

Functionalized Hollow MnFe_2O_4 Nanospheres: Design, Synthesis and Applications in Efficient Adsorption of Heavy Metal Ions

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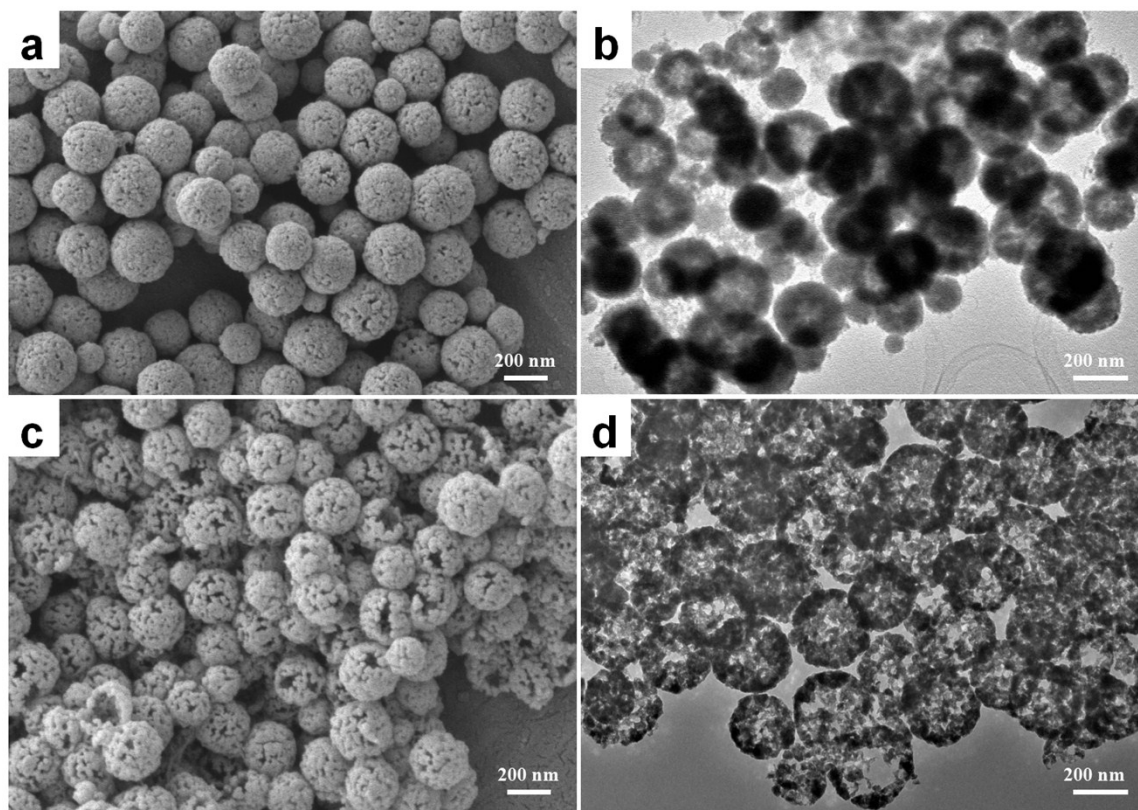


Figure S1 low-magnification SEM images of the as-synthesized of the H- MnFe_2O_4 -Cys samples with different etching times (a) S2, 15 h, (b) S3, 20 h. (c) and (d) the relatively TEM of H- MnFe_2O_4 -Cys.

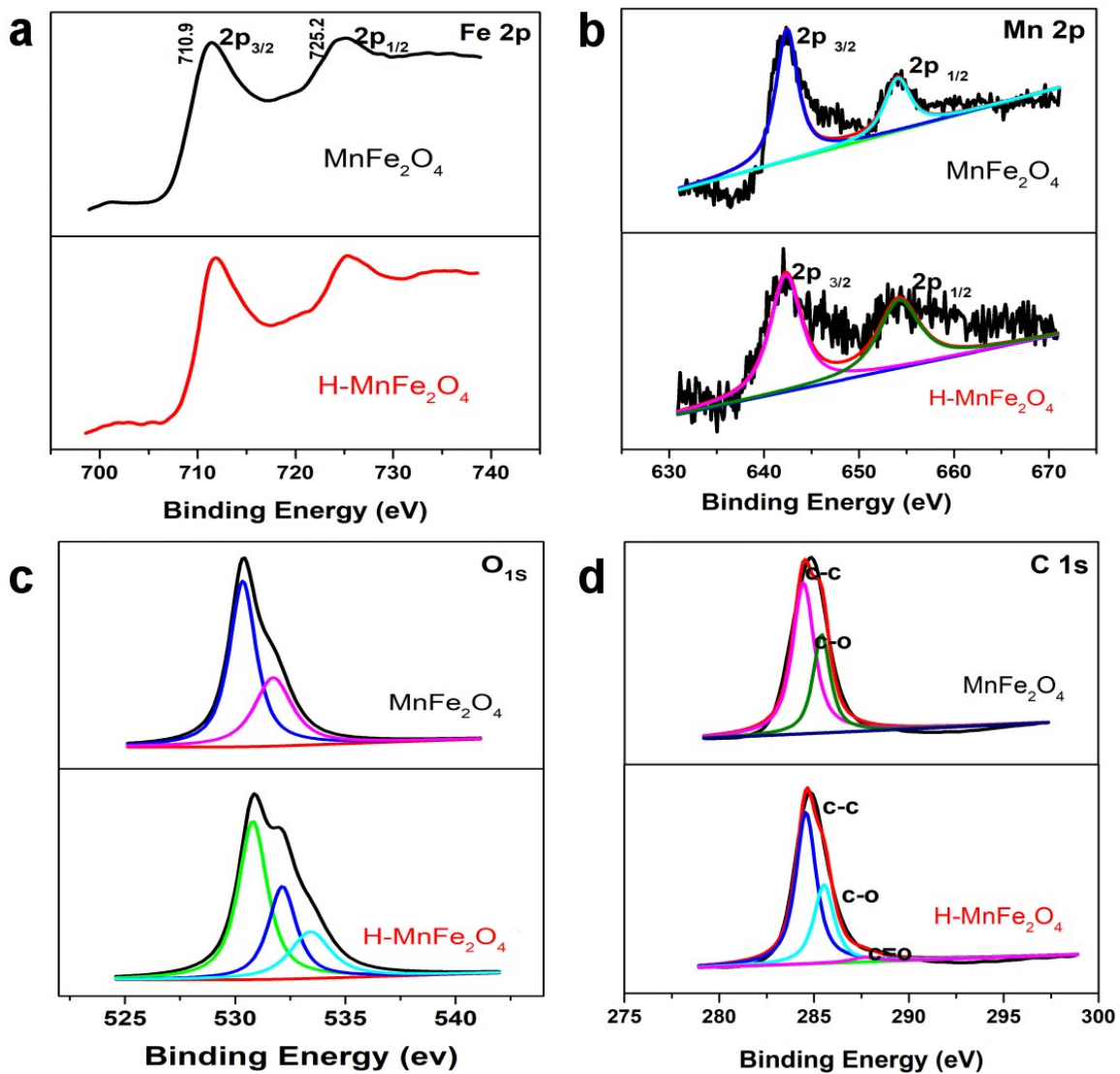


Figure S2 XPS spectra of the MnFe₂O₄ and H-MnFe₂O₄, (a) Fe2p, (b) Mn2p, (c) O1s and (d) C1s.

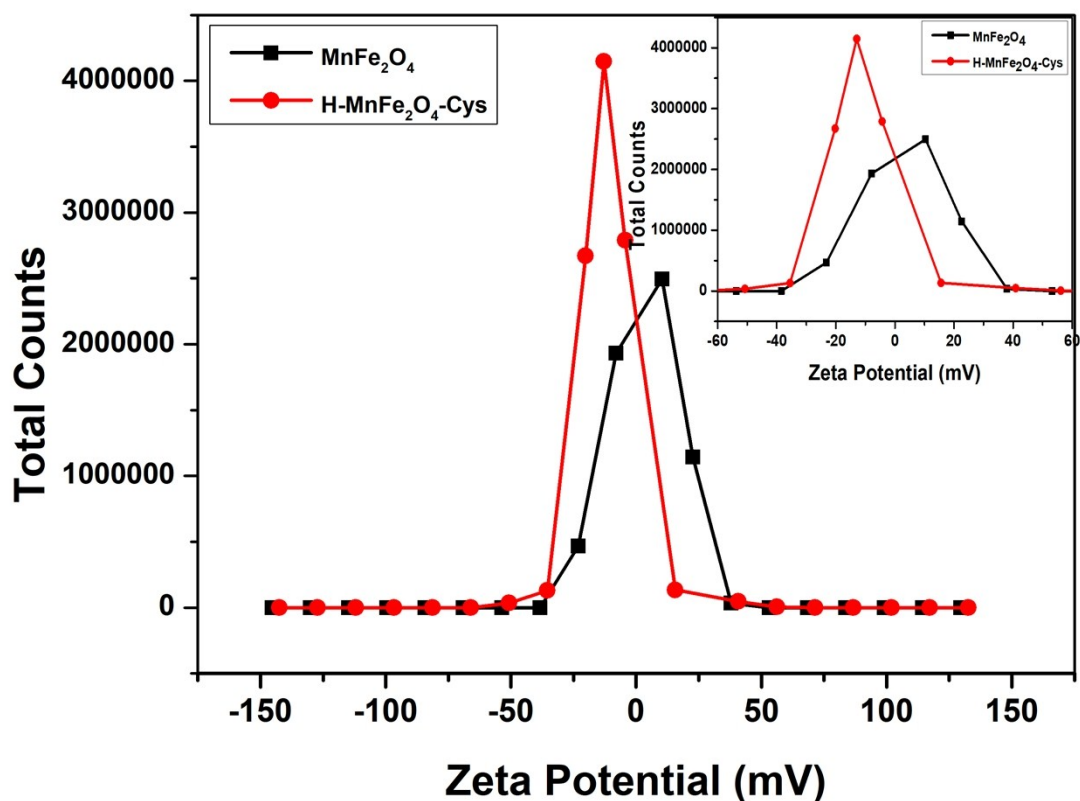


Figure S3 Zeta potential of MnFe₂O₄ and H-MnFe₂O₄-Cys.

Figure S3 shows the surface charge potential of bare H-MnFe₂O₄ and H-MnFe₂O₄-Cys, as obtained from zeta potential technique. The H-MnFe₂O₄ surface charge could be due to the presence of surface hydroxyl groups (Fe-OH). The H-MnFe₂O₄ zeta potential measurement gives positive surface charge of +10.25 mV. The positive H-MnFe₂O₄ surface charge is most likely due to the formation of [+Fe-OH₂] in an acidic environment. After H-MnFe₂O₄ stabilization with L-Cys, the zeta potential measurement showed a negative surface charge of -12.25 mV. The negative surface charge is own to the presence of a carboxyl group above its isoelectric point. Like other amino acids, L-Cys is also a zwitterionic molecule and hence its zeta potential varies with pH. The isoelectric point (pH_{ISP}) of L-Cys is 5.07.¹ Below its isoelectric point, L-Cys is positively charged on account of the presence of ammonium groups and above its isoelectric point it is negatively charged by reason of the presence of carboxyl groups. Thus, H-MnFe₂O₄-Cys had a negative zeta potential.

The schematic of the experimental setup

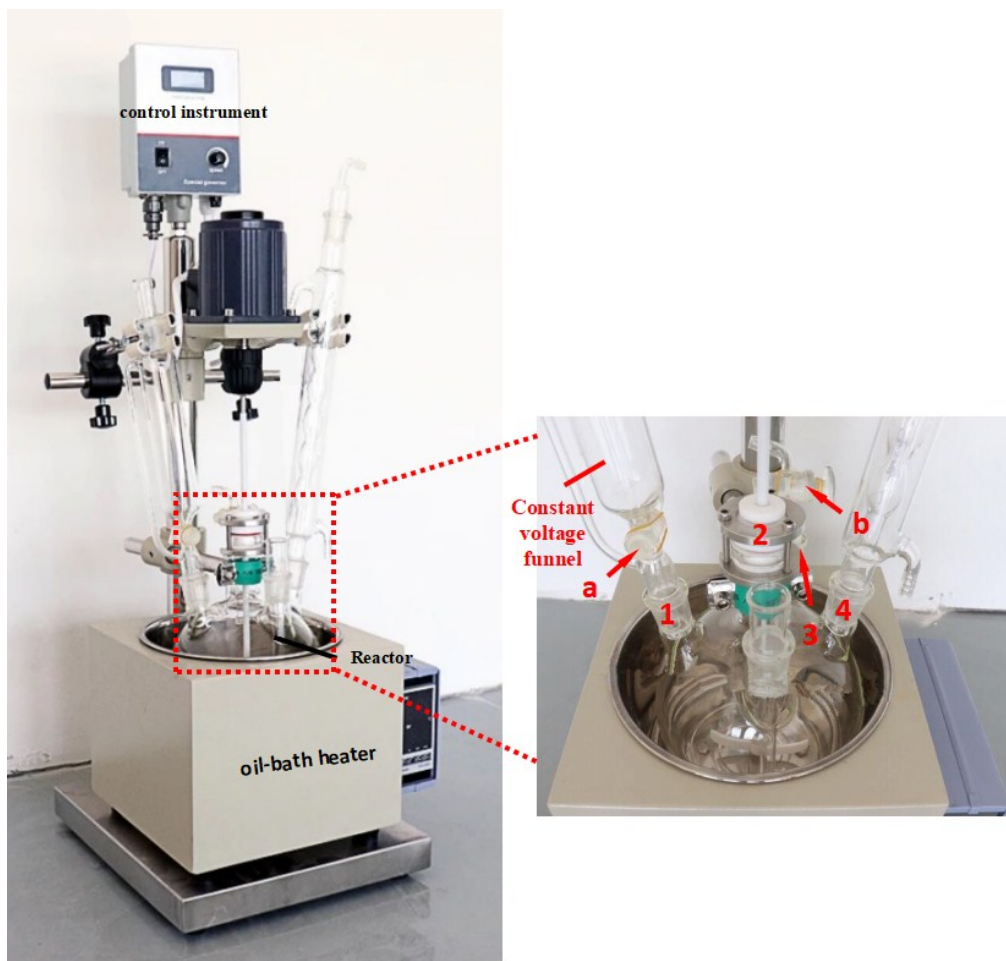


Figure S4 The schematic of the experimental setup. (a) valve of constant voltage funnel, (b) gas valve.

The schematic of the experimental setup is shown in Figure S4. The equipment consists of a liquid storage tube, a mechanical agitation with smart digital display control instrument, a smart digital display oil-bath heater, and a reactor. In detail, 0.5 g anhydrous MnFe_2O_4 , 50 mL $0.02 \text{ mol}\cdot\text{L}^{-1}$ D-galactose solution were placed in an interface morphology control device for premixing (26 h), and the reactor was magnetically stirred for 50 min at $50 \text{ r}\cdot\text{min}^{-1}$ and the reactor was purged with nitrogen 5 times (open the valve (b) to evacuate the air inside from the gas outlet with a mechanical

pump until it reached vacuum, then closed the valve (b), changed the mechanical pump with a nitrogen gas cylinder pump, opened the valve (b) and inject N_2 , the whole reaction vessel would be filled with nitrogen.). Then, the reactor was gradually heated to $60\text{ }^\circ\text{C}$, and the reaction was kept at $160\text{ }^\circ\text{C}$ for 4 h. After the reaction was finished, the autoclave was cooled to room temperature. Opening the mechanical agitation, the stirring speed was kept at $50\text{ r}\cdot\text{min}^{-1}$ for 15 h to mix the mixed acid ions and Carbon- MnFe_2O_4 nanospheres. Adjusting the valve (a) controls, the dropping process takes 15 h. Finally, the black particles were washed with distilled water followed by ethanol to remove the residual mixed acid and vacuum dried for 12 h at $40\text{ }^\circ\text{C}$.

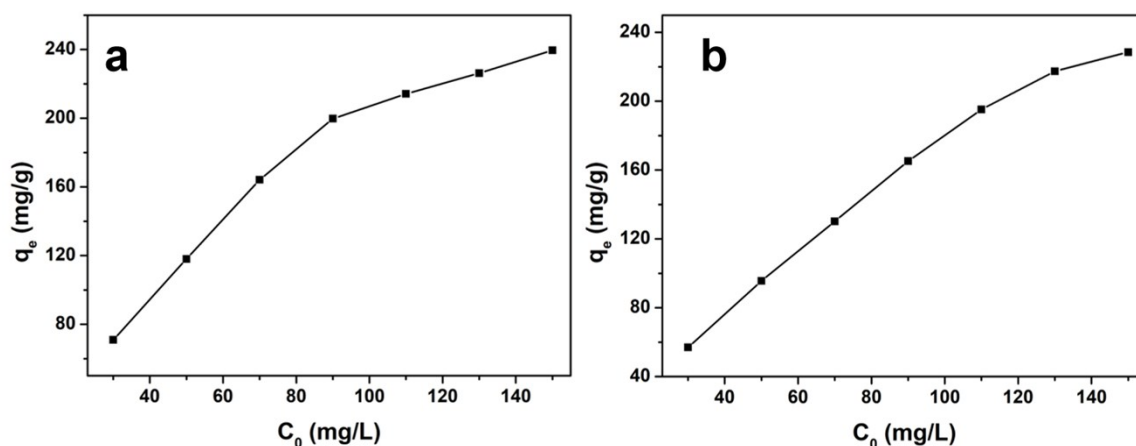


Figure S5 The effect of initial heavy metal concentration on q_e of Pb^{2+} (a) and Cr^{6+} (b) (pH=3.0 for Pb^{2+} and 5.5 for Cr^{6+} , contact time 2 h for Pb^{2+} and Cr^{6+} , $T=293\text{ K}$).

[1] Mocanu, A. Cernica, I. Tomoaia, G. Bobos, L. Horovitz, O. Tomoaia-Cotisel, M. Colloids. Surf. A Physicochem. Eng. Asp., 2009, **338**, 93-101.