Supporting information

Facile fabrication of hierarchically structured single-crystal mesoporous silica nanoparticles

Chemicals

Cetyltrimethyl ammonium bromide (CTAB) and hexadecyl pyridinium chloride (CPC) were obtained from Aladdin, China. Poly(acrylic acid) (PAA) (average molecular weight = 240 000 g/mol, 25% solution in water) was obtained from Acros. In this work, the amount of PAA used in the synthesis means the weight of the 25% solution. Tetraethylsiloxane (TEOS) was purchased from Alfa Aesar. All the chemical agents were used without further purification.

Synthesis

In a typical synthesis of HMSN-1: 0.28 g of CTAB and 2.25 g of PAA solution (average molecular weight 240,000, 25% solution in water) were dissolved in 40 mL of deionized water under stirring, followed by the introduction of 1.0 g of ammonia solution (25%). After further stirring for 20 min, 1.04 g of tetraethylsiloxane (TEOS) was added. The mixture was stirred for 40 min, and then transferred to an autoclave at 80 °C for 48 h.

In a typical synthesis of HMSN-2: 0.11 g of CPC and 0.7 g of PAA solution were dissolved in 100 mL of deionized water under stirring, followed by the introduction of 0.8 g of ammonia solution (25%). After further stirring for 20 min, 0.42 g of tetraethylsiloxane (TEOS) was added.
The mixture was stirred for 40 min, and then transferred to an autoclave at 80 °C for 48 h.

For HMSN-1 and HMSN-2, the as synthesized material was centrifugated, washed with deionized water, and dried at 60 °C. The organic templates were removed by calcination at 550 °C for 5 h.

**Characterization**

Small-angle X-ray scattering (SAXS) experiments were performed on a Bruker Nanostar small angle X-ray scattering system. The X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max-2500 diffractometer, with CuKα Radiation at 40 kV and 100 mA. Scanning electron microscopy (SEM) images were obtained with a Shimadzu SS-550 instrument. Transmission electron microscopy (TEM) observations were performed on a Philips Tecnai F20 and a Tecnai G2 F20 microscope, working at 200 kV. All samples subjected to TEM measurements were dispersed in ethanol ultrasonically and were dropped on copper grids. N₂ adsorption measurements were performed on a BELSORP-mini II sorption analyzer. The specific surface area was calculated by BET (Brunauer-Emmett-Teller) method, the pore size distribution was calculated from the adsorption branch using BJH (Barett-Joyner-Halenda) method and total pore volume was obtained at a relative pressure of p/p₀ = 0.99. Before measurements, the samples were dried under dry N₂ flow at 350 °C for 5 h.