

Supplementary Information

Protocrystallinity of Monodispersed Ultra-Small Templated Mesoporous Silica Nanoparticles

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Table S1. Zeta potential of the reaction solution for ultrasmall MCM-41 nanoparticles, **MSN-20-A**.

Reaction time	Zeta (mV)
(pH 5.5) 5 min	+ 24
(pH 5.5) 4 h	+ 32
(pH 5.5) 3 d	+ 24
(pH 5.5) 4 h → (pH 7) 5 min	+ 42
(pH 5.5) 4 h → (pH 7) 3 d	+ 59

Table S2. Porosity characteristics.

Material	S _{BET} (m ² /g)	Pore diameter ^a (nm)	Pore wall thickness ^b (nm)	Internal Pore volume ^c (cm ³ /g)	Interparticle Pore volume ^c (cm ³ /g)
MSN-23-A	540 ± 20	3,9 ± 0,2	1.8 ± 0,3	0.60 ± 0.02	1.20 ± 0.02
MSN-20	804 ± 30	3.8 ± 0.2	1.2 ± 0,3	0.63 ± 0.02	1,41 ± 0.02
MSN-100-B	920 ± 30	3.5 ± 0,2	n.a.	0.82 ± n.0.02	0.90 ± 0.02
MCM-41	1092 ± 30	3.7 ± 0,2	1.0 ± 0.2	0.88 ± 0.02	0.94 ± n.a 0.09 ± 0.01

a) from N₂ nitrogen and BdB method, b) calculated from pore diameter and XRD assuming a hexagonal channel array, c) calculated at P/P₀ = 0.90

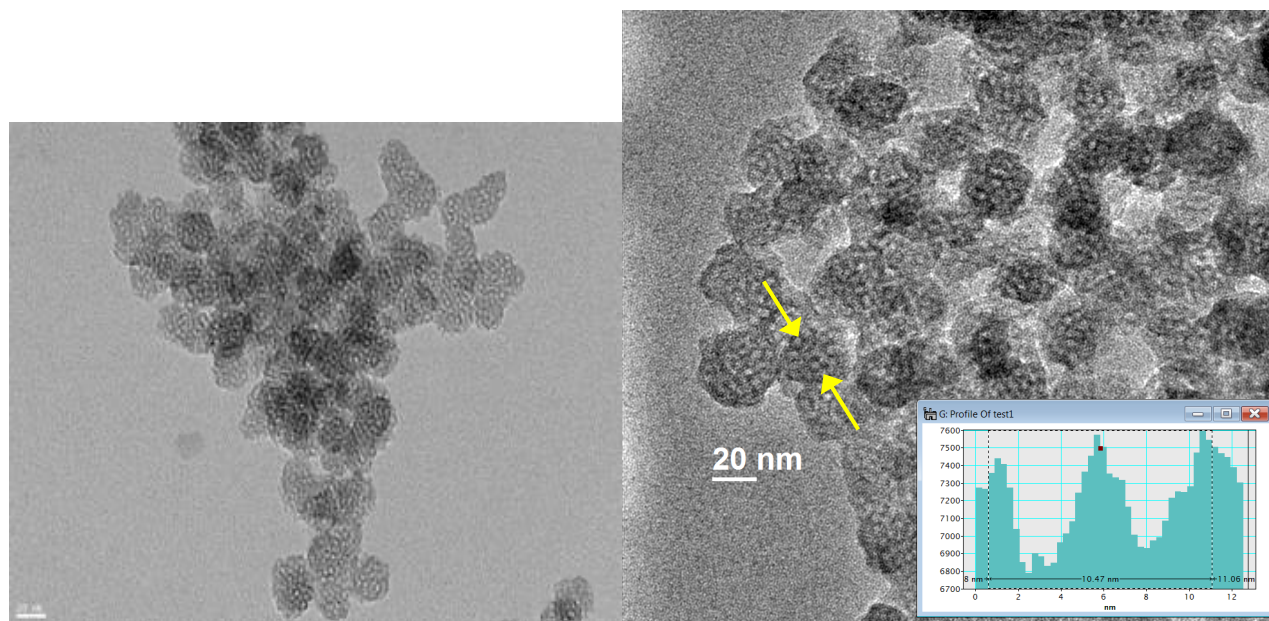


Figure. S1 HRT EM image of calcined : **MSN-23-A** typical (bottom) with insert for intensity profile analysis showing a distance 5.4 ± 0.2 nm between two pores and an average particle size diameter of 22 ± 3 nm prepared as calcined MSN-22-A (top image) with an average size of $22 \text{ nm} \pm 3$ nm.

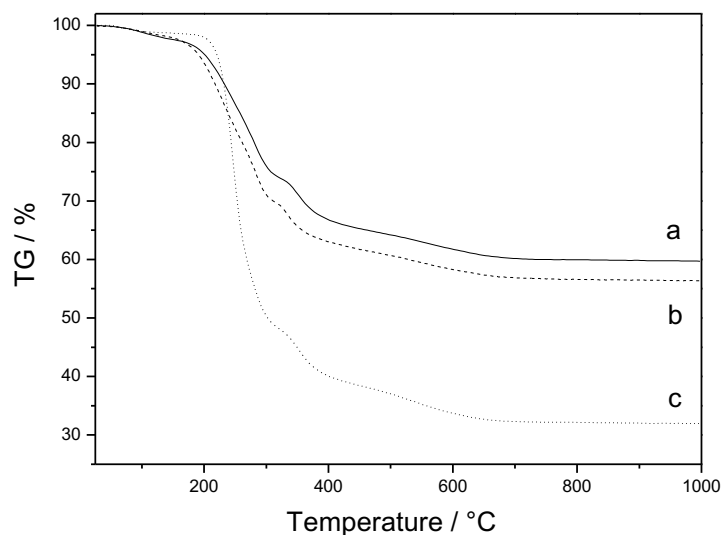
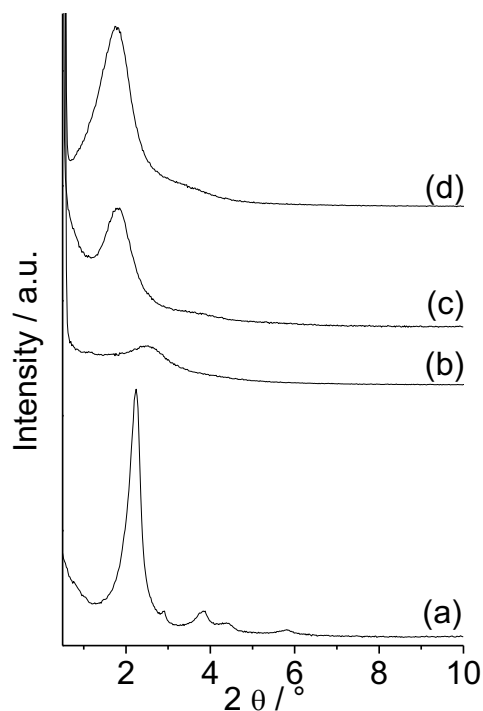


Figure. S2 (left) Comparison of XRD patterns of MSM-100 (a,b) and MSN-20 (c, d) as-synthesized (a, c) and calcined then treated in distilled water (b, d), i. e., i) calcined mesoporous silica powder 0.1 g + distilled water 10 g, stirred at RT overnight, ii) centrifugated and iii) dried at 50°C ; (right) TGA of the as-synthesized nanoparticles of (a) **MSN-20-A**, (b) **MSN-100-A** acid treated (c) **MSN-100** (washed with deionized water).

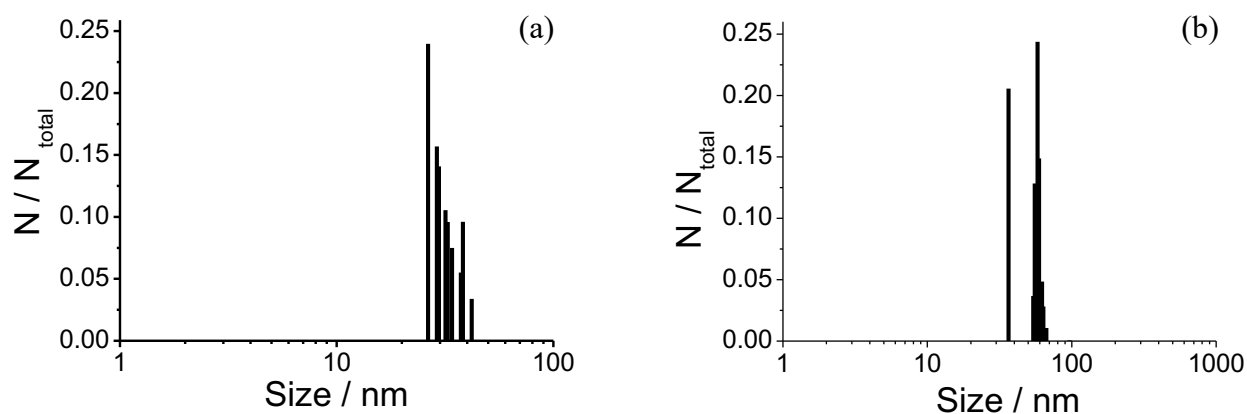


Figure. S3 DLS size distribution of **MSN-20-A**, measured after the synthesis with flocculate comprised between 24 and 41 nm (a) and 3 months later with a single peak at 37 and a distribution in the range 52-69 nm (b).

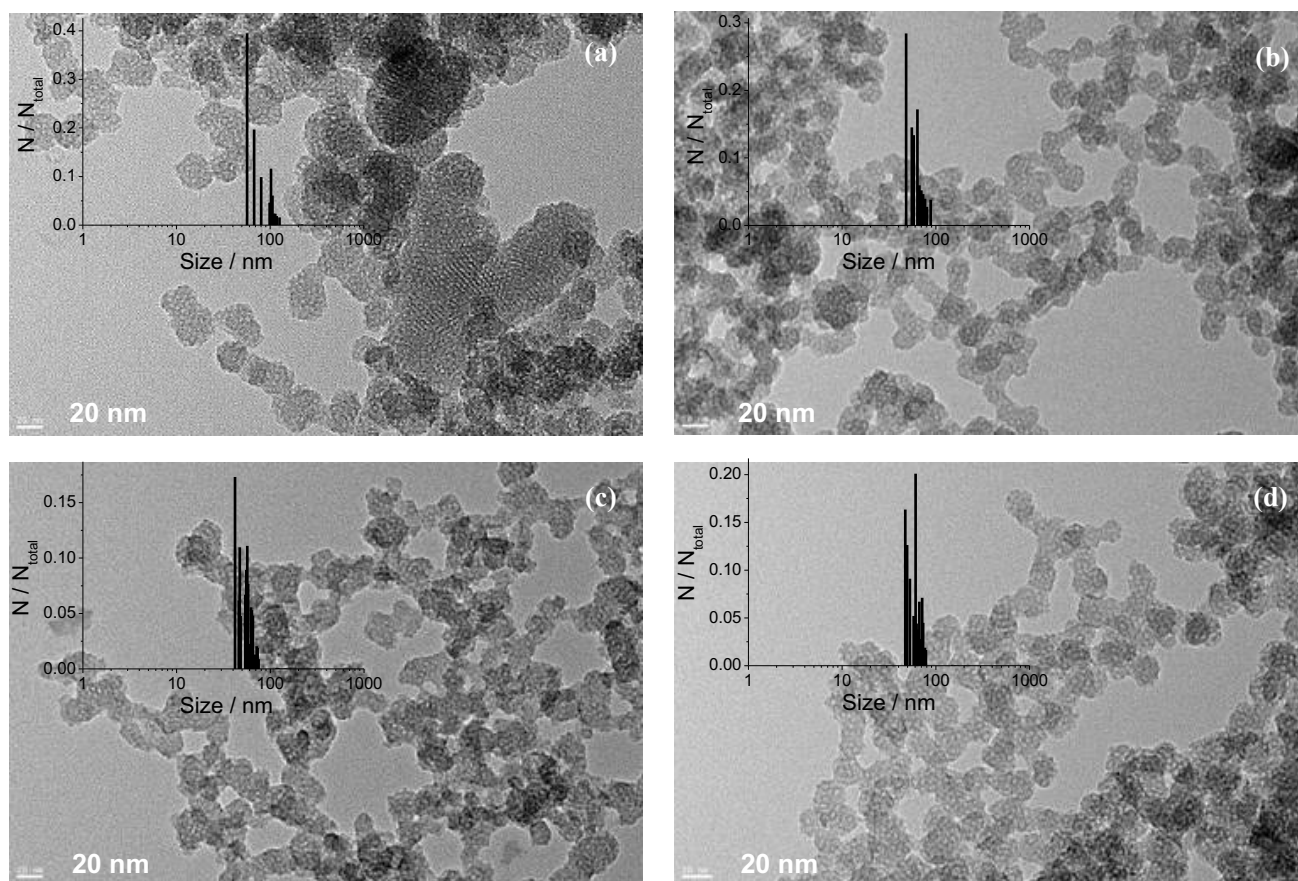


Figure. S4 TEM images of US-MSN obtained from the reaction solution at the molar ratio of 1 SiO_2 : 0.5 NaOH : x CTAB : y F127 : 130 H_2O . (a) $x = 0.12$, $y = 0.000104$ (twice more F127), (b) $x = 0.12$, $y = 0.000026$ (twice less F127), (c) $x = 0.24$ (twice more CTA), $y = 0.000052$, and (d) $x = 0.06$ (twice

less CTA), $y = 0.000052$. Same nucleation quenching using dilution by 6 times. Inserts : corresponding DLS size distribution of the nanoparticle aggregates in the as-synthesized solution (a, b, c, and d).

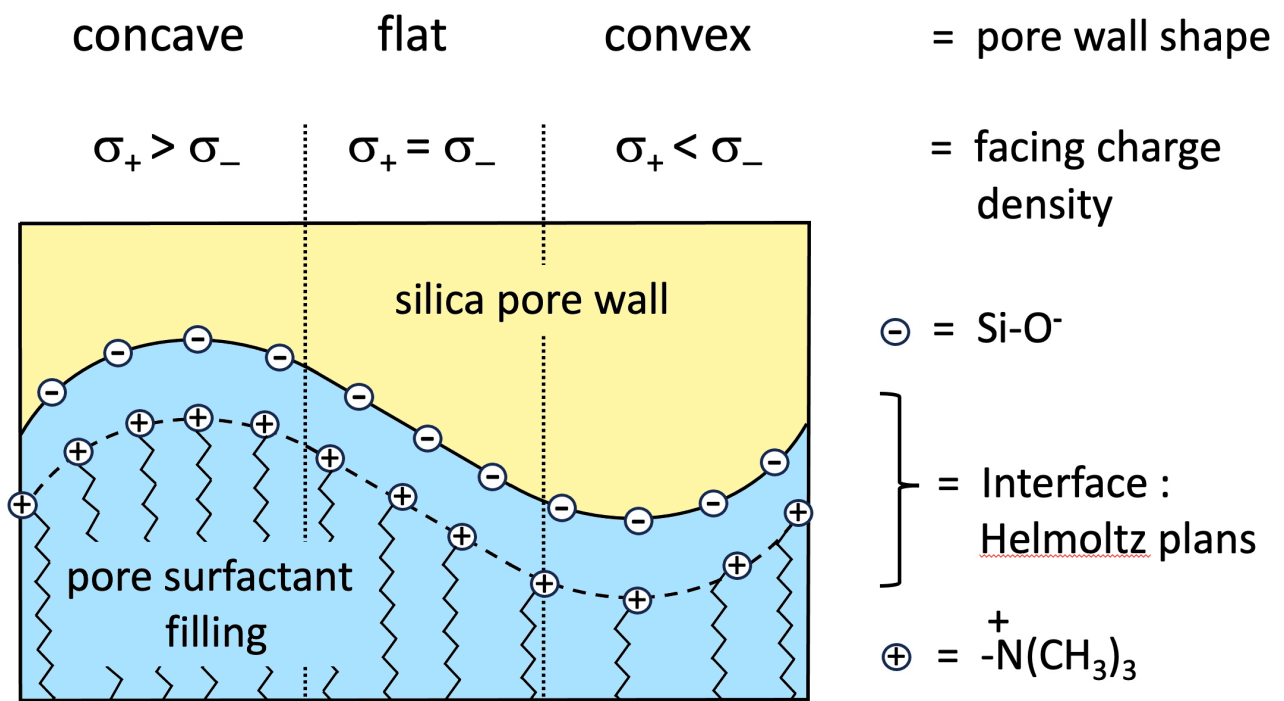


Figure. S5 Surface curvature generated by charge density mismatch between the Helmholtz plans in the silica-surfactant interface inspired from ref. 49 where σ_i and σ_s stand for charge densities on the silica pore wall (Si-O^-) and on the surfactant micelles palisade entrapped in the templated pores (positively charged ammonium heads).

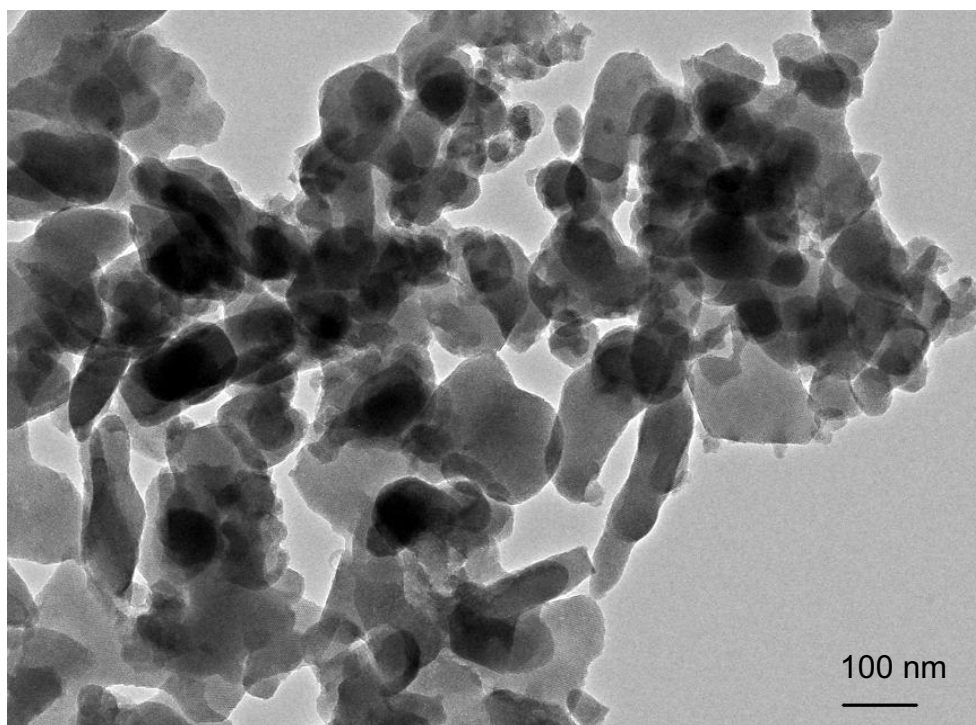


Figure. S6 TEM image of **MSN-100** synthesized in the presence of a large quantity of F127 as reported in ref.11 by Imai et al.; average particle size of 100 nm.