Supporting Information

One-Pot Co-condensation Strategy for Dendritic Mesoporous Organosilica Nanospheres with Fine Size and Morphology Control

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Experimental section

Chemicals

Cetyltrimethylammonium tosylate (CTATos) was purchased from MERCK. Triethanolamine ($TEAH_3$), Tetraethylorthosilicate(TEOS), Chloroauric acidtetrahydrate ($HAuCl_4 \cdot 4H_2O$), benzyl alcohol were purchased from Sinopharm Chemical Reagent. 1,2-Bis(triethoxysilyl)-thane (BTSE), 1,4-bis(triethoxysilyl)-benzeneand (BTSB), 2-Cyanoethyltriethoxysilane (CTSE), N-[3-(Triethoxysilyl)-propyl]-4,5-dihydroimidazole (TSPDI), (3-Aminopropyl) trimethoxysilane (APTMS) were purchased from Aldrich. All chemicals were used without additional purification. Deionized water was used for all experiments.

Synthesis

Synthesis of dendritic mesoporous organosilica nanoparticles (DMOSNs)

The dendritic mesoporous organosilica nanoparticles (DMOSNs) were synthesized using a soft-templating method. High concentrations of precursors were used with a molar composition of $1.0SiO_2$(TEOS+OSP) : 0.06CTATos : $0.026THAH_3$: $80.0H_2O$, where OSP = 1,2-Bis(triethoxysilyl)e-thane (BTSE = 1) or 1,4-bis(triethoxysilyl)-benzeneand (BTSB = 2) or 2-Cyanoethyltriethoxysilane (CTSE = 3) and N-[3-(Triethoxysilyl)propyl]-4,5-dihydroimidazole (TSPDI = 4). A typical synthesis of DMOSNs was performed as follows: A mixture of 5.49 g of cetyl-trimethylammonium tosylate (CTATos), 1.00 g of triethanolamine ($TEAH_3$) and 289 mL of deionized water was stirred at 80 ^oC for 30 minutes. After that 32.96 g of TEOS and 16.31 g BTSE was quickly added into the surfactant solution. The final liquid had the molar composition: $1.0SiO_2$(1.0TEOS : 0.28BTSE) : 0.06CTATos : $0.026TEAH_3$: $80.0H_2O$. The final mixture was stirred for 2 hours. The synthesized DMOSNs were centrifuged, washed and dried in the oven at 100^oC overnight. The products were denoted as DMOSNs-*X,* where *X* represents the different bis(mono)silylated organosilica precursors. Details of the synthesis of SBA-15 silica and MCM-41 slilca can be found in the literature.[1,2]

Synthesis of dendritic mesoporous organosilica nanoparticles loaded with gold nanoparticles (Au@DMOSNs)

The Au@DMOSNs catalysts were fabricated by amino-functionalizing the DMOSNs and then grafting the gold nanoparticles. In a typical process, the as-made DMOSNs-1 (1.0 g) was stirred with ethanol (40 mL) containing HCl (1.5 equiv H^+ per CTA^+ cation in DMOSNs-1) at 60 ^oC for 2 hours. The solid was then centrifuged and

washed with ethanol and acetone, then dried overnight at 80 °C. After this, 40 mL of anhydrous ethanol, 1 g of the HCl treated DMOSNs-1, and 1.5 g of APTMS were introduced into the round bottom flask and the mixture was refluxed at 80 °C for 12 hours. The powder was collected by centrifuged and washed with ethanol, then dried overnight at 80 °C. After that, 0.6 g of solid, 12 mL anhydrous ethanol of $HAuCl_4$ (4.85×10^{-3} mol / L), and 10 mL anhydrous ethanol were mixed and stirred at room temperature for 12 hours, and then 0.144 g of $NaBH_4$ was added into the suspension. The obtained solid material was centrifuged and washed with ethanol, and dried overnight at 80 °C. The Au@SBA-15 and Au@MCM-41 catalysts were use the same approach.

Oxidation of benzyl alcohol

The gas−phase oxidation of benzyl alcohol over Au@DMOSNs was carried out in a fixed-bed continuous-flow quartz tube reactor (14mmi.d.) at atmospheric pressure. The Au@DMOSNs (0.2 g) catalysts were directly heated and exposed to a feed stream with no pretreated. Then, the benzyl alcohol was fed into the reactor in a weight hourly space velocity (WHSV = 20 h^{-1}) using a syringe pump by passing air (43.2 uL/min) along with the reactant at 350 °C. AHP 6850 gas chromatograph equipped with a thermal conductivity detector (TCD) and a 30-m AT-plot capillary column was used to analyze the products. The column temperature was programmed from 40 °C to 160 °C at a ramp of 30 °C/min with a hold time of 3 min at each of the initial and final temperature points. The yield of benzaldehyde was calculated by multiplying the benzyl alcohol conversion by the selectivity for benzaldehyde.

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 of as-made MSNs 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. ^{29}Si and ^{13}C solid-state CP-MAS NMR measurements were obtained on 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 and for ^{29}Si (79.5 MHz), a 4 μs (h = p/2) pulse was used with a repetition time of 360 s.

Figures

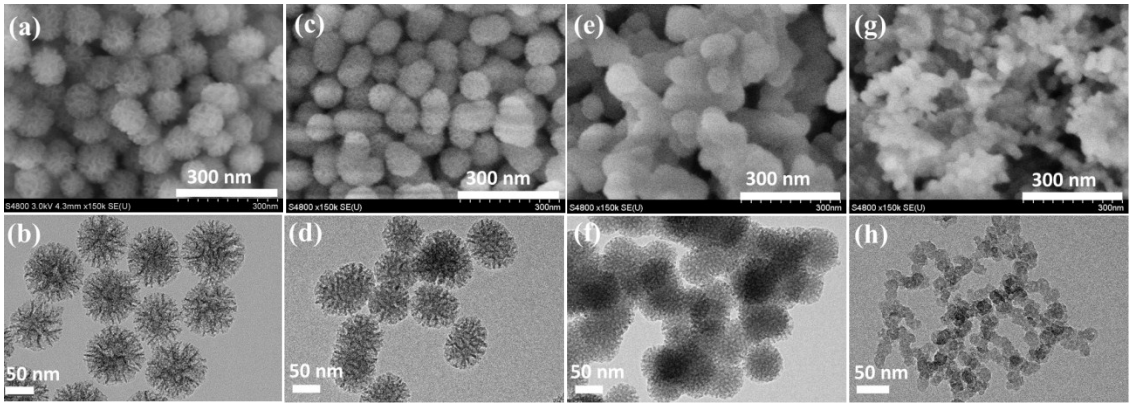

Fig. S1. SEM and TEM images of DMOSNs-1 prepared at various TEOS/BTSE weight ratios of (a, b) 1:0, (c, d) 1:1, (e, f) 0.5:1, (g, h) 0:1.

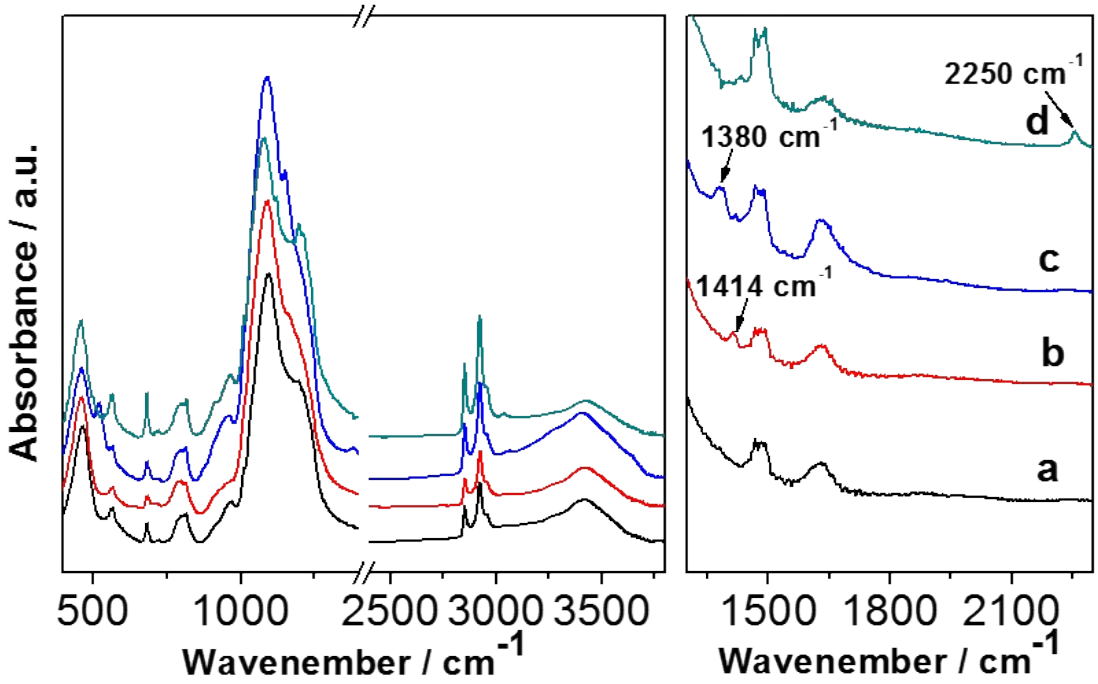

Fig. S2. FT-IR spectra of (a) DMSNs, (b) DMOSNs-1, (c) DMOSNs-2, (d) DMOSNs-3.

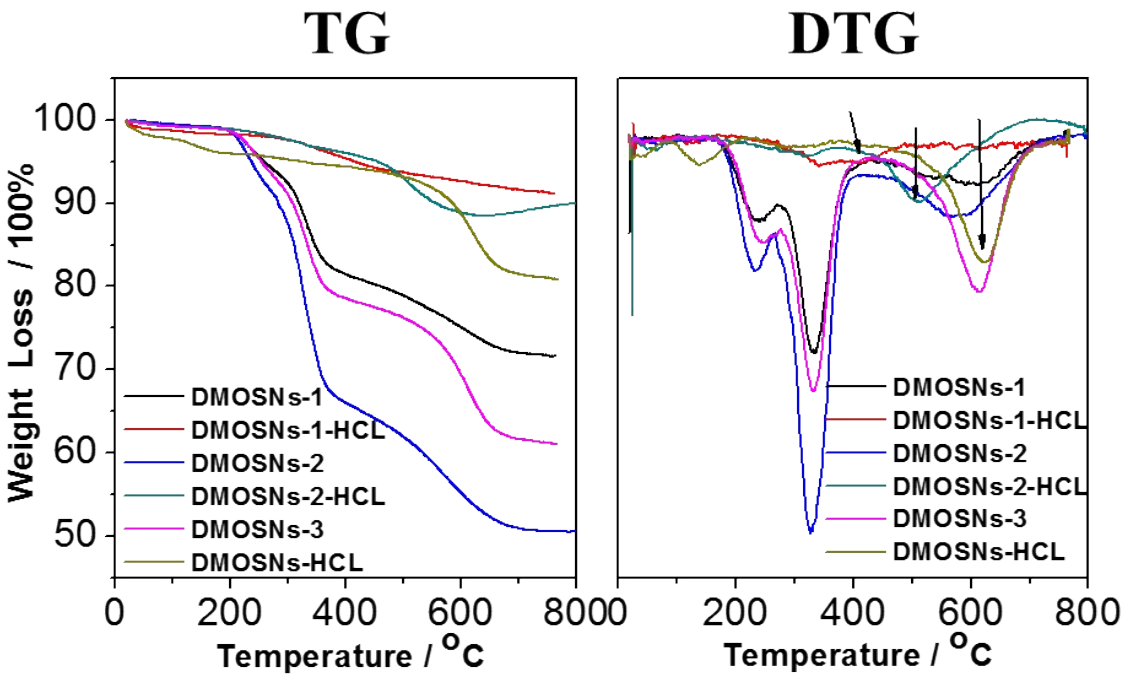

Fig. S3. Thermogravimetric analysis (TG) of as-made DMOSNs-1, DMOSNs-2 and DMOSNs-3 and corresponding surfactant-abstracted DMOSNs by acid washing (1.5 equiv H^+ per CTA^+ cation in DMOSNs) at 60 °C for 2 hours.

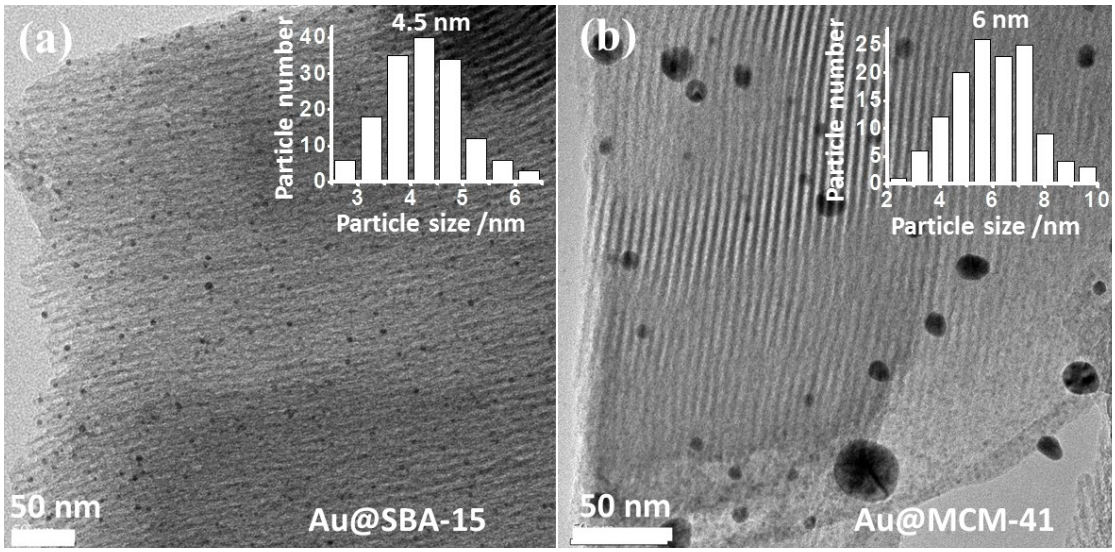

Fig. S4 TEM images of Au@SBA-15 (a) and Au@MCM-41 (b).

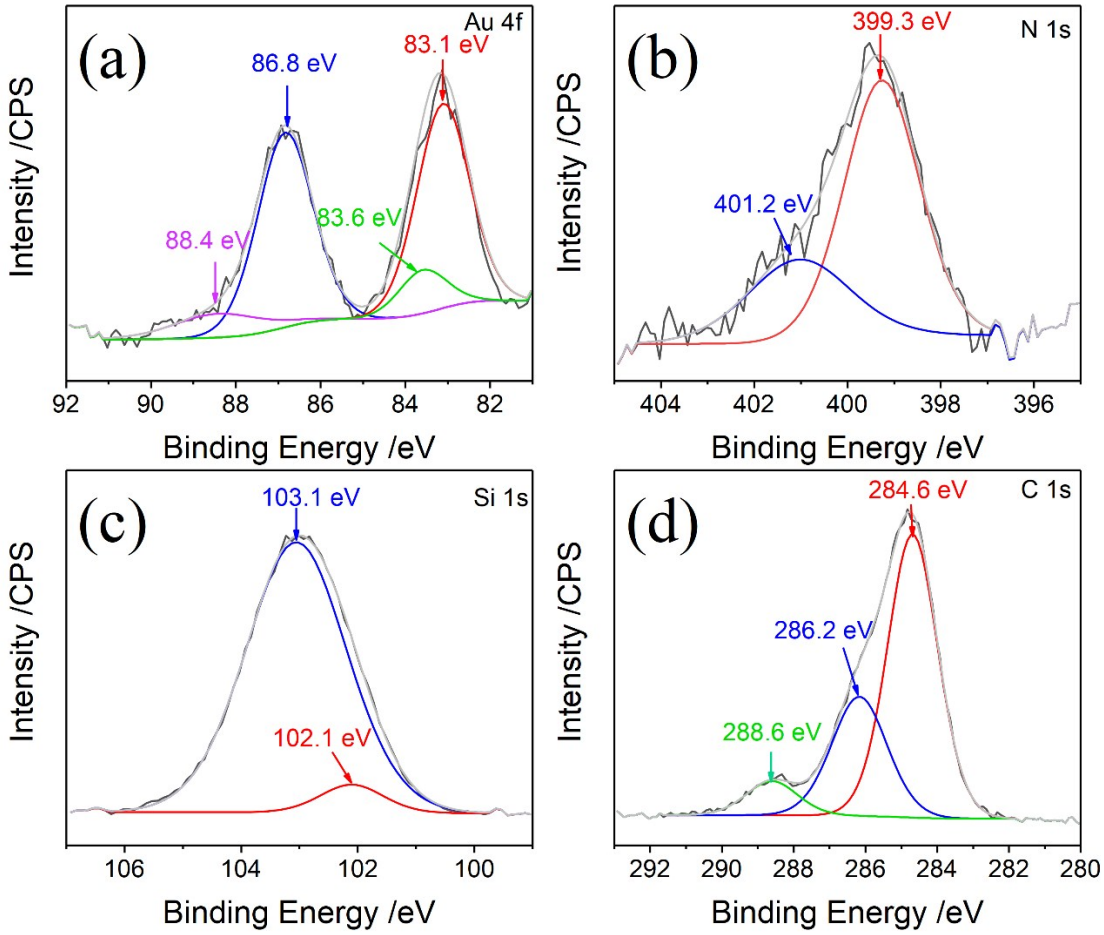

Fig. S5 XPS spectra for Au 4f (a), N 1s (b), Si 1s (c) and C 1s (d) of Au@DMOSNs-1. (**XPS studies were conducted for elucidating surface constitution/elemental chemical states of loading Au NPs. The Au 4f spectra after Shirley background removal for Au are shown in Fig. S5a. The Au species show two peaks due to the Au $4f_{7/2}$ and Au $4f_{5/2}$ transitions. The values of binding energy (BE) will be only referred to the Au $4f_{7/2}$ peak for the simplicity, which was deconvolved to two components at 83.1 and 83.6 eV, corresponding to $Au^{\delta-}$ and Au^0, respectively. Comparing with bulk metallic Au (84.0 eV), the BE shifted remarkably to lower value, probably related to the nano-size effect and / or the strong interaction between Au NPs and silica support. This further confirmed that the nanosized Au particles were highly dispersed into the dendritic pore channel networks of DMOSNs-1.**)

References:

(1) X. J. Ma, Y. J. Yu, J. L. Xing, T. Q. Yang, K. F. Lam, Q. S. Xue, B. Albela, L. Bonneviot and K. Zhang, *Microporous Mesoporous Mater.*, 2014, **200**, 182-189.

(2) K. Zhang, K. F. Lam, B. Albela, T. Xue, L. Khrouz, Q. W. Hou, E. H. Yuan, M. Y. He and L. Bonneviot, *Chem. Eur. J.*, 2011, **17**, 14258-14266.

(3) K. Zhang, L. L. Xu, J. G. Jiang, N. Calin, K. F. Lam, S. J. Zhang, H. H. Wu, G. D. Wu, B. Albela, L. Bonneviot and P. Wu, *J. Am. Chem. Soc.*, 2013, **135**, 2427-

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