instruments), where the temperature ramp was 10 ^{o}C/min and under N_2 atmosphere. The calcination of the silica/microgel composite by removing the microgel particles and fusing the silica particles was carried out in air using a furnace (Ney Vulcan^{TM} 3-400 HTA). The temperature was ramped from room temperature to various temperatures (900, 950, 1000, 1400 ^{o}C) at 3 ^{o}C /min, held at specific temperature (900, 950, 1000, 1400 ^{o}C) for 2 hours, and then cooled to room temperature at 3 ^{o}C /min. For SEM observation, the silica monoliths after the calcination were coated with Au before imaging on a FEI Quanta 400 FEG microscope operating at 5 kV. Intrusion volumes, bulk densities and pore size distribution were characterized with AutoPore IV 9500 V1.05 porosimeter.

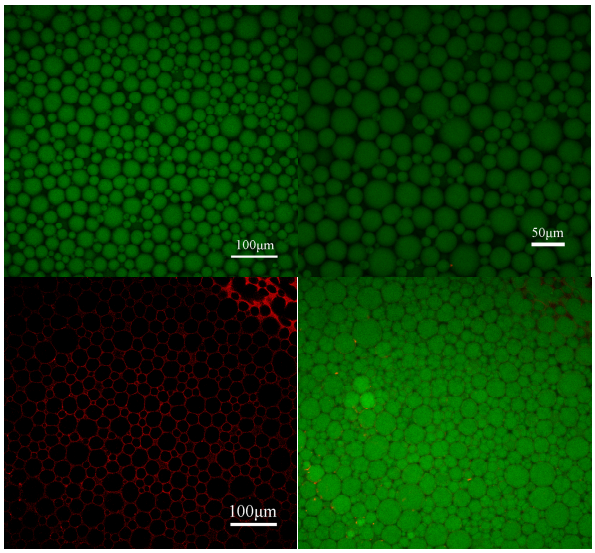

Figure S1. Confocal images of HIPEs stabilized by silica and microgel particles. The green color is attributed to perylene which was dissolved in oil hexane and excited at 408 nm. The red color is due to the MRB-labelled microgel particles that were excited by wavelength at 543 nm. It shows that microgel particles are absorbed to the interface to stabilize the emulsions.

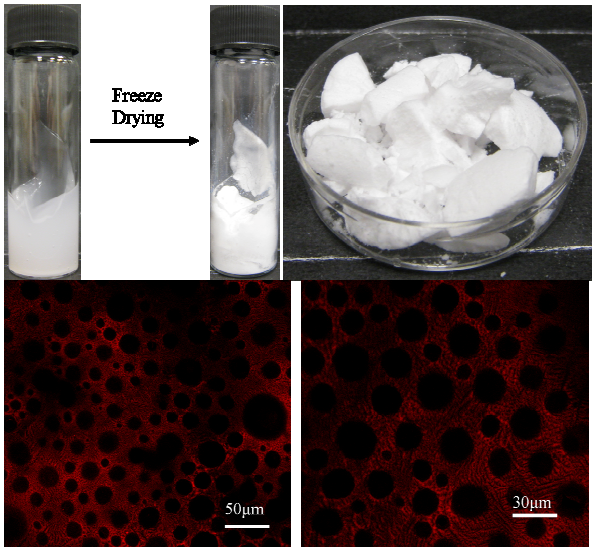

Figure S2. Appearances of the particle (silica and microgels) stabilized HIPEs after freeze drying. The corresponding confocal images confirm that the resulting porous materials consist of cellular macropores 10-30 μm in diameter without the distortion of internal structure.

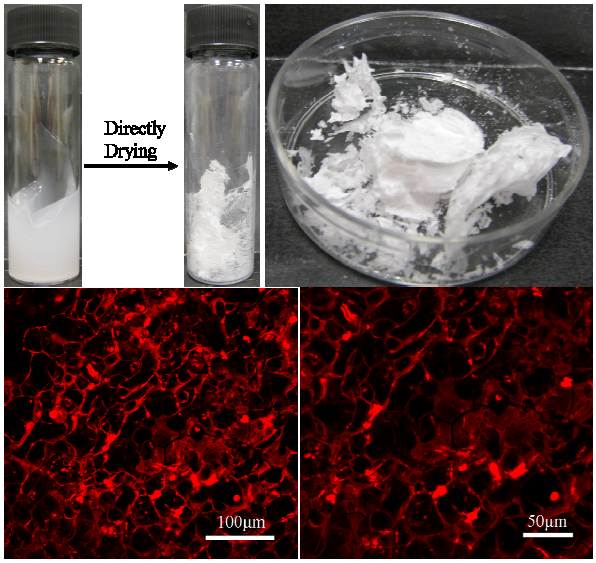

Figure S3. Appearances of the particle (silica and microgel) stabilized HIPEs after directly drying in air. The corresponding confocal images show that the integrity of the porous structures cannot be retained.

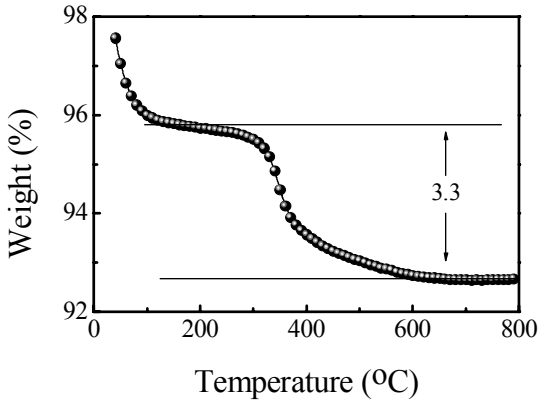

Figure S4. The weight loss dependent on temperature of the silica/microgel composite material, about 3.3% weight was lost between 200 °C and 600 °C, corresponding to the calculated value 3.4% of the microgel particles.

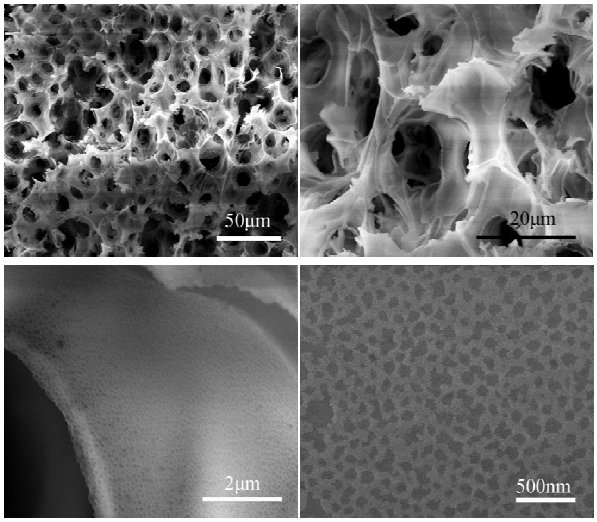

Figure S5. SEM images of the hierarchically macro-pores, interconnected windows and meso-pores templating from HIPE droplets and microgel particles after sintered at 900 °C for 2 hours.

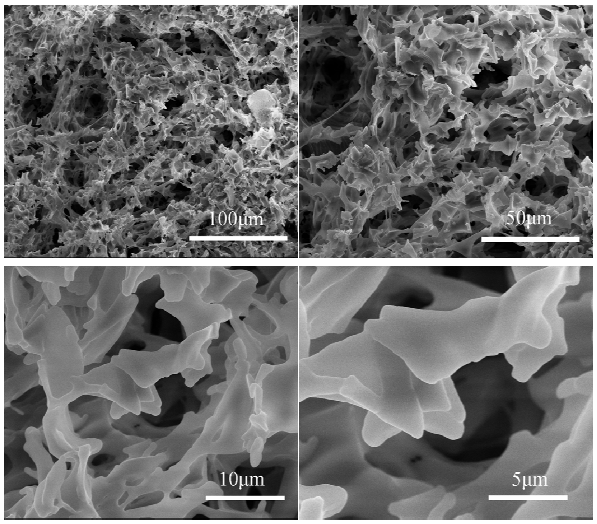

Figure S6. SEM images of the macro-pores and interconnected windows templating from HIPE droplets after sintered at 1000 °C for 2 hours.

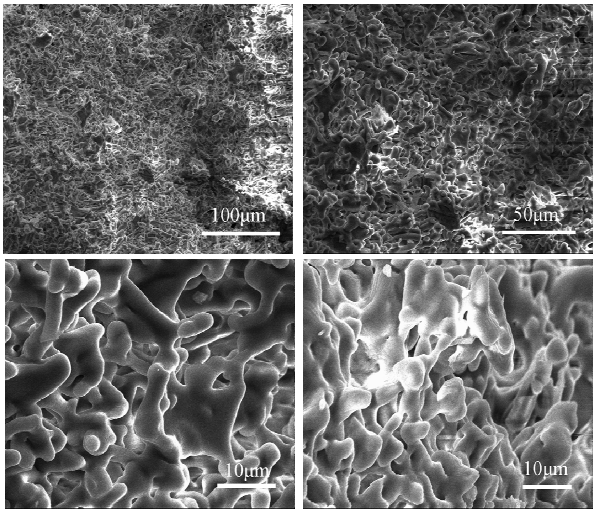

Figure S7. SEM images of the macro-pores templating from HIPE droplets after sintered at 1400 °C for 2 hours.

	Total Intrusion Volume (ml/g)	Total Pore Area (m^2/g)	Bulk Density at 0.50 psia (g/ml)	Apparent Density (g/ml)	Porosity
900	8.82	8.84	0.092	0.490	86.78%
950	7.08	6.04	0.122	0.926	81.27%
1000	1.54	1.10	0.437	1.342	67.38%
1400	0.86	0.42	0.586	1.713	50.21%

Table S1, Properties of the hierarchical porous silica materials after sintering at various temperatures.

References:

1. Z. F. Li, T. Ming, J. F. Wang, T. Ngai, *Angew. Chem. Int. Ed.* **2009**, *48*, 8490.