

Multifunctional nanostructures based on porous silica covered Fe₃O₄@CeO₂/Pt composites: A high thermal stable and magnetic-recycled catalyst system

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Note added after first publication: This Supplementary Information file replaces that originally published on 29th May 2014, which contained an incorrect image for Fig. S8.

Supporting Information

Experimental Section

Synthesis of magnetite microspheres

The Fe₃O₄ microspheres were synthesized according to the method reported previously. Typically, FeCl₃ (0.65 g, 4.0 mmol) and trisodium citrate (0.20 g, 0.68 mmol) were first dissolved in ethylene glycol (20 mL), afterward, NaAc (1.20 g) was added with stirring. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclave was heated at 200 °C and maintained for 10 h, and then allowed to cool to room temperature. The black products were washed with ethanol and deionized water for several times.

Synthesis of Fe₃O₄@CeO₂ composites microspheres

The Fe₃O₄@CeO₂ composites microspheres were prepared by chemical precipitation method in accordance with the following procedure. The obtained 0.1 mmol Fe₃O₄ microspheres were dispersed in 20 mL deionized water and 0.1 mmol Ce(NO₃)₃·6H₂O was dissolved in 20 mL ethanol, then the two solution were mixed together through an ultrasonic treatment process for 15 min. Subsequently, 0.05 mmol hexamethylenetetramine (HMT) dissolved in 0.2 mL deionized water was added to the fully dispersed particle solution. The mixture was then stirred for 0.5 h in an oil bath maintained at 70 °C. Final products were collected by a magnet, washing with deionized water and ethanol for several times to remove any possible ionic remnants, followed by drying overnight at 60°C.

Synthesis of Pt nanoparticles

Pt nanoparticles were synthesized through a facile ultrasound treated method. Typically, 1mmol of H_2PtCl_6 was mixed with Polyvinyl Pyrrolidone (PVP, 0.1g) in the present of 20 ml ethylene glycol, followed by the sonochemistry method. The as-obtained products were then purified by the help of acetone.

Synthesis of $\text{Fe}_3\text{O}_4@ \text{CeO}_2/\text{Pt}$ composites

The obtained $\text{Fe}_3\text{O}_4@ \text{CeO}_2$ composites were treated with 1 mmol L-lysine aqueous solution by sonicating 10 min, then the solution was centrifuged and redispersed into 1mmol of lysine solution to repeated the procedure twice, and then the solution was centrifuged and redispersed in the 10 mL deionized water. In an optimized deposition process, 10 mL of the Pt nanoparticle solution was mixed with above solution by incubation for overnight, and then the obtained $\text{Fe}_3\text{O}_4@ \text{CeO}_2/\text{Pt}$ composites were separated and washed with deionized water for several times.

Synthesis of porous $\text{Fe}_3\text{O}_4@ \text{CeO}_2/\text{Pt}@ \text{mSiO}_2$ composites

$\text{Fe}_3\text{O}_4@ \text{CeO}_2@ \text{Pt}/\text{SiO}_2$ composites were prepared via Stöber sol-gel process. The as-made $\text{Fe}_3\text{O}_4@ \text{CeO}_2/\text{Pt}$ composites (55 mg) were dispersed in a mixed solution containing CTAB (32.8 mg), ethanol (30 mL), concentrated ammonia solution (1.5 mL, 28 wt %), The resultant mixed solution was ultrasonicated for 5 min and then mechanically stirred for 30 min to form a uniform dispersion. Subsequently, 40 μL of TEOS was added dropwise to the dispersion under continuous stirring. After stirring for 6 h at 30 °C, the product was collected with a magnet and washed repeatedly with ethanol and deionized water. Finally, the purified products were redispersed in 100 mL of acetone and refluxed at 80 °C for 48 h to remove the template CTAB.

Characterization

Scanning electron microscopy (SEM) images and the energy-dispersive X-ray spectrum (EDX) were performed on a field emission scanning electron microscope (FESEM, S4800, Hitachi) equipped with an energy-dispersive X-ray spectrum (EDX, JEOLJXA-840). Transmission electron microscopic (TEM) images, high-resolution transmission electron microscopic (HRTEM) images and High-angle annular dark-field scanning transmission-electron microscopy (HAADF-STEM) images were

obtained with a TECNAI G2 high-resolution transmission electron microscope operating at 200 kV. Nitrogen adsorption isotherms were measured at a liquid nitrogen temperature (77 K) with a Micromeritics ASAP 2010M apparatus. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method. The total pore volume was evaluated by the t-plot method, and pore size distribution was analyzed with the supplied BJH software package from the desorption branches of the isotherms. Magnetization measurement was carried out with a Magnetic Property Measurement System (MPMS XL-7) at 300 K. The measurements for all samples were done on pure and dried powders. UV/Vis absorbance spectra were recorded on a Cary 500 scan 117 UV/Vis/NIR spectrophotometer (Varian, Harbor City, CA) at room temperature.

CO oxidization test

A home-made flow reactor system including a stainless steel reaction tube (1 \square \times 60 cm) was used for the catalytic test. In a typical CO oxidation experiment, the different catalysts and 4 g quartz sand were mixed as catalyst, respectively, and the experiment was carried out under a flow of reactant gas mixture (1% CO, 20% O₂, balance He) at a rate of 50 mL min⁻¹. The composition of the gas was monitored on-line by gas chromatography (Agilent technologies, GC-7890A).

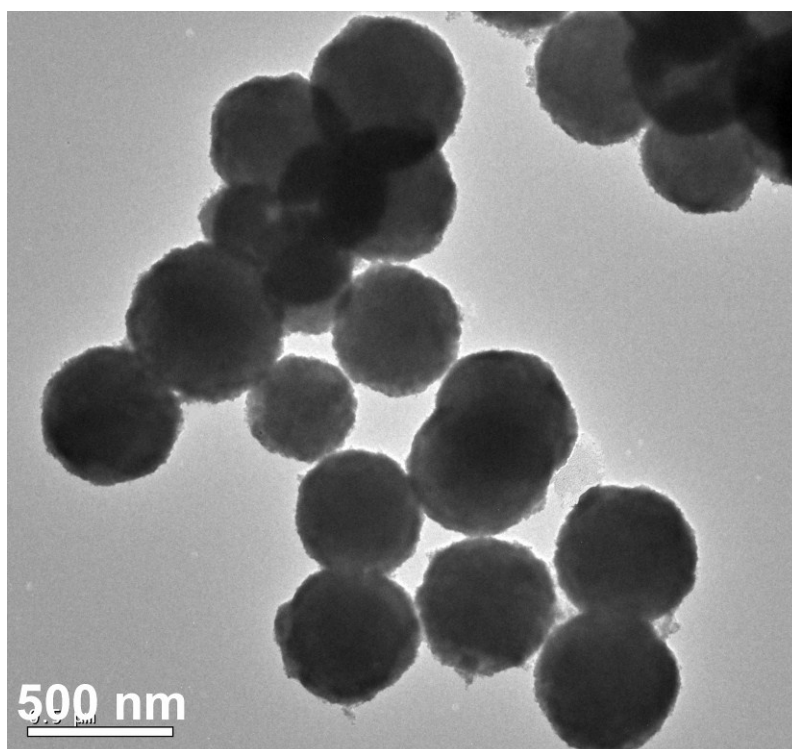


Fig. S1 TEM image of the as-prepared magnetite particles.

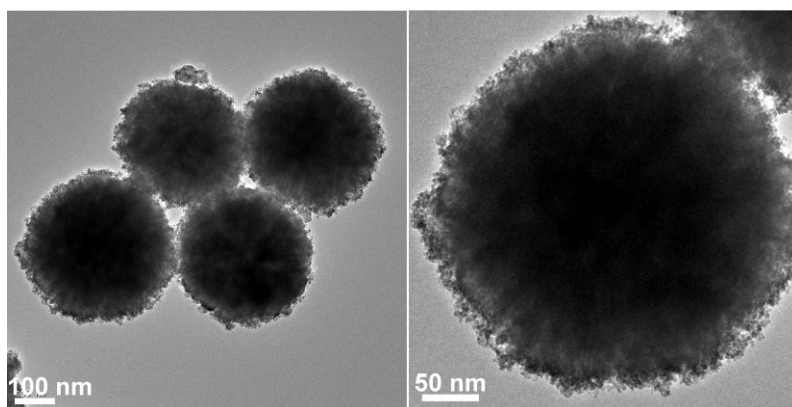


Fig. S2 TEM images of the as-prepared monodisperse Fe₃O₄@CeO₂ composites.

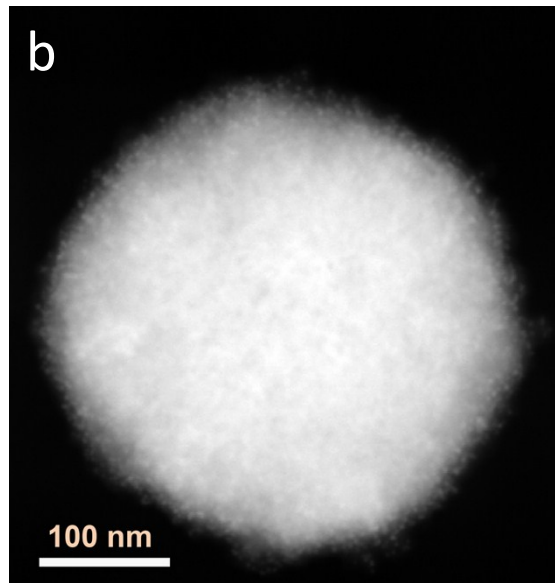
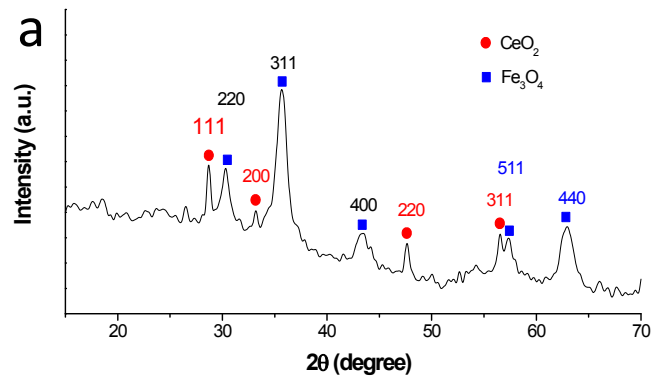


Fig. S3 XRD pattern (a) and high-angle annular dark-field scanning transmission-electron microscopy (HAADF-STEM) image (b) of the Fe₃O₄@CeO₂/Pt composites.

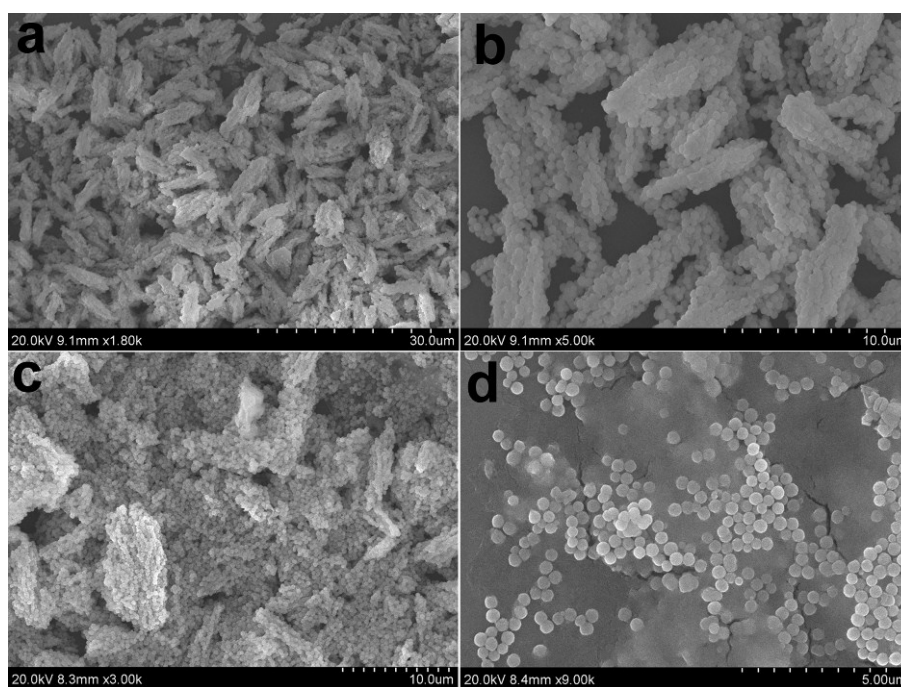


Fig. S4 SEM images of the products prepared with different volume ratio of EtOH/H₂O.

It must be noted that the solvent used here is critical for the evenly precipitation of the CeO₂ on magnetite. As shown in Figure S4a and b, keeping other synthetic condition unchanged, the products assembled and formed the shuttle-like architectures using H₂O as solvent. This may be caused by the rapid nucleation of the CeO₂ nanoparticles in aqueous solution, and the CeO₂ nanoparticles acted as the linker to induce the assemble of magnetic Fe₃O₄ particles together. When small quality of EtOH was added in the aqueous solution with the volume ratio of EtOH/H₂O 1:5 (Figure S4c), the assembled shuttle structures decreased with the nucleation rate of CeO₂ nanoparticles slowing down. The optimal volume ratio of EtOH/H₂O is 1:1, in this condition, the monodisperse Fe₃O₄ coated with CeO₂ nanoparticles formed, as shown in Fig 1a-c and Fig S2. When pure EtOH was used as solvent, the CeO₂ nanoparticles can not be formed, as shown in Figure S4d.

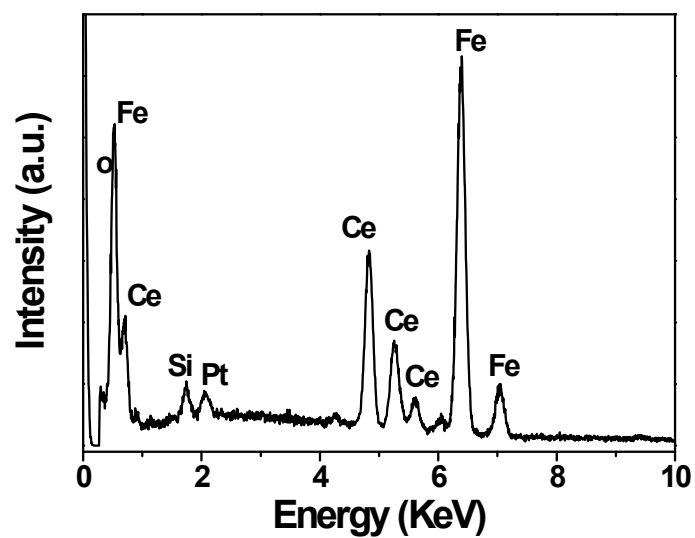


Fig. S5 EDX spectrum of the $\text{Fe}_3\text{O}_4@\text{CeO}_2/\text{Pt}$ composites.

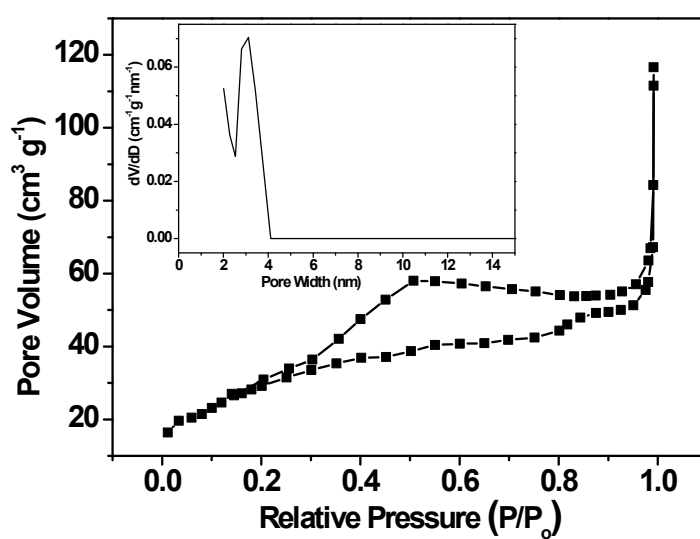


Fig. S6 N_2 adsorption/desorption isotherms of the $\text{Fe}_3\text{O}_4@\text{CeO}_2/\text{Pt}@m\text{SiO}_2$ composites. Inset is the pore volume.

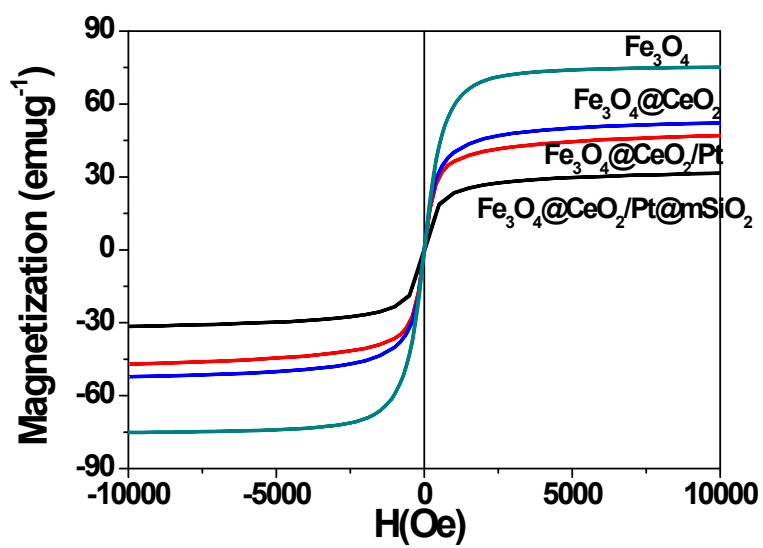


Fig. S7 The hysteresis loops for the as-prepared composites at 300 K.

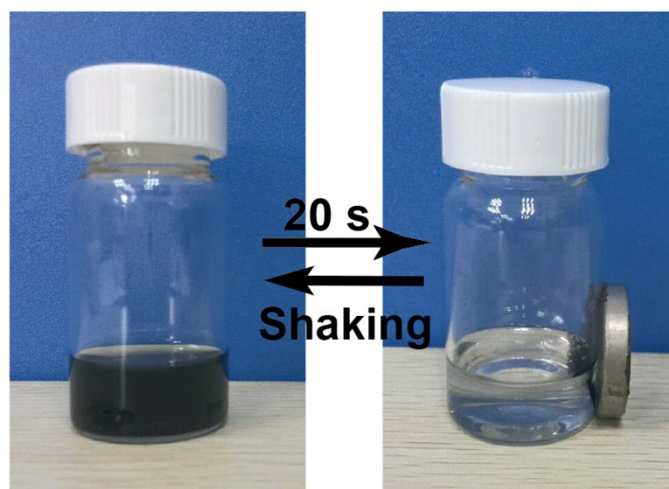


Fig. S8 The dispersion of $\text{Fe}_3\text{O}_4@ \text{CeO}_2/\text{Pt}@ \text{mSiO}_2$ microspheres.

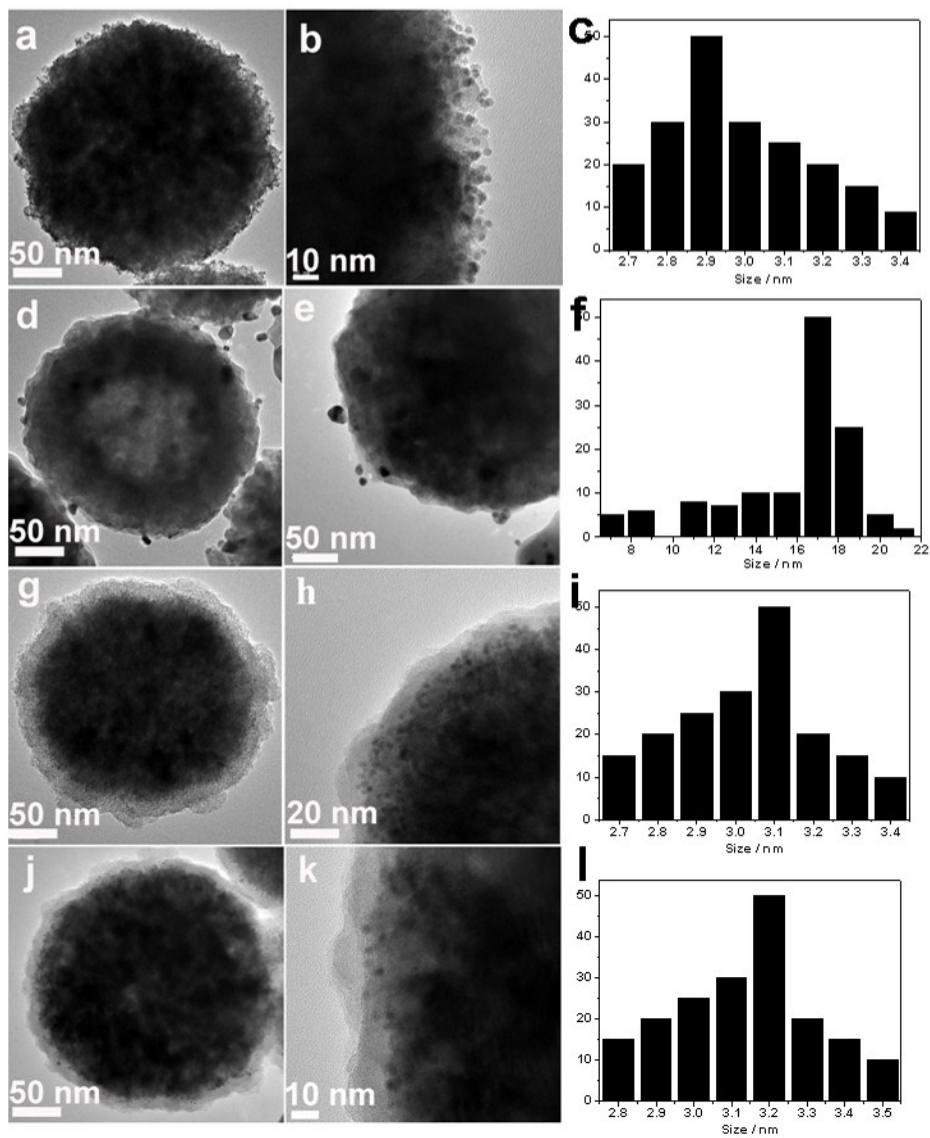


Fig. S9 TEM images of the products calcined at different temperatures and size distribution of the Pt nanoparticles.

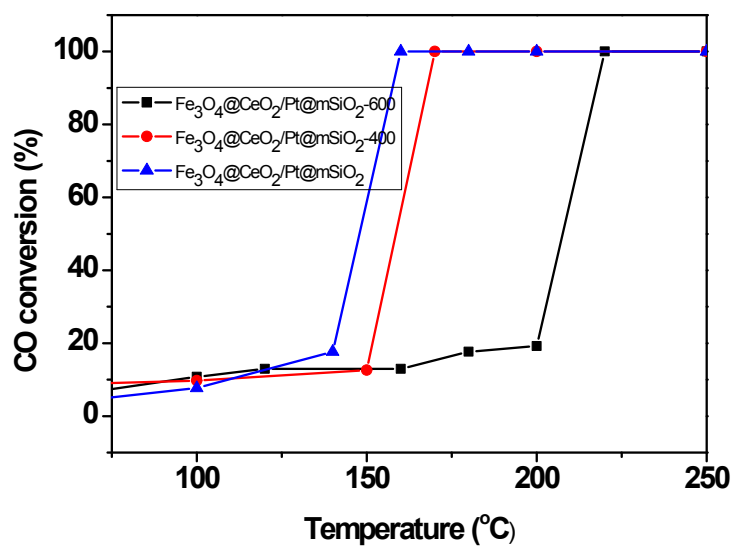


Fig. S10 CO conversion vs reaction temperature over the different catalysts.