

Electronic Supplementary Information:

Yolk-shell structured CoFe₂O₄ microspheres as novel catalyst of peroxymonosulfate activation for efficient degradation of butyl paraben

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Materials and methods

Preparation of yolk-shell structured CoFe₂O₄ microspheres

Yolk-shell structured CoFe₂O₄ microspheres were synthesized by a modified method reported previously.¹ In a typical synthesis, 0.25 mmol of Fe(NO₃)₃·6H₂O, 0.125 mmol of Co(NO₃)₂·6H₂O, and 8 mL of glycerol were dissolved into 40 mL of isopropanol to form a transparent pink solution. The solution was then transferred to a Teflon-lined stainless steel autoclave and kept at 180 °C for 6 h. After cooling to room temperature naturally, the brown precipitate was separated by centrifugation, washed with several times with ethanol and dried in an oven at 80 °C. In order to obtain the yolk-shell structured CoFe₂O₄ microspheres, the as-synthesized FeCo-glycerate is then annealed at 350 °C in air for 2 h with a heating rate of 1 °C min⁻¹. The CoFe₂O₄ microspheres were prepared by annealed FeCo-glycerate at 350 °C in air for 2 h with a heating rate of 10 °C min⁻¹.

Characterizations of samples

X-ray powder diffraction (XRD) was carried out using a Bruker D8 ADVANCE X-ray diffractometer equipped with monochromated Cu K α radiation (λ = 0.1541 nm) at a tube voltage of 40 kV and a tube current of 30 mA. Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800 emission scanning electron microscope. High-resolution electron microscopy (HRTEM) was performed on sample suspensions dried on a carbon coated grid (200 mesh, 3.05 mm in diameter) with a JEOL JEM 2010 FEF electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) spectra of the samples were recorded on a PHI Quantum 2000 Scanning ESCA Microprobe spectrometer with an Al K α incident X-ray beam. The X-ray source was operated at 35 W, and the spectra were recorded at 15 kV. The analysis chamber pressure was 5 × 10⁻⁸ Pa. Hysteresis loops was collected on a Quantum Design superconducting quantum interference device magnetometer (LakeShore 7307) at 300 K.

Catalytic properties measurement

Butyl paraben (BPB) degradation tests were carried out at 25 °C in 250 mL glass vessel with 150 mL of BPB solution at 10 mg L⁻¹ with constant shaking at 300 rpm. First, 15 mg of catalyst was added into the BPB solution for a while, then 23 mg of PMS was added into the solution. At predetermined time intervals, 1 mL of BPB solution was sampled and filtered through a 0.22 μ m

Millipore filter for HPLC analysis. The residual concentrations of BPB in solutions were analyzed using a high performance liquid chromatography (HPLC) system (Agilent 1260, USA) equipped with a diode array detector and a Poroshell 120 EC-C18 column (2.7 μm , 4 $\times$ 100 mm, Agilent). The mobile phase was a mixture of 55/45 (v/v) acetonitrile–water with a flow rate of 1 mL/min at 303 K.

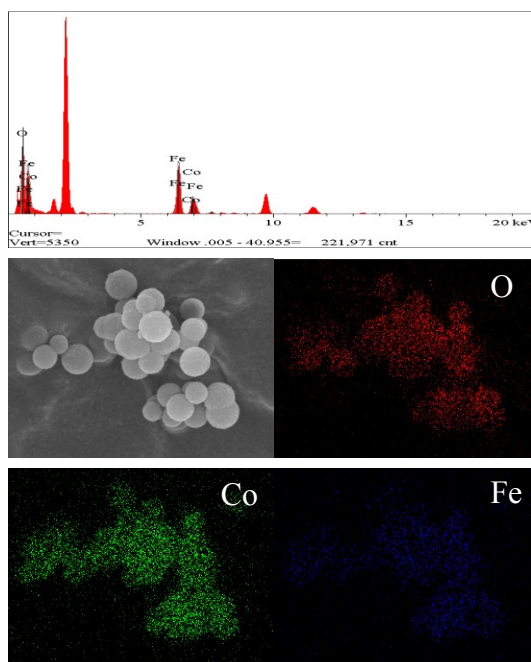


Fig. S1 EDX spectrum and elemental mapping of yolk-shell structured CoFe_2O_4 microspheres.

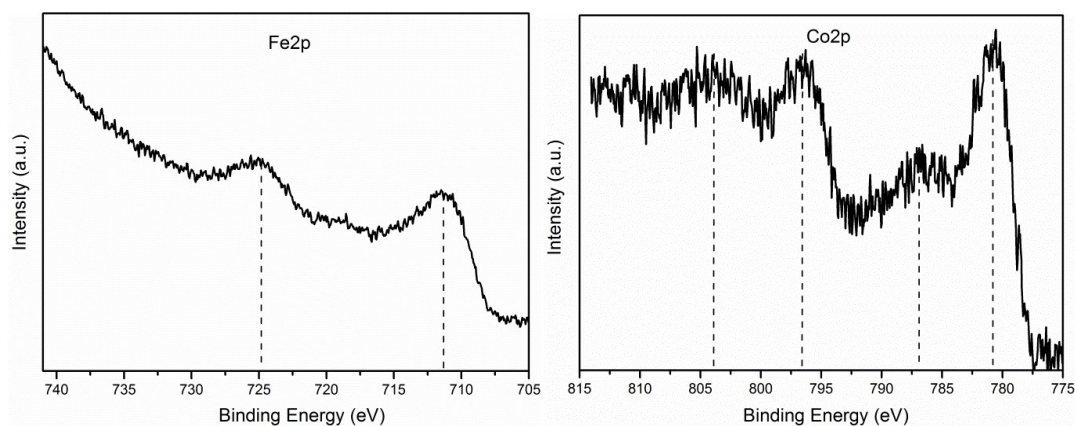


Fig. S2 XPS spectra of the as-synthesized yolk-shell structured CoFe_2O_4 microspheres.

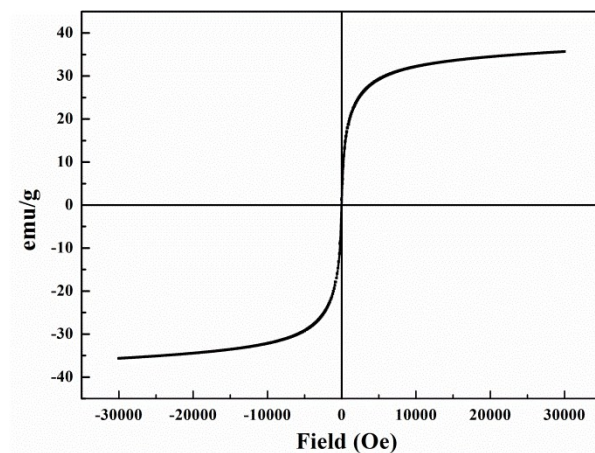


Fig. S3 The magnetization hysteresis of the as-synthesized yolk-shell structured CoFe₂O₄ microspheres.

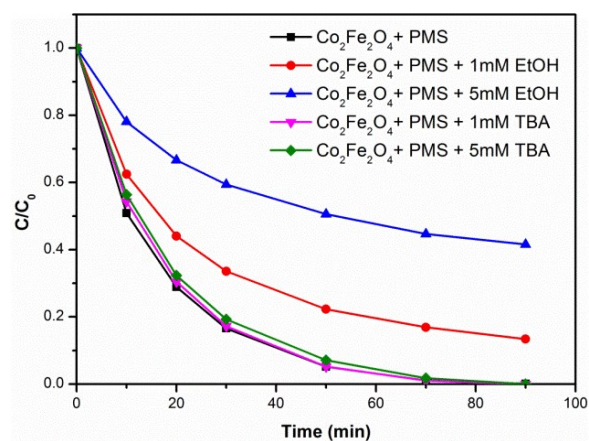


Fig. S4 Degradation of BPB in the system of CoFe₂O₄ yolk-shell microspheres/PMS without and with quenching agents of TBA and EtOH (initial BPB concentration 10 mg L⁻¹, PMS concentration 0.5 mmol L⁻¹, catalyst load 0.1 g L⁻¹).

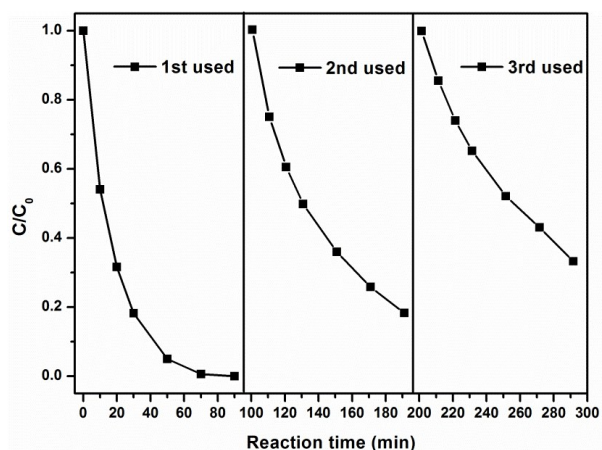


Fig. S5 Time profiles of BPB degradation in different recycles (initial BPB concentration 10 mg L^{-1} , PMS concentration 0.5 mmol L^{-1} , catalyst load 0.1 g L^{-1}).

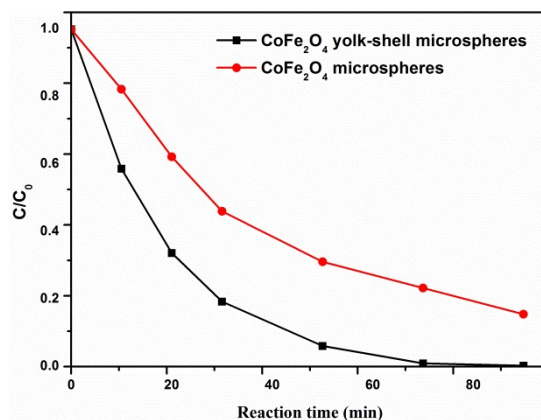


Fig. S6 BPB degradation profiles versus time in different systems (initial BPB concentration 10 mg L^{-1} , PMS concentration 0.5 mmol L^{-1} , catalyst load 0.1 g L^{-1}).

Reference:

1. L. Shen, L. Yu, X.-Y. Yu, X. Zhang and X. W. Lou, *Angewandte Chemie International Edition*, 2015, **54**, 1868-1872.