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Large pore mesostructured cellular silica foams coated magnetic oxide composites with multilamellar vesicle shells for adsorption

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Experimental Section

Chemicals.

All of chemicals were analytical grade and used without further purification. Triblock poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) copolymer Pluronic P123 (PEO_{20}-PPO_{70}-PEO_{20}) was purchased from Acros Corp. $FeCl_3$, trisodium citrate, sodium acetate, ethylene glycol, boric acid, anhydrous magnesium sulfate, tetraethyl orthosilicate (TEOS), hexadecyltrimethylammonium bromide (CTAB), Cytochrome C (12400 Da, 2.6 x 3.2 x 3.3 nm^3) and protein Bovine serum albumin (BSA) (66400 Da, 5.0 x 7.0 x 7.0 nm^3) were purchased from Sinopharm Chemical Reagent Co. (China). Doxorubicin hydrochloride (DOX) was brought from Beijing Hua Feng United Technology Co., Ltd. Deionized water was used in all experiments.

Preparation of Fe_3O_4 nanoparticles.

The highly water dispersible magnetite nanospheres were prepared through a solvothermal method by using trisodium citrate as a stabilizer and $FeCl_3$ as a iron source in ethylene glycol solution according to the reference reported by our group.[1] Typically, 0.54 g of $FeCl_3$ and 0.30 g of trisodium citrate were dissolved in 20 mL ethylene glycol. Afterward, 1.20 g of sodium acetate was added and stirred vigorously for at least 30 minutes to form clear solution. Then, the solution was placed into a 30-mL Teflon-sealed autoclave and maintained at 200 °C for 10 h in oven, subsequently, the autoclave was cooled to room temperature. The black products were washed with ethanol and water for three cycles, and then dried in vacuum at 40 °C over night.

Synthesis of mesoporous cellular silica foams coated magnetic oxide (MO@MCFs).

The core-shell structured MO@MCF composites were achieved using nonionic tri-block copolymer Pluronic P123 as a template without adding swelling agents. In a typical process, 0.1 g of P123 and 3.0 g of boric acid (1.3 mol/L) were firstly dissolved in 40 mL deionized water, then the above Fe_3O_4 nanoparticles (0.15 g) was

added into the aqueous solution. The mixed solution was homogenized *via* ultrasonic treatment to form a uniform dispersion. 0.46 g of TEOS was injected into the solution under vigorous mechanical agitation at 40 °C oil bath. After continuous stirring for 24 h, the solution was transferred into a 50-mL autoclave and maintained at 100 °C for 24 h. The products were collected with a magnet and washed with ethanol and water for several times, and then dried in vacuum at 40 °C for 6 h. The final products (denoted as MO@MCFs) were obtained after being calcined in atmosphere at 550 °C for 5 h to remove the copolymer templates. The mesoporous cellular silica foams coated magnetic oxide composites with multilamellar vesicle shells (MO@MLVs) were prepared similar to the above procedure while adding 0.36 g of $MgSO_4$ as the inorganic salt. The mesoporous cellular silica foams coated magnetic oxide composites with onion-like lamellar shells (MO@MLVs-130H) were prepared with the hydrothermal treatment at 130 °C for 24 h without addition of the inorganic salt. The weight ratios of Fe_3O_4 are calculated to be about 55 and 58 % for MO@MCFs and MO@MLVs, respectively.

Synthesis of the conventional core-shell MO@MCM-41 composite.

The core-shell MO@MCM-41 composite was obtained according to the previous report by using surfactant CTAB as a template.[2] In brief, 50 mg of the Fe_3O_4 particles was mixed with a solution containing 25 mL of H_2O, 15 mL of ethanol, 0.28 mL of ammonia aqueous (28 wt %) and 75 mg of CTAB. The mixture was stirred at room temperature for 30 min, then 0.12 mL of TEOS was injected into the solution and continuous agitated for 6 h. The particles (MO@MCM-41) were collected with a magnet, washed with ethanol for three times, and then dried in room temperature for further use.

Adsorption of Cytochrome C and BSA.

2 mg/mL of Cytochrome C and BSA phosphate buffer solution (PBS, pH = 7.4) were prepared, respectively. Then, 5 mL of the protein solution was shifted to the vessel containing 10 mg of the samples MO@MCM-41, or MO@MCF or MO@MLV composites, respectively. After being sealed, then ultrasonicated for 1 h and shaken at room temperature for 24 h, the samples were separated by external magnetic field.

Then the supernatant liquor was measured by UV-vis spectra, the adsorption wavelengths for Cytochrome C and BSA were selected to be 360 and 277 nm, respectively.

In vitro DOX loading and release.

10 mg of the core-shell structured MO@MCM-41, or MO@MCF or MO@MLV composites was added into 5 mL of DOX (1.0 mg/mL) phosphate buffer solution (PBS, pH = 7.4), and kept on shaking for 48 h in a dark condition at room temperature. The DOX loading composite sample was obtained by centrifugation and washed with PBS solution twice. The supernatant solution containing DOX drug was measured by fluorescence spectra at an excited wavelength of 500 nm to calculate the loading amount of DOX in the composites (The solutions were all diluted twenty times for fluorescent measurement). The loading capacity was evaluated as the weight percentage of DOX drug related to the composites. The DOX release tests were performed by mixing 2.0 mg of DOX loaded composites in 5 mL of PBS solution at 37 °C under gentle shaking in dark condition. The release PBS solution was collected at different time for analysis and replaced with an equal volume of fresh PBS buffer. The release percentage of DOX in the PBS solution was measured by fluorescence spectra at 500 nm.

Characterization.

Scanning electron microscopic (SEM) images were obtained on a Philip XL30 microscope. A thin film of gold was sprayed on the samples before the characterization. Transmission electron microscopy (TEM) measurements were achieved on a JEOL 2011 microscope operated at 200 kV. The samples were suspended in ethanol and dried on a holey carbon film on a Cu grid for TEM measurements. Nitrogen sorption isotherms were measured at 77 K with a Micromeritcs Tristar 3020 analyzer (USA). Before measurements, the samples were degassed in a vacuum at 180 °C for at least 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}), using adsorption data in a relative pressure (P/P_0) range from 0.04 to 0.2. The pore volume and pore size distributions were derived from the adsorption branches of isotherms by using

Barrett-Joyner- Halenda (BJH) model. The total pore volume, V_t, was estimated from the amount adsorbed at a relative pressure P/P_0 of 0.995. Wide-angle X-ray diffraction (XRD) patterns were recorded on a Bruker D4 X-ray diffractometer (Germany) with Ni-filtered Cu Kα radiation (40 kV, 40 mA). UV-Vis absorption spectra were measured on a Jasco spectrophotometer (V-550) (Japan). Fluorescence spectra were recorded on an F-4500 spectrofluorometer (Hitachi High-Technologies). DOX was excited at 500 nm and collected at 520 - 900 nm. The bandpass was set at 5 nm both excitation and emission, scan speed at 1200 nm/min and PMT voltage at 700 V for all measurements.

References:

[1] J. Liu, Z. K. Sun, Y. H. Deng, Y. Zou, C. Y. Li, X. H. Guo, L. Q. Xiong, Y. Gao, F. Y. Li and D. Y. Zhao, *Angew. Chem., Int. Ed.*, 2009, **48**, 5875.

[2] J. P. Yang, F. Zhang, Y. R. Chen, S. Qian, P. Hu, W. Li, Y. H. Deng, Y. Fang, L. Han, M. Luqman and D. Y. Zhao, *Chem. Commun.*, 2011, **47**, 11618.

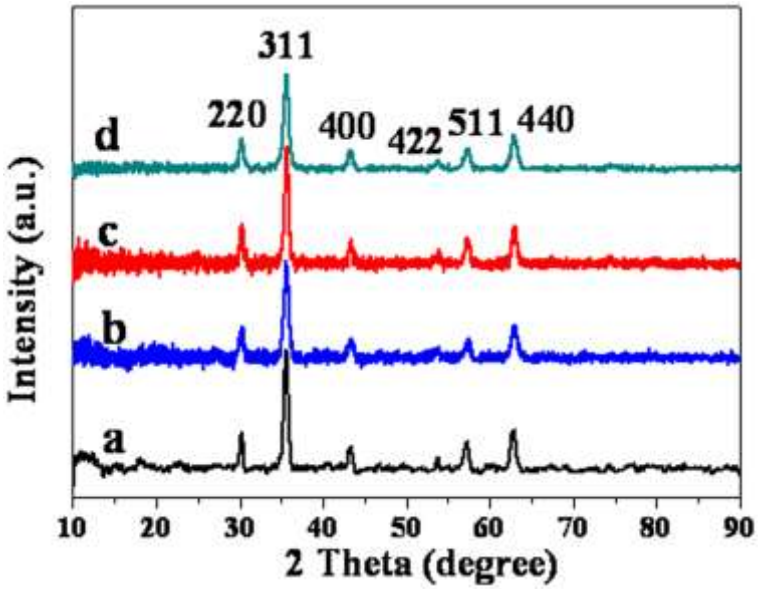

Fig. S1. Wide-angle X-ray diffraction (XRD) patterns of (a) the Fe_3O_4 nanoparticles prepared through a solvothermal method by using trisodium citrate as a stabilizer and $FeCl_3$ as a iron source in ethylene glycol solution, (b) large pore mesoporous cellular silica foams coated magnetic oxide composites (MO@MCFs) prepared in 1.3 mol/L of boric acid medium by using Pluronic P123 as a template with the hydrothermal treatment at 100 °C for 24 h, (c) mesoporous cellular silica foams coated magnetic oxide composites with multilamellar vesicle shells (MO@MLVs) prepared in 1.3 mol/L of boric acid medium by using Pluronic P123 as a template and $MgSO_4$ as the inorganic salt with the hydrothermal treatment at 100 °C for 24 h, and (d) mesoporous cellular silica foams coated magnetic oxide composites with onion-like lamellar shells (MO@MLVs-130H) prepared in 1.3 mol/L of boric acid medium by using Pluronic P123 as a template with the hydrothermal treatment at 130 °C for 24 h.

Table S1. Physicochemical properties of the core-shell structured MO@MCF, MO@MLV and MO@MCM-41 composites.

Samples	S_{BET} (m^2g^{-1})	Pore size (nm)	V_t (cm^3g^{-1})	Adsorption amount ($mg \cdot g^{-1}$)		
				Cyt C	BSA	DOX
MO@MCFs	297	15.1, 42.6	0.49	175	113	33.2 wt %
MO@MLVs -130H	185	12.5, 43.1	0.32			
MO@MLVs	296	10	0.35	142	103	33 wt %
Mesoporous silica tubes	717	9.2	1.72			
MO@MCM-41	290	2.3	0.18	65.6	0	13.2 wt %

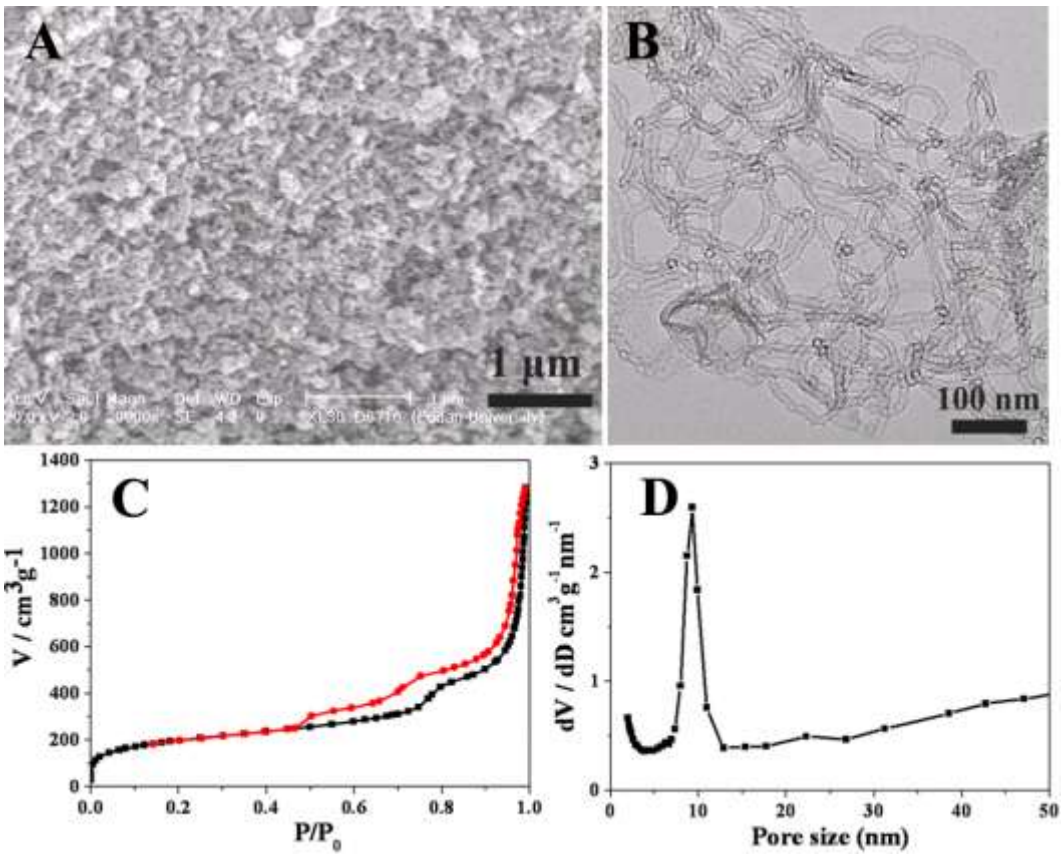

Fig. S2. SEM (A) and TEM images (B), the N_2 sorption isotherm curves (C) and pore size distribution plots (D) of the mesoporous silica nanotubes, prepared in 1.3 mol/L of boric acid medium by using Pluronic P123 as a template without the addition of magnetic oxides.

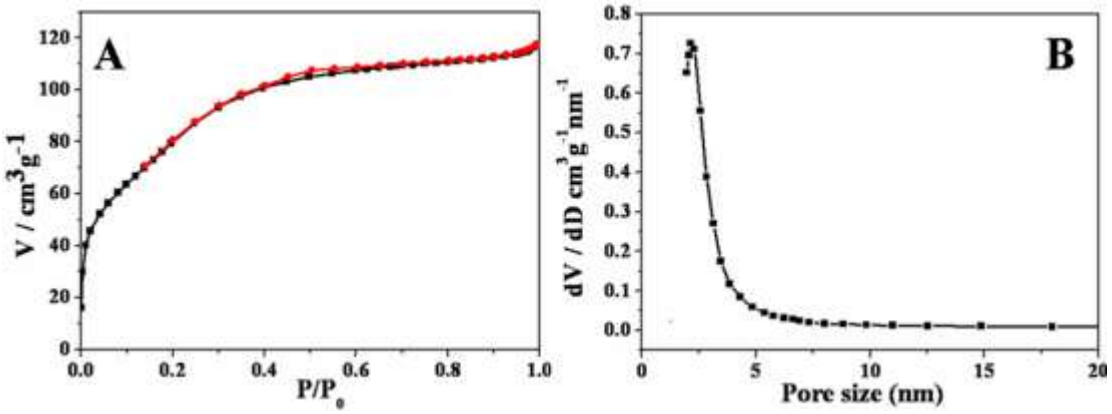

Fig. S3. N_2 sorption isotherm curves (A) and pore size distribution plots (B) of the core-shell structured MO@MCM-41 composites prepared by using surfactant CTAB as a template.