Electronic Supplementary Information (ESI)

Facilely prepared $\text{Fe}_3\text{O}_4$/nitrogen-doped graphene quantum dot hybrid as a robust nonenzymatic catalyst for visual discrimination of phenylenediamine isomers†

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1. Supplementary Figures

**Fig. S1** UV-vis spectra of the as-synthesized N-GQDs and Fe$_3$O$_4$/N-GQDs (a) and XPS spectra of N-GQDs (b). The concentrations of N-GQDs and Fe$_3$O$_4$/N-GQDs were 0.054 mg/mL and 0.018 mg/mL, respectively. Inset of figure S1a: the photograph of N-GQDs (left) and Fe$_3$O$_4$/N-GQDs (right). The concentrations of N-GQDs and Fe$_3$O$_4$/N-GQDs were 5.4 mg/mL and 5.3 mg/mL, respectively.

**Fig. S2** XRD patterns of N-GQDs (a) and Fe$_3$O$_4$/N-GQDs (b).
Fig. S3 XPS analysis of Fe$_3$O$_4$/N-GQDs and Fe2p prepared at different conditions. The concentrations of N-GQDs and NaOH were 12.2 mg/mL and 1 M, respectively. The concentrations of Fe$^{3+}$ were 0.15 M (a,b), 0.5 M (c,d) and 0.6 M (e,f).
**Fig. S4** Energy-dispersive spectrum (EDS) of the Fe$_3$O$_4$/N-GQDs. Note that the strong signal at 8.1 and 8.9 eV assigned to Cu originates from the copper TEM grid.

**Fig. S5.** Room-temperature magnetization curves of the Fe$_3$O$_4$/N-GQDs.
**Fig. S6** C1s XPS spectra of N-GQDs (a) and Fe$_3$O$_4$/N-GQDs (b); N1s XPS spectra of N-GQDs (c) and Fe$_3$O$_4$/N-GQDs (d).
Fig. S7 UV-vis spectra of the Fe$_3$O$_4$/N-GQDs-catalyzed oxidation of ABTS (a) and TMB (b) in 70 μL of 250 mM HAc-NaAc buffer (pH 6.5) at room temperature. The concentrations of Fe$_3$O$_4$/N-GQDs, H$_2$O$_2$, ABTS were 0.454 mg/mL, 100 mM, and 2 mM respectively. (Inset: the colors of final solutions in the absence (left) and presence (right) of Fe$_3$O$_4$/N-GQDs, respectively)
Fig. S8 Relative catalytic activity of Fe$_3$O$_4$/N-GQDs after the treatment by different pH (a) and temperature (b) for 2 h. Experiments were carried out as following: fist, Fe$_3$O$_4$/N-GQDs were incubation at different pH (2.0-12.0) and temperature (10-90 °C) for 2 h, respectively. The obtained mixtures were centrifuged at 12 000 rpm for 10 min. The treated Fe$_3$O$_4$/N-GQDs were dissolved in 40 μL ultrapure water (The final concentration of treated Fe$_3$O$_4$/N-GQDs is 0.454 mg/mL). 10 μL diluted Fe$_3$O$_4$/N-GQDs, 70 μL HAc-NaAc buffer (250 mM, pH 6.5) and 10 μL of 5 mM H$_2$O$_2$ were mixed together. After that, the above mixture were incubated at room temperature for 5 min in the present of 10 μL TMB (10 mM). The absorbance was read at 652 nm.
The peroxidase-like activity of Fe$_3$O$_4$/N-GQDs treated with 2% NaBH$_4$, 2% NaIO$_4$ or H$_2$O under standard conditions at 420 nm using ABTS and H$_2$O$_2$ as substrates.
Fig. S10 Steady-state kinetic assay and catalytic mechanism of Fe$_3$O$_4$/N-GQDs. Experiments were conducted by 10 μL diluted Fe$_3$O$_4$/N-GQDs (0.454 mg/mL), 70 μL HAc-NaAc buffer (250 mM, pH 6.5) at room temperature. (a) The concentration of TMB was 32 μM and H$_2$O$_2$ concentration was varied. (b) The concentration of H$_2$O$_2$ was 0.1 mM and TMB concentration was varied. (c,d) Double reciprocal plots of activity of Fe$_3$O$_4$/N-GQDs with the concentration of one substrate (H$_2$O$_2$ or TMB) fixed and the other varied.
**Fig. S11** Images of oxidation color reaction of OPD (left), MPD (middle), and PPD (right) by H$_2$O$_2$ based on the catalysis of Fe$_3$O$_4$/N-GQDs at room temperature for 20 min. Control experiments were carried out at room temperature for 20 min as follows: (a) 70 μL HAc-NaAc buffer (250 mM, pH 6.5) + 10 μL H$_2$O$_2$ (5 mM) + 10 μL Fe$_3$O$_4$/N-GQDs (0.454 mg/mL) + 10 μL analyte (1 mM); (b) 70 μL HAc-NaAc buffer (250 mM, pH 6.5) + 10 μL Fe$_3$O$_4$/N-GQDs (0.454 mg/mL) + 10 μL analyte (1 mM) + 10 μL H$_2$O; (c) 70 μL HAc-NaAc buffer (250 mM, pH 6.5) + 10 μL H$_2$O$_2$ (5 mM) + 10 μL analyte (1 mM) + 10 μL H$_2$O; (d) 70 μL HAc-NaAc buffer (250 mM, pH 6.5) + 10 μL analyte (1 mM) + 20 μL H$_2$O.
Fig. S12 UV–vis absorption spectra of the reaction mixture under different conditions. Experiments were carried out at room temperature for 20 min, and the concentrations of Fe$_3$O$_4$/N-GQDs, N-GQDs, H$_2$O$_2$, OPD, MPD, and PPD were 0.454 mg/mL, 12.2 mg/mL, 5 mM, 100 μM, 100 μM, and 100 μM, respectively.
Fig. S13 Comparison of the catalytic ability of Fe$_3$O$_4$ and Fe$_3$O$_4$/N-GQDs. The concentrations of Fe$_3$O$_4$, Fe$_3$O$_4$/N-GQDs, H$_2$O$_2$, OPD, MPD, and PPD were 0.454 mg/mL, 0.454 mg/mL, 5 mM, 100 μM, 100 μM, and 100 μM, respectively.
Fig. S14 UV−vis absorption spectra of the reaction mixture in the presence of Fe$_3$O$_4$/N-GQDs and leached Fe$^{3+}$ from Fe$_3$O$_4$/N-GQDs. Fe$_3$O$_4$/N-GQDs were incubated in HAc-NaAc buffer (pH 6.5) for 2 h and then removed from solution. The obtained solution was used to evaluate the catalytic ability of Fe$^{3+}$ leaching from Fe$_3$O$_4$/N-GQDs. The concentrations of H$_2$O$_2$, OPD, MPD, and PPD were 5 mM, 100 μM, 100 μM and 100 μM, respectively.
Fig. S15 Effect of pH (a), temperature (b), concentration of H$_2$O$_2$ (c), doge of Fe$_3$O$_4$/N-GQDs (d), and reaction time (e) on the analysis of OPD and PPD in the presence of Fe$_3$O$_4$/N-GQDs.
Experiments were conducted using 10 μL Fe₃O₄/N-GQDs in 70 μL HAc-NaAc buffer (250 mM, pH 6.5) with 10 μL of 5 mM H₂O₂. Then, 10 μL of 70 μM analyte solution are added to the obtained mixture, and incubated at room temperature for 20 min (ΔA = Aₘₐₓ - A₀, where A₀ is the absorbance of the sensing system in the absence of OPD and PPD, and Aₘₐₓ is the max absorbance in the presence of OPD and PPD).

**Fig. S16** UV−vis absorption spectra of the Fe₃O₄/N-GQDs-H₂O₂ system in the presence of toluene-2,4-diamine (TDM). Experiments were carried out at room temperature for 20 min, and the concentrations of Fe₃O₄/N-GQDs, H₂O₂, and TDM were 0.454 mg/mL, 5 mM, and 200 μM, respectively.
2. Supplementary Tables

Table S1 Comparison of analytical methods for OPD and PPD detection

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<th>Methods</th>
<th>Detection range (μM)</th>
<th>Sensitivity (μM)</th>
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References


