

Supporting information

Non-Surfactant Self-Templating Strategy for Mesoporous Silica Nanospheres : beyond the Stöber Method

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Experiment section:

Materials. tetraethoxysilane (TEOS, Richjoint Chemical, 28.4%), aqueous ammonia (Enox, 25-28%), ethanol (EtOH, SCR, 99.7%), Ultrapure water with a resistivity higher than 18.2 MΩ cm was used in all experiments. All chemicals were analytic grade and used without further purification.

Synthesis of normal SiO₂ nanoparticles using Stöber method. Normal SiO₂ nanoparticles were prepared using a typical modified Stöber method. In a typical synthesis of 270 nm SiO₂ nanoparticles, 21.6 mL of water, 9 mL of ammonia solution, and 19.4 mL of ethanol were mixed. After the mixture was vigorously stirred for 20 min at 40°C to form a homogeneous solution, the mixture of 4.5 mL of TEOS and 45.5mL ethanol was quickly added. The resulting mixture was again vigorously stirred at 40°C for 2.5h. For comparison, the resulting Stöber colloids were also treated by soft etching process.

Characterization. The SEM and TEM images were taken using Hitachi S-4800 microscope and JEOL-JEM- 2100 microscope, respectively. Nitrogen adsorption-desorption isotherms were obtained at 77 K on a BEL SORP after activating the sample under vacuum at 573K for 6 hours. ²⁹Si solid-state CP-MAS NMR measurements were obtained on a VARIAN VNMRS-400WB spectrometer. For ²⁹Si (79.5 MHz), a 4 μs ($h = \pi/2$) pulse was used with a repetition time of 360 s.

Experiment results:

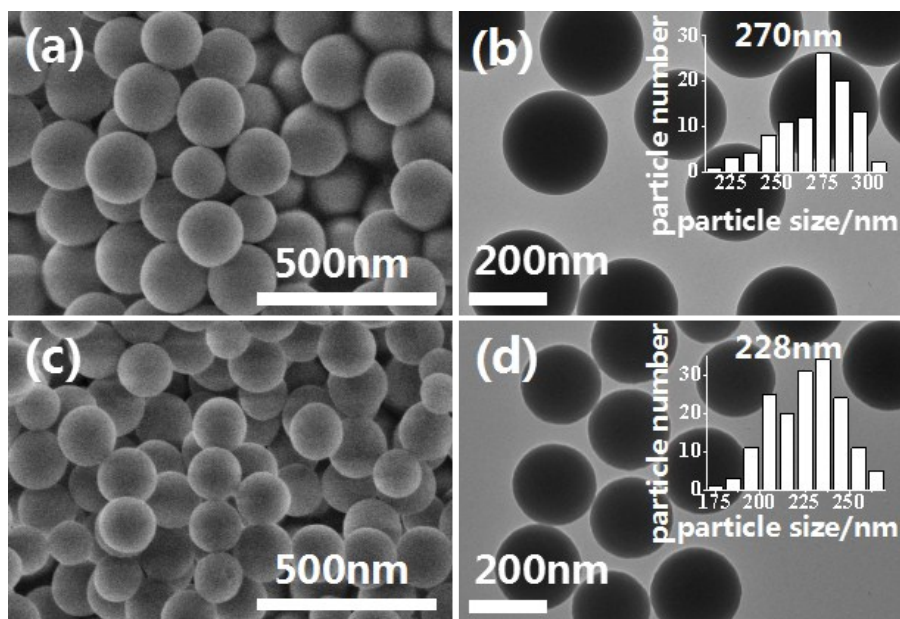


Figure S1. SEM and TEM images of silica nanoparticles obtained from typical Stöber method (a and b named S-1-1), S-1-1 diluted with water to 5 times and then added with ammonia solution to reach to 2.6M (c and d named S-1-5).

Table S1. Textural Characteristics of Calcined parent silica nanoparticles and MSNs Synthesized in Various Reaction Conditions.

Sample ^a	S _{BET} ^b (m ² /g)	V _{Total} ^c (mL/g)	V _{inter} ^d (mL/g)	D _{BJH} ^e (nm)	PSD ^f (nm)	Q ² (%)	Q ³ (%)	Q ⁴ (%)
P-0.3-1	85	0.36	0.069	17	140	9.5	33.4	57.1
M-0.3-5	426	0.87	0.26	3	113	7.4	32.9	59.7
P-0.4-1	19	0.27	0.017	56	180/280	-	-	-
M-0.4-5	418	0.65	0.22	3	130/230	-	-	-
P-1-1	7	0.11	0	60	320	-	-	-
S-1-1	13	0.15	0.011	45	270	2.4	24.2	73.4

^aP, M and S stand for parent silica, MSNs and silica prepared from Stöber method, the intermediate number representation the initial ammonia concentration, the last digit representation the dilution multiple; ^bS_{BET} is the specific surface area measured from N₂ physisorption. ^cV_{total} is the total internal pore volume measured at P/P_o = 0.99. ^dV_{inter} is the internal pore volume measured at P/P_o = 0.80. ^eD_{BJH} is the pore diameter calculated from the BJH theoretical model. ^fParticle size distribution (PSD) was determined by measuring the diameters of at least 100 particles under TEM (Figure 1 and Figure 2). Q², Q³, Q⁴ measured from ²⁹Si MAS solid-state NMR spectra.

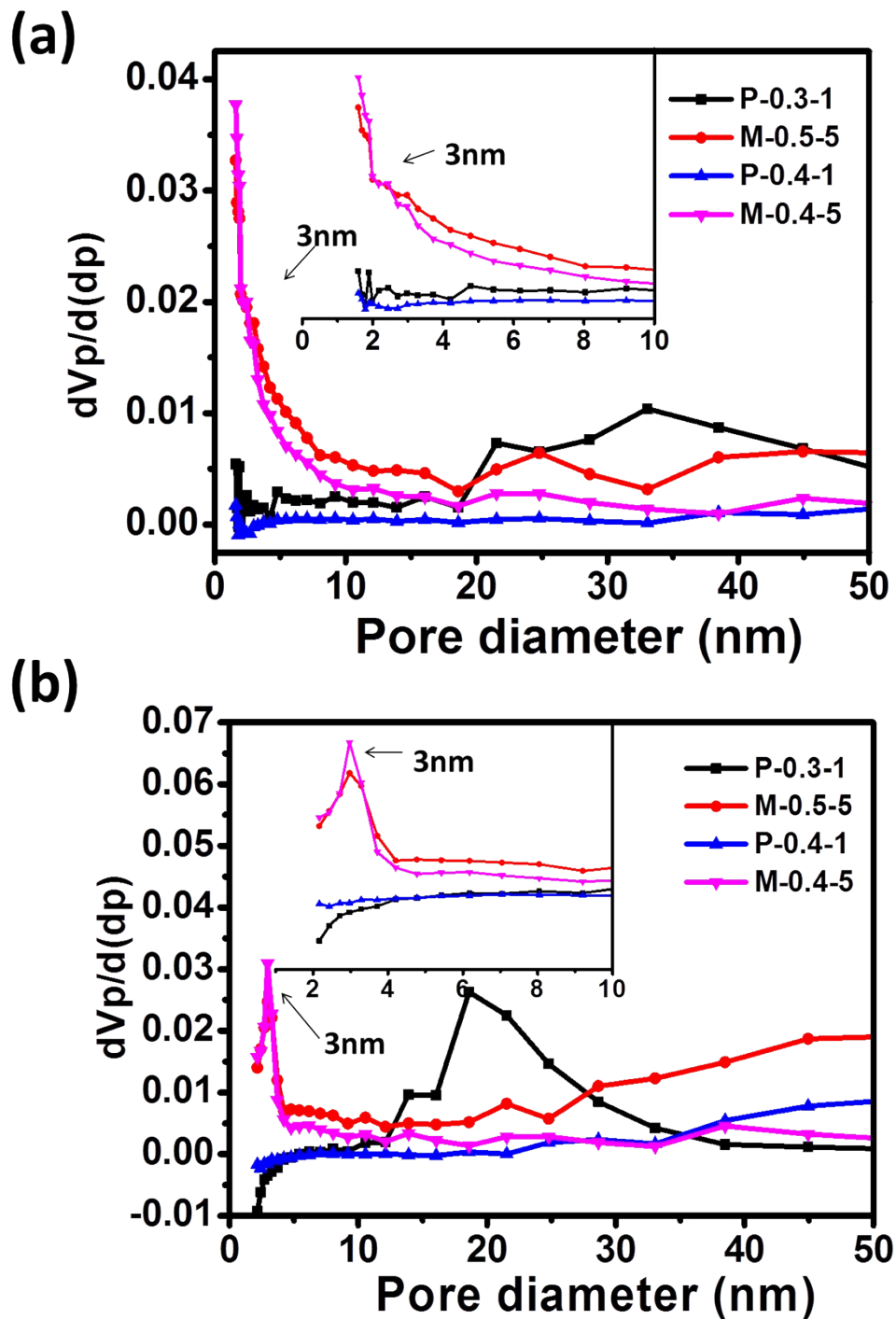


Figure S2. Pore size distribution plots of parent silica nanoparticles and etched MSNs synthesized with different molar of ammonia solution calculated by using the BJH model from adsorption branch (a) and desorption branch (b) respectively.