Electronic Supplementary Information (ESI)

One-step synthesis of hollow periodic mesoporous organosilica spheres with radially oriented mesochannels

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Experimental Section

Materials

Ammonia aqueous solution (25-28%), hydrochloric acid (HCl, 37%) and anhydrous ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Cetyltrimethylammonium bromide (CTAB) and 1,2-Bis(triethoxysilyl) ethane (BTSE) were purchased from Sigma–Aldrich (St. Louis, MO, USA). All regents were of analytical grade and used as supplied without further purification. Deionized water was used in all synthetic experiments.

Synthesis of hollow periodic mesoporous organosilica spheres (HPMOSs)

Nanometer sized HPMOSs were synthesized by a one-step method which based on O/W microemulsion system. Firstly, ethanol (30 ml), ammonia (2 ml) and CTAB (0.64 g) were dissolved in water (150 ml) to form a transparent water solution. Then, an ethanol solution (30 ml) containing BTSE (0.48 g) was added into the above-mentioned water solution under magnetic stirring for 1 minute, the oil (BTSE) droplets dispersed in water forming the O/W microemulsion system. After stirring for 60 minutes under normal temperature and pressure, the white HPMOSs was formed, then being collected by centrifugation and washed by deionized water for three times. The CTAB was removed by extraction in ethanol solution (100 ml) containing HCl (1 ml) for 6 hours at 80°C, and repeated three times. The products were then collected by centrifugation, washed by deionized water for three times and dried for 6 hours at 60°C. The particle size, sphere shell thickness and the hollow void size of the HPMOSs were controlled by tunning the synthetic composition. The samples were synthesized with the various $V_{\text{EtOH}}/V_{\text{water}}$ (the volume ratio of ethanol and H2O) of 0.4, 0.3 and 0.2, which were denoted as HPMOS-1, HPMOS-2 and HPMOS-3, respectively. In order to further increase the hollow void size of the sample, a certain amount of octane was mixed with BTSE and added into the reaction system (based on the synthesis procedure of HPMOS-1), the obtained samples were denoted as HPMOS-4.
Characterization

Transmission electron microscopy (TEM) images were recorded on a HT7700 microscope (Hitachi, Japan) at 100 kV accelerating voltage, and a JEOL 2100F microscope (JEOL, Japan) at 200 kV. The powder samples for the TEM measurements were suspended in ethanol and then dropped onto the Cu grids with holey carbon films. Scanning electron microscopy (SEM) images were obtained by Zeiss Gemini microscope (Carl Zeiss, Germany). The average particle size, hollow void size and shell thickness were calculated from SEM and TEM images using ImageJ software. X-ray power diffraction (XRD) patterns were obtained with a RINT/DMAX-2500 diffractometer (Rigaku, Japan) using Cu-Kα radiation operated at 40 kV and 200 mA. The nitrogen adsorption-desorption measurement was conducted on a Gemini VII 2390 (Mike, USA) at 196 °C. Prior to the measurement, the sample was degassed at 150 °C for at least 6 h. The Brunauer-Emmett-Teller (BET) specific surface area was calculated using adsorption data at a relative pressure range of $P/P_0 = 0.05-0.30$. Pore size distribution was derived from the adsorption branch using nonlocal density functional theory (NLDFT) method. The total pore volume was estimated from the adsorbed amounts at a relative pressure ($P/P_0$) of 0.99. Fourier transform infrared (FTIR) spectra were collected on Vertex 70v Fourier Spectrophotometer (Bruker, Germany) by dispersing powder samples in KBr pellets. $^{29}$Si MAS NMR spectra were recorded on a Bruker AVIII400 spectrometer (Bruker, Germany) with the following experimental parameters: 7mm MAS BB/1H probe, spinning rate of 6.0 kHz, a recycle delay of 120 s. The chemical shifts were referenced to 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS). Dynamic light scattering (DLS) measurements were conducted on Zetasizer Nano ZS90 (Malvern, UK).

Supplementary Figure

![Fig. S1 TEM images of HPMOS](image)
To further explore a possible mechanism of the formation of HPMOSs, we designed a separate experiment to analyze the size distribution of droplets of unreacted microemulsion (Fig. S2). Similar with the synthesis procedure of HPMOS-1, but without adding ammonia which acted as catalysis, as soon as the oil solution (ethanol and BTSE) was added into the upper water phase under magnetic stirring, the microemulsion was analyzed by Zetasizer Nano ZS90. The results show that the average size of the unreacted microemulsion was 50 nm, which was smaller than that of HPMOS-1 (100 nm).
Fig. S4 The white powdery HPMOSs dispersed in aqueous solution, showing typical Tyndall light scattering effect, indicating the high dispersity of HPMOSs.

Fig. S5 SEM images of HPMOSs synthesized with various $V_{\text{EtOH}}/V_{\text{water}}$, (a) 0.4 (HPMOS-1), (b) 0.3 (HPMOS-1), (c) 0.2 (HPMOS-3) and (d) HPMOS-4 synthesized with octane (0.02ml).

Fig. S6 DLS size distributions of HPMOSs synthesized with various $V_{\text{EtOH}}/V_{\text{water}}$, (a) 0.2 (HPMOS-3), (b) 0.3 (HPMOS-2) and (c) 0.4 (HPMOS-1).
Fig. S7  Average particle size, shell thickness and hollow void size of HPMOSs synthesized with various $V_{\text{EtOH/water}}$ of 0.4, 0.3 and 0.2.

Fig. S8 DLS size distribution of droplets of unreacted microemulsion synthesized with various $V_{\text{EtOH/water}}$ (a) 0.2 (HPMOS-3), (b) 0.3 (HPMOS-2) and (c) 0.4 (HPMOS-1).

Fig. S9 SEM and TEM images of HPMOS-5 (0.2 ml octane).