Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Magnetic C-C@Fe_3O_4 double-shelled hollow microspheres *via* aerosol-based Fe_3O_4@C-SiO_2 core-shell particles

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Experimental section

Chemicals

Tetraethyl orthosilicate (TEOS), $FeCl_3 \cdot 6H_2O$, cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich. K_2PtCl_6, 2,4-dihydroxybenzoic acid (RF-COOH, 98%) were obtained from Aladdin (Shanghai, China). Resorcinol, formaldehyde, concentrated ammonia solution (~28%), sucrose, absolute ethanol, and all of the other chemical reagents were of analytical grade and used without further purification (Damao Chemical Company, Tianjin, China). Deionized water was used for all experiments.

Synthesis of Fe_3O_4 and Fe_3O_4@C-SiO_2 core-shell particles

Fe_3O_4 nanoparticles were prepared according to our previous work.[1, 2] A rapid aerosol approach was used to prepare Fe_3O_4@C-SiO_2 core-shell particles. The aerosol precursor solution was prepared by mixing 1.0g $FeCl_3 \cdot 6H_2O$ and 1.1g CTAB in 15ml ethanol solution, followed by sonication for a while to form a clear solution. Then 120mg Fe_3O_4 nanoparticles were added and sonicated for 10min to get a homogeneous dispersion. Finally, 2.0 ml of a 0.1M HCl solution and the dissolution of 1 g of sucrose, 4.5ml TEOS were added to the above dispersion, respectively. The mixture solution was sonicated for 20min to get a brown aerosol solution. The aerosol solution was aerosolized using a commercial atomizer (model HD-130, HOLDER) to form aerosol droplets, which passed through a quartz tube with a heating zone. The temperature of the heating zone was held at 200 °C, and the pressure of carrying gas N_2 was adjusted to yield a droplet residence time of about 20s through the furnace. The aerosol particles were collected by a microfiltration membrane which was maintained at 100℃. The as-synthesized particles were calcined in N_2 at 500℃ for 3 h to obtain Fe_3O_4@C-SiO_2 aerosol core-shell particles.

Synthesis of Fe_3O_4@C-SiO_2@RF-COOH core-shell particles and C-C@Fe_3O_4 double-shelled porous hollow particles

The as-prepared Fe_3O_4@C-SiO_2 aerosol core-shell particles were homogenously dispersed in the mixed solution of deionized water and ethanol by ultrasonication, followed by the addition of CTAB, and stirred at room temperature. The mixed solution was sonicated for 15min to form a uniform dispersion. The surface zeta potential of the Fe_3O_4@C-SiO_2 particles was tested to be -22.8 mV in the mixed solution. Accordingly, the particles can homogenously disperse in the solution after the sonication process and addition of CTAB molecules. 2,4-dihydroxybenzoic acid and formaldehyde were added to the dispersion with continuous stirring for 10min. After the addition of ammonia solution, the weight ratio of (Fe_3O_4@C-SiO_2)-CTAB-(2,4-dihydroxybenzoic acid)-formaldehyde-H_2O-ethanol--ammonia solution was 1 : 1.5 : 0.64 : 1.0 : 600 : 200 : 3.66. The final solution was stirred at 25℃ for 20h, and the Fe_3O_4@C-SiO_2@RF-COOH core-shell particles were collected by centrifugation. The products were washed with water and ethanol several times and then dried at 60℃ in air overnight. The dried particles were then carbonized at 800℃ for 4h in N_2 with a heating rate of 2℃/min. The calcined particles were etched in 2.0M NaOH solution for 24h to remove silica and obtain C-C@Fe_3O_4 particles.

Synthesis of C-C@Fe_3O_4–Pt particles

In a typical deposition process, 1.0mL 0.024M K_2PtCl_6 aqueous solution was added to a 100mL 1:1 (volume/volume) water and ethanol mixed solution containing C-C@Fe_3O_4 particles (20mg). The obtained mixture was subjected to 100℃ for 60min under mechanically stirring, and then allowed to cool to room temperature. The obtained black products C-C@Fe_3O_4–Pt were washed with ethanol and water respectively, and then dried at 60℃.

Catalytic reduction of 4-nitrophenol using C-C@Fe_3O_4–Pt particle

The reduction of 4-nitrophenol was carried out in a quartz cuvette. First, 0.4 mL of aqueous 4-nitrophenol solution (1mM) was mixed with 2mL of fresh $NaBH_4$ solution (0.02M). Subsequently, 2mL of C-C@Fe_3O_4 –Pt dispersion (0.25mg mL^{-1}) was added to the above solution. Then, the final mixture solution was quickly subjected to UV-vis measurements under different reaction times. The catalyst was recycled by an external magnetic field and washed with deionized water for reuse.

Measurements and characterizations

The microstructure of the magnetic composite microspheres was taken using a Hitachi-4800 field emission scanning electron microscope (FE-SEM) and a Tecnai-20 transmission electron microscope (TEM). X-ray diffraction (XRD) patterns were obtained with a D/MAX-2400 diffractometer (Cu Kα radiation, 120 0.154 nm). Magnetic measurements of samples were performed on a Quantum Design SQUID (MPMS XL-7) magnetometer. Element concentrations were determined by an inductively coupled plasma emission (ICP, Optima 2000DV).

Figures

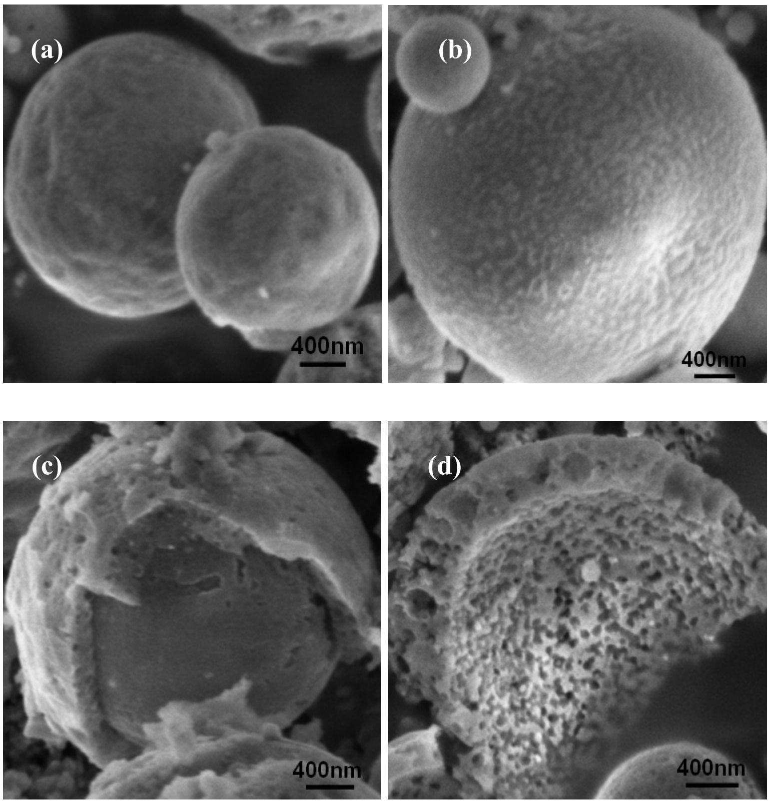


Figure S1 (a) (b) SEM images of Fe_3O_4@C-SiO_2 core-shell aerosol particles, (c) (d) broken C-C@Fe_3O_4 porous hollow particles

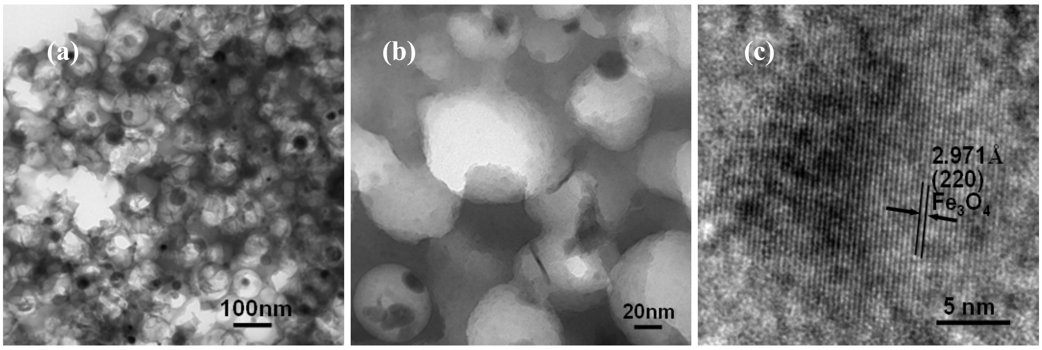


Figure S2 (a) (b) HRTEM images of C-C@Fe_3O_4 porous hollow particles, (c) HRTEM image of the black spot in C-C@Fe_3O_4 porous hollow particles

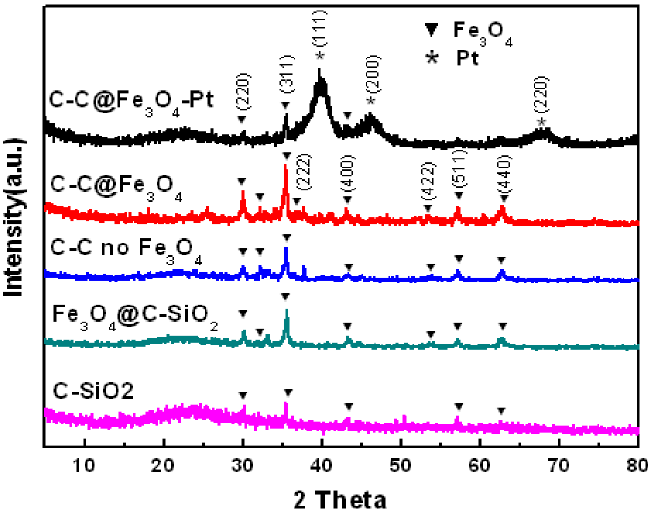


Figure S3 XRD patterns of different magnetic particles

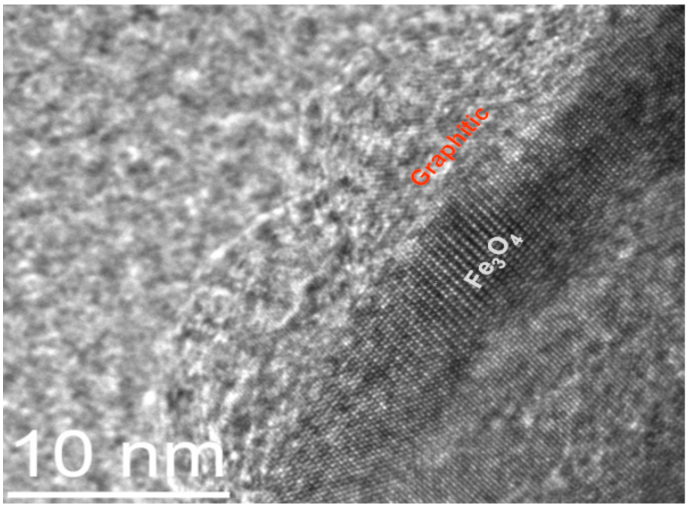
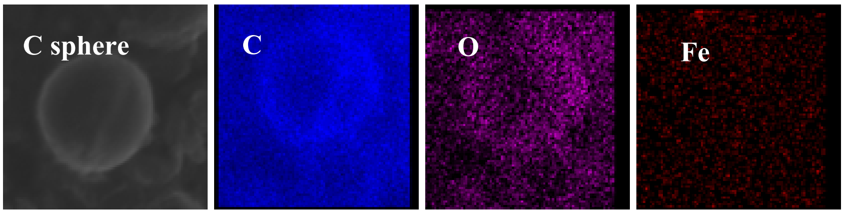
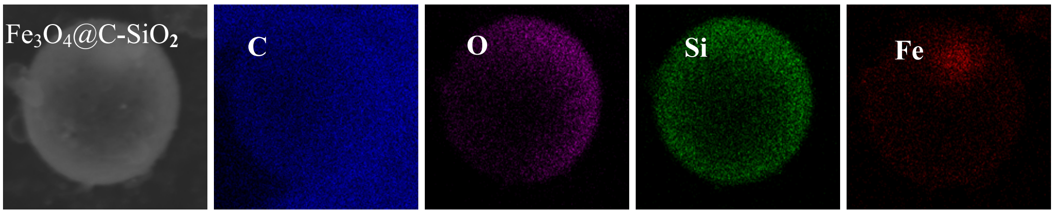


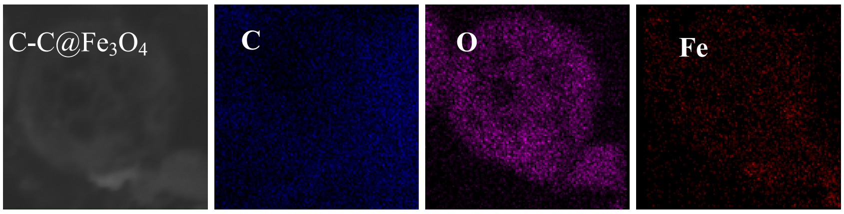
Figure S4 HRTEM image of the C-C@Fe_3O_4 porous hollow particles



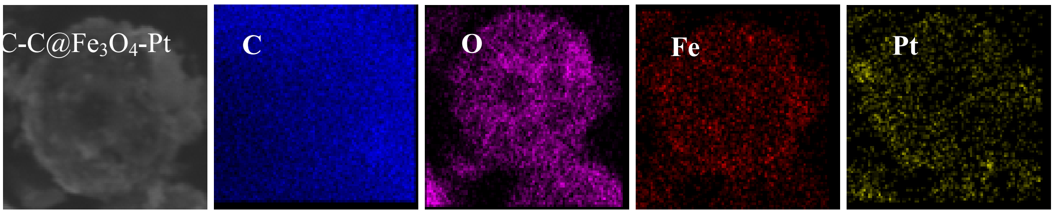
A. Element map of single carbon hollow spheres, which was obtained by etching the C-SiO_2 aerosol particles in HF solution, the iron species distribute homogeneously in the carbon shell



B. Element map of the Fe_3O_4@C-SiO_2 core-shell aerosol particles, the bright red spots can be ascribed to the encapsulated Fe_3O_4 nanoparticles

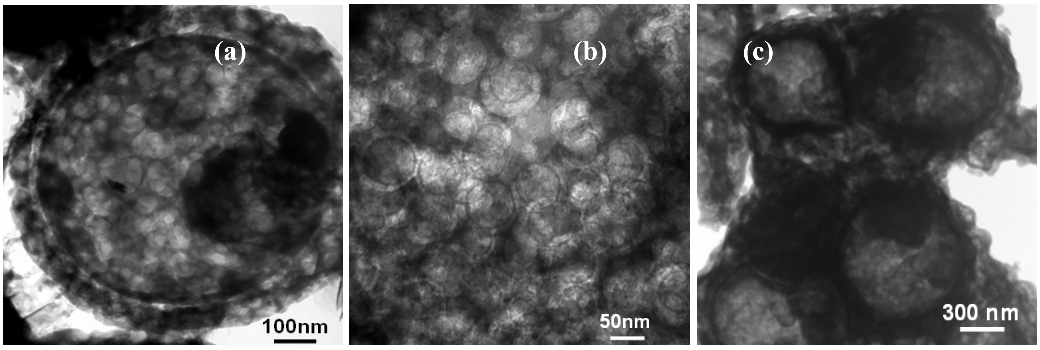


C. Element map of the C-C@Fe_3O_4 porous hollow particles

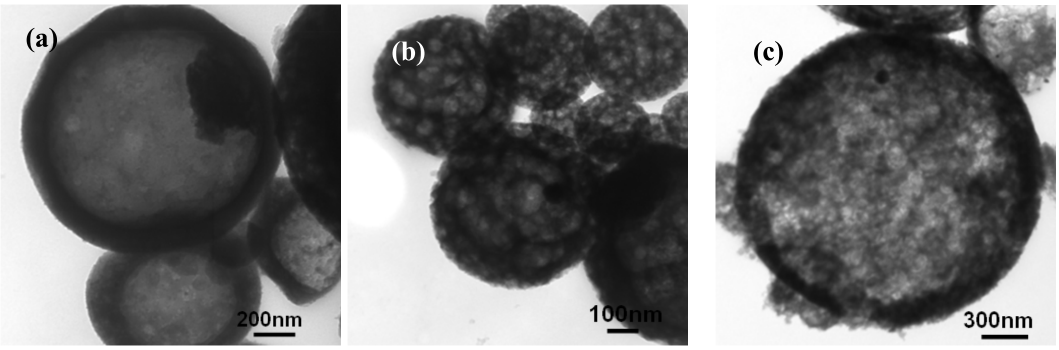


D. Element map of the C-C@Fe_3O_4-Pt porous hollow particles

Figure S5 Distribution of iron species in different hollow spheres



A. (a) (b) TEM images of C-C porous particles, no any Fe_3O_4 was added in the aerosol precursor solution, (c) double-shelled hollow C-C particles without pores in the carbon layer with RF as the carbon source



B. Fe_3O_4@C-SiO_2@RF-COOH core-shell particles, (a) without CTAB and (b) with CTAB, (c) C-C particles obtained from (a)

Figure S6 The controlled experiments show that only C-C porous particles are obtained when no Fe_3O_4 is added in C-SiO_2 aerosol particles while other conditions keep constant, and C-C spheres without porous structure are prepared if RF-COOH is replaced with RF (Fig. S6 A). No obvious pores in Fe_3O_4@C-SiO_2@RF-COOH precursor particles and C-C spheres are formed without the presence of CTAB, revealing the important role of CTAB to template the pores (Fig. S6 B). These results reveal that both the CTAB and the Fe_3O_4 cores play important roles in generation of mesoporous carbon microspheres containing dispersed Fe_3O_4 nanoparticles

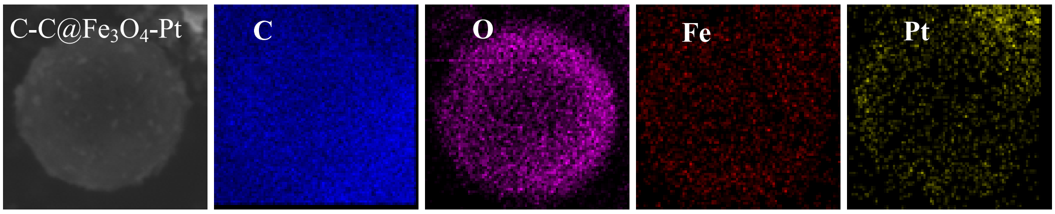


Figure S7. Element map of the C-C@Fe_3O_4-Pt porous hollow particles after five cycle usage

References

1 H. Zhang, X. Li, G. He, J. Zhan and D. Liu, *Ind. Eng. Chem. Res.*, 2013, **52**, 16902.

2 Y. Wang, B. Sunkara, J. Zhan, J. He, L. Miao, G. L. McPherson, V. T. John and L. Spinu, *Langmuir*, 2012, **28**, 13783.