

*Electronic Supplementary Information:*

## **Synthesis of core-shell structured Fe<sub>3</sub>O<sub>4</sub>@ $\alpha$ -MnO<sub>2</sub> microspheres for efficiently catalytic degradation of ciprofloxacin**

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### **Materials and methods**

**Preparation of Fe<sub>3</sub>O<sub>4</sub> microspheres.** The Fe<sub>3</sub>O<sub>4</sub> microspheres were prepared according to Li's method.<sup>1</sup> In a typical preparation procedure, FeCl<sub>3</sub>·6H<sub>2</sub>O (4.05 g, 15 mmol) was dissolved in ethylene glycol (120 mL) to form a clear solution, followed by the addition of NaAc (10.8 g) and polyethylene glycol (3 g). The mixture was stirred vigorously for 30 min and then sealed in a teflon-lined stainless-steel autoclave (200 mL). The autoclave was heated to and maintained at 200 °C for 20 h, and then allowed to cool to room temperature. The black products were collected from the solution with an external magnet and washed with ethanol for a few times. Finally, the black products were dried in a vacuum at 50 °C for 8 h.

**Preparation of core-shell structured Fe<sub>3</sub>O<sub>4</sub>/ $\alpha$ -MnO<sub>2</sub> microspheres.** The magnetic composites were prepared via a simple hydrothermal process. In a typical experiment, 0.1 g of Fe<sub>3</sub>O<sub>4</sub> microspheres and 0.16 g of KMnO<sub>4</sub> were firstly dispersed in 40 mL of distilled water by ultrasonication, and 0.7 mL of acetic acid was then slowly added dropwise. The mixture was transferred to a Teflon-lined autoclave (50 mL) and sealed to heat at 100 °C for 8 h. The obtained products were washed with distilled water and ethanol for a few times and dried in a vacuum at 60 °C for 8 h.

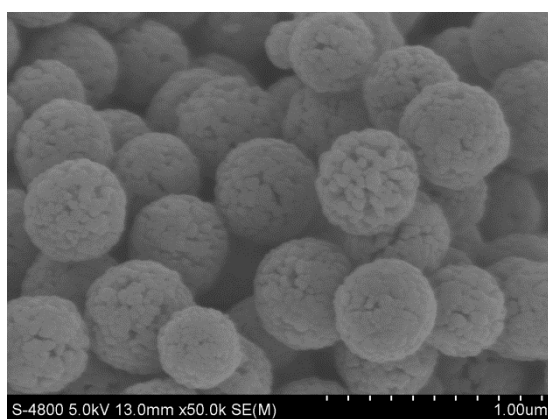
### **Characterizations of samples**

X-ray powder diffraction (XRD) was carried out using a Bruker D8 ADVANCE X-ray diffractometer equipped with monochromated Cu K $\alpha$  radiation ( $\lambda = 0.1541$  nm) at a tube voltage of 40 kV and a tube current of 40 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. A Quantachrome Autosorb-1 instrument was used to measure the surface areas and micropore size distributions of the materials. Samples were degassed in a vacuum at 250 °C for about 10 h to remove water and other physically adsorbed species. N<sub>2</sub> isothermal adsorption and desorption experiments were performed at relative pressures (P/P<sub>0</sub>) from 10<sup>-6</sup> to 0.9916 and from 0.9916 to 0.047, respectively. Hysteresis loops were collected on a Quantum Design superconducting quantum interference device magnetometer (LakeShore 7307) at 300 K.

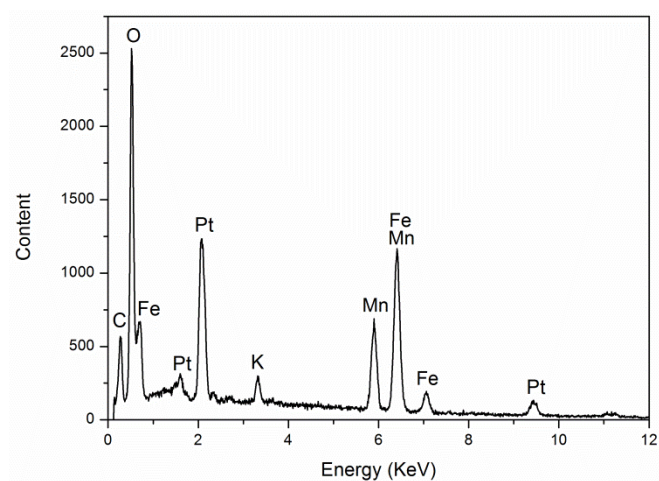
### **Catalytic degradation of CIP**

CIP degradation tests were carried out at 25 °C in 50 mL glass vessel with 30 mL of CIP solution at 50 mg L<sup>-1</sup> with constant shaking at 300 rpm. First, 30 mg of catalyst was added into the CIP solution for a while, then 120 mg of PDS was added into the solution. At predetermined time

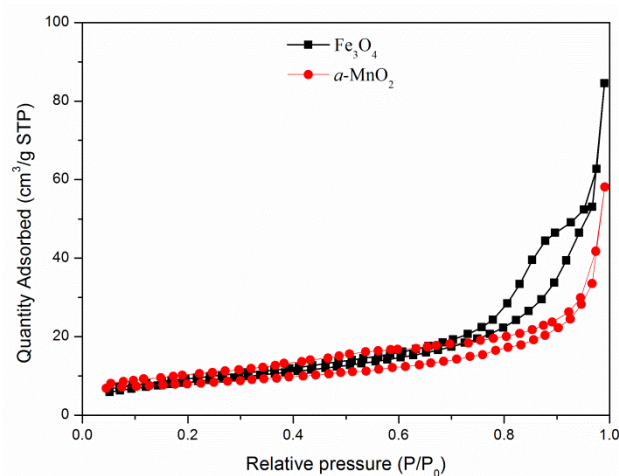
internals, 1 mL of CIP solution was sampled and filtered through a 0.22  $\mu\text{m}$  Millipore filter for HPLC analysis. The concentration of CIP was analyzed by an Agilent Technologies 1260 Series high performance liquid chromatography system (HPLC) equipped with an UV-VIS diode array detector (DAD). Analytical separation was performed by a C18 Agilent column (250  $\times$  4.6 mm<sup>2</sup>, 5  $\mu\text{m}$  particle size) at 25  $^{\circ}\text{C}$ . The isocratic elution consisted of 20% acetonitrile and 80% 20 mM phosphate buffer solution with a flow rate of 1 mL min<sup>-1</sup>. The detection wavelength was 278 nm for CIP. Total organic carbon (TOC) concentration was measured using TOC VCPH analyzer (Shimadzu).



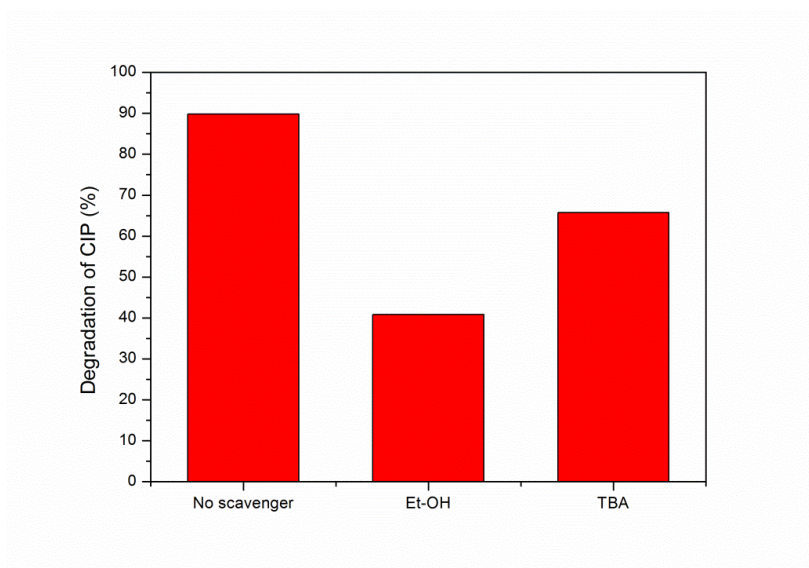
**Fig. S1** SEM image of the synthesized Fe<sub>3</sub>O<sub>4</sub> microspheres.



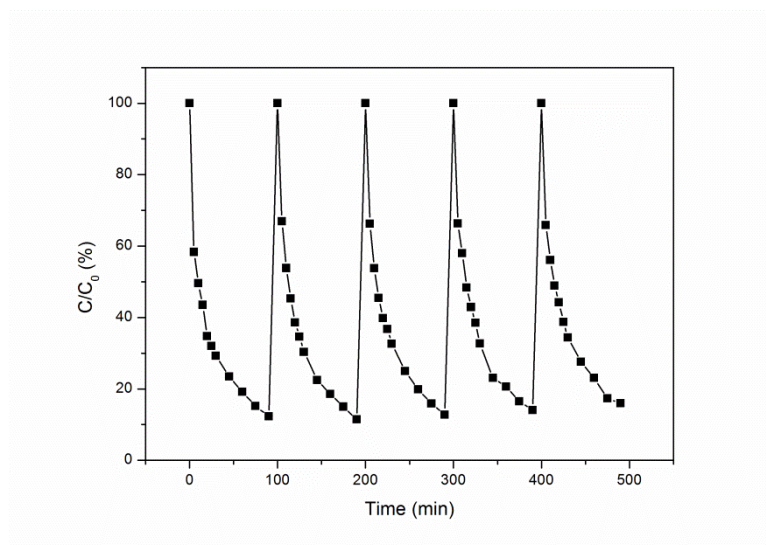
**Fig. S2** EDX spectrum of the Fe<sub>3</sub>O<sub>4</sub>@ $\alpha$ -MnO<sub>2</sub> microspheres.



**Fig. S3** N<sub>2</sub> adsorption/desorption isotherms of the pure Fe<sub>3</sub>O<sub>4</sub> microspheres and α-MnO<sub>2</sub>.



**Fig. S4** Degradation of CIP in the system of PS/Fe<sub>3</sub>O<sub>4</sub>@α-MnO<sub>2</sub> without and with quenching agents of TBA (15 mmol L<sup>-1</sup>) and EtOH (15 mmol L<sup>-1</sup>) (initial CIP concentration 50 mg L<sup>-1</sup>, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration 2 g L<sup>-1</sup>, catalyst load 1 g L<sup>-1</sup>).



**Fig. S5** Time profiles of CIP degradation in different recycles (initial CIP concentration 50 mg L<sup>-1</sup>, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration 2 g L<sup>-1</sup>, catalyst load 1 g L<sup>-1</sup>).

**Reference:**

1. H. Deng, X. Li, Q. Peng, X. Wang, J. Chen and Y. Li, *Angewandte Chemie*, 2005, **117**, 2842.