

Electronic Supplementary Information:

Fabrication of 3D porous Mn doped α -Fe₂O₃ nanostructures for removal of heavy metals from wastewater

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Experimental section

Preparation of porous Mn doped α -Fe₂O₃ nanostructures

In a typical procedure, 48 mmol of FeSO₄·7H₂O, 12 mmol of MnSO₄·H₂O and 3.6 g of glucose were added to 40 mL deionized water with vigorous stirring. The resulting solution was transferred to a Teflon autoclave, which was then heated at 160 °C in an electric oven for 4 h. The products were collected by centrifugation and washed with water and ethanol for several times, then dried at 60 °C for 12 h in an oven. The resulting sample was calcined at 500 °C for 3 h to producing 3D porous Mn doped α -Fe₂O₃ nanostructures.

Characterizations

X-ray powder diffraction (XRD) was carried out using a Bruker D8 ADVANCE X-ray diffractometer equipped with monochromated Cu K α radiation ($\lambda = 0.1541$ 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. 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. N₂ isothermal adsorption and desorption experiments were performed at relative pressures (P/P₀) from 10⁻⁶ to 0.9916 and from 0.9916 to 0.047, respectively. Hysteresis loops were collected with a Quantum Design superconducting quantum interference device (SQUID) magnetometer (Lake Shore 7307) at 300 K. The SQUID measurements for all the samples were done on the pure and dried powders. 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. The metal contents were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, PerkinElmer, Optima 7000DV).

Removal of heavy metal ions

To study the equilibrium adsorption isotherm tests, 30 mg of Mn doped α -Fe₂O₃ was added to 30 mL of aqueous Pb(II) and Cr(VI) solutions with different concentrations at pH 5.0 and pH 3.0, respectively. As(III) adsorption isotherms were determined with a sorbent loading of 0.05 g L⁻¹ at

pH 7.0. The adsorption experiments were carried out in conical flasks mounted on a shaker at 260 rpm under ambient conditions for 20 h. Then, the suspension was filtered with a 220 nm membrane filter, and ICP-MS was used to measure the concentration of metal ions in the solution. All of the adsorption tests were performed in triplicate.

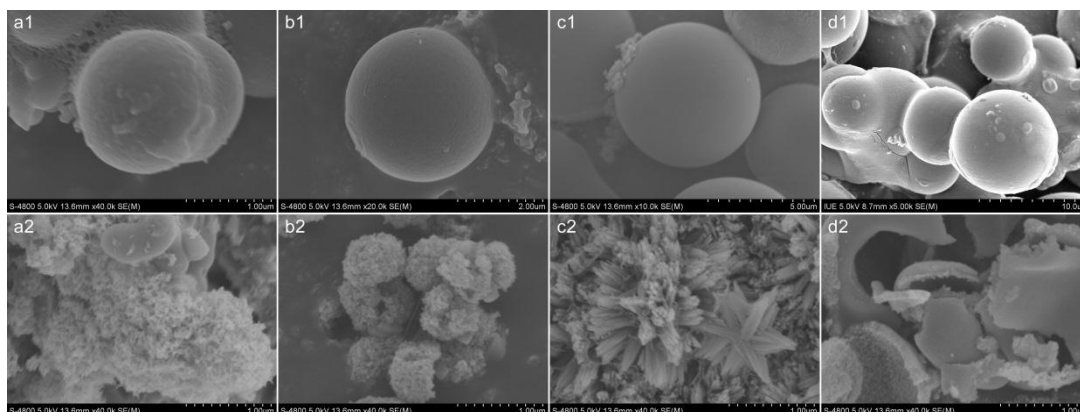


Fig. S1 SEM images of the carbon spheres containing Fe(II) and Mn(II) precursor (initial solutions containing 30 mmol of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 10 mmol of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$) and final calcined products with different amount glucose: (a) 1.2 g; (b) 2.4 g; (c) 3.6 g; (d) 4.8 g.

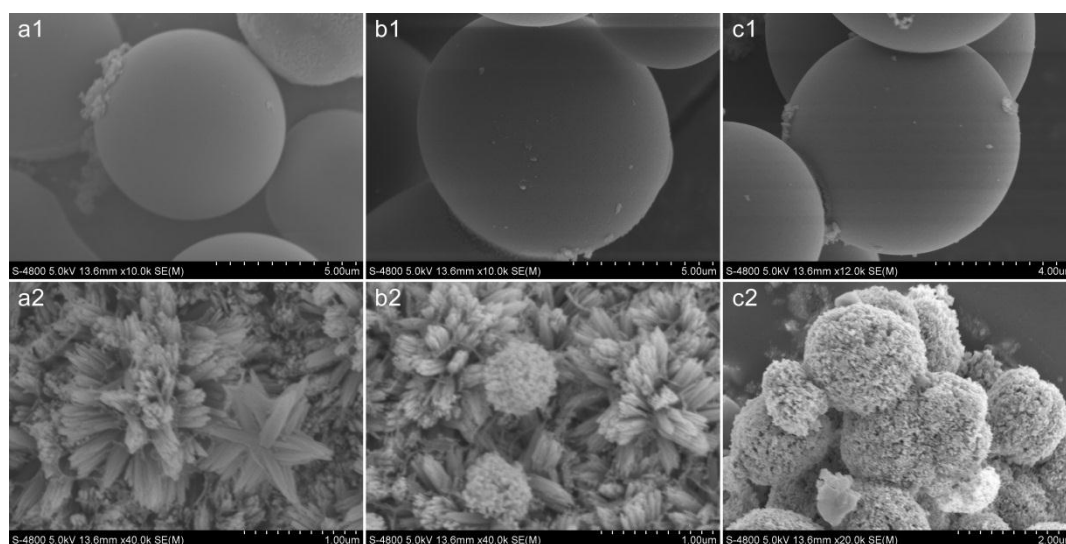


Fig. S2 SEM images of the carbon spheres containing Fe(II) and Mn(II) precursor (initial Fe(II)/Mn(II) molar ratio is 3:1) and final calcined products with different total amounts of Fe(II) and Mn(II): (a) 40 mmol; (b) 60 mmol; (c) 80 mmol

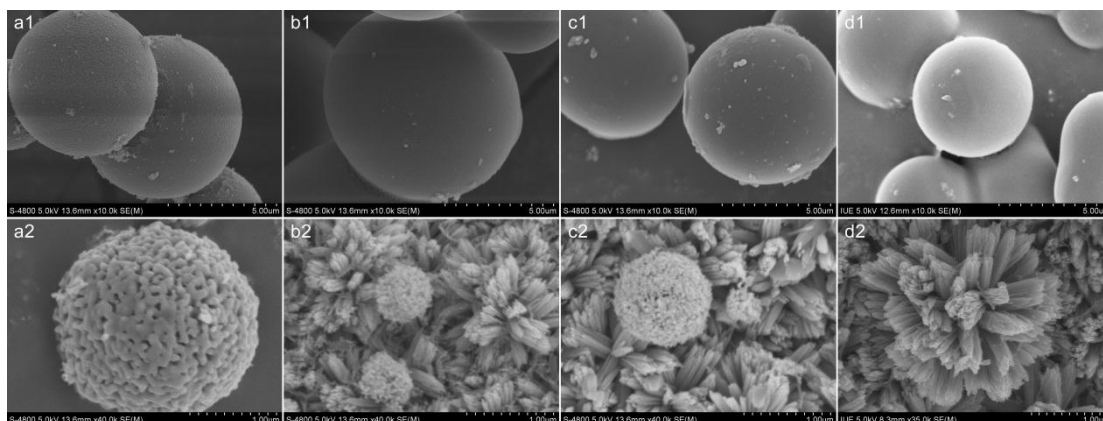


Fig. S3 SEM images of the carbon spheres containing Fe(II) and Mn(II) precursor (initial solutions containing 3.6 g of glucose, and total amount Fe(II) and Mn(II) is 60 mmol) and the final calcined products with different Fe(II)/Mn(II) molar ratio: (a) 1:1; (b) 2:1; (c) 3:1; (d) 4:1.

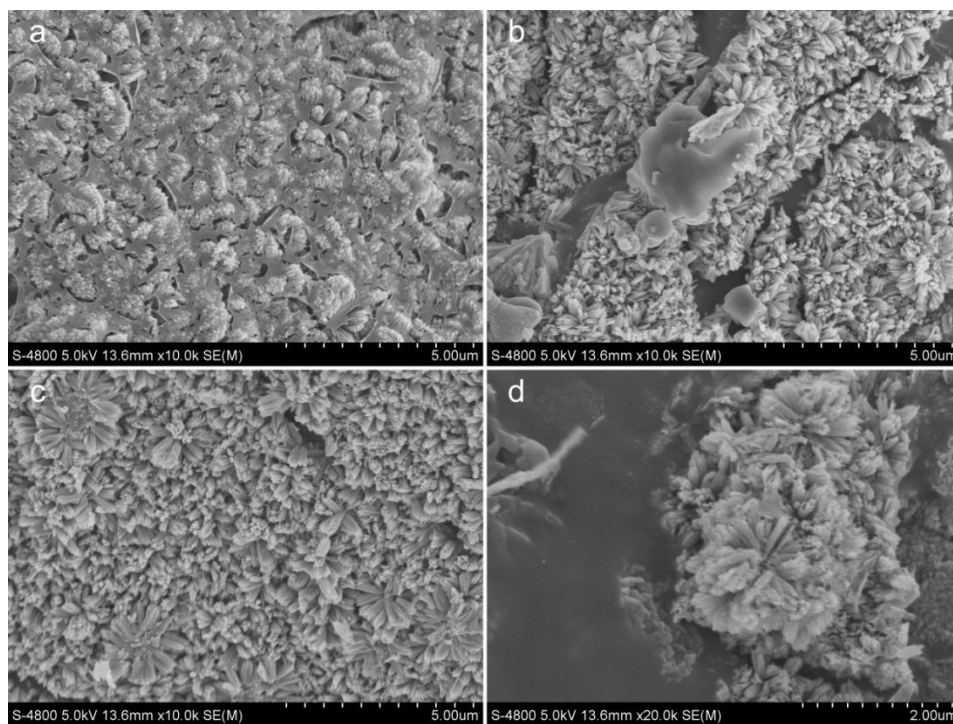


Fig. S4 SEM images of the final products with different calcined temperatures (initial solutions containing 48 mmol of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 12 mmol of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 20 mmol of glucose): (a) 300°C; (b) 400°C; (c) 500°C; (d) 550°C

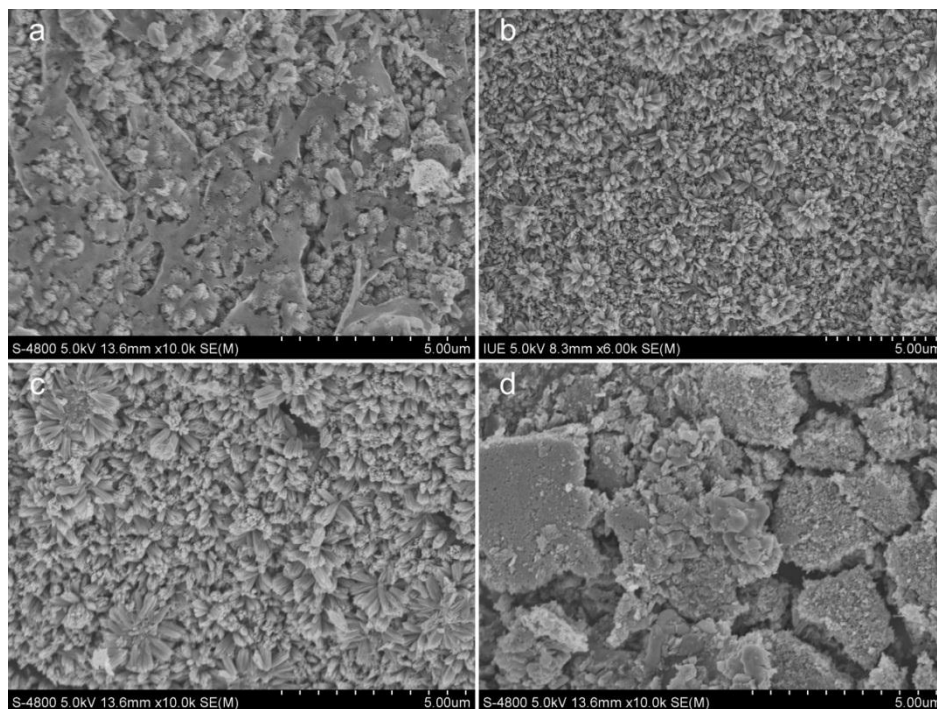


Fig. S5 SEM images of the products calcined at 500 °C for different time (initial solutions containing 48 mmol of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 12 mmol of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 20 mmol of glucose): (a) 2 h; (b) 3 h; (c) 4 h; (d) 5 h

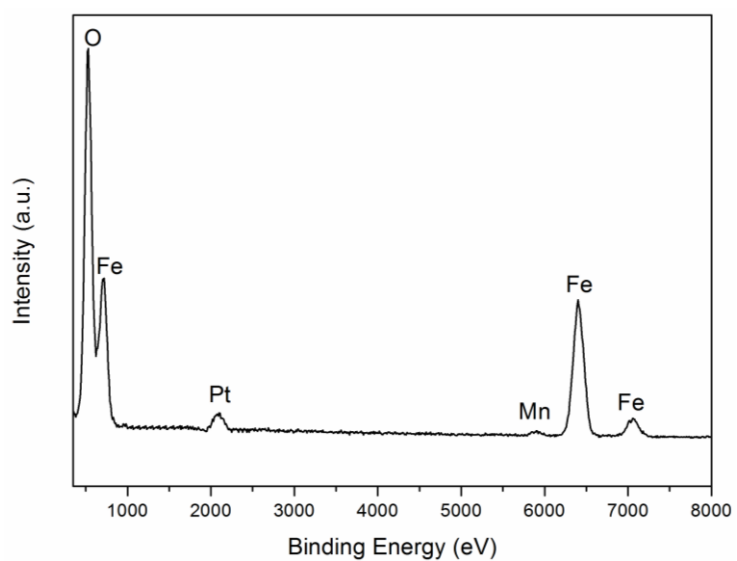


Fig. S6 EDX spectrum of the as-synthetic Mn doped $\alpha\text{-Fe}_2\text{O}_3$.

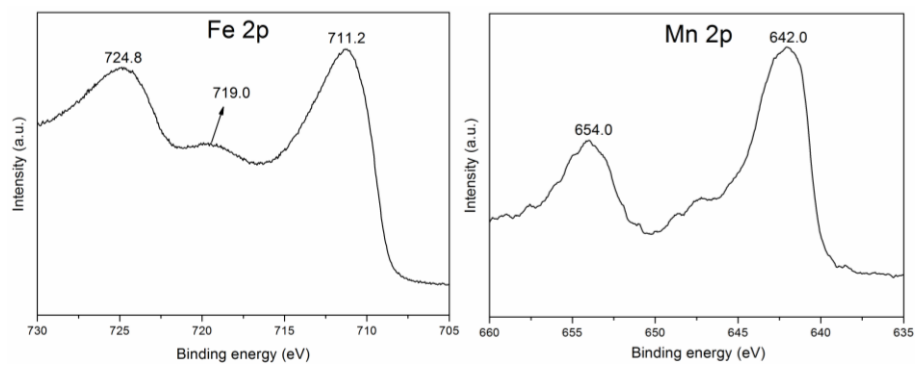


Fig. S7 XPS spectra of Fe 2p (a) and Mn 2p (b) in the as-synthesized Mn doped α -Fe₂O₃.