

Supporting Information

Size and shape-dependent peroxidase-like catalytic activity of MnFe₂O₄ Nanoparticles and their applications in Highly efficient colorimetric detection of target cancer cell

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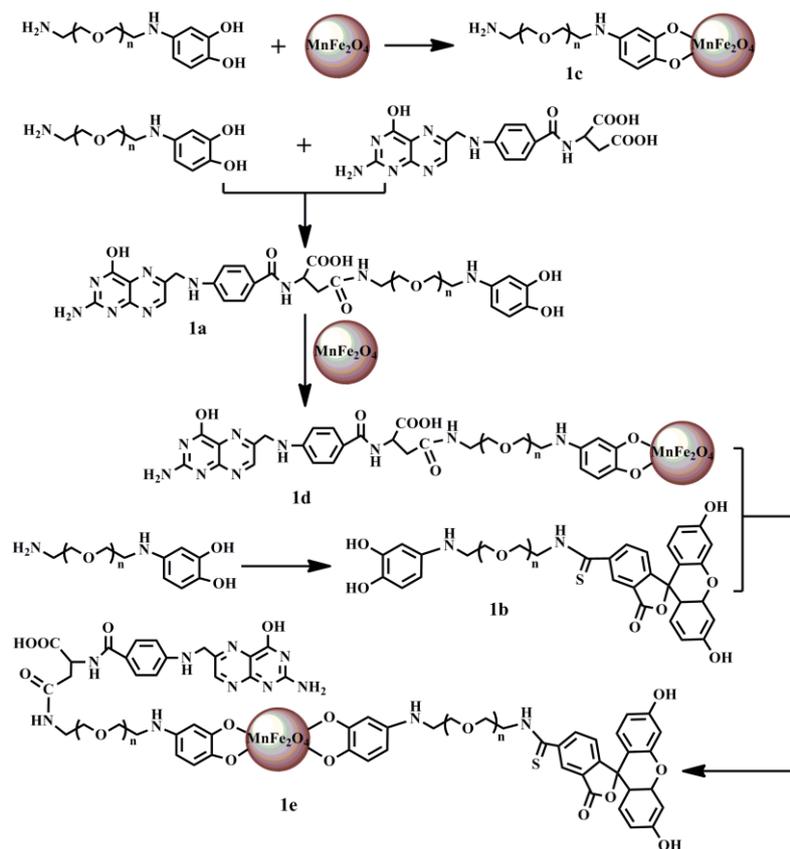
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Synthesis of 16 nm MnFe₂O₄ NPs.

4 mmol of Fe(acac)₃ and 2 mmol of Mn(acac)₂ was dissolved in 15 mL of oleic acid. The reaction mixture was dehydrated at 120 °C for 1 h under N₂ atmosphere, then quickly heated to 330 °C, and aged at this temperature for 4 h. After the reaction, the solution was allowed to cool down to room temperature. The MnFe₂O₄ NPs were precipitated upon the addition of 50 mL of isopropyl alcohol and centrifuged. In order to remove the excess oleic acid on the surface of NPs, the NPs was washed by petroleum ether and ethanol mixed solution. Finally, the product was dispersed in hexane.

Synthesis of 18 and 27 nm MnFe₂O₄ NPs.

Under identical conditions, the 18 nm MnFe₂O₄ NPs and 27 nm MnFe₂O₄ NPs were synthesised. The only difference is that 18 nm MnFe₂O₄ NPs corresponds to 2 mmol of Fe(acac)₃ and 1 mmol of Mn(acac)₂, while 27 nm MnFe₂O₄ NPs corresponds to 8 mmol of Fe(acac)₃ and 4 mmol of Mn(acac)₂. Each MnFe₂O₄ NPs were precipitated upon the addition of 50 mL of isopropyl alcohol and centrifuged. In order to remove the excess oleic acid on the surface of NPs, the NPs was washed by petroleum ether and ethanol mixed solution. Finally, the product was dispersed in hexane.



Scheme S1. Synthetic route of DIB-PEH-NH-FA (1a), DIB-PEH-NH-FITC (1b), MnFe₂O₄-DIB-PEG-NH₂ (1c), MnFe₂O₄-DIB-PEG-NH₂-FA (1d) and MnFe₂O₄-DIB-PEG-NH-FITC (1e).

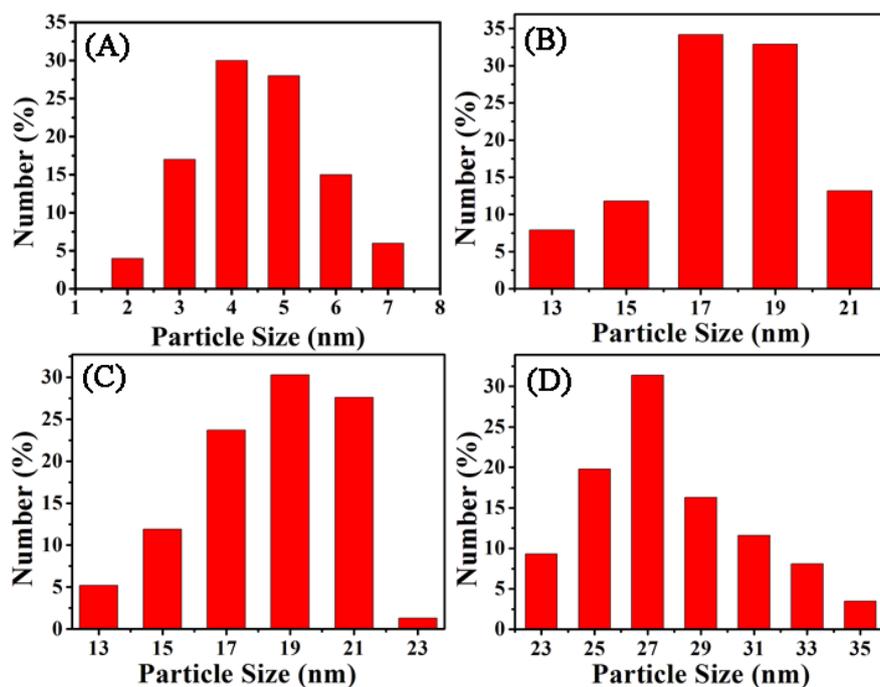


Figure S2. The size distribution histograms of as-prepared MnFe₂O₄ NPs with the different average sizes of (A) 4 nm, (B) 16 nm, (C) 18 nm, and (D) 27 nm.

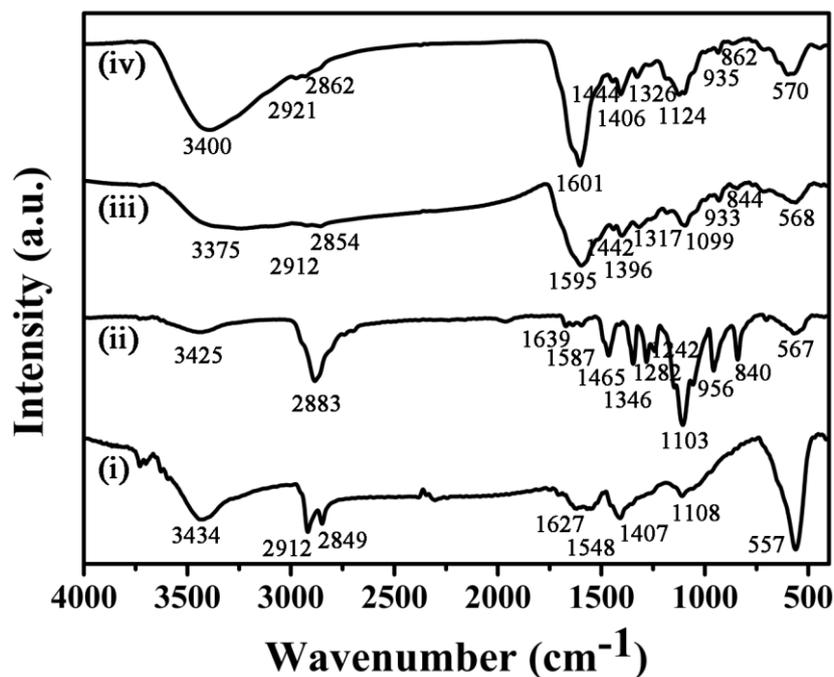


Figure S3. The IR spectra of (A) as-synthesized MnFe_2O_4 NPs, (B) MnFe_2O_4 -DIB-PEG- NH_2 (**1c**), (C) MnFe_2O_4 -DIB-PEG- NH_2 -FA(**1d**) and (D) MnFe_2O_4 -DIB-PEG-NH-FA, FITC (**1e**).

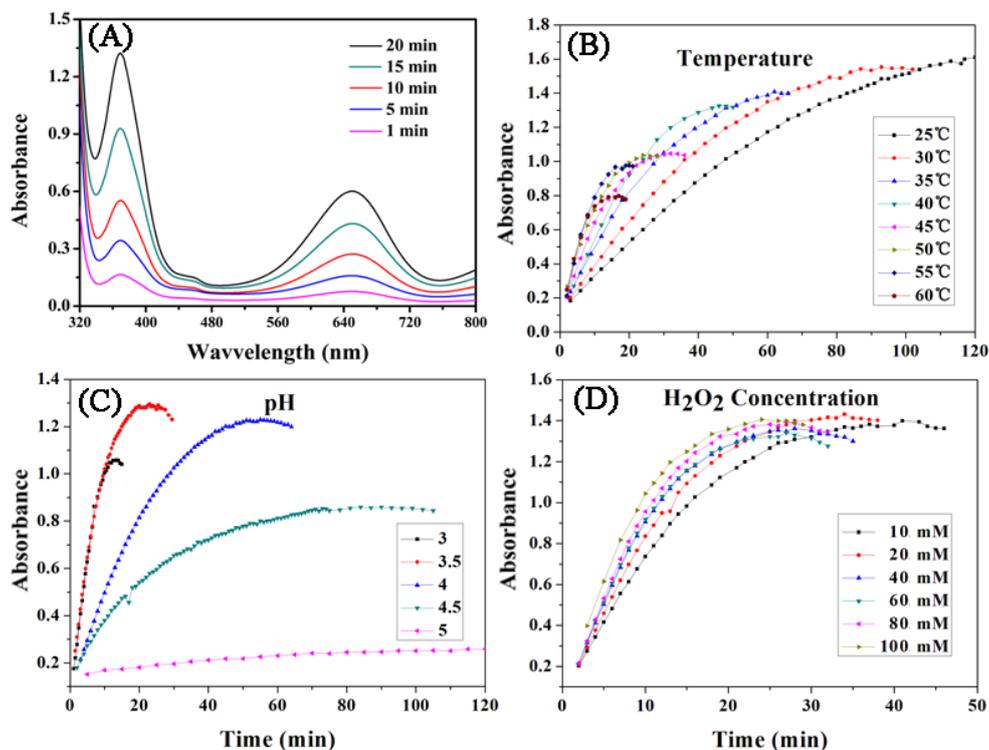


Figure S4. (A) UV absorbance curve of the HAC-NaAc solution (pH = 4.0) containing 10.0 mM H_2O_2 and 1.5 mM TMB, catalysed by the MnFe_2O_4 -DIB-PEG- NH_2 (**1c**) with different reaction time; (B) showed an optimal temperature around 40 °C, (C) optimal PH=3.5 and (D) optimal concentration of H_2O_2 was 0.10 mM.

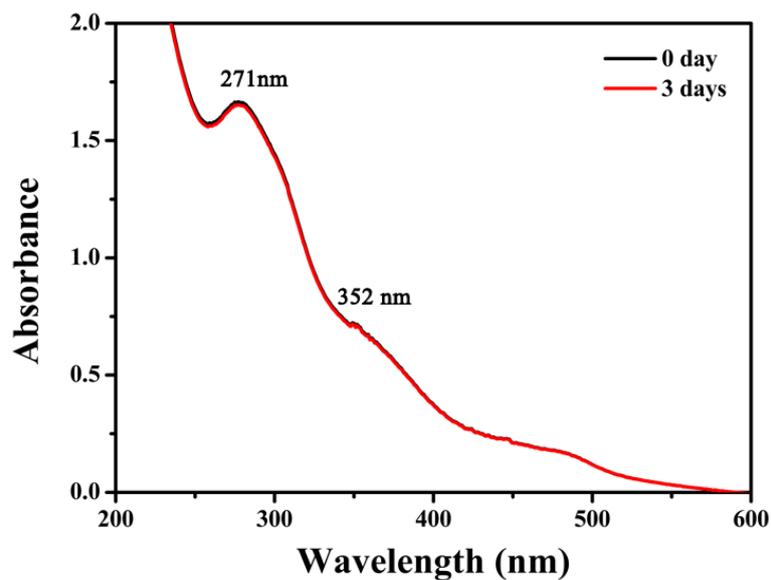


Figure S5. UV-vis spectra of 1d for 0 day (black line) and 3 days (red line). The absorption peak at 271 nm and 352 nm is attributable to FA.

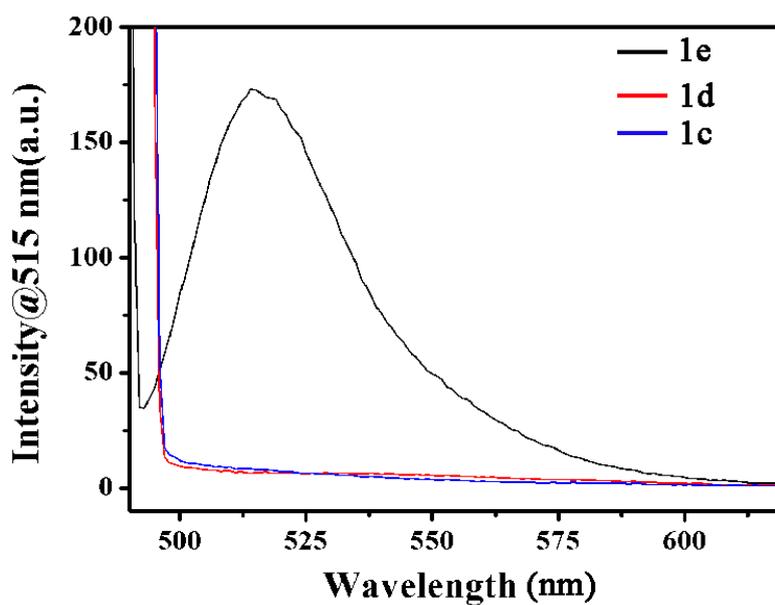


Figure S6. Fluorescence spectra of $\text{MnFe}_2\text{O}_4\text{-DIB-PEG-NH}_2$ (**1c**), $\text{MnFe}_2\text{O}_4\text{-DIB-PEG-NH}_2\text{-FA}$ (**1d**) and $\text{MnFe}_2\text{O}_4\text{-DIB-PEG-NH-FA, FITC}$ (**1e**) in aqueous solution.

Table S1. Comparison of the Kinetic Parameters of different NPs when changing the concentrations of TMB. K_m is the Michaelis constant, v_{\max} is the maximal reaction rate.

MnFe_2O_4	K_m [mM]	v_{\max} [M s^{-1}]
4 nm	1.46×10^{-3}	6.98×10^{-3}

16 nm	9.64×10^{-2}	3.53×10^{-4}
18 nm	2.58×10^{-2}	1.55×10^{-3}
27 nm	3.30×10^{-2}	7.30×10^{-4}

Table S2. Comparison of the Kinetic Parameters of different NPs when changing the concentrations of H_2O_2 (TMB as a substrate). K_m is the Michaelis constant, v_{max} is the maximal reaction rate.

MnFe ₂ O ₄	K_m [mM]	v_{max} [M s ⁻¹]
4 nm	0.112	7.15×10^{-3}
16 nm	0.543	5.15×10^{-4}
18 nm	0.242	4.94×10^{-3}
27 nm	0.304	1.76×10^{-3}

Table S3. Comparison of the Kinetic Parameters of Fe₃O₄ (4 nm), dumbbell Au-Fe₃O₄ and MnFe₂O₄ (4 nm) when changing the concentrations of TMB (TMB as a substrate). K_m is the Michaelis constant.

Nanoparticles	K_m [mM]
Fe ₃ O ₄	0.062
dumbbell Au-Fe ₃ O ₄	0.021
MnFe ₂ O ₄	0.00146