

Supporting information for

## **Double Mesoporous Silica Shelled Spherical/Ellipsoidal Nanostructures: Synthesis and Hydrophilic/Hydrophobic Anticancer Drug Delivery**

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### **Experimental section**

**Synthesis of sSiO<sub>2</sub>@mSiO<sub>2</sub> core/shell nanostructure using C<sub>16</sub>TAB as structural directing**

**agent:** The synthetic procedure was according to previous reports (*J. Mater. Chem.*, **2007**, *17*, 1758; *Colloids and Surface A: Physicochem. Eng. Aspects*, **2008**, *313-314*, 77).

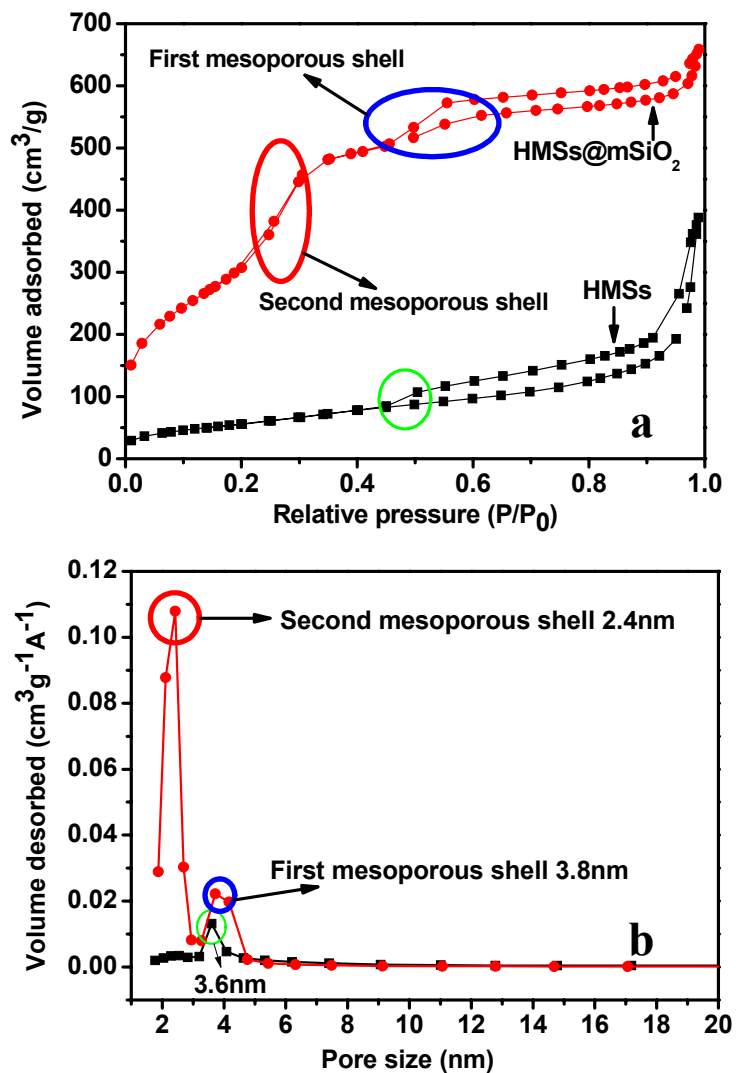
**Synthesis of sSiO<sub>2</sub>@mSiO<sub>2</sub> core/shell nanostructure using C<sub>18</sub>TMS as structural directing**

**agent:** Typically, 142.8 mL of ethanol, 20 mL of deionized water and 3.14 mL of ammonia solution were mixed and heated to 30°C. Then 6 mL of TEOS was added rapidly and the mixture were magnetically stirred for 1 h. Afterwards, 5 mL of TEOS and 2 mL of C<sub>18</sub>TMS were then mixed and added into above mixture quickly, which was magnetically stirred for another 1 h (*ACS Nano*, **2010**, *1*, 529; *Chem. Commu.*, **2009**, 6071, *Adv. Mater.* **1998**, *10*, 1036).

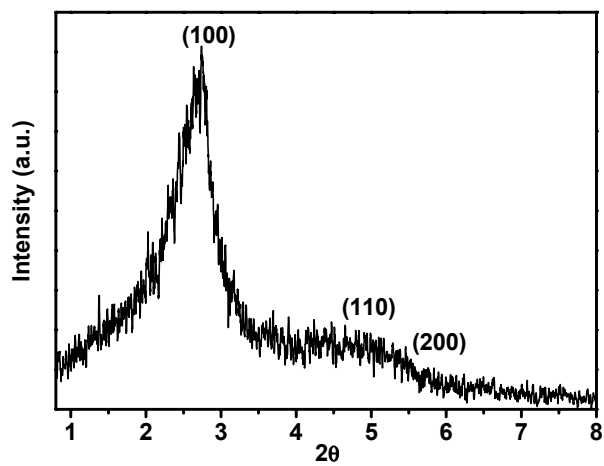
**Synthesis of ellipsoidal Fe<sub>2</sub>O<sub>3</sub> nanocrystals:** Ellipsoidal Fe<sub>2</sub>O<sub>3</sub> were synthesized by aging a solution containing 11.6 g of Fe(ClO<sub>4</sub>)<sub>3</sub>•6H<sub>2</sub>O, 1.5 g of urea and 0.16 g of NaH<sub>2</sub>PO<sub>4</sub> dissolved in 250 mL of deionized water at 100 °C for 24 h. The product was collected by centrifugation and washed with water for 3 times. Then the sample was dried under vacuum at room temperature for further use (*ACS Nano*, **2010**, *1*, 529; *Angew. Chem. Int. Ed.*, **2008**, *47*, 5806).

**Synthesis of FITC-HMSs@mSiO<sub>2</sub>:** FITC (15mg) was reacted with 3-aminopropyltriethoxysilane (APTES, 100 µL) in ethanol (5 mL) under dark conditions for 24 h. Subsequently, HMSs@mSiO<sub>2</sub> (20 mg) were reacted with FITC-APTES stock solution (1 mL) under dark conditions for 24 h. The FITC grafted particles were collected by centrifugation and washed with ethanol several times to remove the unreacted FITC-APTES. Finally, the FITC-HMSs@mSiO<sub>2</sub> were dried under vacuum at room temperature.

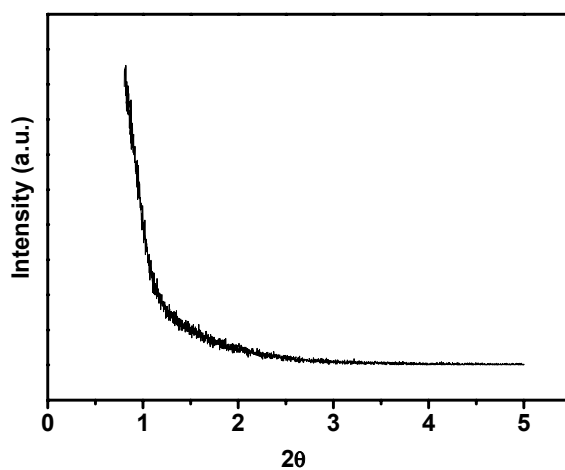
**Synthesis of MCM-41 type mesoporous silica spheres:** Typically, 0.28 g of NaOH was dissolved into 480 mL of H<sub>2</sub>O under magnetic stirring at room temperature. Then 1 g of C<sub>16</sub>TAB was added into above solution and the temperature of the mixture was raised to 80 °C. 5 mL of TEOS was added dropwise to the solution under vigorous stirring. The reaction was continued for 2 h to give rise to a white precipitation. The product was collected by filtration and washed with deionized water and ethanol several times. After the sample was dried at 100 °C, the surfactant (C<sub>16</sub>TAB) was removed by calcination in air at 600 °C for 6 h (*Microporous Mesoporous Mater.*, **2007**, *102*, 151).



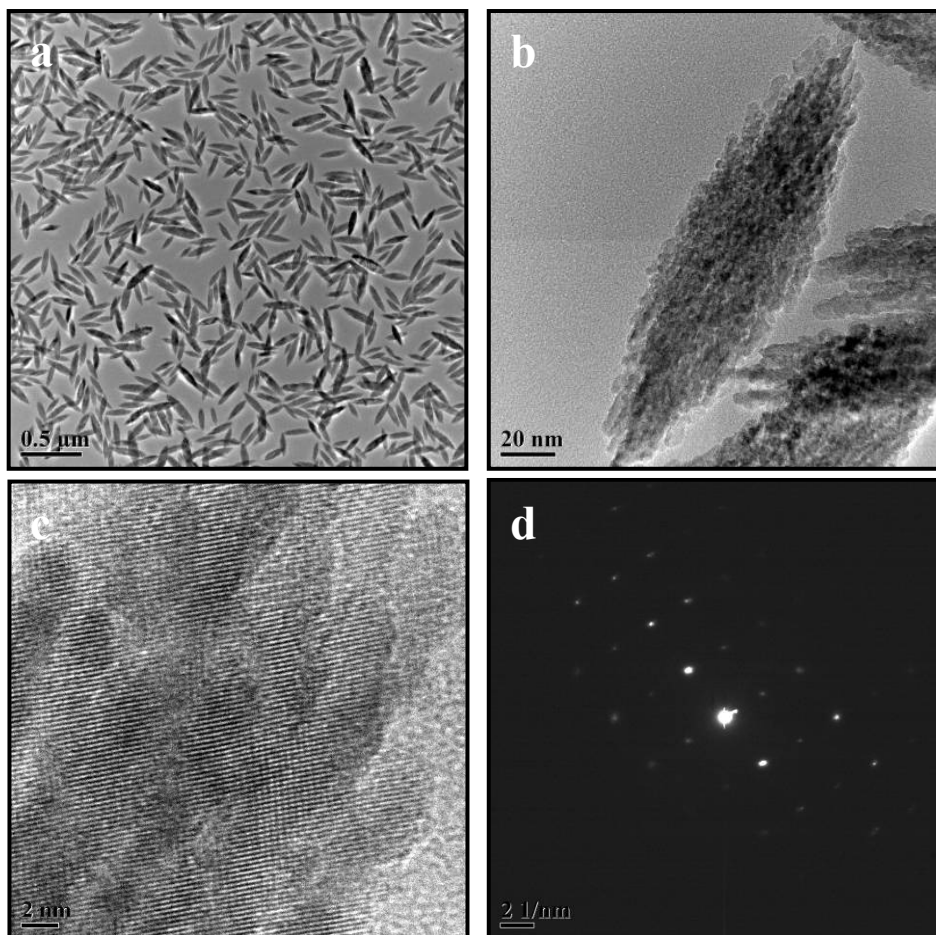
**Figure S1**  $N_2$  adsorption-desorption isotherms (a) and corresponding pore size distributions (b) of HMSs and HMSs@mSiO<sub>2</sub>.



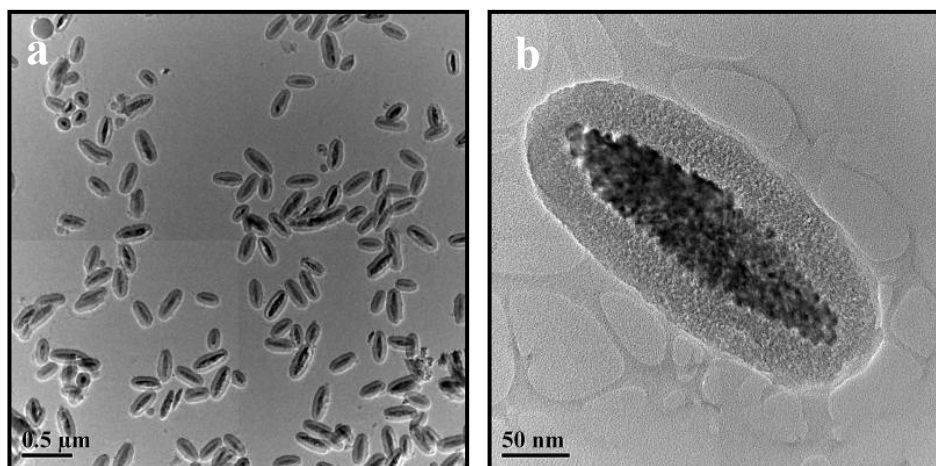
**Figure S2** Small angle X-ray diffraction pattern of HMSs@mSiO<sub>2</sub>.



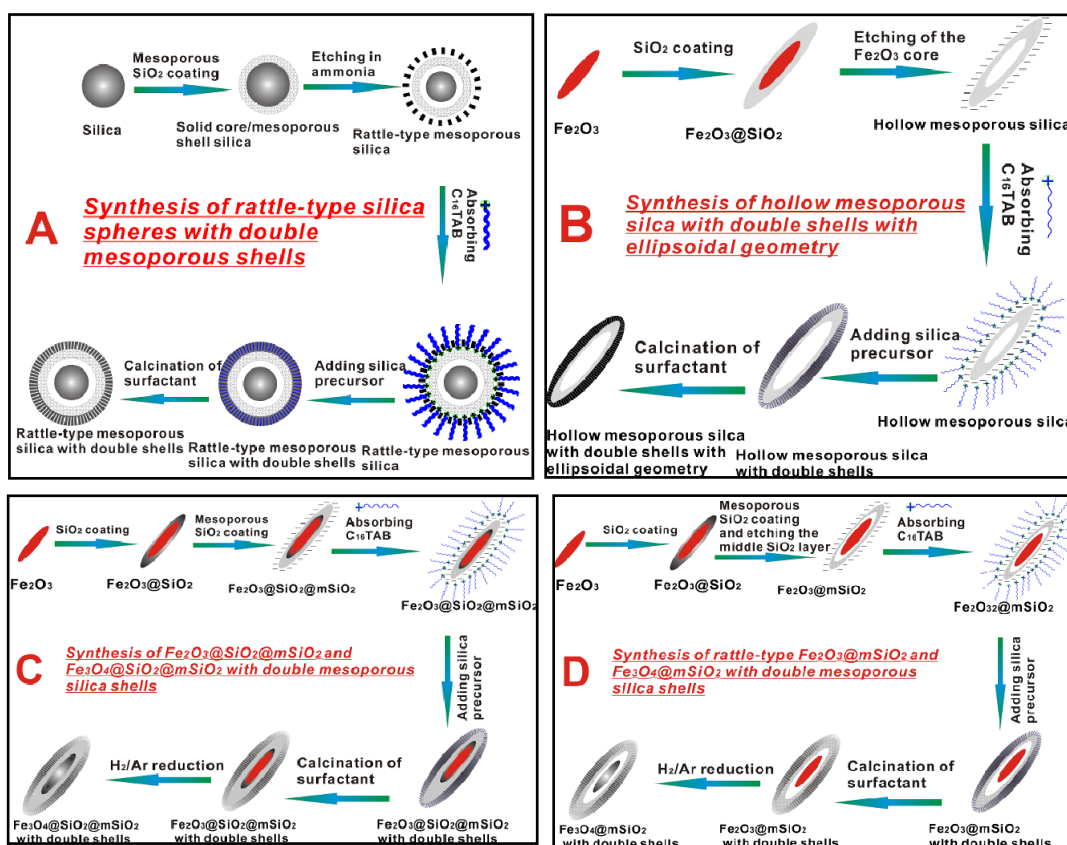
**Figure S3** Small angle X-ray diffraction pattern of HMSs with single mesoporous shell.



**Figure S4** TEM images (a, b) of ellipsoidal  $\text{Fe}_2\text{O}_3$  nanocrystals under different magnifications; High resolution TEM image (HRTEM, c) of  $\text{Fe}_2\text{O}_3$  nanocrystals; (d) Selected area electron diffraction (SAED, d) of  $\text{Fe}_2\text{O}_3$  nanocrystals.



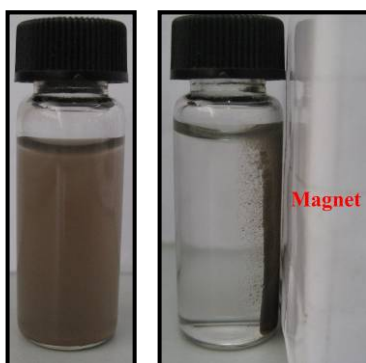
**Figure S5** TEM image (a, b) of  $\text{Fe}_2\text{O}_3@\text{mSiO}_2$  before removing  $\text{C}_{18}\text{TMS}$  under different magnifications.



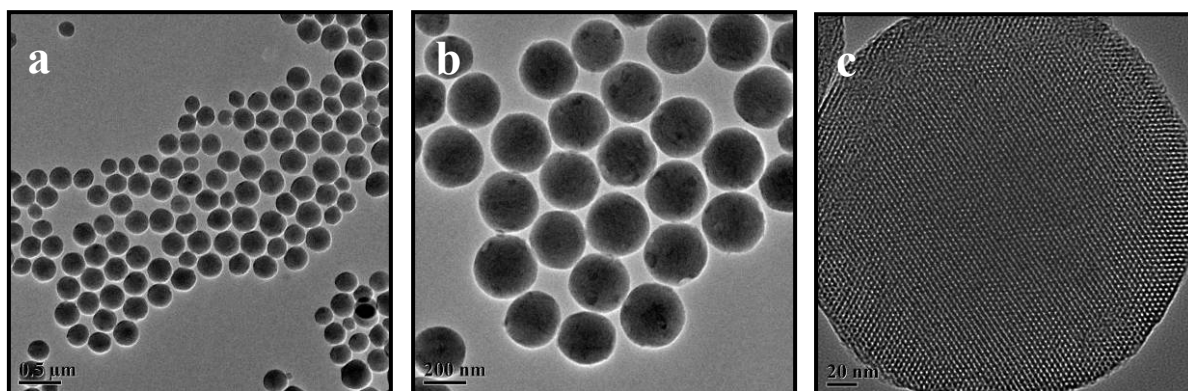
**Figure S6** Schematic illustration of the whole procedures for the preparation of various nanostructures with double mesoporous silica shells. (A) Double shelled homogeneous rattle-type silica spheres: Firstly, solid silica surface was coated by a layer of  $\text{C}_{18}\text{TMS}$  templated mesoporous silica shell ( $\text{sSiO}_2@m\text{SiO}_2$ ). Then, the obtained  $\text{sSiO}_2@m\text{SiO}_2$  nanoparticles were dispersed in 0.12 M ammonium solution and under hydrothermal treatment at  $150^\circ\text{C}$  for 24 h to create the interstitial space between solid core and mesoporous shell. After adding  $\text{C}_{16}\text{TAB}$  into the reaction medium, the positively charged  $\text{C}_{16}\text{TAB}$  were absorbed onto the surface of rattle-type  $\text{sSiO}_2@m\text{SiO}_2$ . When the silica precursor was added, a mesoporous silica shell templated by  $\text{C}_{16}\text{TAB}$  was formed on the surface of rattle-type  $\text{sSiO}_2@m\text{SiO}_2$ . Finally, both  $\text{C}_{18}\text{TMS}$  and  $\text{C}_{16}\text{TAB}$  were removed by calcination under high temperature; (B) Double shelled ellipsoidal hollow mesoporous silica nanoparticles by employing ellipsoidal  $\text{Fe}_2\text{O}_3$  as the morphology-deciding template: The coating of a

mesoporous silica shell onto the surface of ellipsoidal hollow mesoporous nanoparticles was similar to the process for HMSs@mSiO<sub>2</sub> and rattle-type mesoporous sSiO<sub>2</sub>@mSiO<sub>2</sub>; (C) Double shelled Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@mSiO<sub>2</sub> nanostructure by using modified Stöber method and coating process of HMSs@mSiO<sub>2</sub>; (D) Double shelled rattle-type mesoporous nanostructures with functional Fe<sub>2</sub>O<sub>3</sub> (or Fe<sub>3</sub>O<sub>4</sub>) as the core and huge interstitial space between the core and shell: An ammonium etching process was employed to create the cavities between the core and shell, and modified Stöber method and coating process of HMSs@mSiO<sub>2</sub> were used for double mesoporous shell deposition.





**Figure S7** Digital photographs of double-shelled  $\text{Fe}_3\text{O}_4@\text{SiO}_2@m\text{SiO}_2$  nanostructure in water (left) and manipulated by external magnetic field (right).



**Figure S8** TEM images of MCM-41 type mesoporous silica spheres under different magnifications.