Supporting Information

Facile preparation of ellipsoidal-like MCM-41 with parallel channels along the short axis for drug delivery and assembly of Ag nanoparticles for catalysis

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Materials and Methods

1. Materials

Cetyltrimethylammonium bromide (CTAB), sodium dodecylbenzenesulfonate (SDBS), tetraethyl orthosilicate (TEOS), aqueous ammonia, $AgNO_3$, $NaBH_4$, and 4-nitrophenol (4-NP) were obtained from Beijing Chemical Reagents Company (China). Doxorubicin was purchased from Huafeng United Technology Co. (Beijing). All chemicals were used as received without any further purification.

2. Synthesis of mesoporous silica nanoparticles

Ellipsoidal-like MCM-41 with parallel channels along the short axis: Ellipsoidal-like MCM-41-type mesoporous silica nanoparticles were synthesized with tetraethoxysilane (TEOS) as silica precursor, and a surfactant mixture of cetyltrimethylammonium bromide (CTAB) and sodium dodecylbenzenesulfonate (SDBS) as template in diluted ammonia aqueous solution. In brief, 0.8 g CTAB and 0.2 g SDBS were dissolved in 400 ml H_2O, and 5 ml $NH_3 \cdot H_2O$ (25%~28%) was added with stirring for 30 min at room temperature. 5 ml TEOS was then added with stirring for another 5 h. After collected by centrifugation and followed by washed three times with deionic water, the resulting solid products were dried at 80 °C overnight. Surfactant templates were then removed with a heating rate of 1 °C/min in static air up to 600 °C.

Rod-like MCM-41 with parallel channels along the long axis: Rod-like MCM-41-type mesoporous silica nanoparticles were synthesized under the similar conditions to the

preparation procedure of ellipsoidal-like MCM-41 without the addition of SDBS. Briefly, 0.8 g CTAB was dissolved in 400 ml H_2O, and 5 ml $NH_3 \cdot H_2O$ (25%~28%) was added with stirring for 30 min at room temperature. 5 ml TEOS was then added with stirring for another 5 h. After collected by centrifugation and followed by washed three times with deionic water, the resulting solid products were dried at 80 °C overnight. Surfactant templates were then removed with a heating rate of 1 °C/min in static air up to 600 °C.

3. Drug Loading and Release

To load Doxorubicin (Dox) into the ellipsoidal-like MCM-41 nanoparticles, the nanoparticles were dispersed in Dox solution (20mg mL^{-1}, keeping the weight ratio of nanoparticles to drug at 1:1) and stirred for 24 h at 37 °C, followed by centrifugation and washing once with saline to obtain the drug-loaded ellipsoidal-like MCM-41 nanoparticles. The concentration of Dox was determined by UV/vis spectroscopy measurements at a wavelength of 233 nm. For drug release assay, the Dox-loaded ellipsoidal-like MCM-41 nanoparticles samples were immersed in PBS (pH=4.5), and the supernatant was collected at given time intervals for determining the concentration of Dox. Drug loading and release tests of rod-like MCM-41 with parallel channels along the long axis were same to that of ellipsoidal-like MCM-41. The amount of Dox loaded into rod-like MCM-41 was calculated to be 486 mg per gram nanoparticles.

4. Assembly of Ag nanoparticles on ellipsoidal-like MCM-41

To assemble Ag nanoparticles on ellipsoidal-like MCM-41, 300 mg silica host was soaked into 10 ml $AgNO_3$ (1 wt%) solution for 24 h. After filtered and rinsed thoroughly with deionized water, the product was dried at 60 °C, and then the solid products were treated at 500 °C directly in static air for 1 h to make $AgNO_3$ decompose into Ag. Assembly test of rod-like MCM-41 were same to that of ellipsoidal-like MCM-41. The content of Ag nanoparticles in rod-like MCM-41 supported Ag nanocomposite was estimated to be 3.62 wt% according to the EDX spectrum result.

5. Application of the ellipsoidal-like MCM-41 supported Ag nanocomposite for catalytic reduction of 4-nitrophenol

The reduction of the 4-nitrophenol (4-NP) compound by the ellipsoidal-like MCM-41 supported Ag nanocomposite in the presence of $NaBH_4$ was carried out to examine the catalytic activity and reusability of the ellipsoidal-like MCM-41 supported Ag nanocomposite. Typically, an aqueous solution of $NaBH_4$ (2×10^{-3} mol L^{-1}) was mixed with aqueous 4-NP solution (2.7×10^{-4} mol L^{-1}) in the quartz cell. Then, ellipsoidal-like MCM-41 supported Ag nanocomposite catalysts (0.1×10^{-4} mol L^{-1} relative to Ag nanoparticles) were added to the mixture and quickly placed in the cell holder of the spectrophotometer. The progress of the

conversion of 4-NP to 4-aminophenol (4-AP) was then monitored via UV/vis spectroscopy by recording the time-dependent absorbance spectra of the reaction mixture in a scanning range of 200−600 nm at ambient temperature. Catalytic test of rod-like MCM-41 were same to that of ellipsoidal-like MCM-41.

6. Characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a JEOL JEM 2010F electron microscope operating at 200 kV. The energy-dispersive X-ray (EDX) spectroscopic measurements were performed with the spectrometer attached on the JEOL-2010F HRTEM. A JASCO V-570 spectrophotometer was used to measure the UV/vis spectra of the nanoparticles at room temperature. Fourier transform infrared spectrometry (FT-IR) was performed on an Excalibur 3100 Fourier transform infrared spectrometer. X-ray diffraction (XRD) patterns were obtained using Cu Kα radiation (λKα1 = 1.5406Å) and a wide-angle graphite monochromator. Nitrogen adsorption–desorption measurements were carried out to determine the textural properties of silica materials by using a Quantachrome NOVA 4200e surface area analyzer at −196 °C. The prepared products were dried at 300 °C before analysis. Pore-size distributions were estimated from adsorption branches of the isotherms by using the Barrett–Joyner–Halenda (BJH) method. Pore volumes were determined from the amounts of N_2 adsorbed at the single point of P/P_0 =0.98.

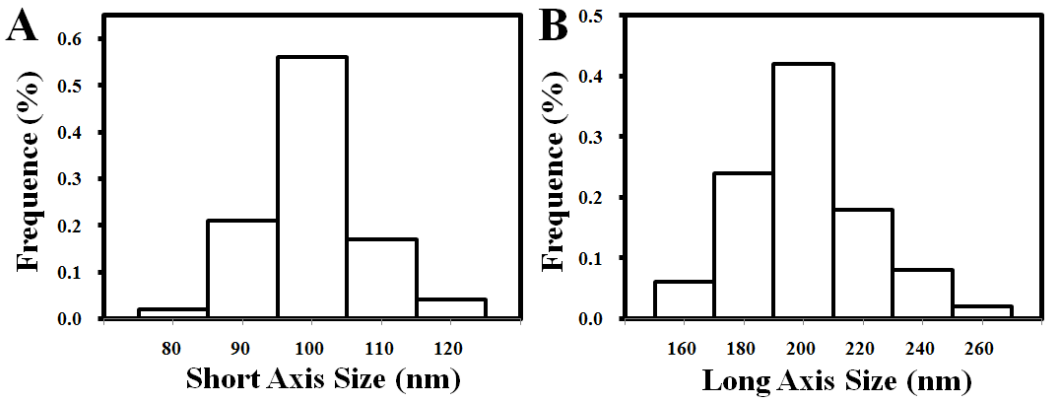

Figure S1. Statistical short axis (A) and long axis (B) size distribution of ellipsoidal-like MCM-41 nanoparticles from 200 particles in the TEM images.

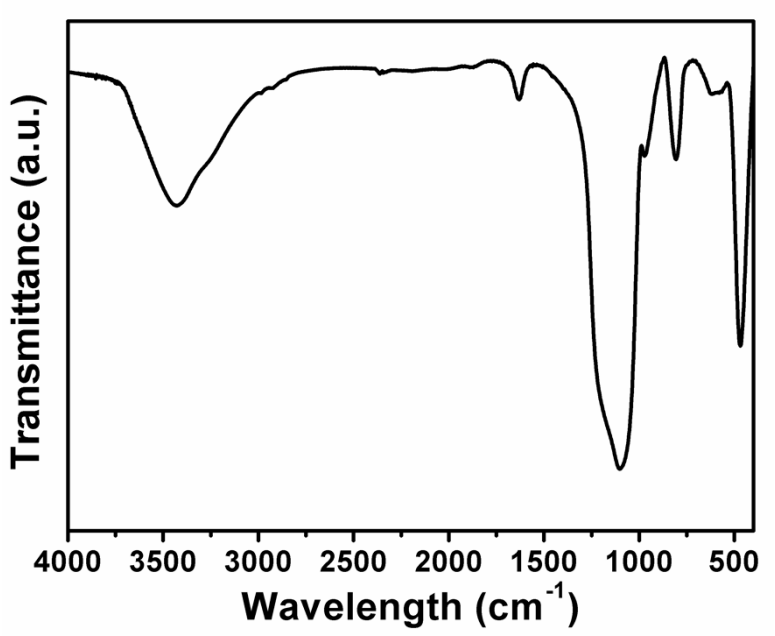

Figure S2. FT-IR spectra for the ellipsoidal-like MCM-41 nanoparticles after calcination treatment.

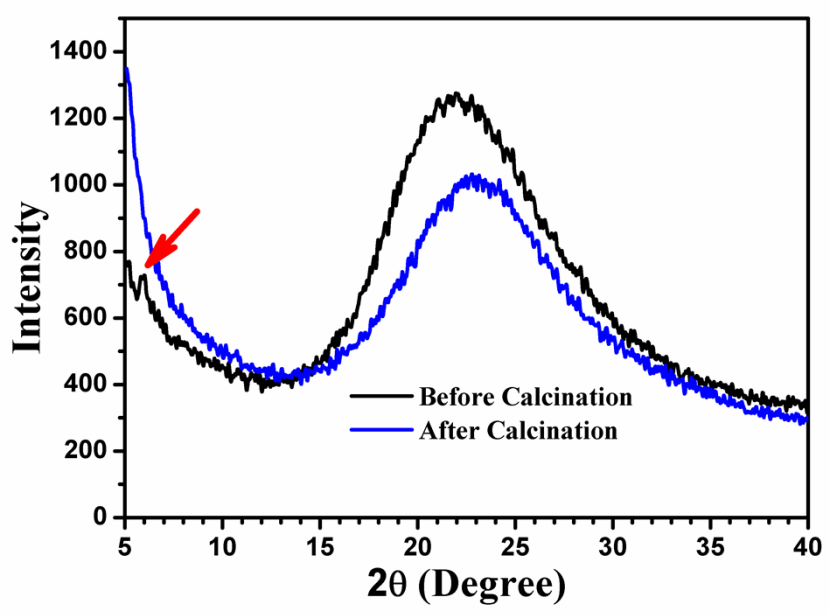

Figure S3. X-ray diffraction patterns of the ellipsoidal-like MCM-41 nanoparticles before and after calcination treatment.

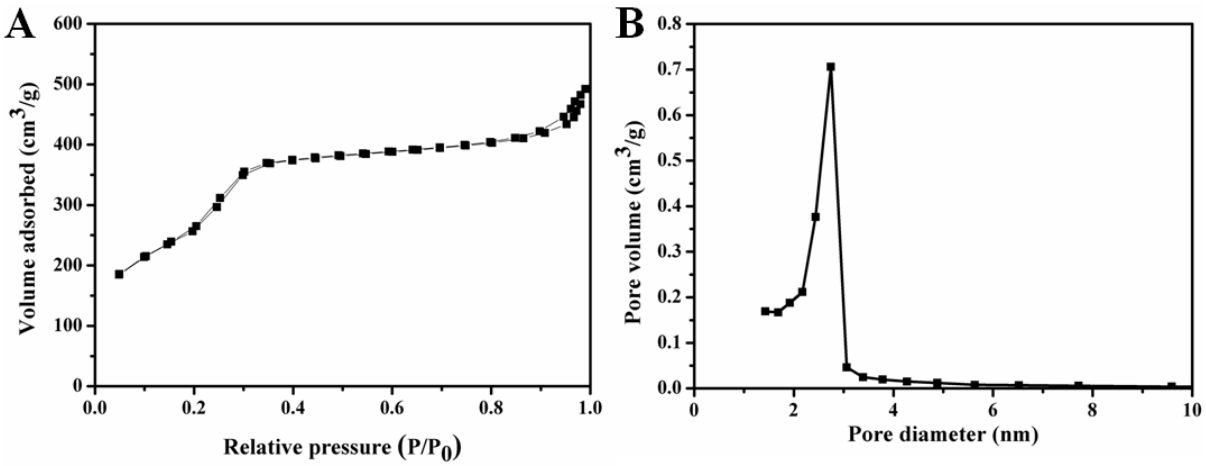

Figure S4. (A) N2 adsorption-desorption isotherm of calcined ellipsoidal-like MCM-41; (B) The corresponding adsorption pore size distribution plot by BJH method.

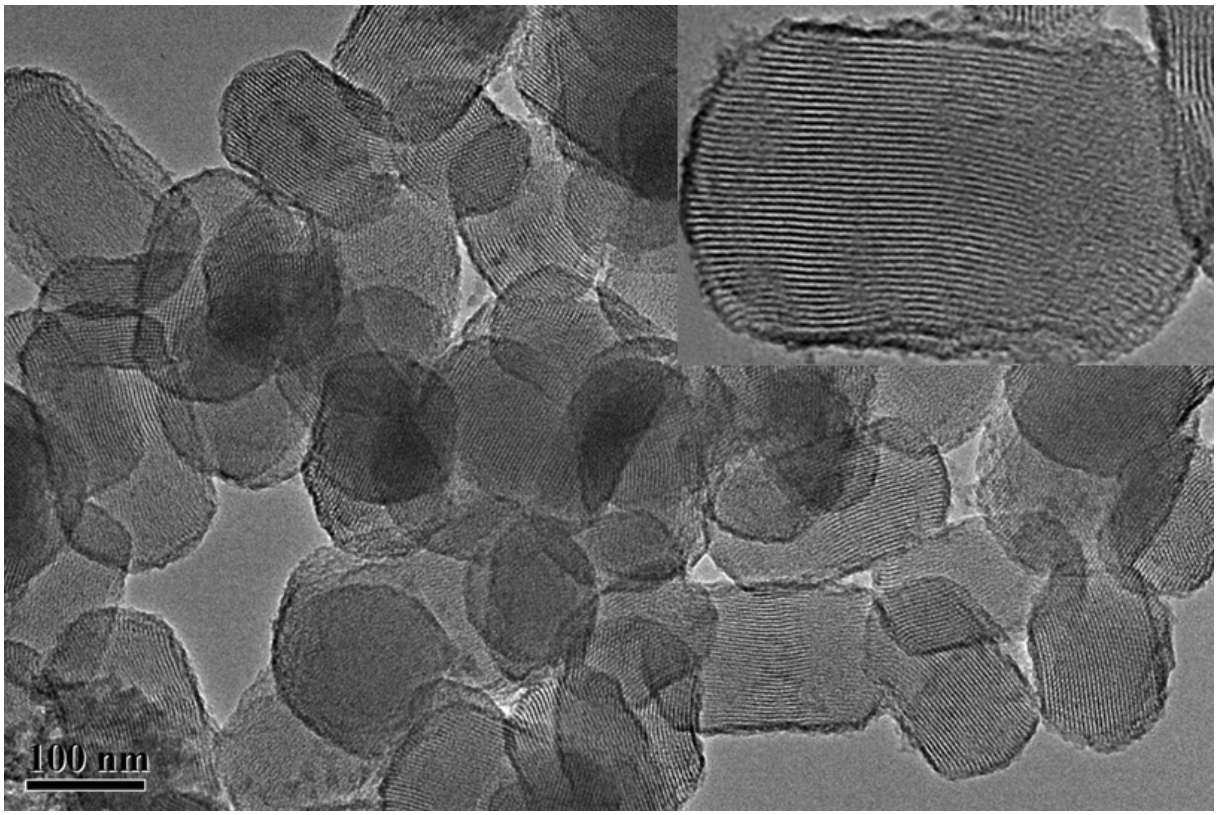

Figure S5. TEM image of rod-like MCM-41 with parallel channels along the long axis. The inset of TEM image with higher magnification shows ordered mesoporous structure with straight channels.

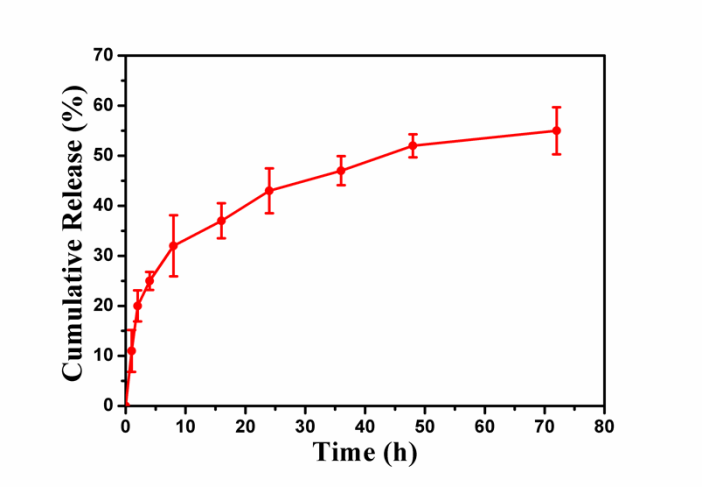

Figure S6. Released profile of Doxorubicin from drug-loaded rod-like MCM-41 with channels oriented along the long axis in PBS solution (pH=4.5). Points shown indicate mean of three replicates. Data represent the mean ± SD.

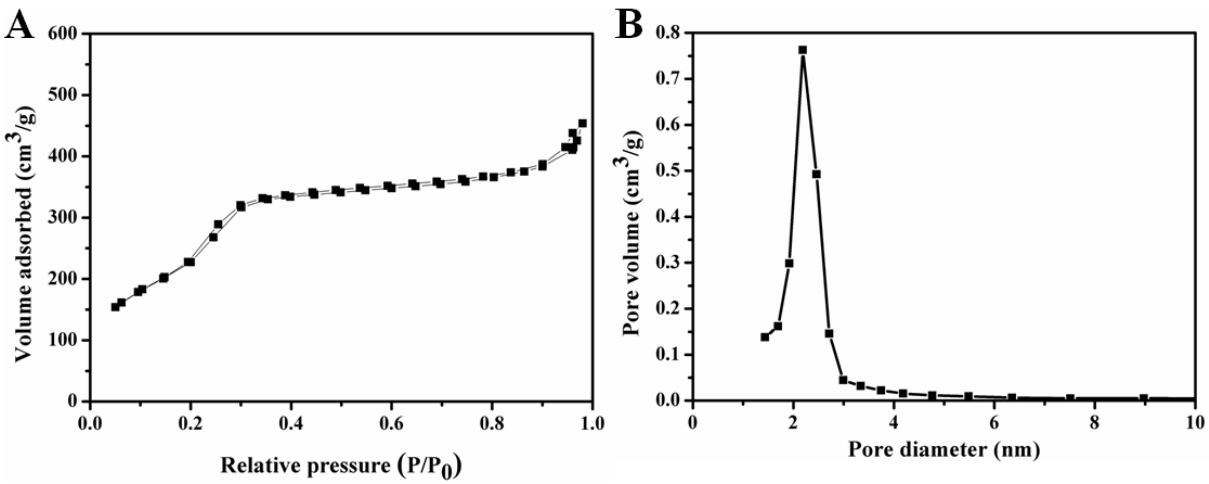

Figure S7. (A) N2 adsorption-desorption isotherm of ellipsoidal-like MCM-41 supported Ag nanocomposite; (B) The corresponding adsorption pore size distribution plot by BJH method.

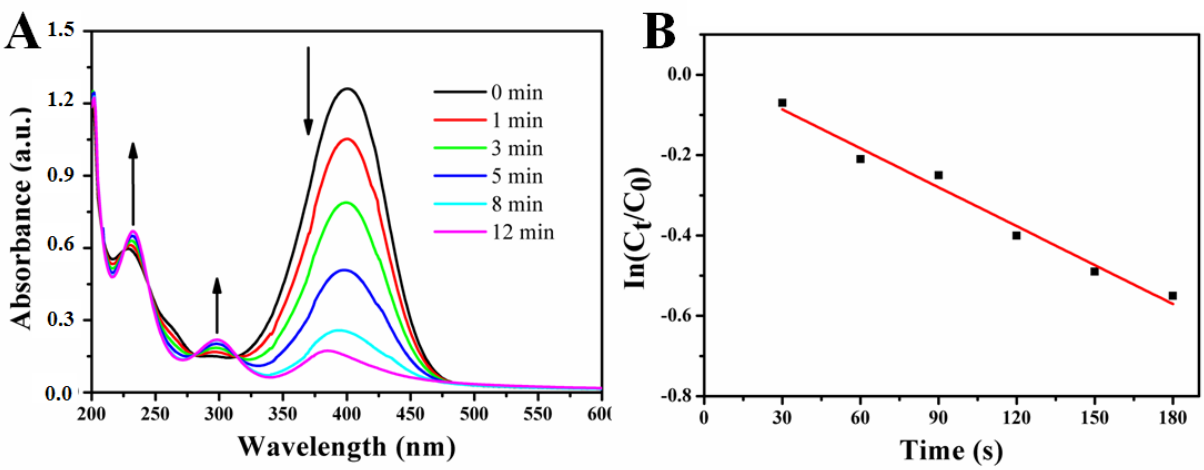

Figure S8. (A) UV/Vis absorption spectrum of 4-nitrophenol catalyzed by the rod-like MCM-41 supported Ag nanocomposite; (B) Linear relationship between $\ln(C_t/C_0)$ and time for 4-nitrophenol (400 nm), the ratios of 4-NP concentration (C_t at time t) to its initial value C_0 (t = 0) were directly given by the relative intensity of the respective absorbance A_t/A_0.