Supporting Information

Controllable fabrication of dendritic mesoporous silicacarbon nanospheres for anthracene removal

Jianping Yang ${}^{a,b,\perp}$, Wangyuan Chen ${}^{a,\perp}$, Dengke Shen b , Yong Wei b , Xianqiang Ran a , Wei Teng a , Jianwei Fan a* , Wei-xian Zhang a* and

Dongyuan Zhao ^b

- ^a College of Environmental Science and Engineering, State Key Laboratory of Pollution Control and Resources Reuse, Tongji University, Shanghai 200092, P. R. China
- ^b Department of Chemistry, Laboratory of Advanced Materials, Fudan University, Shanghai 200433, P. R. China
- $^{\perp}$ These authors contributed equally to this work.

E-mail: fanjianwei@tongji.edu.cn, zhangwx@tongji.edu.cn Tel: 86-21-65985885

Experimental Section

Chemicals. Acetonitrile was chromatographic pure, other chemicals were of analytical grade and used without further purification. Tetraethyl orthosilicate (TEOS) was purchased from Aladdin Reagent Co., Ltd. Cetyltrimethylammonium chloride (CTAC) solution (25 wt % in H_2O) and triethanolamine (TEA) were brought from Sigma-Aldrich (UK). Cyclohexane, acetonitrile and anthracene were obtained from Sinopharm Chemical Reagent Co., Ltd. Deionized water was used in all experiments.

Synthesis of dendritic mesoporous silica nanospheres. The dendritic mesoporous silica nanospheres (DMSNs) with diameter about 110 nm were synthesized by using an oil-water biphase stratification approach. For a typical preparation procedure, a mixture solution containing 72 mL of H₂O, 48 mL of CTAC (25 wt % in H₂O) and 0.36 mL of TEA were added into a 250-mL round bottom flask and stirred for 1 h at 60 °C. Then 40 mL of TEOS (20 v / v % in cyclohexane) was gently dropped and capped with condenser pipe. The reaction was maintained at 60 °C for 20 h in an oil bath with reflux under magnetic stirring (100 rpm). The products were collected after removal of the upper oil layer, then centrifugation and washed with ethanol and water for several cycles. The as-made dendritic mesoporous silica nanosphe res (DMSNs) sample was dried in vacuum at 40 °C over night. The obtained white powder was about 2.16 g. DMSNs-O2 were obtained after the as-made DMSNs sample calcination in a tubular furnace under air atmosphere at 600 °C for 3 h. DMSNs-Ar were prepared after the as-made sample treatment under argon atmosphere at 600 °C for 3 h. The DMSCNs were produced via a H₂SO₄ pretreated approach before calcination under argon atmosphere. Briefly, 1.5 mL of 10 wt % H_2SO_4 was dropped on the white powder of as-made DMSNs samples (0.8 g) and placed at room temperature for 2 h. The powder was transferred into oven at 100 °C for 12 h then at 160 °C for 12 h, followed calcination under argon atmosphere at 600 °C for 3 h.

Adsorption of anthracene in cyclohexane solution. Detection were completed in 48 min by using High Performance Liquid Chromatography(HPLC, Waters, Milford, USA) with a C18 column (Milford, USA), acetonitrile-water gradient elution and

ultraviolet (UV, Waters, Milford, USA) absorption detection. 10 μ L of the solution were injected into the column by utilizing the sample injector. The flow rates of the mobile phase were fixed at 1 mLmin⁻¹. The UV detector was set at 210 nm. Their programs of gradient elution for the separation are listed in Table S1.

segment	Time (min)	A % (H ₂ O)	B % (acetonitrile)
0	0	60	40
1	28	18	82
2	48	0	100

Table S1 The programs of gradient elution for the separation

For the measurement of adsorption isotherms. 10 mg of the DMSNs-O₂, DMSNs-Ar and DMSCNs were firstly suspended in 10 mL of cyclohexane solution with various concentrations of anthracene (2, 3, 4, 5 and 8 mgL⁻¹), and then vibrated at 25 °C for 12 h. After separation of DMSNs-O₂, DMSNs-Ar and DMSCNs, the equilibrium concentrations of anthracene were detected by HPLC-UV. All the analyses were performed in duplicate and the mean values were chosen.

For the measurement of adsorption kinetics curves. 10 mg of the DMSNs-O₂, DMSNs-Ar and DMSCNs were suspended in 100 mL cyclohexane solution with 4 mgL⁻¹ anthracene. The binding kinetics of samples for anthracene were tested by monitoring the temporal evolution of anthracene concentration in the cyclohexane solution.

Characterizations. The small-angle X-ray scattering (SAXS) measurements were taken on a Nanostar U small-angle X-ray scattering system (Bruker, Germany) using Cu K α radiation. Field-emission scanning electron microscopy (FESEM) images were obtained on a Hitachi S-4800 microscope (Japan). Transmission electron microscopy (TEM) measurements were carried out on a JEM 2100F microscope (Japan) operated at 200 kV. The samples were first dispersed in ethanol and then collected using copper grids covered with carbon films for measurements. Nitrogen sorption isotherms were measured at 77 K with a Micromerites Tristar 3020 analyzer (USA). Before measurements, the samples were degassed under vacuum at 180 °C for 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 range from 0.04 to 0.2. The pore volumes and pore size distributions were derived from the adsorption branches of isotherms 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. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 X-ray diffractometer (Germany) with Ni-filtered Cu Ka radiation (40 kV, 40 mA). Fourier transform infra-red (FTIR) spectra were collected on Nicolet Fourier spectrophotometer with spectral width of 4000 - 400 cm⁻¹, using KBr pellets of the solid samples. The thermal decomposition behaviors of the products were monitored by using Mettler Toledo TGA/SDTA851 analyzer from 50 to 900 °C under nitrogen with a heating rate of 5 °C/min. Raman spectra were measured on the micro-Raman spectrometer with 633 nm laser excitation (Renishaw in Via Reflex, UK). The spectra were collected in the wavelength of 1000-2000 cm⁻¹ and the peak intensities were normalized the standard sample silicon wafer 520 cm⁻¹. to of at



Fig. S1 SEM images of (A) the as-made dendritic mesoporous silica nanospheres (DMSNs) sample prepared by using an oil-water biphase stratification approach, (B) DMSNs-O₂ (calcined under air atmosphere), (C) DMSNs-Ar (calcined under argon atmosphere) and (D) DMSCNs (pretreated with H_2SO_4 before calcination under argon atmosphere).

Table S2.	Physicochemic	al propert	les of	the DN	$15NS-O_2$ (calc	cined	under	air
atmosphere)	, DMSNs-Ar	(calcined	under	argon	atmosphere)	and	DMSC	CNs
(pretreated w	with H ₂ SO ₄ befo	ore calcinati	on unde	r argon	atmosphere).			

Samples	$S_{BET} (m^2 g^{-1})$	Pore size (nm)	$V_t (cm^3 g^{-1})$
DMSNs-O ₂	585	6.7	1.2
DMSNs-Ar	640	7.2	1.3
DMSCNs	646	7.3	1.4



Fig. S2 Small angle XRD patterns of (a) the as-made dendritic mesoporous silica nanospheres (DMSNs), (b) DMSNs-O₂, (c) DMSNs-Ar and (d) DMSCNs.



Fig. S3 TGA curve of the as-made dendritic mesoporous silica nanospheres (DMSNs) sample prepared by using an oil-water biphase stratification approach in the air atmosphere.



Fig. S4 Fourier transform infrared (FTIR) spectra of (a) the as-made dendritic mesoporous silica nanospheres (DMSNs), (b) DMSNs-O₂, (c) DMSNs-Ar and (d) DMSCNs. The strong absorption bands around 2925 cm⁻¹ and 2850 cm⁻¹ were assigned the stretching of the C–H bonds of the CTAC molecules. The adsorption bands around 2850-2925 cm⁻¹ were disappeared after calcination, suggesting that the CTAC molecules are completely removed.



Fig. S5 SEM image (A) and elemental mapping of Si, O and C (B-D) of DMSCNs (pretreated with H_2SO_4 before calcination under argon atmosphere). The samples were first dispersed in ethanol and then dropped on copper foil for measurements. The elemental mapping of Si, O and C reveals that the carbon species are homogeneously dispersed in the mesoporous channels of dendritic mesoporous nanospheres.



Fig. S6 TEM image of DMSCNs (pretreated with H_2SO_4 before calcination under argon atmosphere) after treatment with 5 wt % HF for removal the silica sphere framework. This result demonstrates that the existence of tiny carbon nanoparticle species in dendritic mesoporous nanospheres.



Fig. S7 Photographs of aqueous dispersions (50 mgmL⁻¹) of the as-made dendritic mesoporous silica nanospheres (DMSNs) sample prepared by using an oil-water biphase stratification approach, DMSNs-O₂ (calcined under air atmosphere), DMSNs-Ar (calcined under argon atmosphere) and DMSCNs (pretreated with H_2SO_4 before calcination under argon atmosphere).



Fig. S8 XRD patterns of (a) the as-made dendritic mesoporous silica nanospheres (DMSNs), (b) DMSNs-O₂, (c) DMSNs-Ar and (d) DMSCNs.



Fig. S9 Adsorption kinetics of DMSNs-O₂ (calcined under air atmosphere) and SBA-15 (2D-hexagonal mesostructured silica with the pore size ~ 6.4 nm, surface area ~ 770 m²g⁻¹, and pore volume ~ 0.95 cm³g⁻¹) in cyclohexane for anthracene. This phenomena indicates that the advantage of dendritic-like architectures for promoting the fast molecular diffusion.