

Electronic Supplementary Information for

**Formation of uniform hollow nanocages with heteroatom-doped MCM-41
structures**

Jiazhi Chen,^{a,b} Fang Lu,^{*a} and Jie Xu^{*a}

^a *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory of Clean Energy, Dalian 116023, P. R. China.*

^b *University of Chinese Academy of Sciences, Beijing 100049, P. R. China*

** Corresponding author: E-mail: lufang@dicp.ac.cn; xujie@dicp.ac.cn*

Table of Contents

Section S1. Experimental details

Chemicals and reagents

Synthesis of heteroatom (Al, Sn, Nb, Fe, Ti) -doped hollow MCM-41 nanocages

Synthesis of MCM-41 nanoparticle (MSN)

Synthesis of aluminum-doped MCM-41 (Al-MCM-41)

Characterization

Catalytic activity test

Section S2. Characterization results

Fig. S1 SEM image of HMASN and photograph of HMASN suspended in water

Fig. S2 XRD patterns of HMASN and MSN

Fig. S3 Solid state ^{29}Si and ^{27}Al MAS NMR spectra of HMMASN and MSN

Fig. S4 Nitrogen sorption isotherms and pore size distributions of HMASN and MSN

Fig. S5 Pyridine and 2,6-di-tert-butyl-pyridine adsorbed FT-IR spectra of HMASN

Fig. S6 HAADF images and EDX profiles of intermediate aluminosilica samples

Fig. S7 TEM images of the “silicon-doped” MSN

Fig. S8 Schematic illustration of the mesostructure of the silica seeds controlling the fabrication of hollow MCM-41 nanostructures

Fig. S9 SEM image and XRD pattern of Al-MCM-41

References

Section S1. Experimental details

Chemicals and reagents

Tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB) were purchased from J&K Chemical Ltd.. Aluminum isopropoxide ($\text{Al}(\text{O}^i\text{Pr})_3$) was purchased from Acros Organics. Ammonia solution (25 wt.%), ethanol, tin tetrachloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$), tetra-n-butyl titanate ($\text{Ti}(\text{O}^n\text{Bu})_4$), niobium chloride (NbCl_5), iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Cellobiose and glucose were purchased from J&K Chemical Ltd.. All the reagents were used without further purification. Milli-Q water was used in all experiments. Microporous HZSM-5 zeolite was purchased from the Catalyst Plant of Nankai University and calcined at 550 °C before uses.

Synthesis of heteroatom (Al, Sn, Nb, Fe, Ti) -doped hollow MCM-41 nanocages

In a typical experiment for the synthesis of Al-doped hollow MCM-41 nanocage (HMASN). 0.58 g of CTAB was dissolved in an aqueous ammonia solution (300 g) containing 12 g of 25 wt.% ammonia solution. The solution was sealed and stirred at 50 °C for 10 min. 5 mL of TEOS ethanolic solution (0.2 M) was added into the mixture. After reaction for 5 h, 5 mL of concentrated TEOS ethanolic solution (0.9 M) was dropped under vigorous stirring, and the unsealed mixture was stirred for 1 h, resulting in the formation of white silica seeds. Then 5 mL of $\text{Al}(\text{O}^i\text{Pr})_3$ ethanolic solution (0.06 M) was added dropwise to the solution and the mixture was stirred for 1 h, followed by an aging process for 20 h. The resulting white samples were collected by centrifugation, washed with water and ethanol, dried at 80 °C overnight and calcined at 550 °C for 10 h.

For Sn-doped hollow MCM-41 nanocage. The white silica seeds were pre-synthesized following the typical experiment. Then 5 mL of SnCl_4 ethanolic solution (0.06 M) was dropped to the solution. This mixture was stirred for 1 h at 50 °C, followed by an aging process for 20 h at 60 °C. The resulting white samples were collected by centrifugation, washed with water and ethanol, dried at 80 °C overnight and calcined at 550 °C for 10 h.

For Nb-doped hollow MCM-41 nanocage. 0.75 g of CTAB was dissolved in an aqueous ammonia solution (300 g) containing 12 g of 25 wt.% ammonia solution. The solution was sealed and stirred at 50 °C for 10 min. 5 mL of TEOS ethanolic solution (0.2 M) was added into the mixture. After reaction for 5 h, 5 mL of concentrated

TEOS ethanolic solution (0.9 M) was dropped under vigorous stirring, and the unsealed mixture was stirred for 2 h, resulting in the formation of white silica seeds. Then the solution was rapidly cooled to room temperature and 5 mL of NbCl₅ ethanolic solution (0.06 M) was dropped. The mixture was stirred for 1 h at 50 °C, followed by an aging process for 20 h at 130 °C. The resulting white samples were collected by centrifugation, washed with water and ethanol, dried at 80 °C overnight and calcined at 550 °C for 10 h.

For Fe-doped hollow MCM-41 nanocage. 0.90 g of CTAB was dissolved in an aqueous ammonia solution (300 g) containing 12 g of 25 wt.% ammonia solution. The solution was sealed and stirred at 50 °C for 10 min. 5 mL of TEOS ethanolic solution (0.2 M) was added into the mixture. After reaction for 5 h, 5 mL of concentrated TEOS ethanolic solution (0.9 M) was dropped under vigorous stirring, and the unsealed mixture was stirred for 2 h, resulting in the formation of white silica seeds. Then the solution was rapidly cooled to room temperature and 5 mL of NbCl₅ ethanolic solution (0.06 M) was dropped. The mixture was stirred for 1 h at 50 °C, followed by an aging process for 20 h at 80 °C. The resulting white samples were collected by centrifugation, washed with water and ethanol, dried at 80 °C overnight and calcined at 550 °C for 10 h.

For Ti-doped hollow MCM-41 nanocage. HMSN-Ti, 0.58 g of CTAB was dissolved in an aqueous ammonia solution (300 g) containing 12 g of 25 wt.% ammonia solution. The solution was sealed and stirred at 50 °C for 10 min. 5 mL of TEOS ethanolic solution (0.2 M) was added into the mixture. After reaction for 5 h, 5 mL of concentrated TEOS ethanolic solution (0.9 M) was dropped under vigorous stirring, and the unsealed mixture was stirred for 2 h, resulting in the formation of white silica seeds. Then the solution was rapidly cooled to room temperature and 5 mL of NbCl₅ ethanolic solution (0.06 M) was dropped. The mixture was stirred for 1 h at 50 °C, followed by an aging process for 20 h at 50 °C. The resulting white samples were collected by centrifugation, washed with water and ethanol, dried at 80 °C overnight and calcined at 550 °C for 10 h.

Synthesis of MCM-41 nanoparticle (MSN)

MSN was synthesized following our reported two-step method.¹ 5 mL of TEOS (0.2 M in ethanolic solution) was added to an aqueous solution (300 g) containing 0.58 g CTAB and 12 g of ammonia solution (25 wt.%) at 50 °C. Silica nuclei were formed after reaction for 5 h. Then 5 mL of concentrated TEOS ethanolic solution (0.9 M) was dropped under vigorous stirring and the obtained white silica colloids

were aging at 50 °C for 20 h. The resulting white samples were collected by centrifugation, washed with water and ethanol, dried at 80 °C overnight and calcined at 550 °C for 10 h.

Synthesis of aluminum-doped MCM-41 (Al-MCM-41)

Al-MCM-41 was synthesized following the procedure described by Akihiko et al.². In a typical synthesis, 2 g of CTAB was dissolved in 120 g of water, and 9.5 g of aqueous ammonia (25 wt.%) was added to the solution. 10 mL of TEOS was mixed with an isopropanolic solution of Al(OⁱPr)₃ (0.46 g). While stirring at room temperature, the TEOS/Al(OⁱPr)₃ solution was dropped slowly into the surfactant-ammonia solution over a period of 15 min. After vigorously stirring for 2 h, the white suspension was filtered out and washed with water. Then the sample was dried at 80 °C overnight followed by calcining at 550 °C for 10 h.

Characterization

SEM and STEM images were taken on a JEM-7800F microscope at a low landing energy (0.8 kV, in gentle-beam mode) and a Hitachi S5500 microscope at 30 kV, respectively. TEM images were taken on a JEM-2000EX microscope operated at 120 kV. FFT of the hexagonal core region in TEM images was measured with the Gatan Digital Micrograph software. High-angle annular-dark field (HAADF) images and energy dispersive X-ray (EDX) line scanning profiles were conducted on a FEI Tecnai G² F30 S-Twin microscope. The samples for TEM and HAADF observations were dropped onto carbon coated copper grid after ultrasonically dispersing in anhydrous ethanol.

The particle size distribution was measured by dynamic light scattering (DLS) technique employing a Nano ZS90 laser particle analyzer (Malvern Instruments, UK) at 25 °C.

Power X-ray diffraction (XRD) data were collected on a Rigaku D/Max 2500PC diffractometer with Cu K α radiation. The small-angle patterns were recorded from 1° to 8° (2 θ) at 40 kV / 30 mA.

The BET specific surface area and the porous property were determined by nitrogen adsorption-desorption measurement using a Quantachrome Autosorb-1 apparatus. The total pore volume (V_P) was obtained from the amount of adsorbed nitrogen at 0.99 P/P₀. The pore size (D_P) distribution was determined from the nitrogen adsorption plot by Barrett-Joyner-Halenda (BJH) method.

²⁹Si and ²⁷Al MAS NMR experiments were performed on a Varian Infinity-plus

400 spectrometer operating at a magnetic field strength of 9.4 T. The frequencies used were 79.4 MHz for ^{29}Si and 104.2 MHz for ^{27}Al . The pulse widths were 2.0 and 0.5 μs , the recycle delays were 4 and 1 s, and the spinning rates were 6 kHz and 8 kHz for ^{29}Si and ^{27}Al , respectively. The ^{29}Si and ^{27}Al chemical shifts were referenced to TMS and 1 M $\text{Al}(\text{NO}_3)_3$ solution, respectively.

The silicon and aluminum concentrations in the solids and in the reaction filtrates were determined by the ICP-OES method with the Optima 7300DV (PerkinElmer) spectrometer. The solids were pretreated for analysis in the following steps³: 4 mg of powder was placed in the plastic volumetric flask. HCl/HF (70/30, 1.6 mL) solution was added to the flask and the suspension was sonicated for 15 min until all of the solid were completely dissolved. Then, 0.6 mL of concentrated nitric acid was added and the total volume was adjusted to 100 mL with Milli-Q water.

To evaluate the type and the concentration of acid sites, pyridine (kinetic diameter 5.5 \AA)⁴ adsorption on the solid samples was performed on a Bruker Tensor 27 spectrometer and the spectra were collected at room temperature at a spectral resolution of 2 cm^{-1} . Prior to adsorption of pyridine, the self-supporting wafers (approx. 15 mg) were dehydrated by evacuation at $400 \text{ }^\circ\text{C}$ under high vacuum and were measured as the reference spectra. Pyridine adsorption was performed at room temperature until saturation followed by evacuation of the wafers at $150 \text{ }^\circ\text{C}$ for 30 min. FT-IR spectra were collected after cooling the wafers to room temperature. The quantitative calculation of Brønsted acid sites was made with respect to the integrated area of the absorption band at approximately 1545 cm^{-1} ($\epsilon_B = 1.67 \text{ cm } \mu\text{mol}^{-1}$).⁵ To distinguish the accessible acid sites, 2,6-di-tert-butylpyridine (DTBPy) with a diameter of 10.5 \AA ⁴ was used as a probe molecule. The adsorption of DTBPy proceeded at $150 \text{ }^\circ\text{C}$ by equilibrating the wafer for 15 min followed by degassing for 1 h at the same temperature and by collecting the spectrum at room temperature. For the quantitative evaluation of the concentration of accessible Brønsted acid sites, the molar extinction coefficient (ϵ_B) of pyridine was used.^{4,6}

Catalytic activity test

In a typical experiment, an aqueous solution (2.5 mL) that contained 25 mg of cellobiose and 12.5 mg of catalyst was added to the glass pressure tube. The reactor were then sealed and placed in a preheated oil bath at $165 \text{ }^\circ\text{C}$. The mixture was stirred at 800 rpm and maintained for 4 h. After reaction, the reactor was cooled in an ice-water bath and the mixture was centrifugated to remove catalysts. Product analysis was performed in a Waters 2695 HPLC system equipped with 2414 refractive index

detector at 30 °C. The products were separated using a high performance carbohydrate column (4 µm, 4.6 mm × 250 mm) at 30 °C, with acetonitrile/water (75/25, v/v) as the mobile phase at a flow rate of 1.4 mL min⁻¹, and were identified by retention time compared to standard samples and quantified by use of a standard calibration curve. Conversion of cellobiose = (molar amount of cellobiose converted / molar amount of cellobiose added) × 100%. Yield of glucose = (molar amount of glucose obtained / twice molar amount of cellobiose added) × 100%.

Section S2. Characterization results

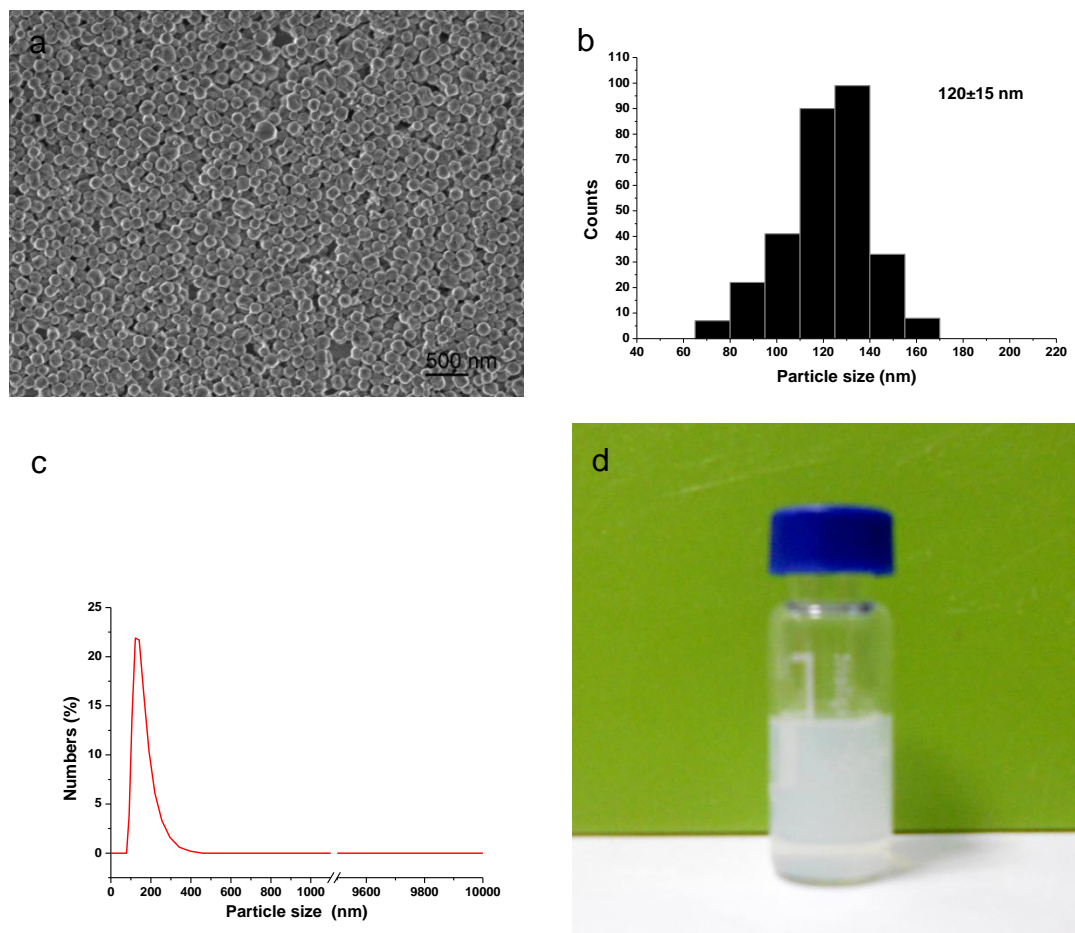


Fig. S1 (a) Low magnification SEM image of HMASN, (b) particle size distribution of HMASN determined by counting 300 particles in the micrograph, (c) the DLS particle size distribution, (d) photograph of well-suspended HMASN in water.

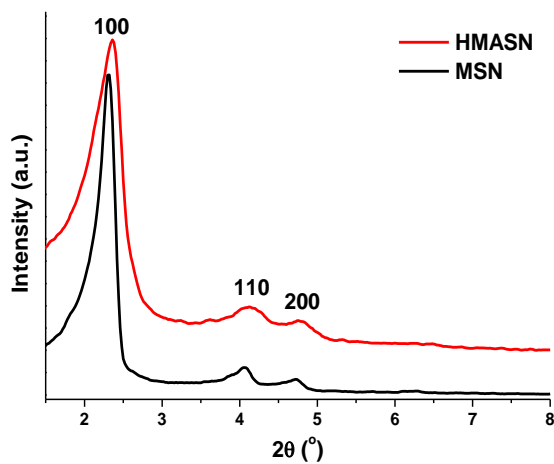


Fig. S2 XRD patterns of HMASN and MSN.

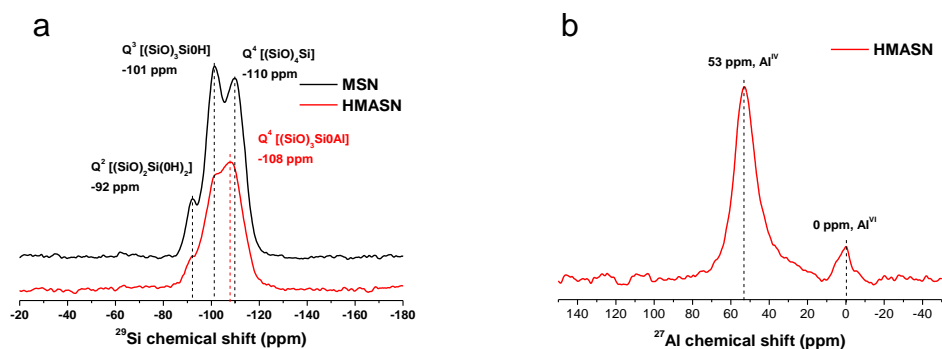


Fig. S3 (a) Solid-state ^{29}Si MAS NMR spectra of MSN and HMMASN, (b) ^{27}Al MAS NMR spectrum of HMMASN.

The ^{29}Si NMR spectrum of MCM-41 nanoparticle (MSN) (Fig. S3a) shows resonance signals centered at -92, -101, and -110, assigned to Q^2 $[(\text{SiO})_2\text{Si}(\text{OH})_2]$, Q^3 $[(\text{SiO})_3\text{SiOH}]$, and Q^4 $[(\text{SiO})_4\text{Si}]$ siloxane units, respectively. Notably, a more positive Q^4 ^{29}Si signal in the spectrum of HMMASN appears at -108 ppm, which could be attributed to Q^4 $[(\text{SiO})_3\text{SiOAl}]$ ^{29}Si species.⁷ The ^{27}Al NMR spectrum of HMMASN (Fig. S3b) is dominated by the signal of tetrahedrally coordinated Al^{IV} species at 53 ppm, indicating that a large number of Al atoms have been incorporated into the silica framework. The weak ^{27}Al signal at 0 ppm is explained by octahedrally coordinated Al^{VI} species that are located at extraframework or defect sites.^{7,8}

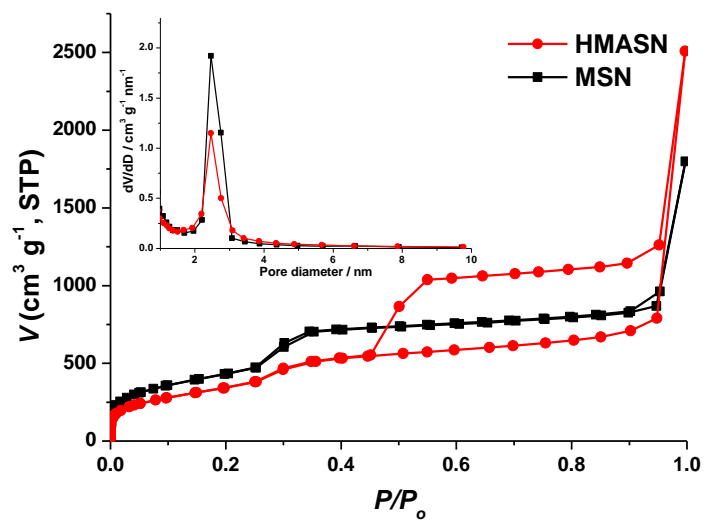


Fig. S4 Nitrogen sorption isotherms of HMASN and MSN, the inset: the pore size distributions calculated from the adsorption branch by the BJH method.

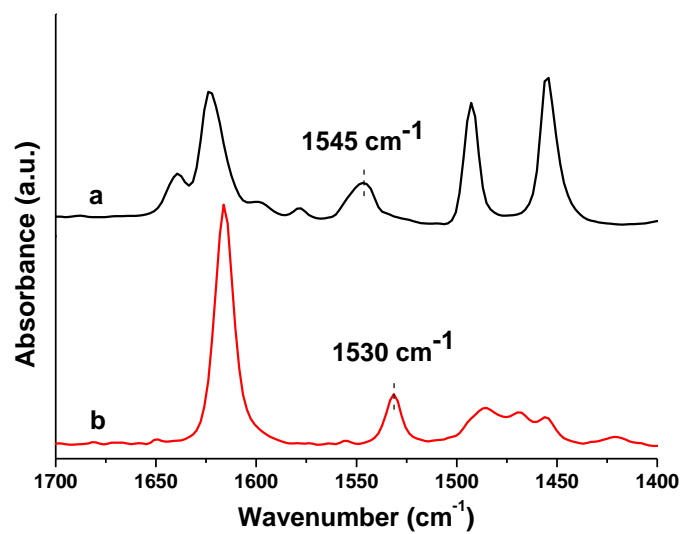


Fig. S5 Subtracted FT-IR spectra of (a) adsorbed pyridine region and (b) adsorbed 2,6-di-tert-butyl-pyridine region in HMASN.

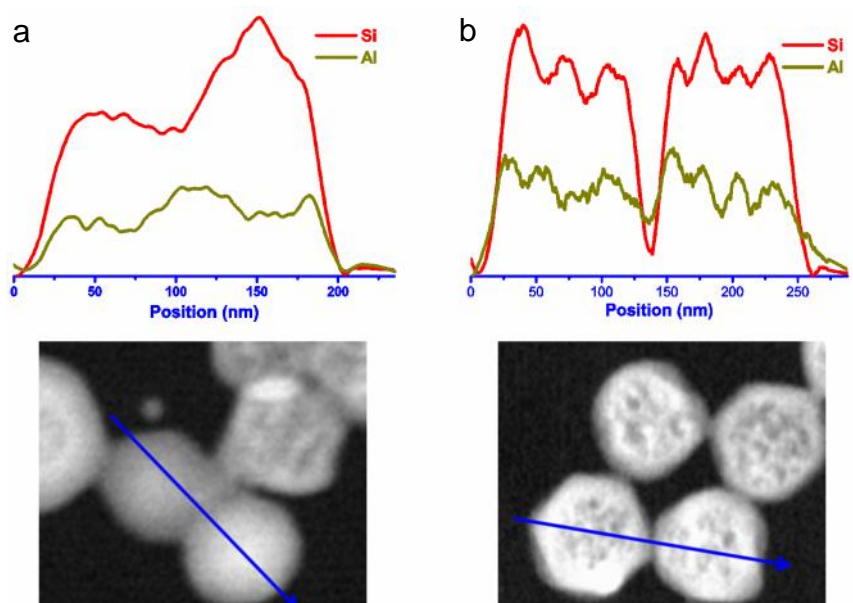


Fig. S6 HAADF images of the intermediate aluminosilica samples after Al species adding for (a) 0 h, and (b) 1h and the corresponding EDX line scanning profiles of Si and Al.

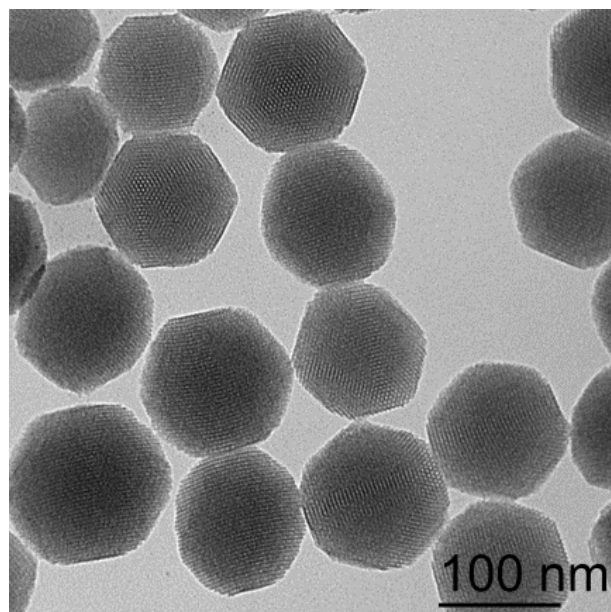


Fig. S7 TEM image of the “silicon-doped” MSN after aging at 50 °C for 20 h.

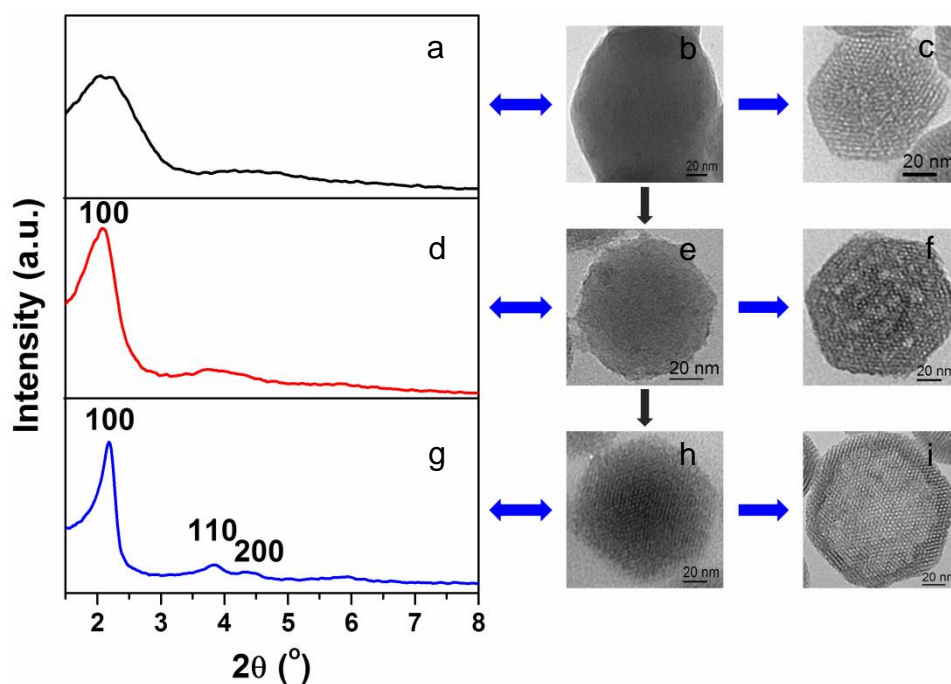


Fig. S8 Schematic illustration of the mesostructure of the silica seeds controlling the fabrication of Al-doped hollow MCM-41 nanostructures. (a, d, g) XRD patterns and (b, e, h) corresponding TEM images of various pre-synthesized silica seeds (which were collected for the measurements at the time interval of 0 min, 10 min, 60 min after that the concentrated TEOS ethanolic solution was dropped), (c, f, i) the calcined mesoporous aluminosilica nanoparticles derived from the related silica seeds.

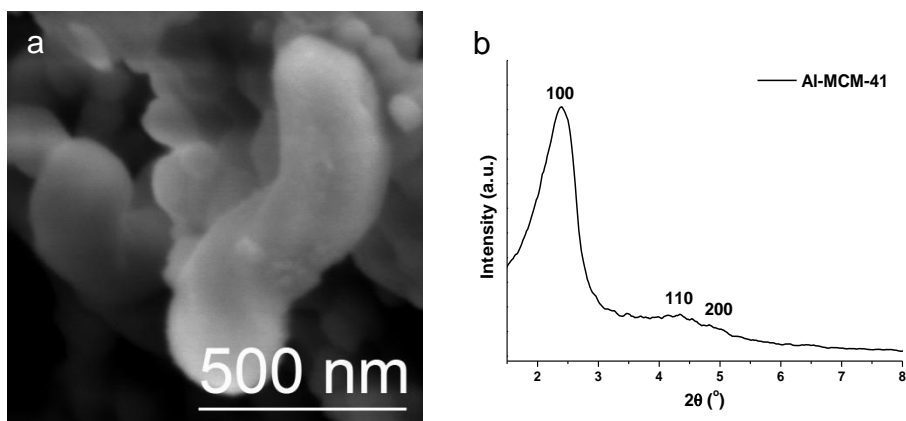


Fig. S9 (a) SEM image of Al-MCM-41, (b) XRD pattern of Al-MCM-41.

The obtained Al-MCM-41 shows a solid microtubule shape and MCM-41 type mesostructure.

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