Electronic Supplementary Information

Iron oxide nanozyme catalyzed synthesis of fluorescent polydopamine for light-up Zn²⁺ detection

Biwu Liu, Xiao Han, and Juewen Liu*

Department of Chemistry, Waterloo Institute for Nanotechnology,

University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.

Email: liujw@uwaterloo.ca



Figure S1. Characterization of Fe₃O₄ NPs used in this work by TEM. The scale bar is 100 nm.



Figure S2. Fluorescence emission spectra of FPD under various excitation wavelengths. FPD prepared from 0.5 mM dopamine in acetate buffer (pH 4, 50 mM) was used for measurement without dilution.



Figure S3. TEM micrographs of the synthesized FPD. The scale bar is 20 nm.



Figure S4. Quantum yield measurement of our prepared FPD. Calibration curves of integrated fluorescence intensity against the absorbance at 480 nm for (A) fluorescein, and (B) our sample. The quantum yield is calculated based on the following equation:

$$\Phi_X = \Phi_{ST} \times \frac{Slope_X}{Slope_{ST}} \times \frac{{\eta_X}^2}{{\eta_{ST}}^2}$$

Where the subscripts ST and X denote the standard and our sample, respectively,

 Φ is quantum yield, which is 0.79 for fluorescein in 0.1 M NaOH,^{S1}

Slope is the slope of the calibration curves in Figure S4, 27333 for fluorescein, and 308 for our sample.

 η is the refractive index of the solvent, 1.33 for 0.1 M NaOH, and 1.34 for 0.05 mM pH 4 acetate buffer.

Finally the quantum yield of our FPD is determined to be 1.0%.



Figure S5. Effect of using Fe₂O₃ NPs on the dopamine oxidation by H₂O₂. Top: image in ambient visible light, bottom: fluorescence image under a 470 nm LED lamp excitation. Dopamine (0.5 mM) was incubated with H₂O₂ (5 mM) in the presence of Fe₂O₃ NPs for 2 hours. The supernatant was collected for imaging.



Figure S6. The UV-vis spectra of dopamine after the oxidation reactions (if any) catalyzed by different nanomaterials in the (A) absence and (B) presence of H_2O_2 . The reaction was carried out at pH 4 (acetate buffer, 50 mM). The concentration of metal oxides was 500 μ g/mL, AuNPs 5 nM, and GO 200 μ g/mL.



Figure S7. Fluorescent spectra of oxidized dopamine at (A) pH 4 (acetate buffer), (B) pH 5 (acetate buffer), (C) pH 6 (MES buffer), (D) pH 7 (HEPES buffer), (E) pH 8 (HEPES buffer), and (F) pH 8.5 (Tris buffer). The concentration of each buffer was 50 mM.



Figure S8. UV-vis absorption spectra of oxidized dopamine prepared at different salt concentrations. The presence of NaCl (50 mM or higher) enhanced the oxidation of dopamine as indicated by the increased absorbance peak at 450 nm. The addition of divalent Mg^{2+} (5 mM) did not induce any further increase.



Figure S9. ζ -potential of Fe₃O₄ NPs (50 µg/mL) at pH 4.0 (acetate buffer, 20 mM) and 7.6 (HEPES buffer, 20 mM).



Figure S10. The stability of FPD at different (A) pH, (B) ionic strength, and (C) divalent metal ions. Typically, 50 μ L of the prepared FPD in acetate buffer (10 mM, PH 4) was added into 50 μ L of buffer solutions (100 mM) with designed pH values. The fluorescence spectra were measured after overnight incubation. The divalent metal ions were 1 mM.



Figure S11. The calibration curve of Zn^{2+} in diluted serum (1%). The error bars represent the standard deviations from three independent measurements.

Additional reference

S1. J. Q. Umberger and V. K. LaMer, J. Am. Chem. Soc., 1945, 67, 1099-1109.