Supporting Information

Large-pore monodispersed mesoporous silica spheres: synthesis and application in HPLC

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A: General Information and Starting Materials

General. The ^{1}H-NMR was recorded on a Bruke DRX 500 (500 MHz) instrument. Chromatography was carried out by using Agilent HPLC 1200 Series. Biological microscope was used to observe the appearance of the product immediately during the synthesis process. Small-angle X-ray powder diffraction (XRD) was carried out on an X-ray diffractometer model D/MAX 2550 (Rigaku, Japan). Scanning electron microscope (SEM) examination of the particles was performed on a JSM-6360LV (JEOL, Japan). Materials were characterized by nitrogen adsorption-desorption at 77 K (Micromeritics ASAP 2010).

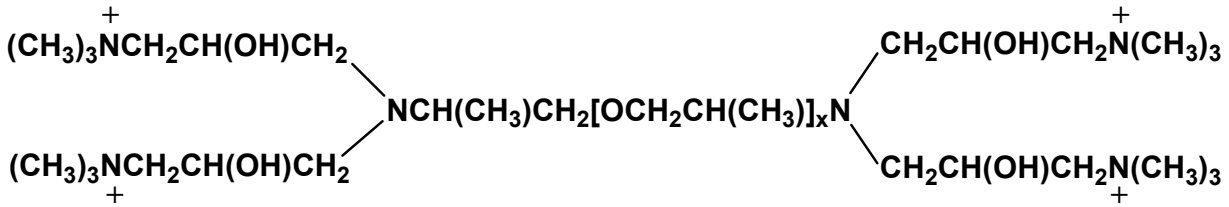
Materials. All solvent and inorganic reagents were of p.a. quality and used without purification. Unless otherwise noted, materials were obtained from commercial sources and used without purification.

B: General Procedure for the synthesis of d-D4000 and q-D4000 [1]

d-D4000

Prepared from (PPOA)s and iodomethane. 5 g of (PPOA)s and 1.42 g of iodomethane were mixed with 100 ml dehydrated alcohol with a magnetic stirrer at room temperature for 48 hrs, and then evaporated to get rid of alcohol and excess iosomethane. The solid product was light yellow. Compared with the proton signals of (PPOA)s, there is a singlet at δ 2.06. It indicated that the methyl groups have been linked with quaternary ammonium.

q-D4000



Prepared from (PPOA)s, 2-(chloromethyl)oxirane and trimethylamine. 5 g of (PPOA)s and 0.92g of 2-(chloromethyl)oxirane were mixed with 100 ml of dehydrated ethanol, and stirred at room

temperature overnight. Then the mixture was evaporated to get rid of excess 2-(chloromethyl)oxirane. The solid was then mixed with 0.59g of trimethylamine in 50 ml of dehydrated ethanol solution, and refluxed for 5 hrs. The light yellow solid product was yielded via evaporation at 55^{o}C. Compared with the proton signals of (PPOA)s, there is also a singlet at δ2.18, which indicated that the methyl groups had a linkage with quaternary ammonium.

C: Synthesis of mesoporous silica spheres under different conditions

Table 1 Synthetic Condition and Porous Properties of Silica Spheres

Sample	Aging temperature (^{o}C)	Surfactant	Surfactant concentration (mg·ml^{-1})	Methanol :water ratio (v/v)	Si source	BET surface area (m^2 g^{-1})	Average pore size (Å)	Pore volume (cm^{3}g^{-1})
D-MSS-1	55	d-D4000	6.7	1.50	TMOS	644.74	69.30	1.12
	75					459.98	86.63	1.00
	95					402.81	103.08	1.04
	115 (24 h)					364.40	152.45	1.39
	115 (48 h)					328.63	163.07	1.34
D-MSS-2	100		5.6	1.14		500.18	136.87	1.71
Q-MSS-1	55	q-D4000	6.7	1.14	TMOS	478.00	67.53	0.81
	75					399.25	96.57	0.96
	95					217.23	131.61	0.72
	115 (24 h)					154.27	195.39	0.75
	115 (48 h)					161.52	190.29	0.77
Q-MSS-2	95		5.4	1.05		220.47	147.36	0.81
Q-MSS-3					TEOS	301.40	132.96	1.00

(1) D-MSS-1 synthesis

5 g of d-D4000 was mixed with 450 g of water and 300 ml of methanol and stirred at room temperature for 1 hr, and then kept at 40 ˚C for 2 hrs. To this solution was added 1.5 ml of $NH_3 \cdot H_2O$ and 25.0 g of TMOS and the solution was stirred for 5 hrs or longer. The solid product was then filtered and dried in air at ambient temperature. The dried solid product was mixed with water before transferring into five Teflon bottles and aged at different temperatures respectively. The resulting solutions were filtered, washed with water, and dried overnight. The samples were then heated from room temperature to 600 ˚C for 2 hrs, and kept at 600˚C for 6 hrs.

(2) D-MSS-2 synthesis

4.2 g of d-D4000 was mixed with 400 g of water and 350 ml of methanol and stirred at room temperature for 1 hr, and then kept at 30 ˚C for 2 hrs. To this solution was added 1.5 ml of $NH_3 \cdot H_2O$ and 25.0 g of TMOS and the solution was stirred overnight. The post-treatment at 100^oC is similar to that of D-MSS-1.

(3) Q-MSS-1 synthesis

5 g of q-D4000 was mixed with 400 g of water and 350 ml of methanol and stirred at room temperature for 1 hr, and then kept at 40 ˚C for 2 hrs. To this solution was added 1.5 ml of $NH_3 \cdot H_2O$ and 25.0 g of TMOS and the solution was stirred for 5 hrs or longer. The solid product was then filtered and dried in air at ambient temperature. The dried solid product was mixed with water before transferring into five Teflon bottles and aged at different temperatures respectively. The resulting solutions were filtered, washed with water, and dried overnight. The samples were then heated from room temperature to 600 ˚C for 2 hrs, and kept at 600˚C for 6 hrs.

(4) Q-MSS-2 synthesis

4.2 g of q-D4000 was mixed with 400 g of water and 380 ml of methanol and stirred at room temperature for 1 hr, and then kept at 30 ˚C for 2 hrs. To this solution was added 1.5 ml of $NH_3 \cdot H_2O$ and 25.0 g of TMOS and the solution was stirred overnight. The post-treatment at 95^oC is identical to that of Q-MSS-1.

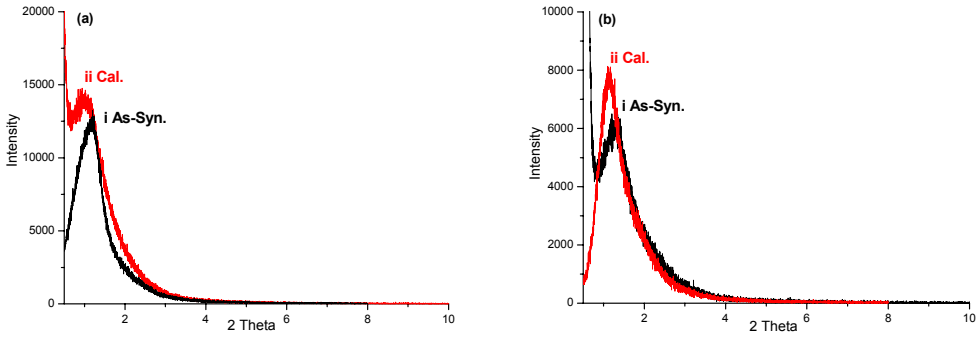
(5) Q-MSS-3 synthesis

4.2 g of q-D4000 was mixed with 400 g of water and 380 ml of ethanol and stirred at room temperature for 1 hr, and then kept at 30 ˚C for 2 hrs. To this solution was added 1.5 ml of $NH_3 \cdot H_2O$ and 25.0 g of TEOS and the solution was stirred overnight. The post-treatment at 95^oC is identical to that of Q-MSS-1.

D: Characterization of **Small Angle XRD**

Small angle XRD patterns and corresponding unit cell parameters obtained for both D-MSS-1 and Q-MSS-1 with post-treatment at 55^oC were shown. The broadness of the peak at the 2θ values suggested that the pores in these materials were not well-aligned, typical of samples prepared

under homogeneous conditions [2]. A reflected a unit cell parameter of 75.83 Å. And the average pore size calculated by the BJH formula (table 1) is smaller than the distance (a= d (100)*2/√3=87.6 Å) determined by XRD, the latter of which also includes the average thickness of the silica walls is 18.3 Å. B reflected a unit cell parameter of d (100) =73.31 Å, and the average silica wall thickness of Q-MSS is 17.1 Å.



Small angle XRD patterns of D-MSS-1 (a) and Q-MSS-1 (b), as-synthesized (black line) and calcined (red line) with template of d-D4000 and q-D4000, respectively

E: Column packing

Q-MSS-7 was packed into 50 mm×2.1 mm stainless steel columns using high-pressure slurry techniques [3, 4]. An amount of 0.15g of orient silica was added to 10 ml acetone/water solution, and the slurry was dispersed and sonicated for 10 min. Then, the suspension was poured into the reservoir of the packing system, an additional volume of acetone/water mixture was added and the system was topped off. The column was downward packed at 65MPa using methanol as propulsion solvent.

F: References

1. Ikeda Sao, and Zhenggang Cui, *China Surfactant Detergent & Cosmetics*, **2001**, *4*, 36-38
2. R. I. Nooney, T. Dhanasekaran, and Y. Chen, *Chem. Mater.,* **2002**, *14*, 4721-4728
3. L. Snyder, J. Kirkland, *An Introduction to Modern Liquid Chromatography, second ed.*, Wiley-Interscience, New York, **1979** (Chapter 6)
4. Xiaodong Liu, Andrei Bordunov, Mark Tracy, and Christopher Pohl, *J. Chromatogr. A*, **2006**, *1119*, 120-127