Supporting Information

Dual-templating Strategy for Green and Scale-up Synthesis of Dendritic Mesoporous Silica Nanospheres

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Materials

Cetyl-trimethylammonium bromide (CTAB), Sodium dodecyl benzene sulfonate (SDBS), Sodium dodecyl sulfate (SDS), Sodium laurate (SL), Sodium stearate (SS), Sodium sulfate (Na_2SO_4), Sodium methanesulfonate ($NaSO_3$-CH_3), Triethanolamine ($TEAH_3$) Tetraethylorthosilicate (TEOS), Tetra-butyl ortho-titanate (TBOT) and acetonitrile were purchased from Sinopharm Chemical Reagent Co., Ltd. Cyclohexene, Tert-Butyl Hydroperoxide (TBHP 5.5 M in decane) were purchased from Aldrich. All chemicals were used as received without any further purification. Deionized water was used in all experiments.

Experimental Section

Synthesis of dendritic mesoporous silica nanoparticles (DMSNs)

The DMSNs were prepared via the sol-gel approach by using dual templates at ultralow concentration. In a typical process, 152g of CTAB, 38 g of SDS, 34 g of $TEAH_3$ were dissolved in 50 ml of water and stirred at 80 °C for an hour. After that, 1458 g of TEOS were added and stirred for another two hours. The mother liquid molar ratio is 1.0 TEOS: 0.06 CTAB: 0.02 SDS: 0.026 $TEAH_3$: 80 H_2O. The synthesized DMSNs were filtered, washed and dried at 100 °C overnight. DMSNs were synthesized with high yield (91.7 %) on a large scale (0.52 kg). The products were denoted as DMSNs-SDS. When DMSNs were synthesized by other co-surfactants (SDBS, SL and SS), all the process were the same as above except SDS was replaced by SL or other co-surfactants which were denoted as DMSNs-SDBS, DMSNs-SL and DMSNs-SS. To confirm the co-templating effect of the second

surfactant, Na_2SO_4 and $NaSO_3$-CH_3 were added into the synthesis process respectively instead of the long-alkyl anion surfactants.

Synthesis of silkworm cocoon-like and mono-lamellar vesicle structured mesoporous silica nanoparticles (SW-MSNs and V-MSNs)

The silkworm cocoon-like or *mono-lamellar* vesicular mesoporous silica nanoparticles were synthesized similar to the synthesis of DMSNs at high concentration of dual templates at varied base concentration. The molar ratio of SW-MSNs and V-MSNs was 1.0 TEOS: 0.12 CTAB: 0.06 SDS: 0.026 NaOH: 80 H_2O:0.48 TMB and 1.0 TEOS: 0.12 CTAB: 0.06 SDS: 0.104 NaOH: 80 H_2O:0.48 TMB, respectively.

Synthesis of Ti-containing DMSNs (Ti-DMSNs)

The Ti-DMSNs were synthesized by one-pot dual-template strategy. Due to the fast hydrolysis of TBOT and to maintain the morphology of DMSNs well, Ti species were added when the mother liquid was cooled to room temperature, and then the mixtures were stirred for another 12 hours. In order to reduce the residual sodium introduced within the co-surfactants, the products obtained after that were washed with a large amount of water. At last, the surfactants were removed in two steps. First, the catalyst was stirred in the mixture of ethanol and HCl aqueous solution at 60 °C for 10 hours. After that, the dried samples were calcined at 550 °C for 6 h to remove surfactants completely.

The reference catalysts, TS-1 and Ti-MCM-41 were synthesized according to the literature. [1-2]

Catalytic reaction

To verify the catalytic properties of the materials, the catalytic performance of Ti-DMSNs were investigated by the liquid epoxidation of cyclohexene with TBHP (5.5 M in decane) as the oxide. In a typical run, a mixture of 0.05 g of catalyst, 10 mmol of cyclohexene, 10 mmol of TBHP (5.5 M in decane), and 10 mL of acetonitrile was stirred vigorously in a round-bottom flask equipped with a condenser at 60 °C for 2 h. The products were analyzed on a Shimadzu GC 2014 gas chromatograph equipped

with a 30 m OV-1 capillary column and a flame ionization detector.

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. FT-IR spectra were recorded by Nicolet Fourier transform infrared spectrometer (NEXUS 670) using the KBr technique. Thermogravimetric analysis (TG) was performed on a Mettler TGA/SDTA 851e instrument with a heating rate of 10°C / min under an air flow. Ultraviolet visible (UV-vis) spectroscopy was conducted with a UV2700 UV-vis spectrophotometer.

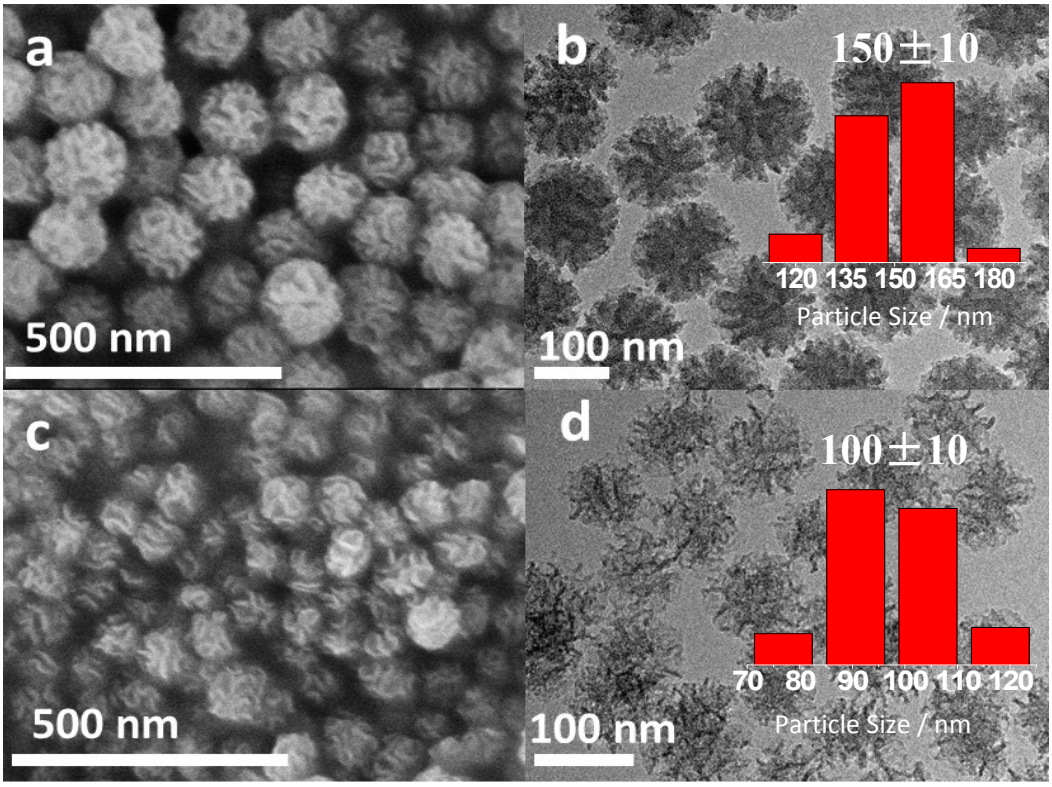

Fig. S1 SEM and TEM images of DMSNs synthesized with DTAB+SDS (a, b) and ODTAB+SDS (c, d)

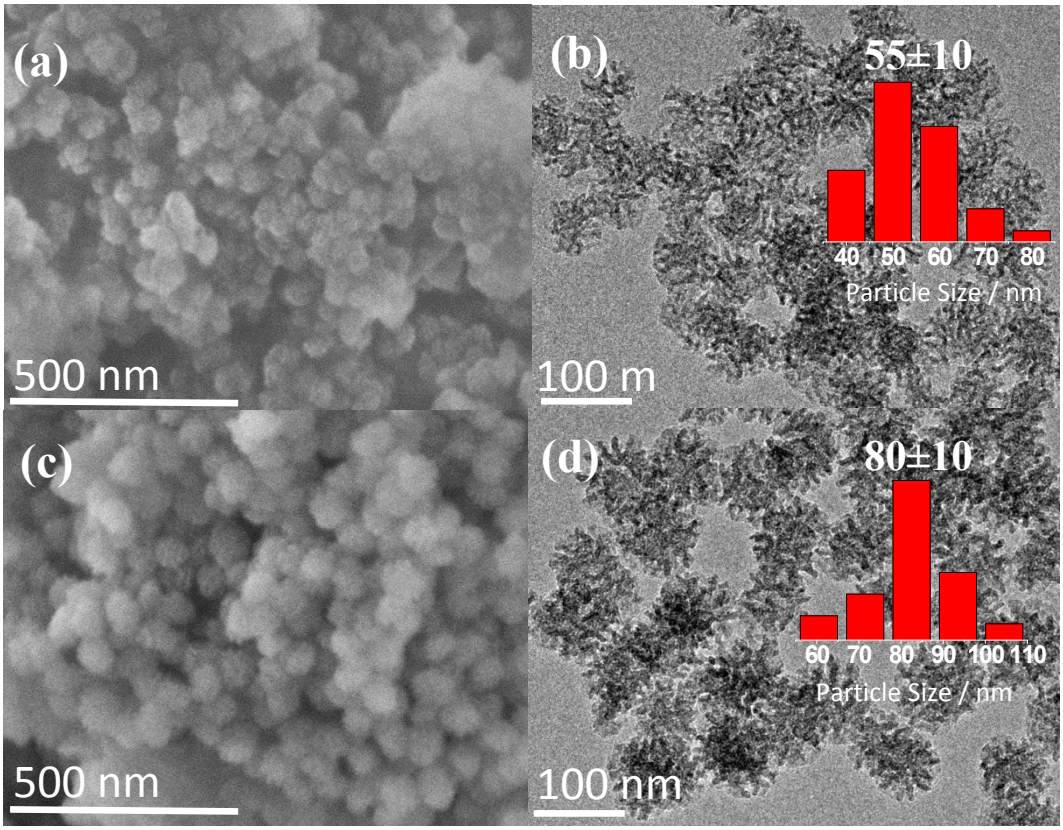

Fig. S2 SEM and TEM images of DMSNs synthesized by NaOH (a, b) and NH_3H_2O (c, d)

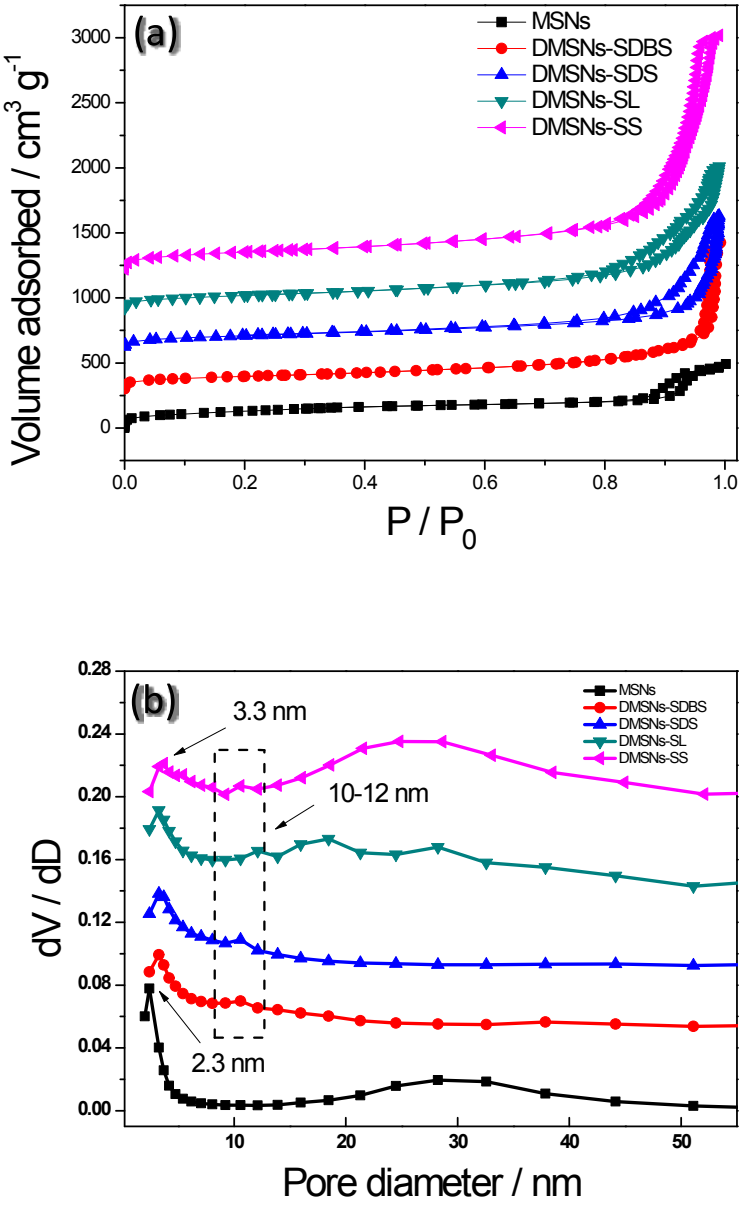

Fig. S3 N_2 adsorption − desorption isotherms (a) and pore size distribution plots (b) of DMSNs with dual templates and MSNs with single surfactant. (Isotherms offset vertically by250 cm^3/g consecutively.)

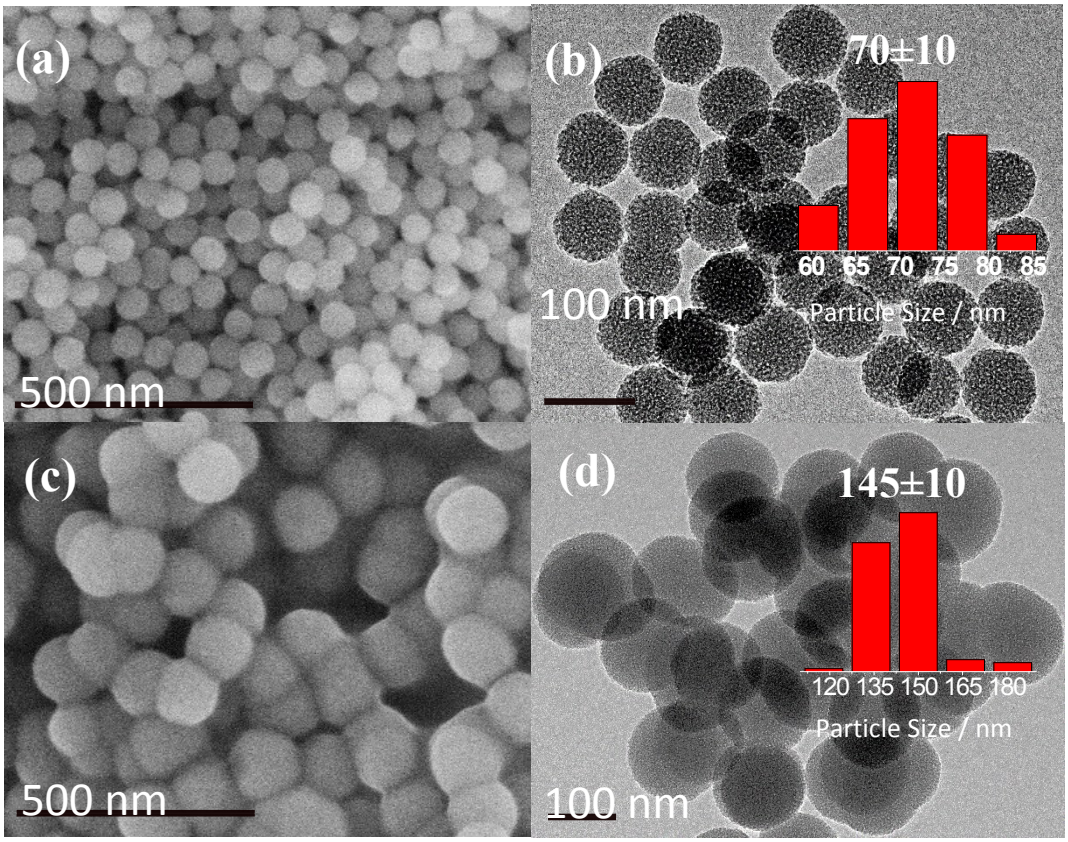

Fig. S4 SEM and TEM images of MSNs synthesized with CTAB+$NaSO_3$-CH_3 (a, b) and CTAB+Na_2SO_4 (c, d)

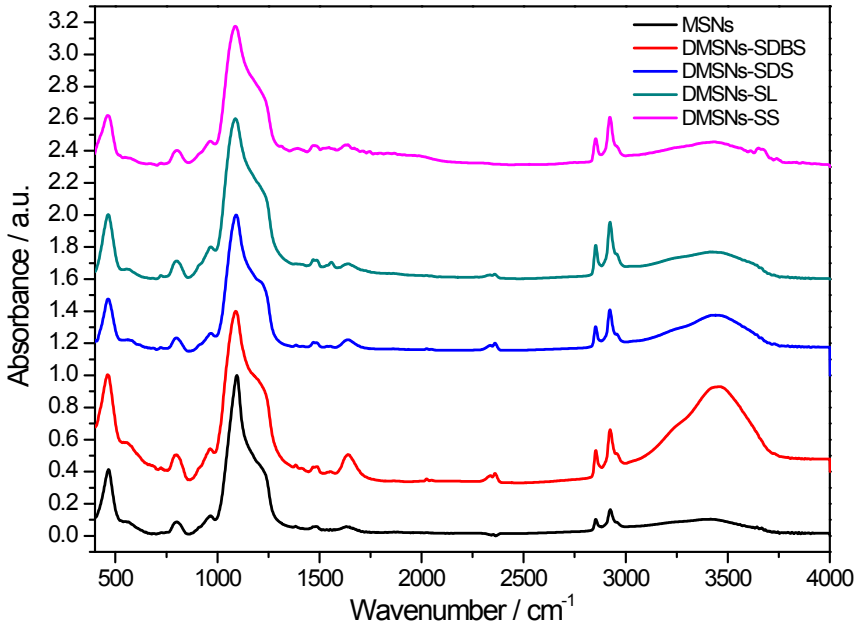

Fig. S5 FT-IR spectra of DMSNs synthesized with dual templates and MSNs synthesized with single surfactant. (These lines are offset regularly.)

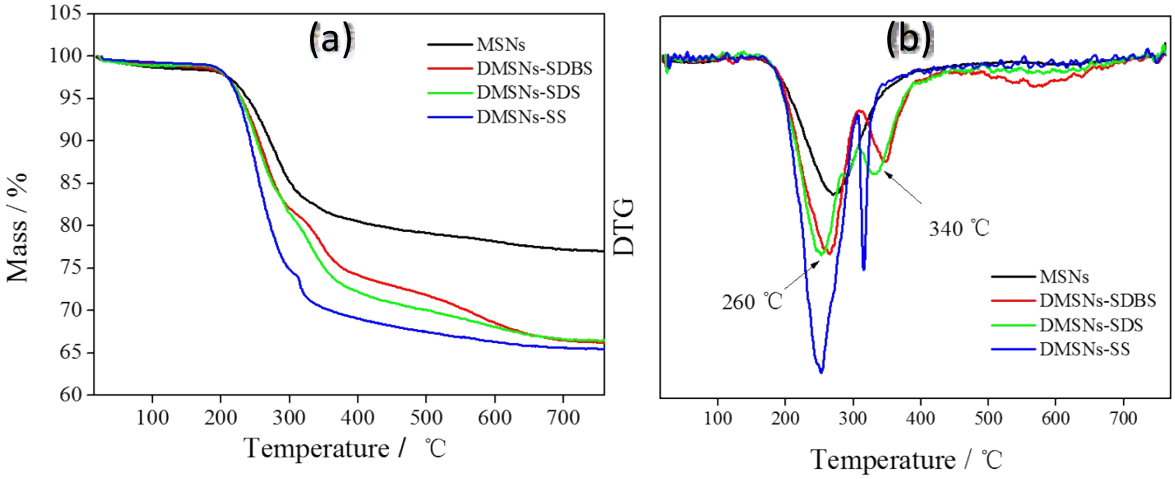

Fig. S6 Thermogravimetric curves (a) and differential thermogravimetric curves (b) of DMSNs with dual templates and MSNs with single surfactant.

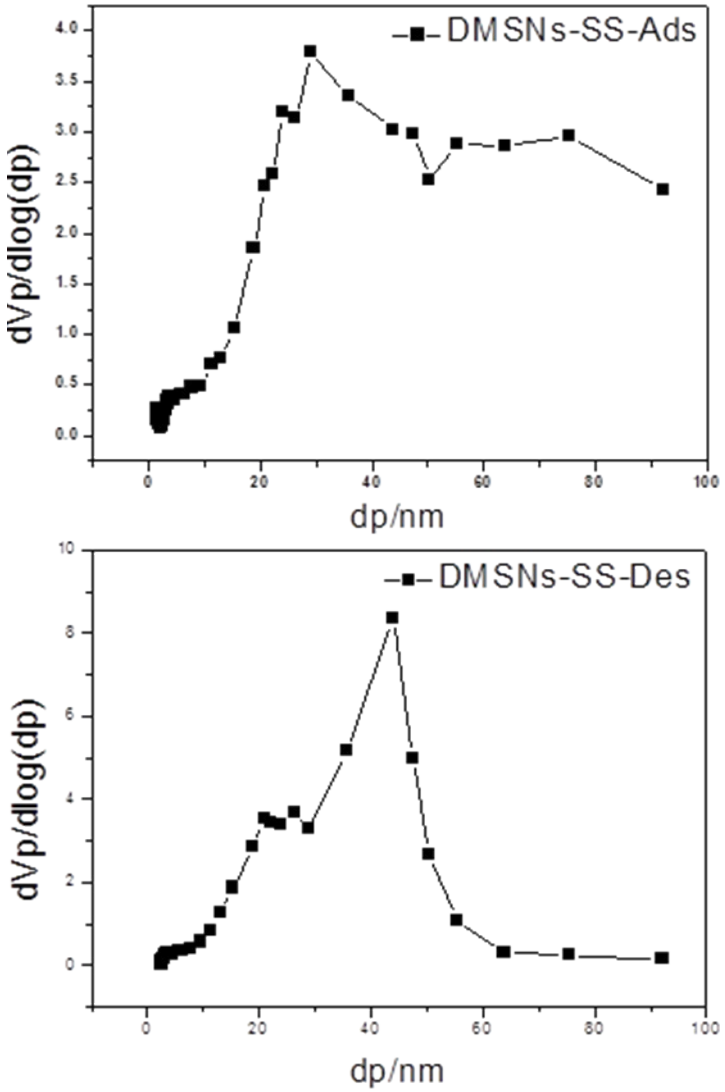

Fig. S7 Pore size distribution (PSD) of typical dendritic MSNs synthesized by dual templating strategy in the presence of anionic sodium stearate (SS) surfactant calculated by BJH method from both adsorption and desorption branch with a scale of vertical axis of dV/dlog(dp).

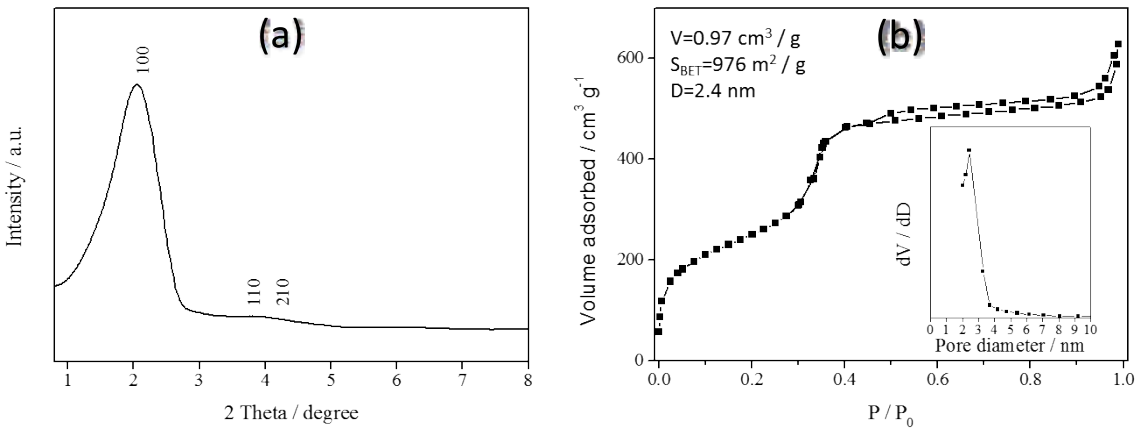

Fig. S8 XRD pattern (a) and N_2 adsorption-desorption isotherms (b) of Ti-MCM-41 (inset is a BJH distribution calculated by adsorption branch).

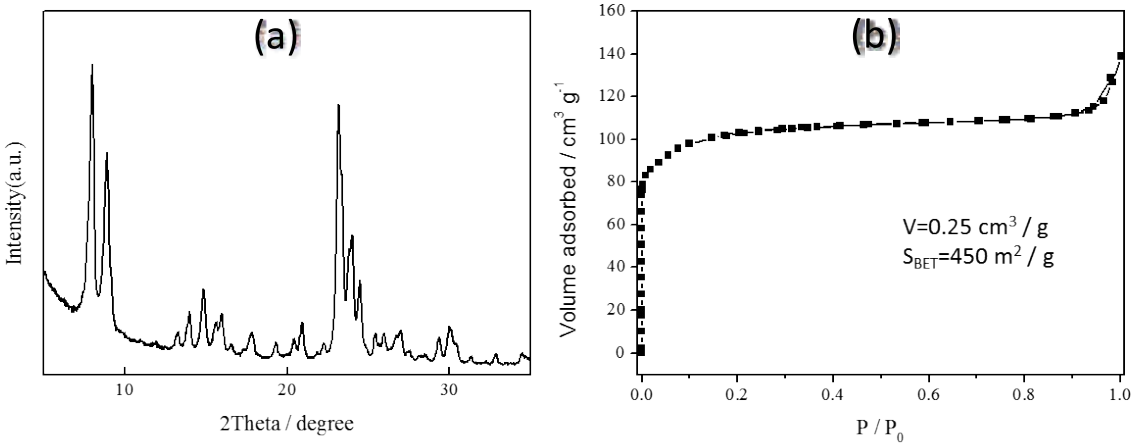

Fig. S9 XRD pattern (a) and N_2 adsorption-desorption isotherms (b) of TS-1.

Table S1. Textural characteristics of calcined DMSNs synthesized with different co-surfactant and MSNs with single surfactant.

[a]MSNs were synthesized with a single surfactant, [a]DMSN were synthesized by CTAB

Sample [a]	**S_{BET}** [b] **(m^2 / g)**	**V_{total}** [c] **(cm^3 / g)**	**D_{BJH}** [d] **(nm)**	**PSD** [e] **(nm)**
MSNs	675	1.27	2.3	50 ± 10
DMSNs-SDBS	346	1.67	3.2 / 10.6	105 ±10
DMSNs-SDS	450	1.59	3.2 / 10.6	120 ±10
DMSNs-SL	424	1.70	3.2 / 10.6	125 ±10
DMSNs-SS	535	2.81	3.3 / 10.6	115 ±10
DMSNs-DTAB	478	1.67	3.2	150±10
DMSNs-ODTAB	450	1.14	3.7	100±10

with SDBS, SDS, SL, and SS, SDS with DTAB and ODTAB respectively. [b] Specific surface area measured from N_2 physisorption. [c] Total pore volume measured at P/P_0= 0.99.[d] Pore diameter calculated from the BJH theoretical model. [e] Particle size distribution was detsermined by measuring the diameters of at least 100 particles under TEM.

References

1. L. Xu, Y. J. Ren, H. H. Wu, Y. M. Liu, Z. D. Wang, Y. T. Zhang, J. J. Xu, H. G. Peng and P. Wu, *J. Mater. Chem*., 2011, **21**, 10852.

2. T. Blasco, A. Corma, M. T. Navarro and J. P. Pariente, *J. Catal*., 1995, **156**, 65.