Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Synthesis of double mesoporous core-shell silica nanospheres with radially oriented mesopores via one-templating step using anionic surfactant

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1. Experimental

1.1 Chemicals

N-lauroylsarcosine sodium (Sar-Na), 3-aminopropyltrimethoxysilane (APMS), polyvinylpyrrolidone (PVP) average Mw ~29,000 and tetraethoxysilane (TEOS) were purchased from Sigma-Aldrich. All the chemical agents were used without further purification.

1.2 Synthesis

1.2.1 Synthesis of solid silica core

Solid core silica particles were synthesized by adding 1.75 ml of aqueous ammonia into a solution containing 37 ml of ethanol and 5 ml of deionized water followed by the addition of 3 ml of TEOS to the solution with vigorous stirring. Then the resulting mixture was heated at 30 ^{o}C for 60 min. The molar composition of the suspension was as follows: TEOS:EtOH:NH_3:H_2O = 1:46.9:3.2:20.5. In order to form the mesoporous silica

shell around the above prepared silica particles, we adopted two different strategies consisting of one and two-pot synthesis routes.

1.2.2 Synthesis of mesoporous core-shell nanosphere by one-pot synthesis route

In the one-pot synthesis route, 10 and 0.10 ml of water and 3-aminopropyltrimethoxysilane (APMS) were added, respectively to the above solution where the mixture was stirred for 30 min. Then a solution of 0.2933 g (1 mmol) *N*-Lauroylsarcosine sodium in 25 ml H_2O, which already has been acidified with 4 ml (0.1 M HCl), was added to the above solution and stirred for further 1 h. Finally 1.5 ml of TEOS was added and kept under stirring at 50 ^oC for 2 h. The resulting molar ratio was: TEOS: EtOH: H_2O: NH_3:APMS: Sar-Na: HCl = 1:31.2:109.4:2.1:0.02: $1x10^{-3}$: $4x10^{-4}$.

1.2.3 Synthesis of mesoporous core-shell nanosphere by two-pot synthesis route

In two-pot synthesis route, and after the silica precipitate was collected by centrifugation and washed three times with water, a 0.3 g of SiO_2 particles was dispersed in 15 ml of H_2O by ultrasonication for 10 min. Thereafter, APMS, and *N*-Lauroylsarcosine sodium acidified solution and TEOS were added, respectively to the reaction mixture similar to one-pot synthesis route with subsequent stirring at 50 ^oC for 2 h. For suppressing the agglomeration of silica cores during two-pot synthesis and to enhance the porosity of silica shell, 1 g/L and 5 mmol of polyvinylpyrrolidone and *N*-Lauroylsarcosine sodium were added, respectively as follows. First, 1 g/L of polyvinylpyrrolidone (PVP) was added to silica core dispersed in water. The dispersion was stirred at room temperature for 1 h. Then, APMS, 5 mmol (1.4465 g) of *N*-Lauroylsarcosine sodium, and TEOS were added, respectively to PVP-silica cores dispersion as mentioned previously. The resulting molar ratio was TEOS: H_2O: APMS: Sar-Na: HCl: PVP = 1:331.6: 0.08: 0.14: 0.06: $5x10^{-3}$.

The final solid was recovered by centrifugation (10000 rpm, 10 min), washed with deionized water for three times and dried in an oven at 60 ^oC for 12 h. Template removal was done by heat-treatment in an air stream at 550 ^oC for 6 h. The resulting calcined one-pot synthesis sample was designated as *OP*, while the calcined two-pot synthesis with 1 and 5 mmol surfactant were designated by *TP-1AS*, and *TP-5AS*, respectively.

1.2.4 Invitro drug storage study

A certain amount of double mesoporous core-shell samples, *TP-1AS*, and *TP-5AS*, was added into 50 mg/ml ketoprofen ethanol solution. The suspension was stirred for 2 h while the evaporation of ethanol was prevented. Then the *TP-1AS*, and *TP-5AS* with drug loaded were separated by high-speed centrifugation and dried in a vacuum oven at 60 ^{o}C. 1.0 ml filtrate was extracted with a vial and diluted to 100 ml, and then was analyzed by UV/vis spectroscopy at a wavelength of 265 nm. Calibration curve of ketoprofen was determined by taking absorbance versus ketoprofen concentration between 0 and 200 mg/ml as parameters.

1.2.5 In vitro drug-release study

Three KBU/*TP-1AS*, KBU/*TP-5AS* samples were separately immersed in simulated body fluid (SBF)[1] at 37 ^{o}C, with stirring at a rate of 100 rpm. Then, 2.0 ml release medium was removed for analysis at given intervals with a syringe, and the same volume of fresh release medium was injected. The extracted medium was diluted to a desired concentration with simulated body fluid, and analyzed by UV/Vis spectroscopy at a wavelength of 265 nm.

1.3 Characterization

TEM analysis was performed using a JEOL JSM-2100F Electron microscope (Japan) operated at 200 kV. Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO MPD (Netherlands) with Ni-filtered Cu KR radiation (45 kV, 40 mA). Nitrogen sorption isotherms were measured at 77 K with a Quantachrome NOVA 4200 analyzer (USA). Before measurements, the samples were degassed in a vacuum at 200°C for at least 18 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (*S*BET) using adsorption data in a relative pressure range from 0.05 to 0.35. By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were derived from the adsorption branches of isotherms, and the total pore volumes (*V*t) were estimated from the adsorbed amount at a relative pressure *P*/*P*0 of 0.992. The UV/Vis absorbance spectra were measured with a Shimadzu UV-2550 UV-Vis Spectrophotometer.

2. Results

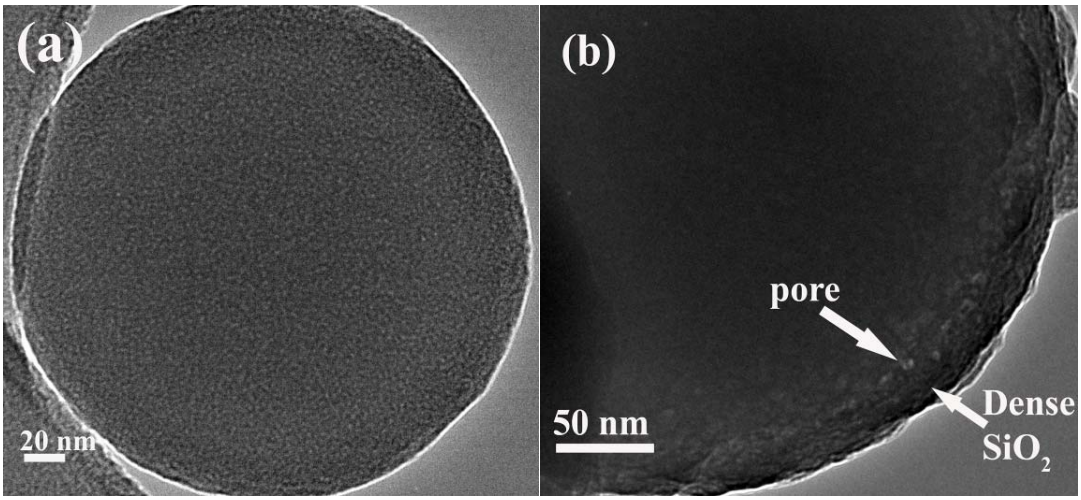

Fig. S1 TEM images of calcined mesoporous core-shell silica nanospheres prepared by (a) two-pot synthesis at 5 mmol *N*-Lauroylsarcosine sodium in absence of TEOS, and (b) one-pot synthesis at higher magnification.

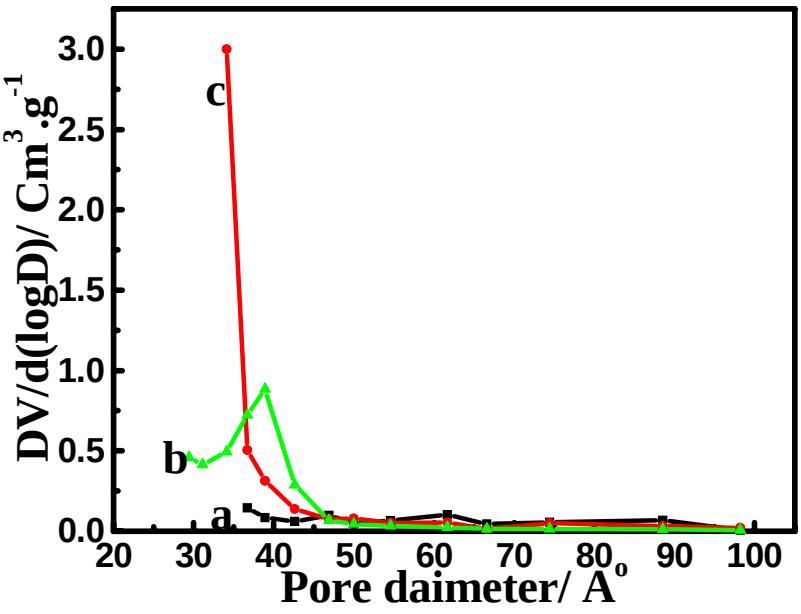

Fig. S2 Pore size distribution curves of calcined mesoporous core-shell silica nanospheres prepared by (a) one-pot synthesis, and two-pot synthesis at (b) 1 mmol and (c) 5 mmol *N*-Lauroylsarcosine sodium calculated from the adsorption branch of N_2 isotherms.

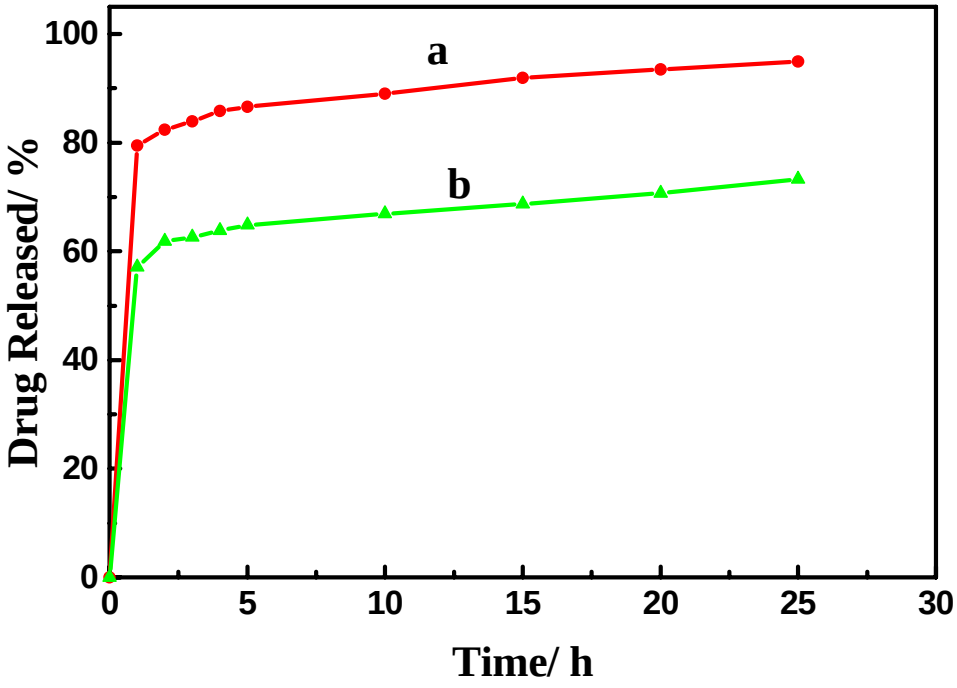

Fig. S3 Cumulative drug release from the double mesoporous core-shell samples prepared by two-pot synthesis at (a) 1 mmol and (b) 5 mmol *N*-Lauroylsarcosine sodium in simulated body fluid.

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Table S1: Structural properties of the mesoporous core-shell silica nanosphere prepared by one and two pot synthesis

Sample name	Particle size/nm [a]	Shell thickness/nm [a]	d-spacing /nm	Unit cell Parameter a_0/nm [b]	BET surface area/$m^2 g^{-1}$	Total pore volume/cc.g^{-1}	Pore size/nm[c]
OP	325	28	-	-	7	0.008	3.66[d]
TP-1AS	305	40	4.34	5.56	226.12	0.184	3.89
TP-5AS	245	38	4.81	5.01	440.73	0.416	3.41

[a] Particle size and mesoporous shell thickness determined from the TEM images. [b] XRD unit cell parameter, $a_0 = 2xd_{100}/3^{1/2}$. [c] Maximum value of the BJH pore size distribution peak calculated from the adsorption branch of the N_2 isotherm. [d] One pot synthesis showed further pore sizes at 46.8, 61.6 nm

References

1 M. Vallet-Regí, A. Rámila, R. P. Del Real, J. Pérez-Pariente, *Chem. Mater.*, 2001, *13*, 308.