Manganese Doped Iron Coordination Polymer Nanoparticles with Enhanced Peroxidase-like Activity for Colorimetric Detection of Antioxidants

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1. Materials and reagents

Ferrous(II) chloride ($FeCl_2$), manganese(II) chloride ($MnCl_2$), o-phenylenediamine (OPD), 3,3′,5,5′-tetramethylbenzidine (TMB), cysteine (Cys), L-proline (Pro), L-serine (Ser), L-phenylalaine (Phe), Glycine (Gly), L-arginine (Arg), L-histidine (His), and ascorbic acid (AA) were purchased from Sigma-Aldrich (USA). Glutathione (GSH), 2,5-dihydroxyterephthalic acid (H_4DHTA), 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid ammonium salt) (ABTS) were supplied by Aladdin Industrial Corporation (Shanghai, China). N, N-Dimethylformamide (DMF), ethanol (EtOH), $CaCl_2 \cdot 2H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, KCl, glucose, maltose, fructose, lactose, sucrose, H_2O_2, acetic acid and sodium acetate were obtained from Sinopharm Chemical Reagent Co., Ltd.

2.2 Material Characterization

The Fourier transform infrared (FTIR) absorption spectra were collected in the range of 400–4000 cm^{-1} on a Nicolet Impact 410 FTIR spectrometer with KBr pellet. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D-Max 2550 diffractometer using Cu-Kα radiation (λ = 0.15418 nm). The ratio of metal ions was determined by an iCAP 7600 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) analyzer. UV-vis absorption spectra were carried out on a UV-8000 spectrophotometer (Metash, China). Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) images and scanning transmission electron microscope (STEM-EDS) elemental mapping were conducted on a JEOL JEM-2100F at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) recorded on a Thermo ESCALAB 250XI photoelectron spectrometer equipped with a monochromatic Al-Kα radiation.

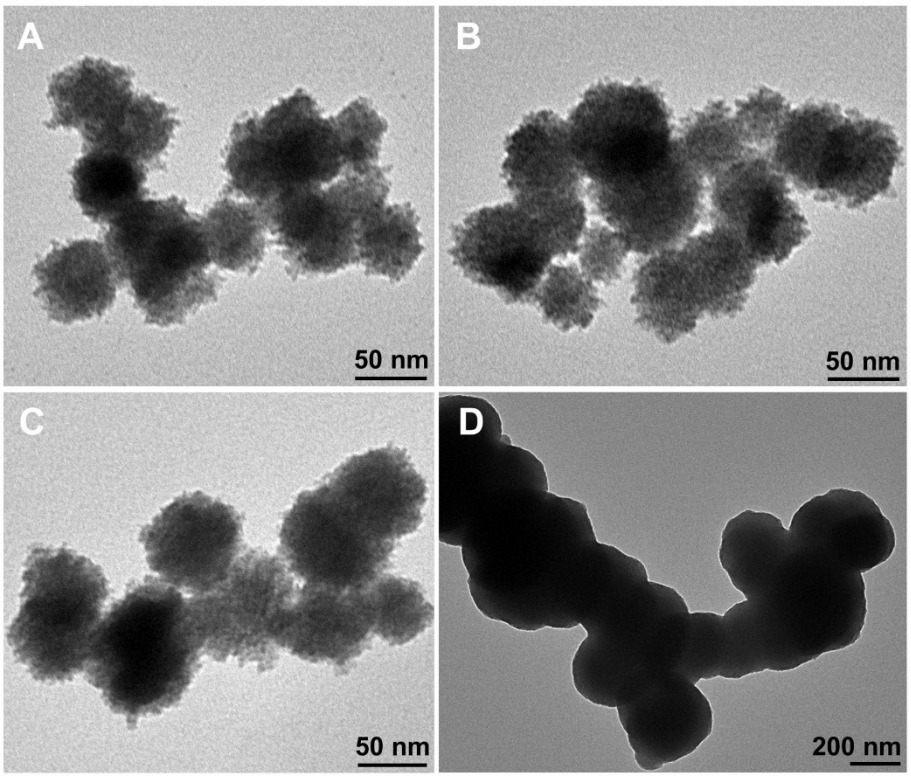

Fig. S1 TEM images of (A) Fe-DHTP, (B) Fe_2Mn-DHTP, (C) Fe_8Mn-DHTP and (D) Mn-DHTP.

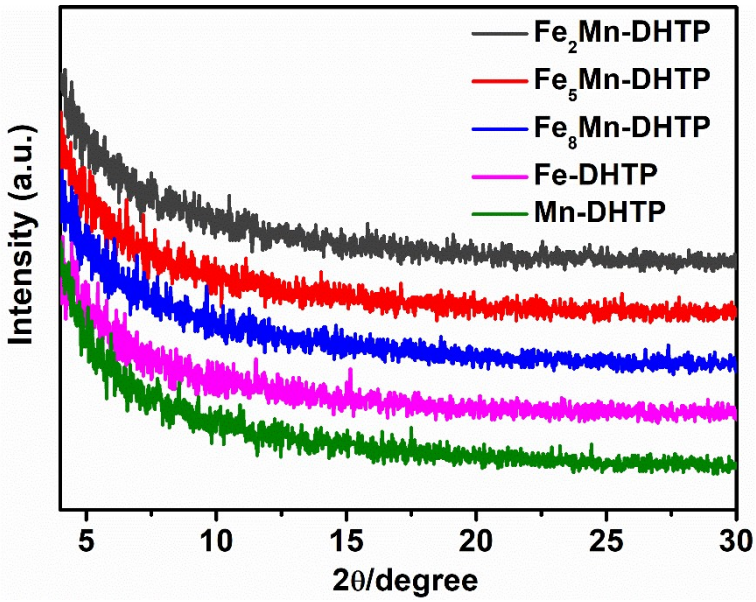

Fig. S2 PXRD patterns of Fe_2Mn-DHTP, Fe_5Mn-DHTP, Fe_8Mn-DHTP, Fe-DHTP and Mn-DHTP.

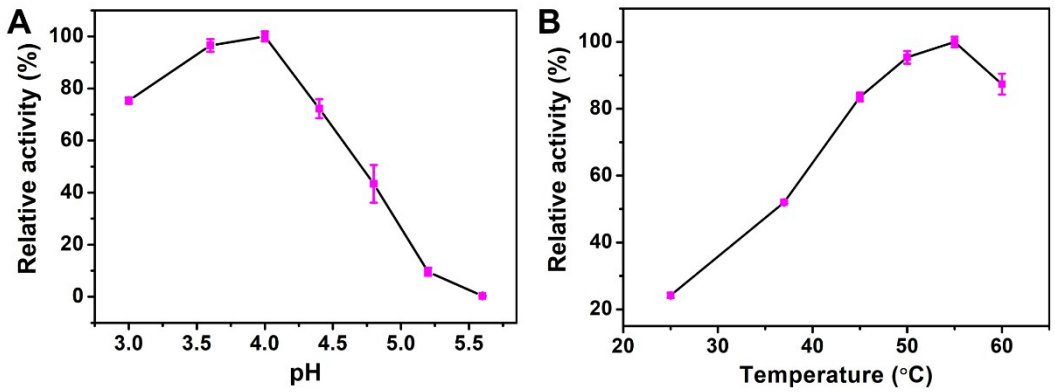

Fig. S3 Relative activity of Fe_5Mn-DHTP as a function of (A) buffer pH and (B) temperature.

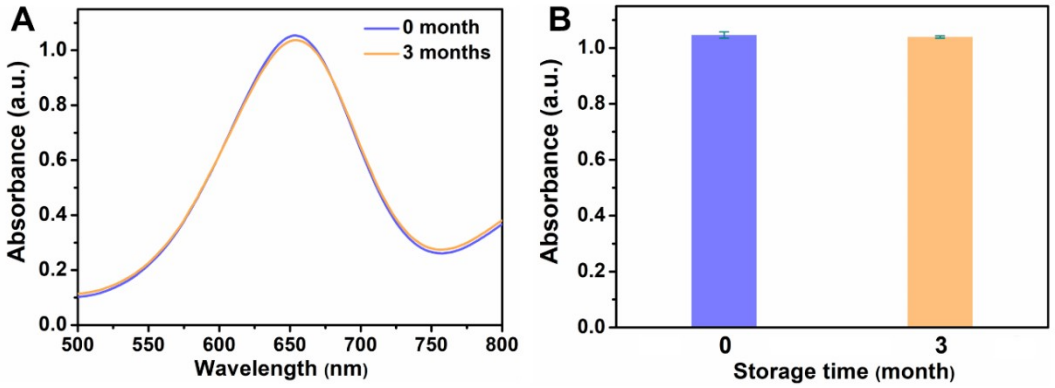

Fig. S4 The storage stability of Fe_5Mn-DHTP.

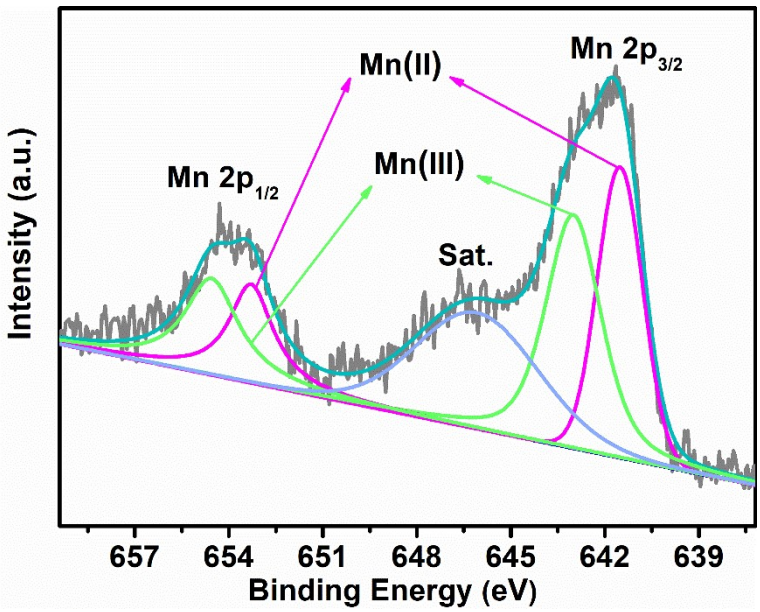

Fig. S5 High resolution XPS spectra of Mn 2p of Fe_5Mn-DHTP.

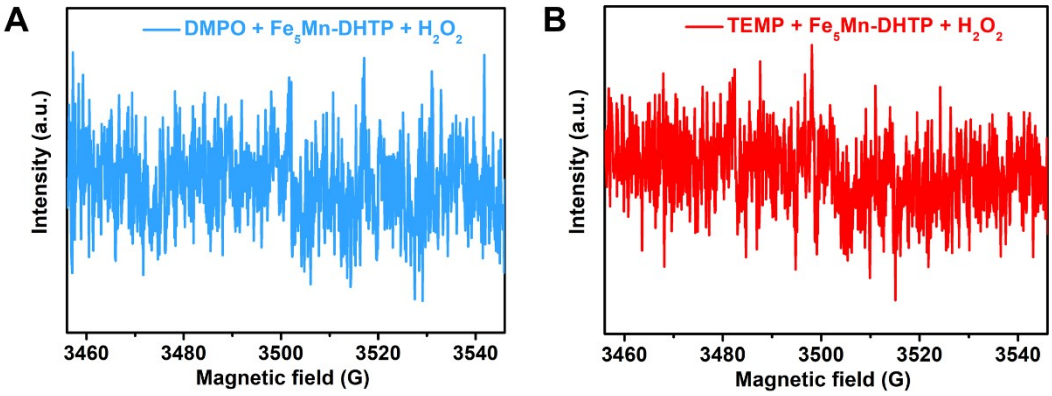

Fig. S6 The EPR spectra of (a) Fe_5Mn-DHTP methanol suspension and (b) Fe_5Mn-DHTP aqueous suspension.

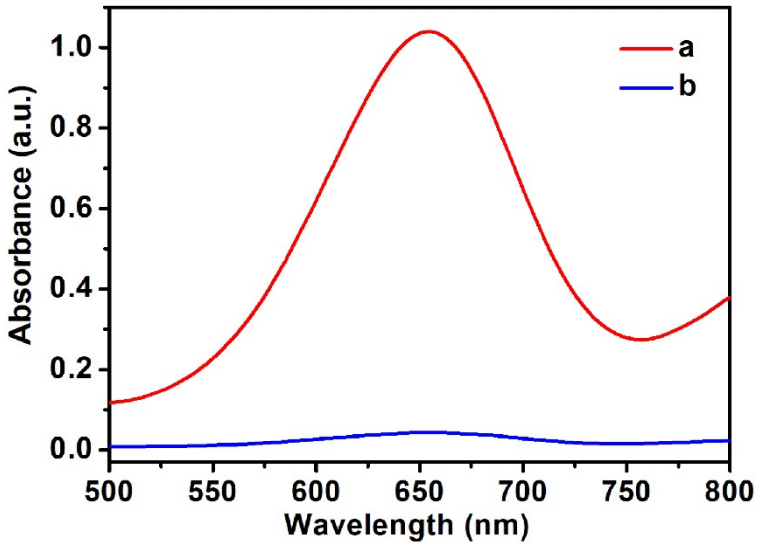

Fig. S7 UV-vis spectra of H_2O_2 + TMB solutions in presence of (a) fresh Fe_5Mn-DHTP and (b) recycled Fe_5Mn-DHTP after treated with Cys.

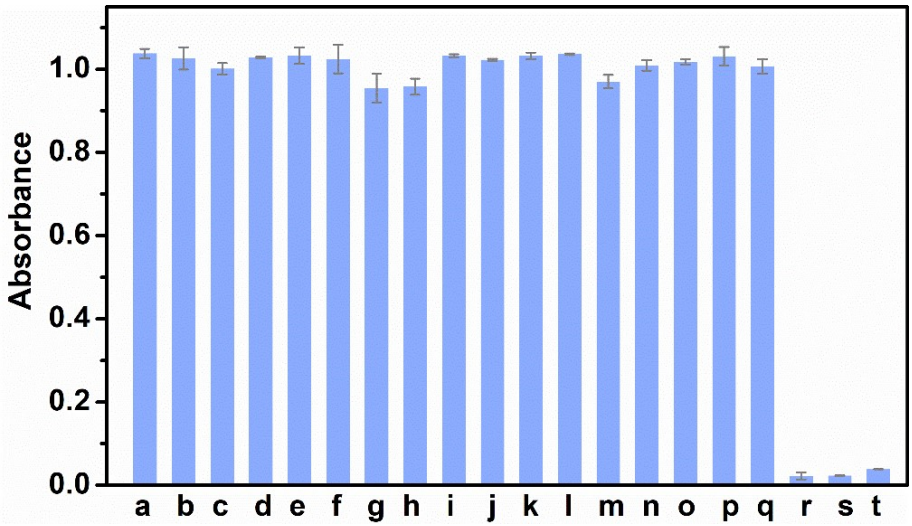

Fig. S8 Specificity of this antioxidant assay toward different interference (a. blank, b. glucose, c. lactose, d. sucrose, e. fructose, f. maltose, g. His, h. Arg, i. Phe, g. Ser, k. Pro, l. Gly, m. Zn^{2+}, n. Ca^{2+}, o. Mg^{2+}, p. K^+ and q. Na^+, r. AA, s. Cys, t. GSH). The concentration for interference and AA was 140 μM, for Cys and GSH was 60 μM.

Table S1. Comparison of the kinetic constants of different nanozymes.

Catalyst	Substrate	K_m (mM)	V_{max} (M s^{-1})	Reference
HRP	TMB	0.434	1×10^{-7}	1
	H_2O_2	3.7	8.71×10^{-8}	
$ZnFe_2O_4$ MNPs	TMB	0.85	1.33×10^{-7}	2
	H_2O_2	1.66	7.74×10^{-8}	
Fe_3O_4 MNPs	TMB	0.098	3.44×10^{-8}	1
	H_2O_2	154	9.78×10^{-8}	
Fe-N-C	TMB	3.6	1.16×10^{-8}	3
	H_2O_2	12.2	3.61×10^{-8}	
$Fe_{0.5}$-N-C	TMB	0.82	1.07×10^{-5}	4
	H_2O_2	20.53	6.17×10^{-6}	
Fe-MSN	TMB	0.407	7.6×10^{-8}	5
	H2O2	0.01	4.33×10^{-8}	
FePPOP-1	TMB	0.064	1.94×10^{-8}	6
	H_2O_2	13.33	2.12×10^{-8}	
Fe-MOF	TMB	2.6	5.6×10^{-8}	7
	H_2O_2	1.3	2.5×10^{-8}	
FeO_x@SHSs-0.05	TMB	0.076	8.59×10^{-8}	8
	H_2O_2	0.154	8.31×10^{-8}	
Mn-DHTP	TMB	0.082	8.92×10^{-9}	This work
	H_2O_2	1.09	2.19×10^{-9}	
Fe-DHTP	TMB	0.051	2.88×10^{-8}	
	H_2O_2	0.88	2.43×10^{-8}	
Fe_5Mn-DHTP	TMB	0.022	6.42×10^{-8}	
	H_2O_2	0.71	4.39×10^{-8}	

Table S2. Comparison of different colorimetric assays for antioxidant.

Materials	Antioxidant	Linear range (μM)	LOD (μM)	Reference
PANi-MnO_2-Pd NWs	AA	0.5−5.0	0.034	9
MIL-68	AA	30-485	6	10
IrO_2/GO	AA	5−70	0.324	11
Co-POP	AA	20–400	1.6	12
AuNCs	AA	0.5−200	0.22	13
Fe_5Mn-DHTP	AA	5−120	1.47	This work
N-MoS_2 NFS	Cys	0−4000	0.68	14
MoS_2-Au@Pt	Cys	0.8–54.4	0.5	15
$NiMo_6$@Co_3O_4	Cys	1–20	0.018	16
MoS_2@$CoFe_2O_4$	Cys	0.5−15	0.1	17
FeOCl	Cys	3–33	2.76	18
Fe_5Mn-DHTP	Cys	1−26	0.33	This work
Co-POP	GSH	5–90 90–300	0.71	12
ZIF-67	GSH	0.1–25	0.07	19
MnO_2/CDs	GSH	0.1−10	0.095	20
Ir/NC	GSH	0.05−15	0.5	21
MnO_2 nanosheets	GSH	1.0−20 20−80	0.94	22
Fe_5Mn-DHTP	GSH	1−40	0.51	This work

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