Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary Information

Yolk-Shell Fe_3O_4@SiO_2@PMO: Amphiphilic Magnetic Nanocomposite as an Adsorbent and Catalyst with High Efficiency and Recyclability

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Experimental Section

Synthesis of yolk-shell structured Fe_3O_4@SiO_2@Pd/PMO(Et)

In a typical synthesis, the core-shell Fe_3O_4@SiO_2 nanoparticles (0.1g) were dispersed in a mixture solution containing deionized water (22mL), ethanol (11mL), CTAB (0.12g) and concentrated ammonia solution (1.0mL, 28wt%) with ultrasonication treatment for 10 min ,and then mechanically stirred for 30 min to form a homogeneous dispersion. Subsequently, 0.27 mL of BTEE was slowly dropwise added to dispersion under continuous stirring. The reaction mixture was stirred for 2h at room temperature. After completely condensation of BTEE, the mixture was transferred to a stainless steel autoclave with a Teflon container and hydrothermally treated at 100℃ for 24h. After cooling down to room temperature, the orange precipitate was collected by a magnet. Finally, the surfactant CTAB was removal by refluxing in ethanol solution containing NH_4NO_3 for three times at 5 h each time.

Pd nanoparticles were loaded into the yolk-shell structured Fe_3O_4@SiO_2@PMO(Et) materials using impregnation and reduction. A certain amount of Fe_3O_4@SiO_2@PMO(Et) was added into 20 mL of 0.0075 M Na_2PdCl_4 aqueous solution with stirring for 24h at room temperature, and 0.2 mL of 0.1M $NaBH_4$ solution was added dropwise, and the mixture was stirred at the room temperature for 2h. Finally, the obtained magnetic catalysts were collected by a magnet and washed with deionized water and ethanol several times.

Synthesis of yolk-shell structured Fe_3O_4 @SiO_2 @NH_2-PMO(Ph)

In a typical synthesis, the core-shell Fe_3O_4 @SiO_2 nanoparticles (0.1g) were dispersed in a mixture solution containing deionized water (22mL), ethanol (11mL), CTAB (0.12g) and concentrated ammonia solution (1.0mL, 28wt%) with ultrasonication treatment for 10 min ,and then mechanically stirred for 30 min to form a homogeneous dispersion. Subsequently, 0.22 mL of BTEB and 0.033mL of APTES were slowly dropwise added to dispersion under continuous stirring. The reaction mixture was stirred for 2h at room temperature. After completely co-condensation of BTEB and APTES, the mixture was transferred to a stainless steel autoclave with a Teflon container and hydrothermally treated at 100℃ for 24h. After cooling down to room temperature, the orange precipitate was collected by a magnet. Finally, the surfactant CTAB was removal by refluxing in ethanol solution containing NH_4NO_3 for three times at 5 h each time.

Loading Pd nanoparticles into Fe_3O_4 @SiO_2 @NH_2-PMO(Ph) for magnetic catalysts

Pd nanoparticles were loaded into the yolk-shell structured Fe_3O_4 @SiO_2 @NH_2-PMO(Ph) materials via an in situ reduction method. A certain amount of Fe_3O_4@SiO_2@NH_2-PMO(Ph) was added into 20 mL of 0.0075 M Na_2PdCl_4 aqueous solution with stirring for 24h at room temperature, and 0.2 mL of 0.1M $NaBH_4$ solution was added dropwise, and the mixture was stirred at the room temperature for 2h. Finally, the obtained magnetic catalysts were collected by a magnet and washed with deionized water and ethanol several times.

Supplementary Figures and Legends

Table S1 The Pd binding energy of Pd-SH and Na_2PdCl_4.

Sample	**3d$_{3/2}$**	**3d$_{5/2}$**
Na_2PdCl_4	**343.6eV**	**338.5eV**
Pd^{2+}-HS-PMO(Et)	**343.5eV**	**338.2eV**
Pd NPs-HS-PMO(Et)	**342.1eV**	**336.8eV**
Pd NPs	**341.2eV**	**335.9eV**

Table S2 Pd^{2+} Adsorption behavior of adsorbents in a homoionic solution.

Adsorbent	**Uptake/%**	**Kd/(mL g^{-1})**
Fe_3O_4@SiO_2@HS-PMO	**99.97**	**3.23*106**
Fe_3O_4@SiO_2@NH_2-PMO	**97.46**	**3.76*104**

K_d (mL g^{-1}) = concentration of metal ion in the adsorbent (mmol g^{-1})/concentration of metal ion in an aqueous solution (mmol mL^{-1})

Table S3 Textural parameters of Yolk-Shell Fe_3O_4 @SiO_2@PMO

Sample (PMO Shell)	**BET surface area (m^{2}g^{-1})**	**Pore volume (cm^{3}g^{-1})**	**Pore size (nm)**
PMO(Et)	**635**	**0.39**	**2.3**
HS-PMO(Et)	**480**	**0.30**	**2.1**
PMO(Ph)	**793**	**0.46**	**2.3**
NH_2-PMO(Ph)	**649**	**0.32**	**2.0**
HS-PMO(Ph)	**599**	**0.34**	**2.2**

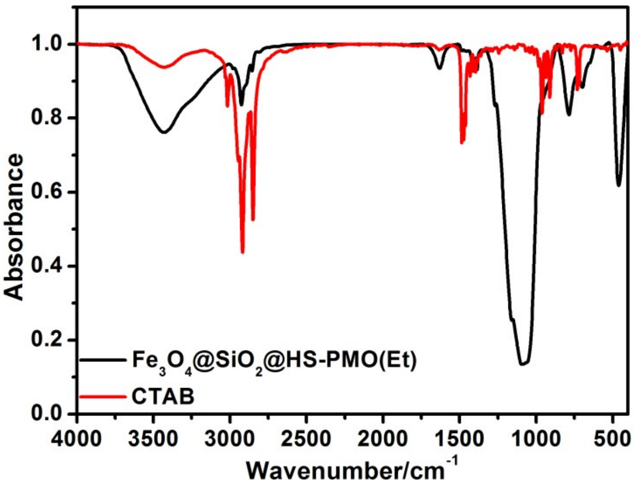

Fig.S1 FT-IR spectra of $Fe_3O_4@SiO_2@HS-PMO(Et)$ and CTAB.

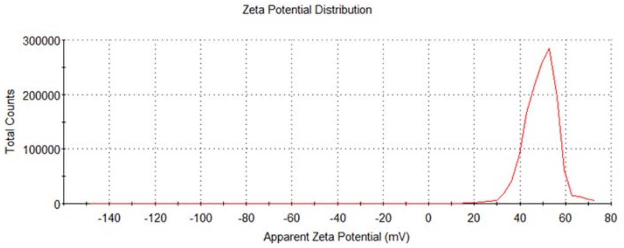

Fig.S2 Zeta potential spectrum of $Fe_3O_4@SiO_2@HS-PMO(Et)$.

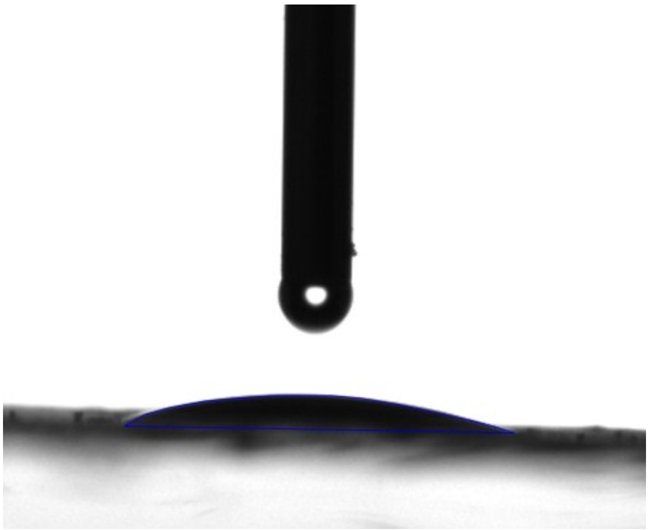

Fig.S3 Water contact-angle of $Fe_3O_4@SiO_2@HS-PMO(Et)$.

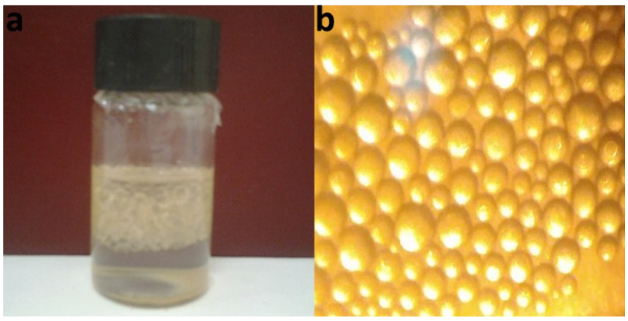

Fig.S4 (a) Digital photograph of the water in oil emulsion of the toluene-water system obtained through extracting the magnetic amphiphilic nanocomposite in water using toluene. (b) Microphotograph of the water in oil emulsion in (a).

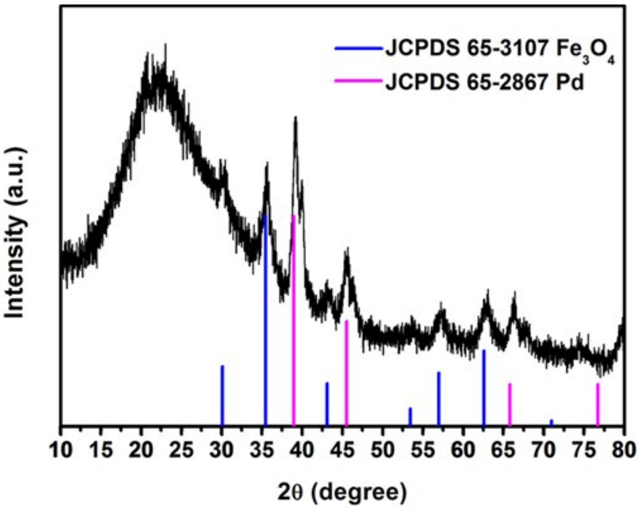

Fig.S5 Wide-angle XRD patterns of Fe_3O_4@SiO_2@Pd/HS-PMO(Et).

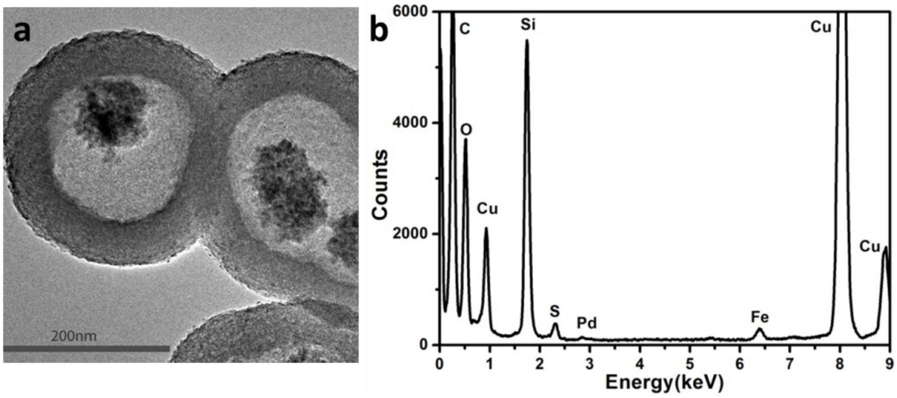

Fig.S6 (a) TEM image and (b) EDS spectra of Fe_3O_4@SiO_2@Pd/HS-PMO(Et) recovered after successive recycling ten times for oxidation of 4-methoxybenzyl alcohol.

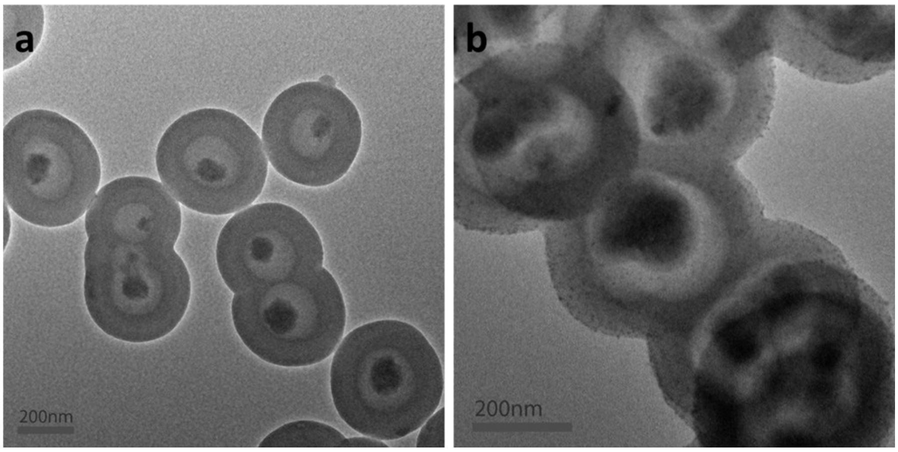

Fig.S7 TEM images of (a) Fe_3O_4@SiO_2@NH_2-PMO(Ph) and (b) Fe_3O_4@SiO_2@Pd/NH_2-PMO(Ph).