Supplementary Material (ESI) for Chemical Communications

Supporting information

A facile approach to fabricate functionalized superparamagnetic copolymer-silica nanocomposite spheres

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Experimental

Synthesis of PS_{100}-b-PAA_{16} and monodisperse magnetite nanoparticles: Monodisperse 5 nm sized Fe_3O_4 nanoparticles were prepared following the method from the literature protocol by Sun et al [1]. Amphiphilic block copolymer, polystyrene$_{100}$-block-poly (acrylic acid)$_{16}$ (PS_{100}-b-PAA_{16}) was synthesized via sequential atomic transfer radical polymerization (ATRP) as previously reported [2].

***Synthesis of magnetic polymeric spheres*:** 200µl of PS_{100}-*b*-PAA_{16} solution (10 mg/ml in DMF) was diluted with a mixture solution of 4.5ml of THF and 4.8ml of DMF. To this solution 500µl of 5nm Fe_3O_4 nanoparticles stock solution (1.0 mg/ml in THF) was added slowly with vigorous stirring, such that $[Fe_3O_4]_{initial}$ = 0.05 mg/ml, $[PS_{100}$-*b*-$PAA_{16}]_{initial}$ = 0.20 mg/ml in 50:50 mixture of DMF/THF (total volume of solution 10ml). Then, 40ml of H_2O was added to the solution at a rate of 80ml/h with vigorous stirring. As water was added, the solution gradually turned a light grey milky suspension in color, indicating the formation of micelle suspension. After stirring for 30 min, the resulting suspension was subjected to the dialysis against Millipore water (18 MΩ) for over 48 h (Spectra/Por® 4 Regenerated Cellulose Membrane, MWCO = 12-14K) to remove THF and DMF. After the dialysis of magnetic micellar solution, 2.0µl of the resulting solution was deposited on the TEM grid, dried in air before taking TEM images.

***Synthesis of NH_2-SMCSNs*:** Firstly, 30g of ethanol were added to the magnetic micellar solution and the pH value of the solution was adjusted to around 10 with a diluted NaOH solution (0.1M). Then, 200µL of the mixture solution containing 0.1g of APTMS, 0.5g of TEOS and 3ml of ethanol was added dropwise to the solution with continuous stirring. After reaction for 12h, the obtained solution was subjected to centrifugation (11,000 r/min, 30 min). The upper 90% of the solution was removed and the same volume of Millipore water was added to the solution. This procedure was repeated three times, and the NH_2-SMCSNs were finally produced.

***Synthesis of SH-SMCSNs*:** 30g of ethanol were added to the magnetic micellar solution and the pH value of the solution was adjusted to 11.40 with 1ml of ammonia. Then, 300µL of MPTMS solution (0.5g of MPTMS in 3ml ethanol) was added in the

solution. After stirring for 12h, the obtained solution was subjected to centrifugation (11,000 r/min, 30 min). The upper 90% of the solution was removed and the same volume of Millipore water was added to the solution. This procedure was repeated three times, and the SH-SMCSNs were finally produced.

***Characterization*:** The XRD pattern of prepared powder sample was collected using a Rigaku D/Max-2200PC X-ray diffractometer with Cu target (40KV, 40mA) from 10 to 80^{o}. TEM (Field Emission Transmission Electron Microscopy) analysis was conducted on a JEM 2100F electron microscope operated at 200 KV. FESEM (Field Emission Scanning Electron Microscopy) analysis was conducted on JEOL JSM6700F electron microscope. The magnetization curve was measured at room temperature under a varying magnetic field with VSM. Fourier-transform infrared (FT-IR) spectra were collected on Nicolet Fourier spectrophotometer using KBr pellets (USA).

References

[1] Sun, S. H.; Zeng, H.; Robinson, D. B.; Raoux, S.; Rice, P. M.; Wang, S. X.; Li, G. X. *J. Am. Chem. Soc.* **2004**, *126*, 273-279.

[2] Kang, Y.; Taton, T. A., *Angew. Chem., Int. Ed.* **2005**, *44*, 409-412.

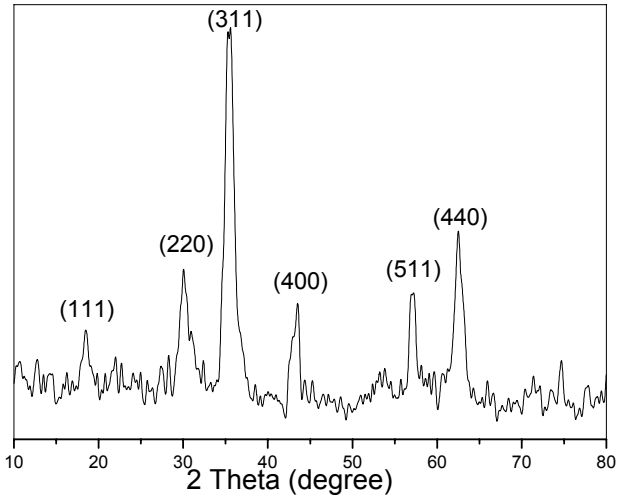

Figure S1. XRD pattern of 5nm-sized Fe_3O_4 nanoparticles.

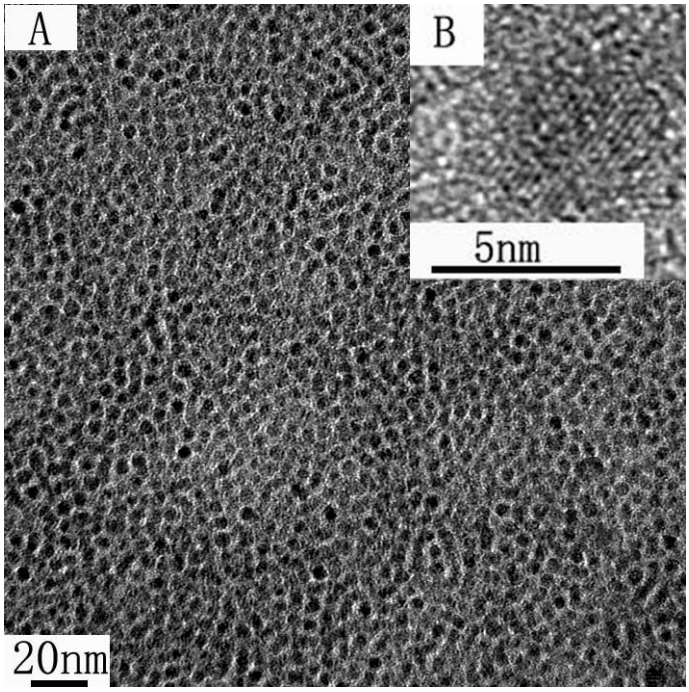

Figure S2. TEM (A) and HR-TEM (B) images of monodispersed Fe_3O_4 nanoparticles.

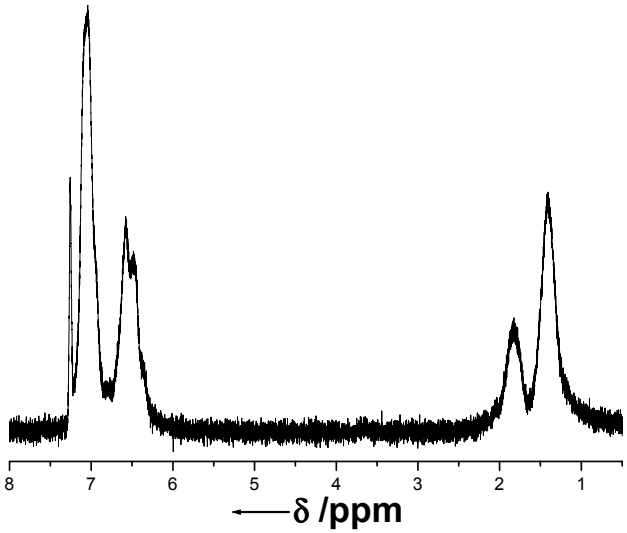

Figure S3. ^{1}H NMR spectrum of polystyrene$_{100}$-block-poly (acrylic acid)$_{16}$ in $CDCl_3$: δ= 6.30-7.30 (broad, -CHC$_6$**H**$_5$-), 1.70-2.20 (broad, -C**H**C$_6$H$_5$-), 1.2-1.7 (broad, -C**H**$_2$-C6H$_5$-).

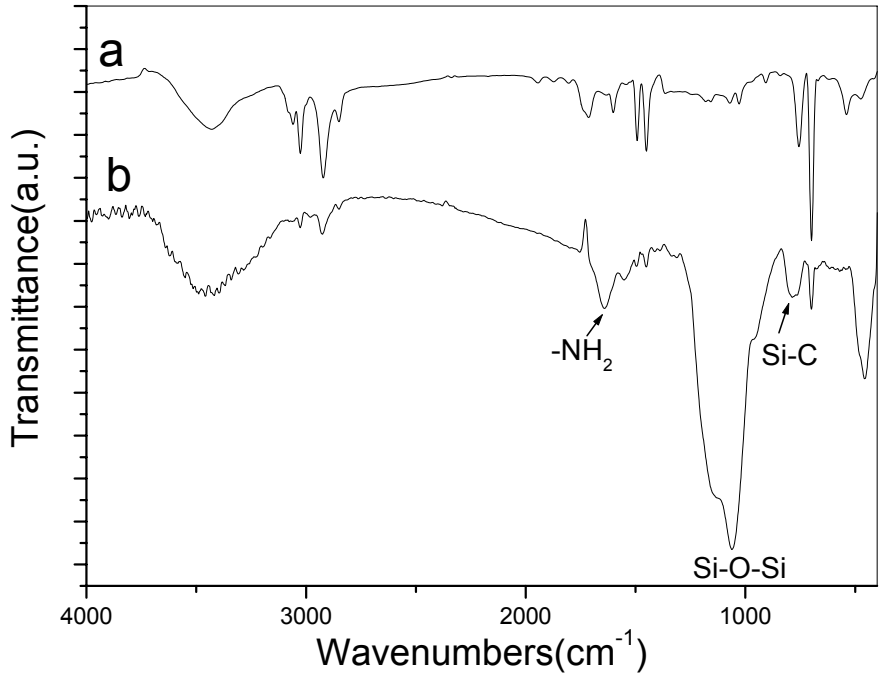

Figure S4. FT-IR spectra of (a) pure block copolymer and (b) NH_2-SMCSNs.

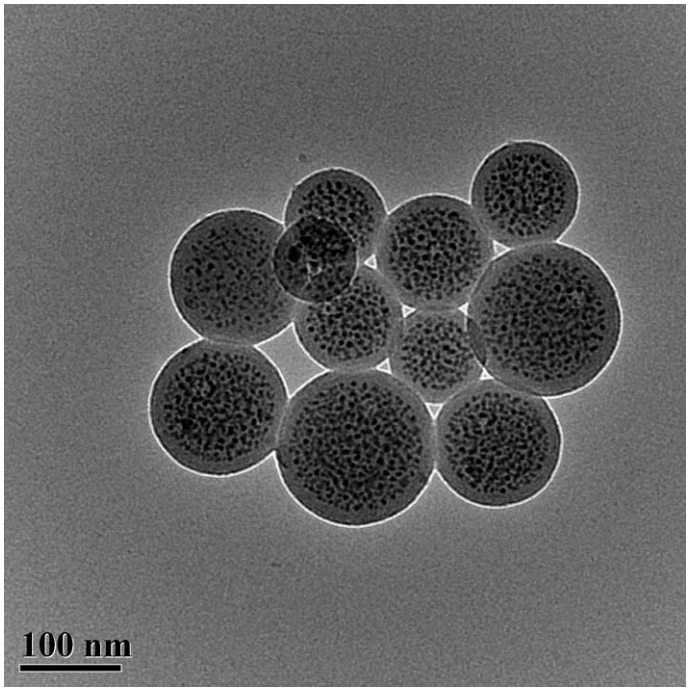

Figure S5. TEM image of SMCSNs without adding APTMS.

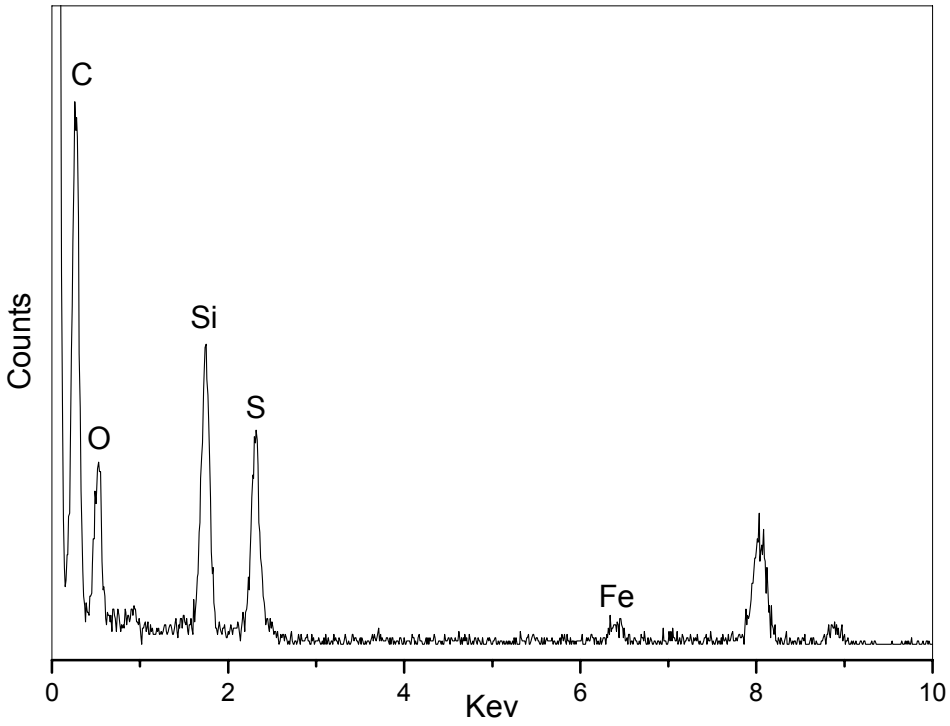

Figure S6. EDS results of SH-SMCSNs (25nm thickness silica shell).

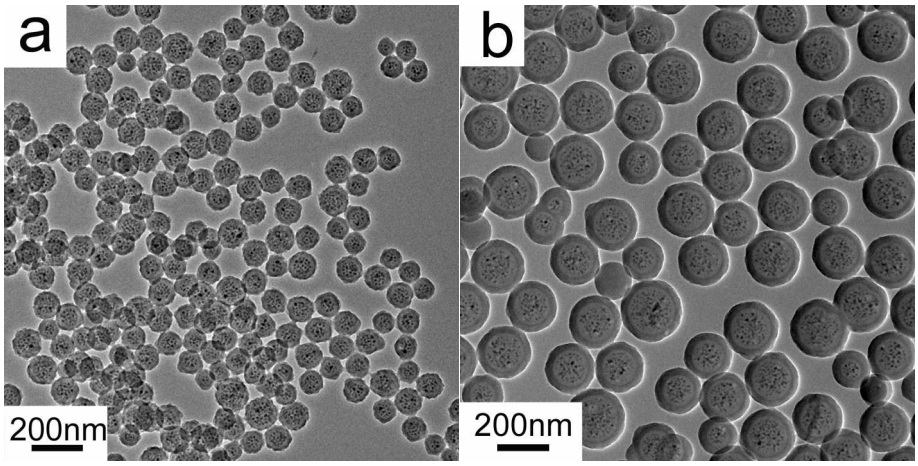

Figure S7. TEM images of SH-SMCSNs with 10nm thickness silica shell(a),and 25nm thickness silica shell (b), prepared by adding 21mg and 43mg MPTMS, respectively.

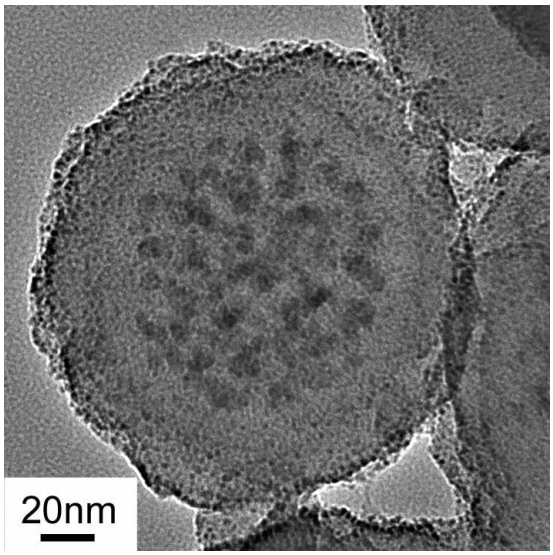

Figure S8. TEM image of Pd-SH-SMCSNs obtained by absorption of Pd^{2+} on the surface of SH-SMCSNs using $PdCl_2$, followed by in situ reduction using $NaBH_4$.