Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

In situ synthesis of phosphate binding mesocellular siliceous foams impregnated with iron oxide nanoparticles

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Experimental

Preparation of magnetite nanoparticles

Monodispersed magnetite nanoparticles were synthesized following a method reported by Sun et. al.[1] Iron(III) acetylacetonate [Fe(acac)$_3$], 1,2-tetradecanediol, oleic acid, benzyl ether and oleylamine were purchased from Sigma Aldrich and used without further purification: 508.5 mg of Fe(acac)$_3$, 2306.6 mg of 1, 2-tetradecanediol, 21 mL of benzyl ether, 1.69 g of oleic acid and 1.69 g of oleylamine were mixed using a magnetic stirrer under nitrogen (N_2). The mixture was heated to 200 ˚C for 2 hours, then under reflux at 300 ˚C for another hour under a blanket of N_2. The mixture was then cooled to the room temperature and the black precipitate separated by centrifugation. The magnetite was dispersed in hexane and kept under an argon purged round-bottom flask to prevent any oxidation.

Preparation of MCFs with iron oxides nanoparticles

Mesocellular siliceous foam loaded with magnetic nanoparticles was synthesized using a modified literature procedure.[2] Firstly, 2.0 g Pluronic® P-123 ($EO_{20}PO_{70}EO_{20}$, averaged Mw = 5800, Sigma Aldrich) was dissolved in 50 mL of deionized water in a 250 ml conical flask. The solution was stirred vigorously in a water bath with the temperature controlled between 40 to 45 °C to dissolve the P-123. After an hour, 10 mL of 10 mM magnetite in hexane solution was added into the P-123 solution and stirring was continued. After 30 min, 4.4 mL of tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich) was added dropwise and the resulting mixture stirred for 20 hours whereupon it was transferred to a Teflon-lined autoclave and placed in an oven at an aging temperature of 110 °C for 24 hours. The mixture was then filtered, washed with deionized water, and dried at 80 °C overnight. The resulting solid was calcined in air at 500 °C for 6 hours to remove the polymer template.

Characterization techniques

The calcined materials were characterized using a ZEISS 1555 instrument for scanning electron micrographs (SEM) at an accelerating voltage of 5 – 15 kV.

Transmission electron micrographs (TEM) were obtained using a JEOL 2100 instrument with an operating voltage of 120 kV. Nitrogen adsorption- desorption studies were performed using a Micromeritics TriStar^{TM} II 3020 system. The samples were outgassed at 110 °C for 16 hours prior to gas adsorption which was carried out at 77 K. The specific surface area, SBET, was determined from the linear part of the BET equation (P/P_o = 0.09 – 0.30). The pore size distribution and pore volume were evaluated using the Barrett–Joyner–Halenda (BJH) method. The total pore volume reported was taken from the amount of gas adsorbed at a relative pressure (P/P_o) at 0.995. Magnetic properties were determined using a superconducting quantum interference device (SQUID) magnetometer. The final iron content was obtained using inductively coupled plasma mass spectrometry (ICP-MS), at TSW Analytical Pty. Ltd. (Perth, WA).

Preparation for phosphate removal study

Iron oxides/MCFs samples were individually mixed with an artificial aquatic-medium with a buffered pH close to 7.5, which mainly includes phosphates, nitrates, carbonate buffer, micronutrients and vitamins.[3] Three different loadings of the same adsorbent (10 mg; 25 mg; 50 mg) were separately mixed with phosphate containing aquatic media (1.5 mL). Each mixture was then hand-vortexed for about 30 seconds, followed by gentle mixing throughout the entire experiment with an Eppendorf tube Rotator (Stuart Rotator, SB3) at a constant rotational speed of 20 rpm. Mixtures were centrifuged at 10000 rpm for 5 minutes, and particle-free supernatants were collected for spectrophotometric analysis. Collected liquid samples were subjected to phosphate analysis using the colorimetric "ascorbic acid" method,[4] which is a standard water-analyzing procedure recognized by the United States Environmental Protection Agency. Phosphate analyzing kits in the form of powder pillows (HACH®, PhosVer® 3 Phosphate Reagent) were employed before reading the phosphate concentration of the supernatant by a colorimeter (HACH® DR/870).

Characterization data:

TEM image of magnetite, for a hexane suspension of the material drop cast onto a continuous carbon coated grid, which was then allowed to dry in air.

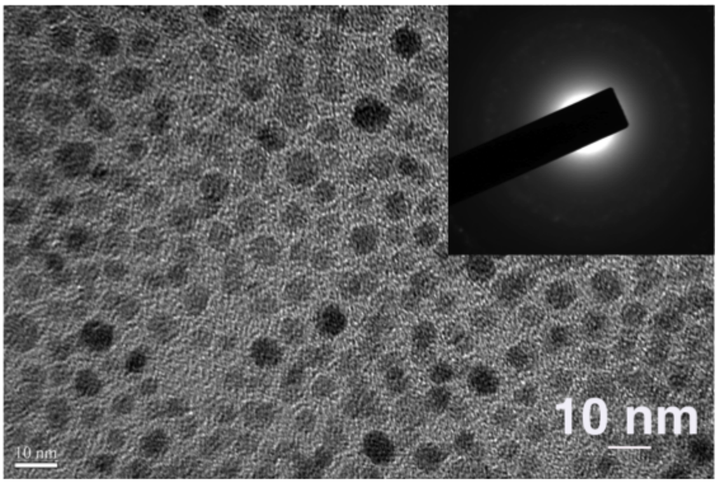

Figure S1. TEM image of magnetite nanoparticles dispersed in hexane, and the diffraction pattern of magnetite (inset).

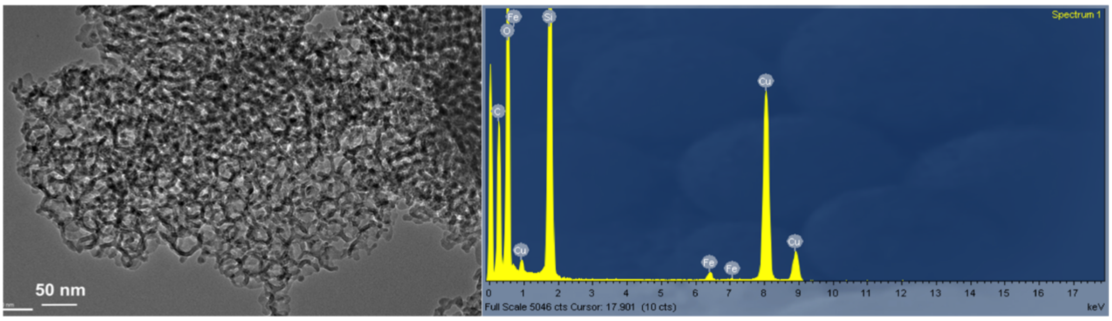

Figure S2. TEM image of MCF-1 (left), and the elemental analysis spectrum using energy-dispersive X-ray spectroscopy (EDS) (right).

X-Ray diffraction (XRD) pattern of MCF-1 revealed a broad amorphous peak.

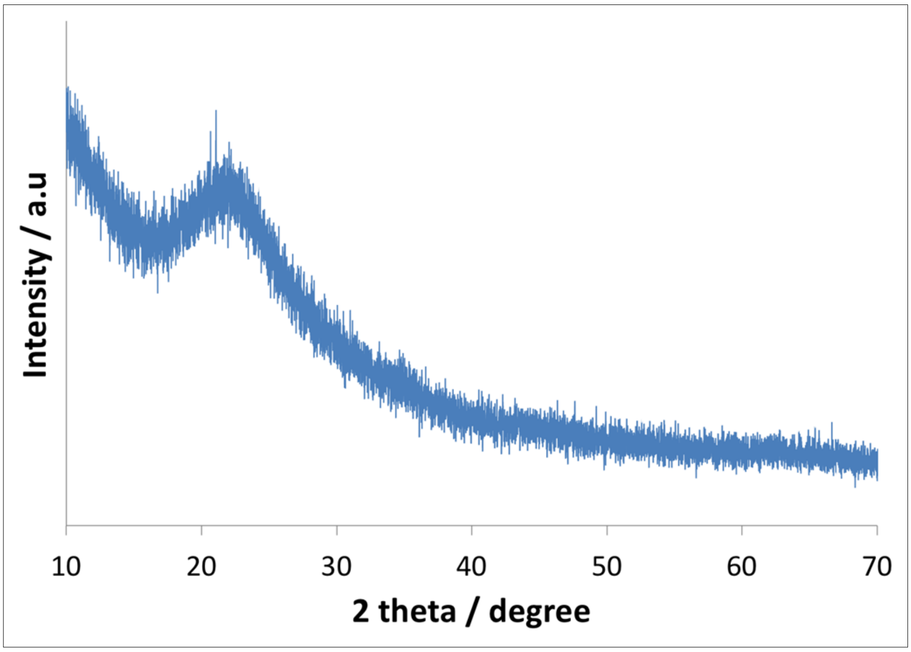

Figure S3. XRD profile for sample MCF-1.

Magnetic properties were determined using a superconducting quantum interference device (SQUID) magnetometer.

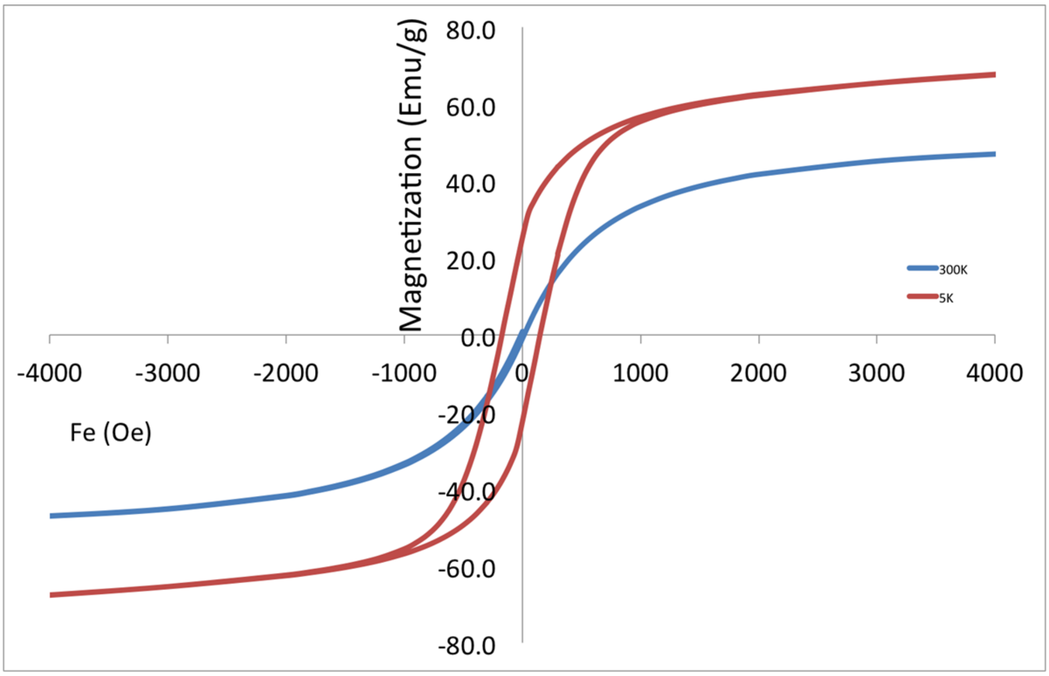

Figure S4. Magnetic hysteresis loops at 5K and 300K for sample MCF-1.

Physiosorption properties of samples MCF- 1 and MCF-2 for nitrogen adsorption desorption isotherms.

Table S1. **Physiochemical properties of the mesocellular siliceous foams**

Sample ID	S_{BET} (m^2/g)	V_t (cm^3/g)	Pore diameter (nm)
MCF-1	438.13	3.5	27.8
MCF-2	581.51	1.6	13.4

Table S2. **Amount of phosphate (PO_4^{3-}) adsorbed from aqueous media in mg.L^{-1} (Initial [PO_4^{3-}]: 16 mg/L) at various time intervals for three different loading concentrations of sample MCF-1.**

Time (h)	Amount of adsorbent		
	10 mg	**25 mg**	**50 mg**
0.5	0.8	1	1.2
4	1.2	1.2	1.4
24	0.8	1	1.2

References:

1. S. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang and G. Li, *Journal of the American Chemical Society*, 2003, 126, 273-279.
2. J. S. Lettow, Y. J. Han, P. Schmidt-Winkel, P. Yang, D. Zhao, G. D. Stucky and J. Y. Ying, Langmuir, 2000, 16, 8291-8295.
3. C. S. Bolch and S. Blackburn, *J Appl Phycol*, 1996, 8, 5-13.
4. APHA, ed., *Standard methods for the examination of water and wastewater*, Washington DC, 1992.