Supporting information

Facile Large-Scale Synthesis of Monodisperse Mesoporous Silica Nanoparticles with Tunable Pore Structure

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Experimental section:

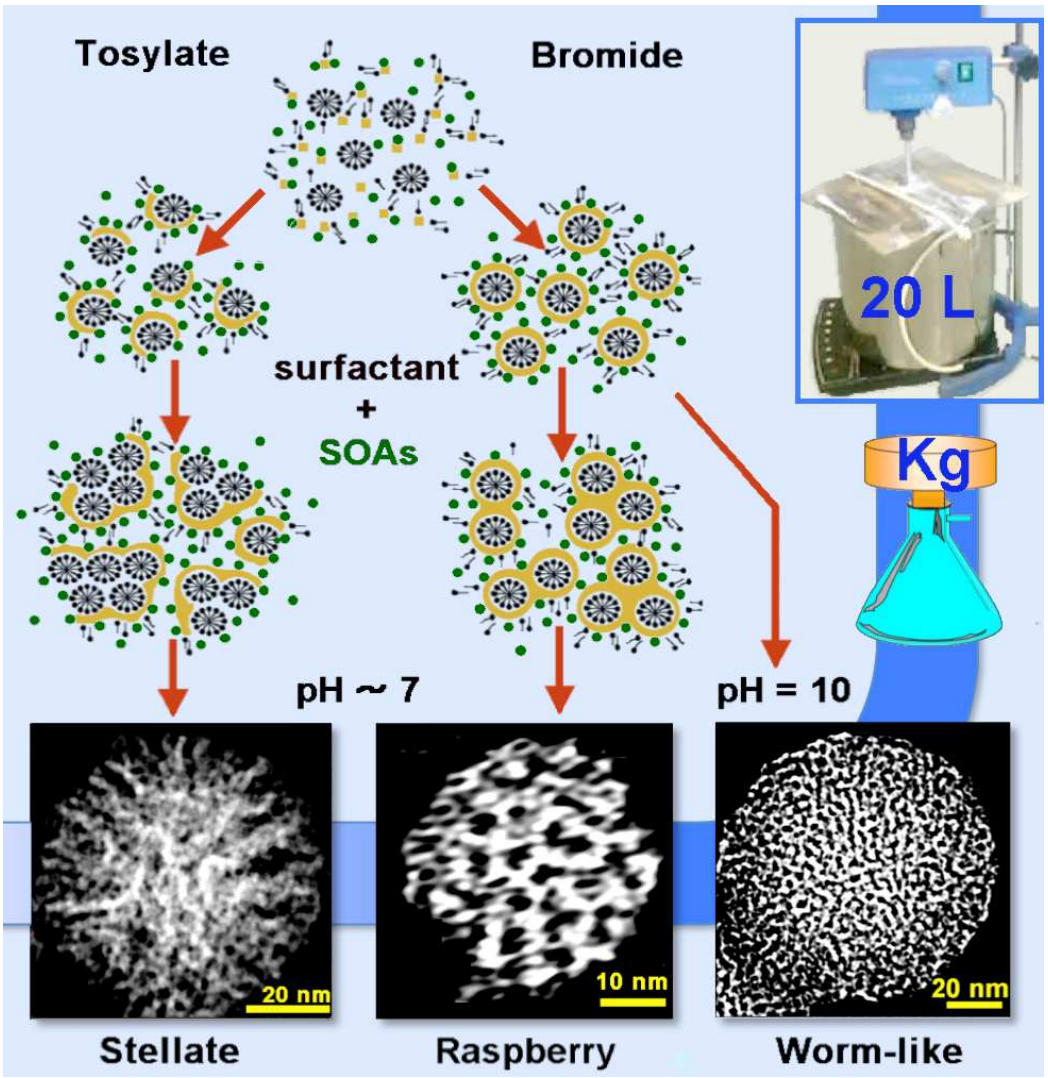
The MSNs were synthesized using a soft-templating method. High concentrations of precursors were used with a molar composition of $1.0SiO_2$:0.06CTATos/CTABr:xSOA:$80.0H_2O$, x=0.026-8, where SOA = triethyleneamine (TEA = *1*, pk_a = 11.1) or triethanolamine ($TEAH_3$ = *2*, pk_a = 7.8) and 2-amino-2-(hydroxymethyl)-propane-1,3-diol (AHMPD = *3,* pk_a = 8.1)

A typical synthesis of MSNs with stellate morphology (MSN-L-T2) was performed as follows: A mixture of 192.0 g of cetyl-trimethylammonium tosylate (CTATos, MERK), 34.7 g of triethanolamine ($TEAH_3$) and 10 L of deionized water was stirred at 80 ^oC for 1 hour, and then 1458.0 g of tetraethyl-orthosilicate (TEOS) was quickly added into the surfactant solution. *It is important to note that, TEOS was quickly added only after the surfactant was completely dissolved in water containing the small organic amine (SOA).* The final mixture had the molar composition: $1.0SiO_2$:0.06CTATos:0.026SOA:$80.0H_2O$. The mixture was stirred at 80 ^oC with a stirring speed of 1200 rpm for another 2 hours. The synthesized MSNs were filtered (final pH = 7.3 for *2* and 7.5 for *3*), washed, and dried in the oven at 100 ^oC for 20 hours. The final yield of the collected product was around 560 g (93% in silica and 85% in surfactant). The yield was 462 g for SOA *3*. *When triethylamine (TEA) was used as the mineralizing agent, the final product* MSN-L-T2 could only *be collected after high-rate centrifugation (final pH = 6.5).*

The synthesis of MSNs with raspberry morphology denoted as MSN-L-B2 was as follows:

the process was the same as described above for MSN-L-T2 with the use of cetyl-trimethylammonium bromide (CTABr) as template. The mother liquor molar composition was $1.0SiO_2$:0.06CTABr:0.026SOA:$80.0H_2O$. The final pH was 7.2. (Yield, 490g)

The synthesis of $TEAH_3$/TEOS with a molar ratio above *2* followed the same recipe for mother liquor molar composition of $1.0SiO_2$:0.06CTATos: $8.0TEAH_3$: $80.0H_2O$. The sample was denoted MSN-L-T2 (Final pH = 10.0). (Yield 594 g)



Scheme S1. Facile kilogram scale synthesis of mesoporous silica nanoparticles

Material characterization:

The X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer with CuKα radiation (λ=1.5405 Å) at 40 kV and 40 mA. Nitrogen adsorption-desorption isotherms were recorded at 77°K on a Quancachrome (O2108-KR-1) after activating the sample under vacuum at 473°K for at least 10 hours. The SEM images were captured by a Hitachi S-4800 microscope. TEM analysis was performed using a JEOL 2010F microscope equipped with a field

emission gun and operating at 200 kV. Thermogravimetric analysis (TG) was performed using a Mettler TGA/SDTA 851e instrument with a heating rate of 10 ^{o}C / min under an air flow. Solid ^{13}C CP-MAS NMR measurements were collected using a VARIAN VNMRS-400WB spectrometer. For ^{13}C (100.6 MHz), a 6 µs (h = p/2) pulse was used with a repetition time of 3 s.

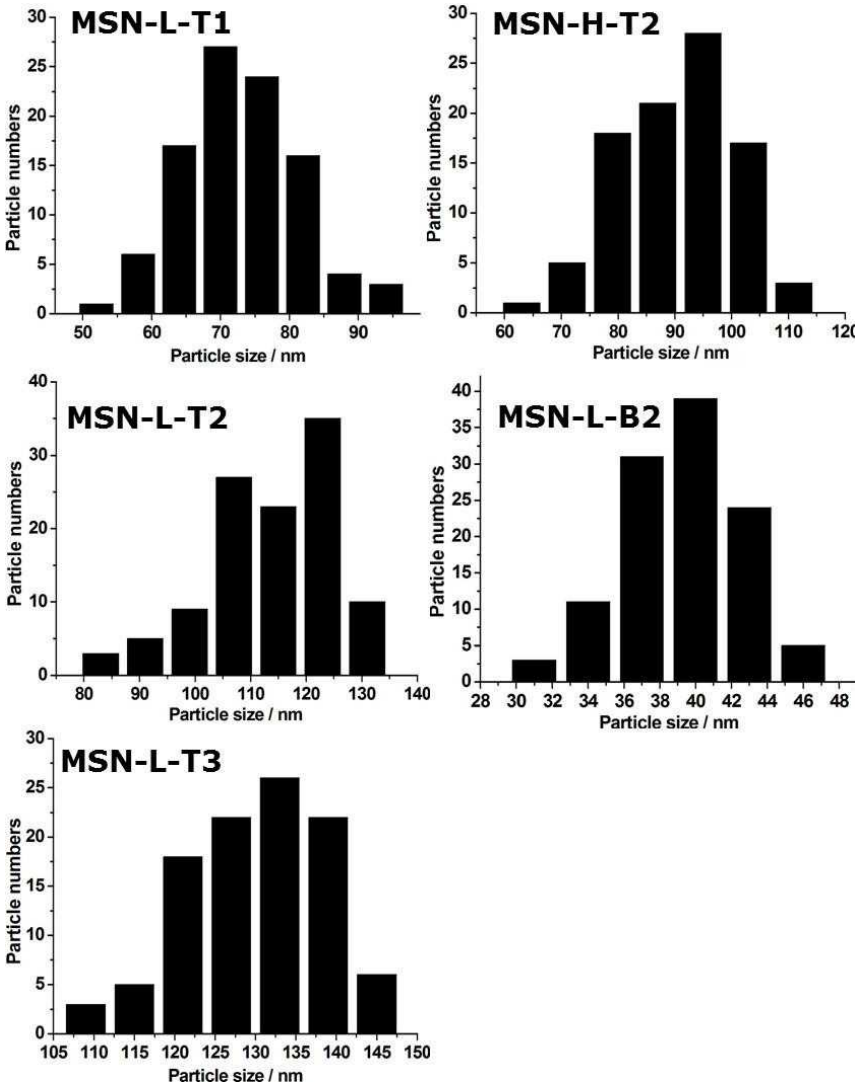


Figure S1. Particle size distribution from TEM pictures

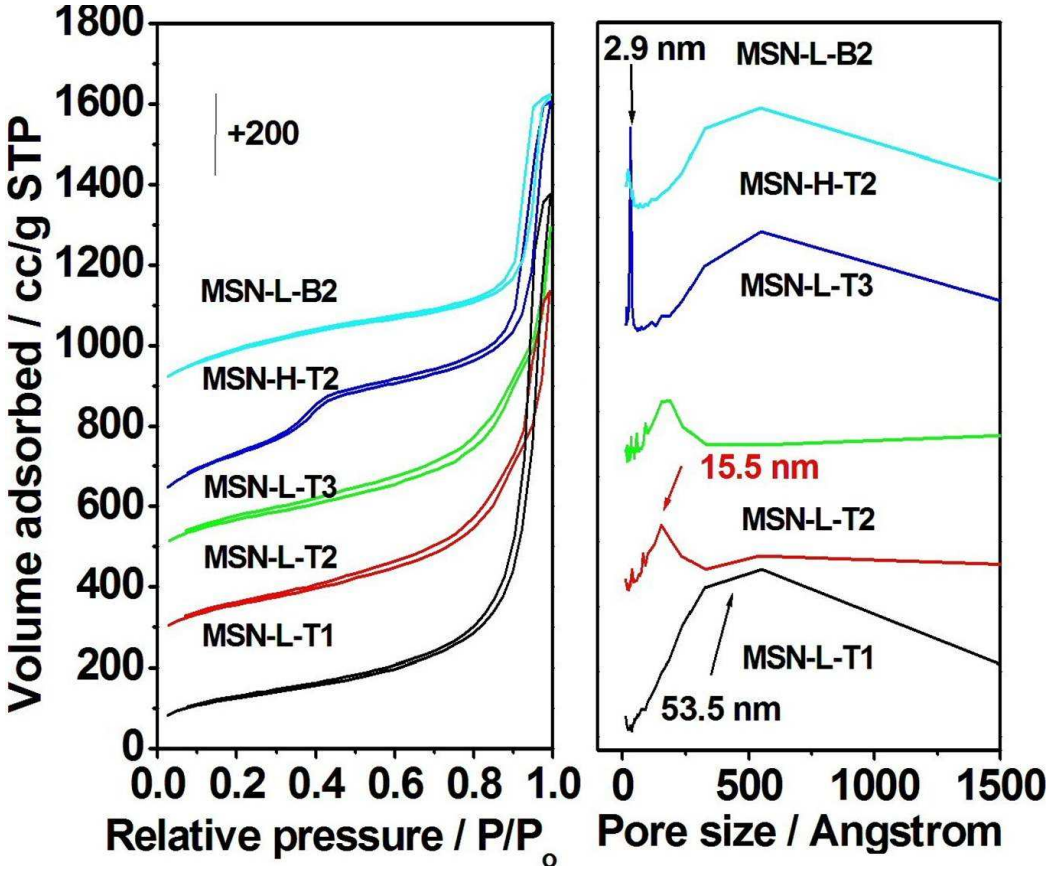


Figure S2. N_2 physisorption isotherms of the mesoporous silica nanoparticles (left) and their corresponding pore size distribution curves calculated by the BJH method (right). *Note that the large distribution of pores above 200 Angström (i e., 20 nm) belongs to inter particle voids between the packed MSNs. The pore distribution centered at 15-16 nm was assigned to the conical pores of the stellate MSNs. The absence of the latter distribution in MSN-L-T1 was assigned to a strong coupled adsorption profile with a broader distribution of interparticle voids that was likely due to a different packing mode leading indeed to a higher external pore volume (Table 1).*

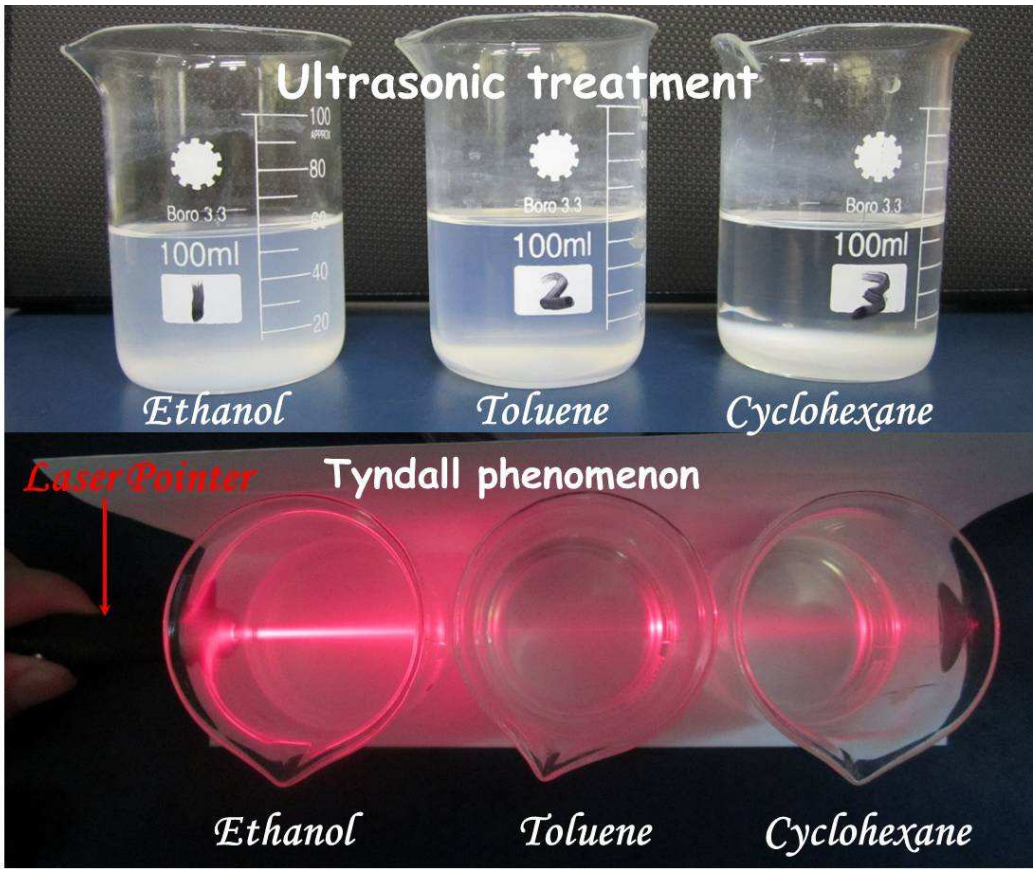


Figure S3. Dispersed MSN-L-T2 (1g/L) in three solvents after classical ultrasonic treatment for 1 h shows the Tyndall effect for particles in non-polar protic solvents where the colloidal suspension was stable. After re-dispersion in water or ethanol, the MSNs cannot be collected by filtration alone.

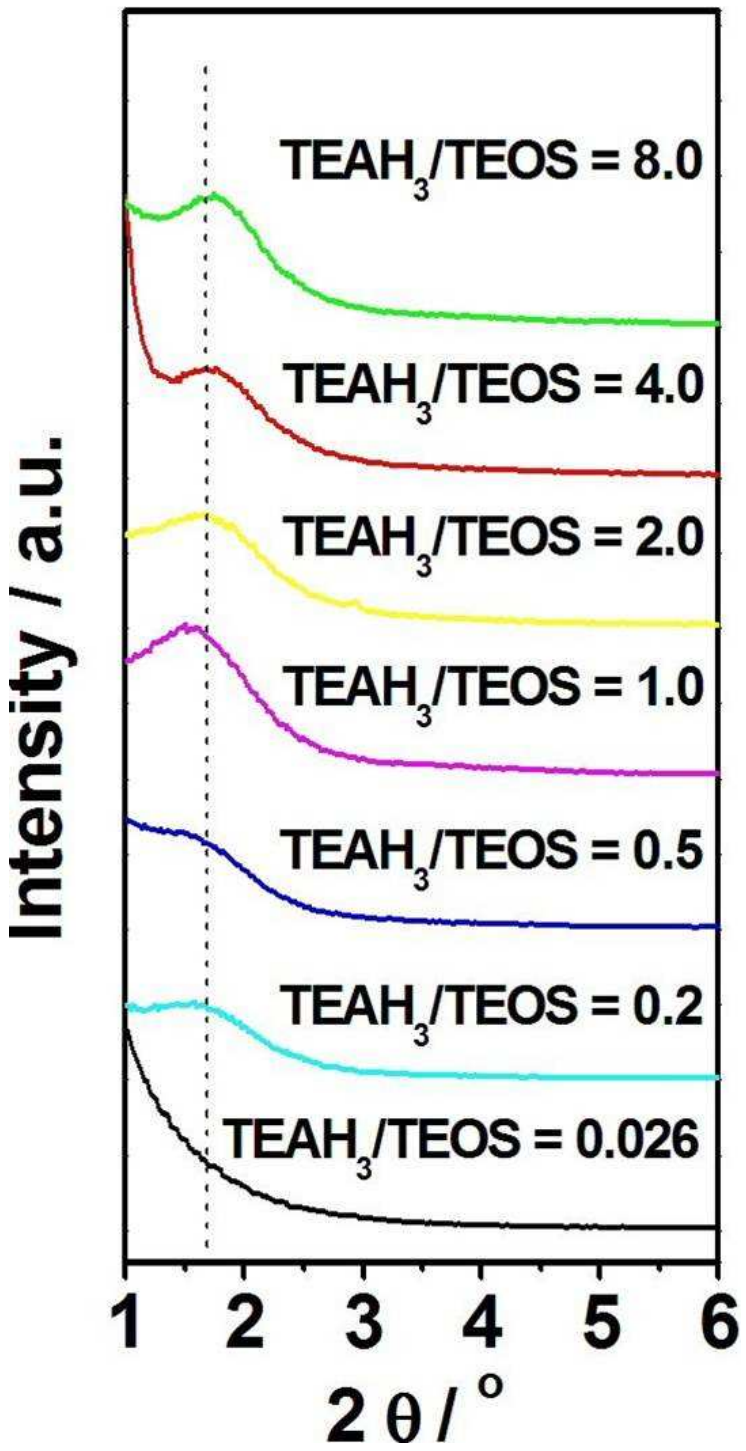


Figure S4. XRD patterns of MSN-X-T1 synthesized at various molar ratios of $TEAH_3$/TEOS.

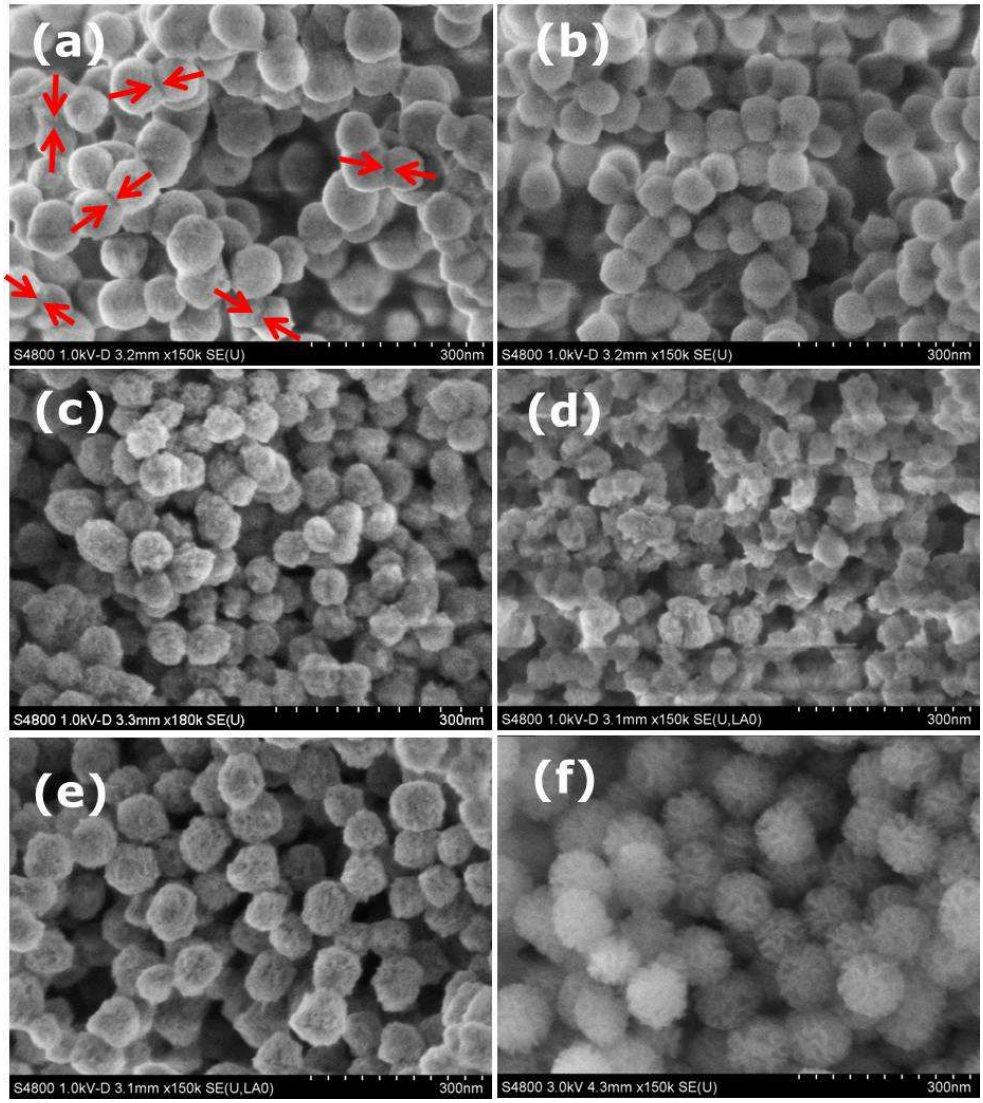


Figure S5. SEM images of MSN-X-T2 synthesized at various molar ratios of $TEAH_3$/TEOS: (a) 8.0; (b) 4.0, (c) 2.0; (d) 0.5; (e) 0.2, and (f) 0.026. *Some particles appeared geminated as revealed by formation of thin bridges featuring porous channels between mesoporous particles. The so-called "geminate nanoparticles" are indicated by red arrows in figure S4(a). The low content of water (H_2O/TEOS molar ratio of 80) and the large quantity of hygroscopic$TEAH_3$ liquid (for $TEAH_3$/TEOS, a molar ratio in the range of 1.0~8.0) resulted in high viscosity which limited diffusion of MSNs. This facilitated the formation of geminate nanoparticles. Similar particle merging was also reported by Mann et al. and Bein et al..* [1, 2, 3]

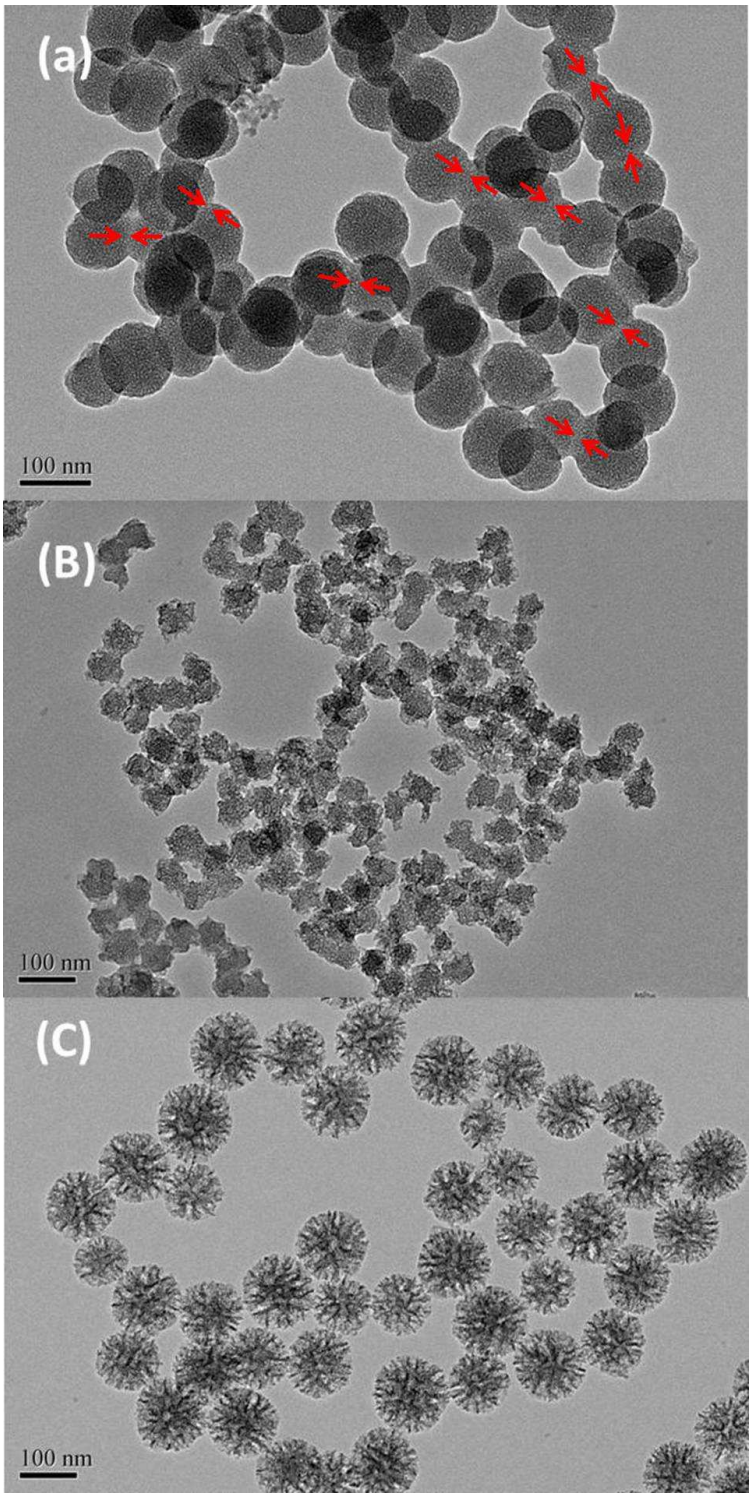


Figure S6. TEM images of MSN-X-T2 synthesized at various molar ratios of $TEAH_3$/TEOS: (a) 8.0; (b) 0.5; and (c) 0.026. *A significant proportion of geminate nanoparticles were seen under HR-TEM using a high molar ratio of $TEAH_3$/TEOS (highlighted by red arrows in figure S5(a)). This was consistent with the SEM results shown on figure 4Sa.*

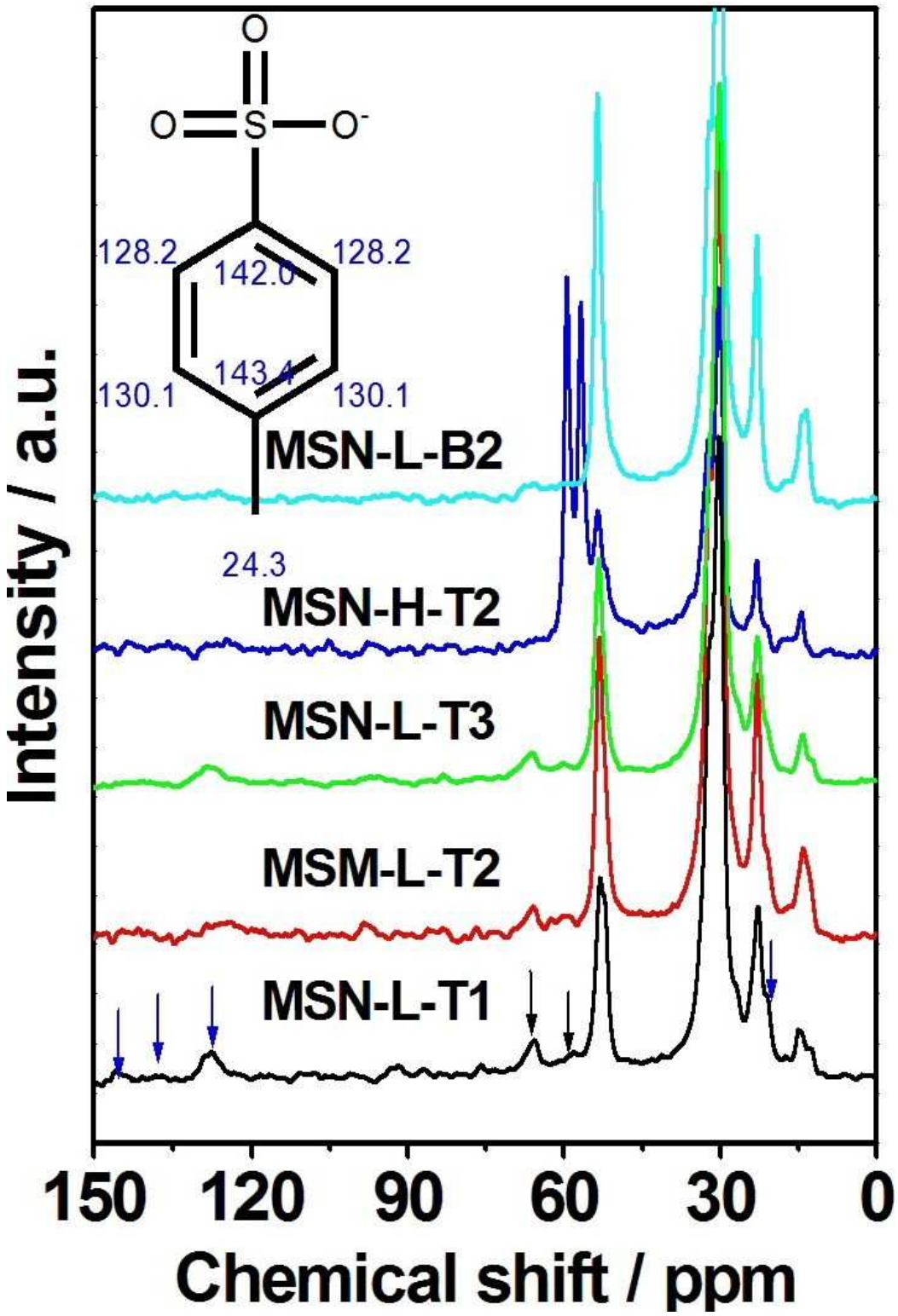


Figure S7. ^{13}C CP MAS NMR spectra of MSNs synthesized at various reaction conditions; *black arrows point out characteristic chemical shifts of Tos^- anions; blue arrows mark the presence of small organic amine (SOA). The presence of Tos^- anions was detected only at low $TEAH_3/TEOS$ molar ratios for MSNs with radial-oriented pores.*

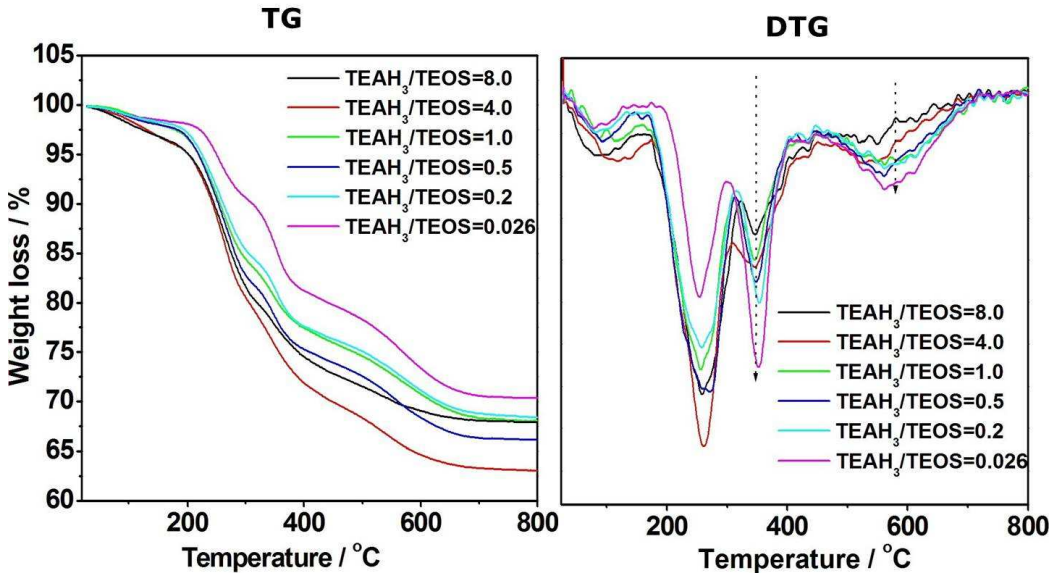


Figure S8. Thermogravimetric analysis (TG) of MSN-X-T2 synthesized at various $TEAH_3$/TEOS molar ratios: (a) 8.0; (b) 4.0, (c) 2.0; (d) 0.5; (e) 0.2, and (f) 0.026. *At increasing $TEAH_3$/TEOS, the weight loss characterized on the DTG curve had a minimum centered at 350 ^oC. This was attributed to decreasing CTA^+-adsorbed onto its tosylate counterion (for assignment see also Figure S9). The peak minima centered at 250^oC was due to CTA^+ interacting directly with silanol groups (SiO^-) and increased with decreasing ratio. The peak at 600 ^oC was attributed to water evolution from silanol condensation.*

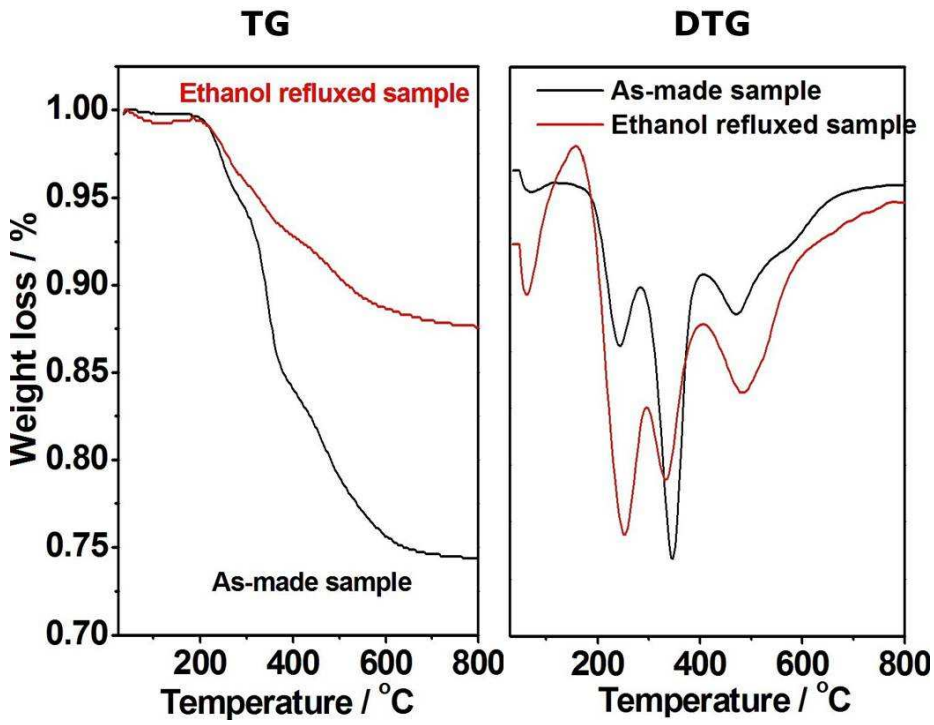


Figure S9. Thermogravimetric analysis (TG) of MSN-L-T2 using anhydrous ethanol extraction. *To check whether physically adsorbed CTATos and electrostatically interacting CTA^+ corresponded to mass loss at 250 and 350 °C (shown in figure S7), an experiment was designed to better characterize the physical characteristics. Since physically adsorbed surfactant or hydrogen-bonded polymer should be extracted by an organic solvent (for example ethanol) a TG curve should evolve consistently.*[4] *Indeed, after ethanol extraction of MSNs, a stellate morphology (*MSN-L-T2*) was seen. The weight loss centered at 250 °C and was almost unchanged. The weight loss centered at 350 °C and 600 °C decreased significantly. When the MSNs with worm-like pores were extracted using anhydrous ethanol, the weight losses of the three peaks were not changed. This was consistent with higher templating efficiency occurring with a higher proportion of electrostatically retained CTA^+ surfactant.*

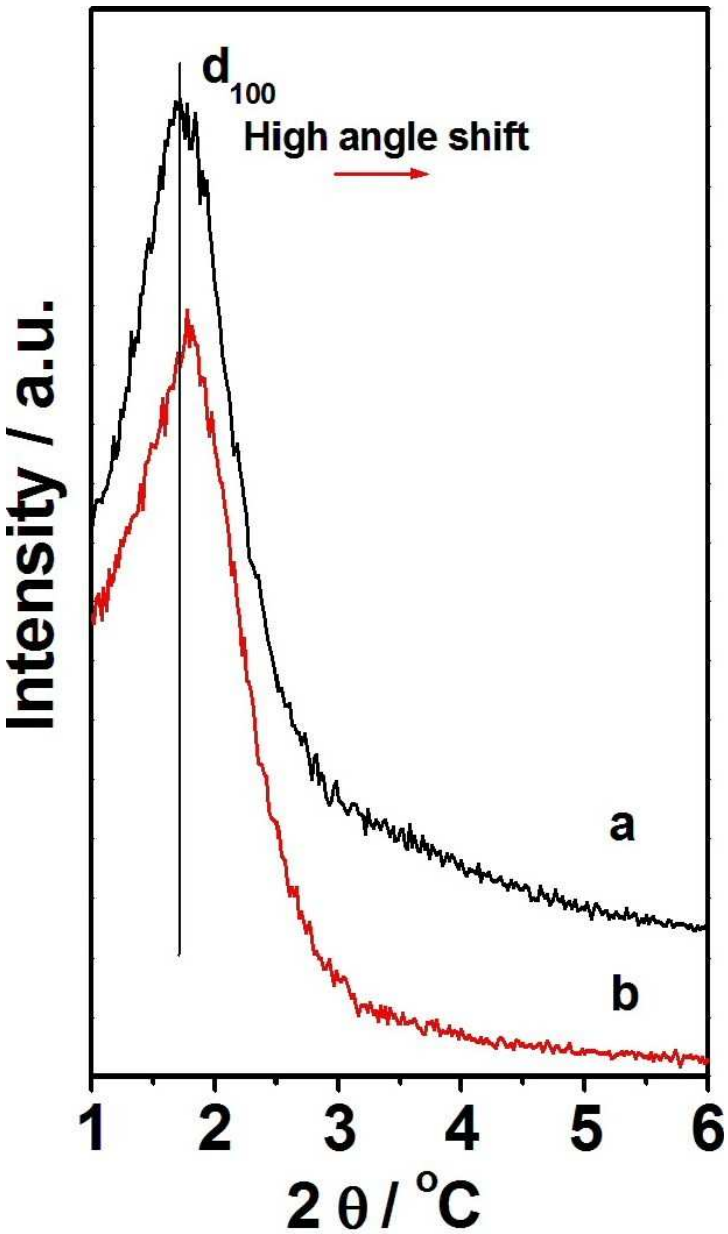


Figure S10. XRD patterns of calcined sample MSN-H-T2 before (a) and after (b) saturated water stream treatment at 700 °C for 6 h. *The comparison of both intensity and shape of the XRD patterns revealed an excellent resistance of the structure to stream treatment. The slight shift of the peak towards a larger angle suggests a small lattice expansion (< 10%).*

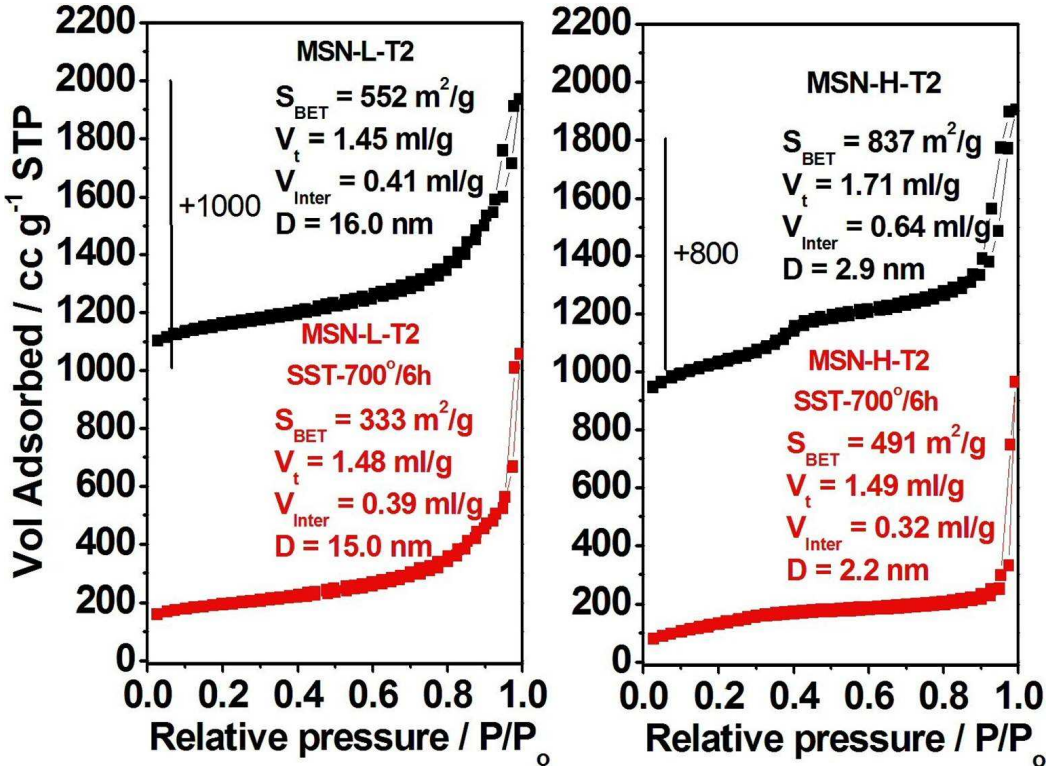


Figure S11. N_2 physisorption isotherms of MSN-L-T2 (left) and MSN-H-T2 (right) before and after saturated water stream treatment at 700 ^{o}C for 6 h. *Even though the BET surface area was reduced after water stream treatment, the mesoporous structure was maintained.*

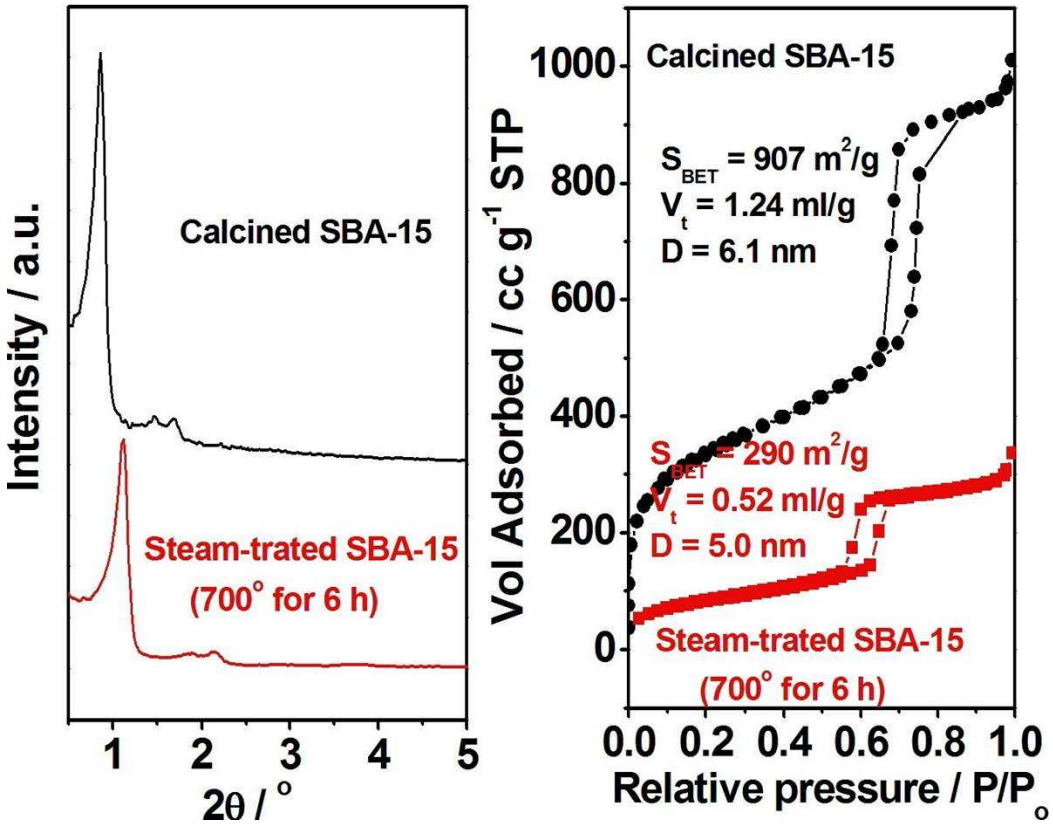


Figure S12. XRD patterns (left) and N_2 adsorption isotherms (right) of calcined SBA-15 after similar saturated water stream treatment at 700 °C for 6 h. *The XRD patterns demonstrated structure integrity after stream treatment, however, the BET surface area was drastically decreased.*

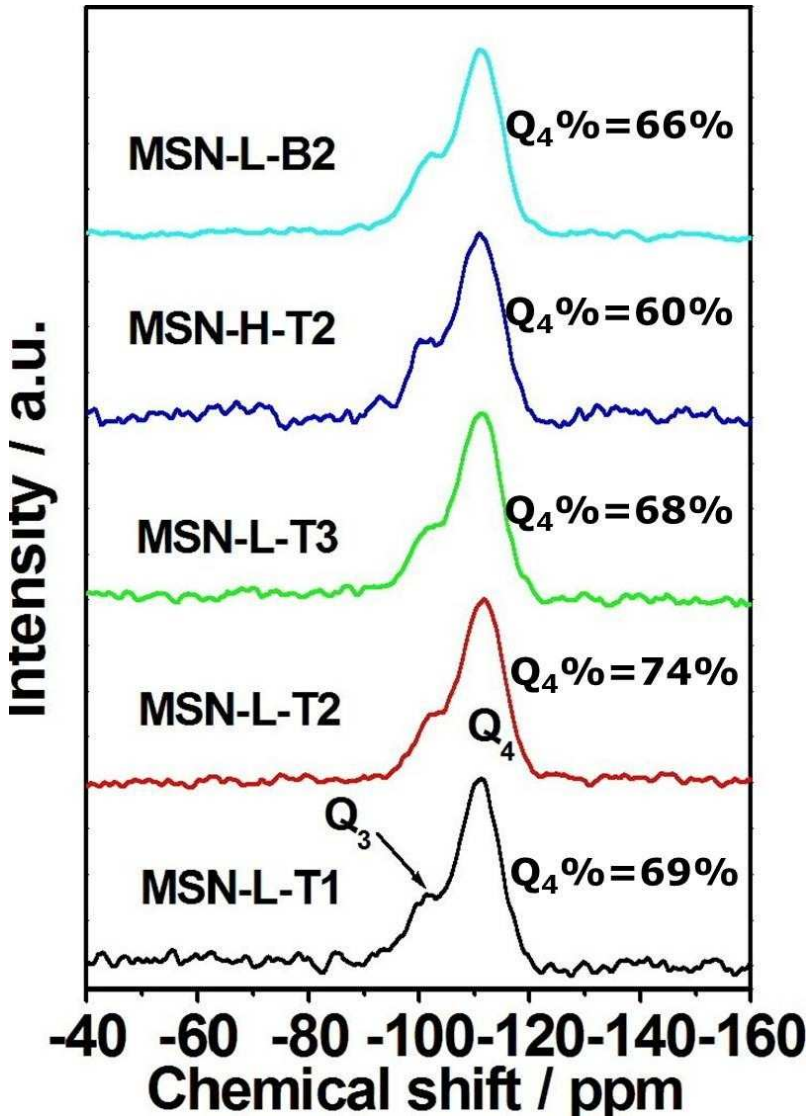


Figure S13. ^{29}Si MAS NMR spectra of as-made MSN-L-Tn and MSN-L-B2 and MSN-H-B2 recorded with single Hahn echo to quantify Q_n species, n = 2-4. $Q_n = [Si(O\text{-}Si)_n(OH)_{4-n}]$. No Q_1 was observed, showing that no pending terminal $Si(O\text{-}Si)_1(OH)_3$ *could be detected. Q_2 was detected only in MSN-H-T2 for the worm-like morphology obtained at high SOA concentration. This indicates a lower level of condensation than in the MSN-L-X_n series. The concentration of Q_3 was low (ca. 30%) with a high Q_4 fraction of ca. 70%. In comparison, MCM-41 silicas calcined at 600°C for 5 hours and as-made SBA-15 silica still possessed ca. 60% and ca. 82.1% of Q_4, indicating that currently synthesized MSNs have similar hydrothermal stability to that of SBA-15.* [4,5]

References:

(1) Fowler, C. E.; Khushalani, D.; Lebeau, B.; Mann, S. *Adv. Mater.* 2001, *13*, 649-652.

(2) Sadasivan, S.; Fowler, C. E.; Khushalani, D.; Mann, S. *Angew. Chem.Int. Ed.* 2002, *41*, 2151-2153.

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(4) Zhao, D. Y.; Feng, J. L.; Huo, Q. S.; Melosh, N.; Fredrickson, G. H; Chmelka, B. F.; Stucky, G. D. *Science* 1998, *279*, 548-552.

(5) Li, Y. R.; Song, M. J.; Gu, H. F.; Huang, Y.; Niu, G. X.; Zhao D. Y. *Chin. J. Catal.*, 2012, *33*, 1360–1366.