A Facile Two Step Synthesis of Novel Chrysanthemum-like Mesoporous Silica Nanoparticles for Controlled Pyrene Release

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Supporting Information

Experimental

1. Materials

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification. Cetyltrimethylammonium bromide (CTAB) (≧99%), ammonia solution (NH₄OH) (25-28%), ethyl ether (≧99.5%) and tetraethoxysilane (TEOS) (99.9%) were analytic purity, supplied by Sinopharm Chemical Reagent Co, Ltd. Pyrene (99%) was purchased from Beijing HuaFeng United Technology CO, Ltd.

2. Preparation of mesoporous silica nanoparticles

The mesoporous silica nanoparticles (MSNs) were prepared by using CTAB as the structure-directing agent (SDA) and ethyl ether as the cosolvent under mild conditions. In a typical synthesis procedure, 8 mL H₂O, 40 mL ethyl ether and 1 mL ammonia solution (25-28 %) in sequence were added in a closed vessel under vigorous stirring at room temperature. After the solution became homogeneous, 2 mL TEOS as the silicon source was dropwise added and stirred continuously for 3 h. Then, 2 mL of TEOS was dripped to the mixture before 1.0 g CTAB was added. Vigorous stirring was continued for 12 h. The as-synthesized materials were centrifugated, washed for three times with distilled water, and then dried overnight at 60 °C. In order to remove CTAB and other organic components, the final products were calcined in air at 550 °C.
for 6 h to obtain the MSNs.

3. In situ encapsulation of fluorescent pyrene into mesoporous silica nanoparticles

The pyrene-encapsulated mesoporous silica nanoparticles (MSNs) were prepared by using CTAB as the structure-directing agent (SDA) and ethyl ether as the cosolvent. In a typical synthesis, 8 mL H$_2$O, 40 mL ethyl ether pyrene solution (contained 0.2 g pyrene) and 1 mL ammonia solution (25-28 %) were added in a closed vessel and vigorously stirred at room temperature. When the solution became homogeneous, 2 mL TEOS was added and stirred continuously for 3 h. Then, to the mixture was dripped 2 mL of TEOS and added 1.0 g CTAB, and the resulting mixture was vigorously stirred for 12 h. The products were collected by centrifugating, washing repeatedly for three times with distilled water, and then drying overnight at 60 °C. Finally, a white solid powder was obtained, namely pyrene-encapsulated MSNs.

4. Controlled Release Experiments

Typically, 0.05 g as-synthesized pyrene-encapsulated silica nanoparticles were dispersed in 100 mL distilled water in dark under magnetic stirring in neutral aqueous media. 2.0 mL above mixture sample was extracted out at given time. Then, the extracted suspension was centrifugated to separate any suspended solid. The upper solution was measured by UV-vis absorption analysis. After being measured, the upper solution and precipitation were immediately poured back.
5. Characterizations

X-ray powder diffraction (XRD) patterns were obtained on the Japan Rigakul D/max-2550 instrument operating at 40 kV and 40 mA using CuKα radiation (\( \lambda = 0.154 \) nm), scanning range 2\( \theta \) of the small-angle and the wide-angle are from 0.5° to 5° and from 5° to 70°, respectively. The structural properties and morphology of the products were studied by transmission electron microscopy (TEM, JEOL 200CX), scanning electron microscopy (SEM, Hitachi S-4800), electron energy disperse spectroscopy (EDS, OXFORD INCA), high resolution transmission electron microscopy (HR-TEM, JSM-2010F). \( \text{N}_2 \) adsorption-desorption isotherms were recorded on a Micromeritics ASAP 2020 M instrument at 77 K after the as-prepared product were annealed at 200 °C. The specific surface areas were calculated by Brunauer-Emmett-Teller (BET) method. Pore size distributions were calculated from the desorption branch using the Barrett-Joyner-Halenda (BJH) method and pore volumes measured at \( P/P_0 = 0.98 \). UV-vis absorption spectra of pyrene-encapsulated MSNs (dispersed in water) were collected on a HITACHI U-3010 UV-vis spectrophotometer in the range of 220-400 nm. Fluorescence spectrum of pyrene-encapsulated MSNs (dispersed in water) was obtained on a HITACHII F-7000 fluorescence spectrometer with an excitation laser operating at 324 nm in the range of 350-600 nm. Confocal image was obtained with the Japan Olympus FV1000 confocal fluorescence microscope with an excitation laser operating at 405 nm.
Fig. S1 HRTEM images of chrysanthemum-like mesoporous silica nanoparticles
Fig. S2 Wide-angle XRD patterns of (a) mesoporous silica nanoparticles, (b) pyrene-encapsulated mesoporous silica nanoparticles
**Fig. S3** UV-vis absorption spectrum of pyrene-encapsulated mesoporous silica nanoparticles

**Fig. S4** UV-vis absorption spectra at different times of the aqueous media in which pyrene was released from pyrene-encapsulated mesoporous silica nanoparticles