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A simple and facile strategy based on Fenton-induced DNA cleavage for fluorescent turn-on detection of hydroxyl radicals and Fe^{2+}

Wei Tao Huang, Wan Yi Xie, Yan Shi, Hong Qun Luo*, and Nian Bing Li*

Key Laboratory of Eco-environments in Three Gorges Reservoir Region (Ministry of Education), School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, P.R. China

1. Preparation of P1-GO Bioconjugate

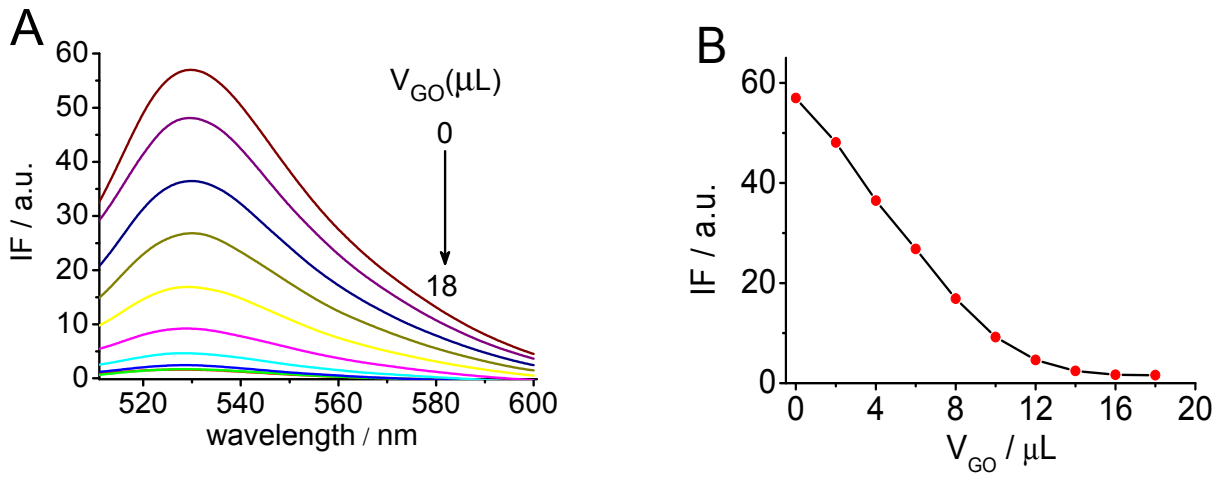

Figure S1. (A) Fluorescence emission spectra recorded during the process of titration of P1 aqueous solution (50 nM) with various volumes of 0.844 mg/mL GO dispersion. (B) Fluorescence quenching of P1 as a function of volumes of GO dispersion (V_{GO}). Excitation wavelength: 480 nm; emission wavelength: 530 nm. Buffer: 10 mM HEPES, 0.2 M NaAc, pH = 7.4.

2. Discrimination of Fe^{2+} and Fe^{3+} Based on the Fenton-DNA Cleavage Switch

Though many fluorescence probes for transition metal ions have been extensively studied, very little information on the interaction between different chemical species of an element (for example, Fe^{2+} and Fe^{3+}) is available. As shown in Figure S2, Fe^{2+} in the presence of H_2O_2 induced significant fluorescence enhancement of P1-GO because Fe^{2+} can efficiently catalyze the formation of HO• from H_2O_2 via the Fenton reaction, resulting in dye-labeled P1 fragments releasing from GO surface, whereas no such effects were observed when Fe^{3+} was used to replace Fe^{2+}.

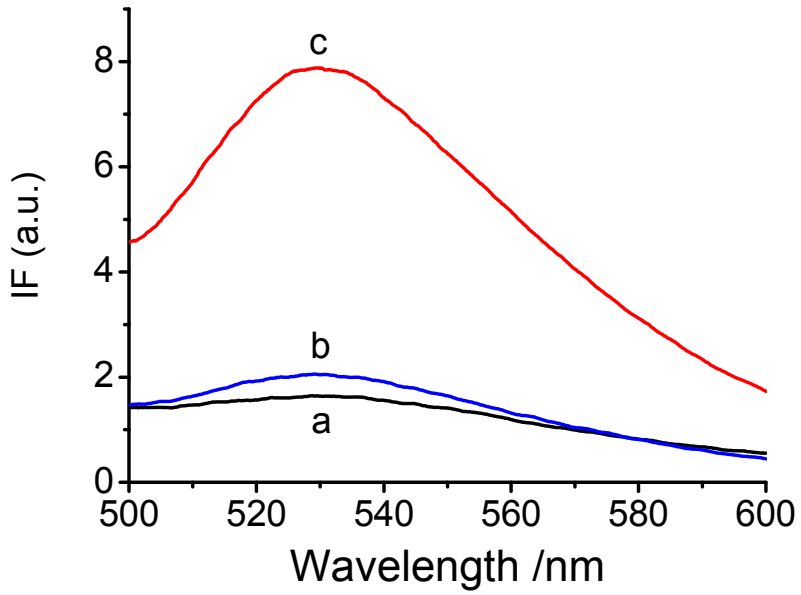

Figure S2. Fluorescence emission spectra of P1 (50 nM) at different conditions: (a) P1 + GO; buffer: 10 mM HEPES, 0.2 M NaAc, pH = 7.4; (b) P1 + GO + Fe^{3+}-EDTA (50 μM) + H_2O_2 (300 μM); (c) P1 + GO + Fe^{2+}-EDTA (50 μM) + H_2O_2 (300 μM).

3. Preparation of the Fluorescein Dyes-GO Complexes and the Fluorescence Response of the Fluorescein Dyes-GO Complexes to HO•

To further confirm that the increase in fluorescence emission was indeed attributed to the HO•-induced breakdown of DNA chains, we also prepared the fluorescein dyes-GO complexes for the control experiment. Due to π-stacking interactions of the fluorescein dye with the aromatic regions of the graphene,[1] the fluorescein dye was titrated with GO (0.844 mg/mL), resulting in fluorescence quenching of the fluorescein dye (see Figure S3 A and B). Upon addition of the Fenton reagent, there was no obvious fluorescence enhancement of the fluorescein dyes-GO complexes (see Figure S3 C). Thus, we conclude that the occurrence of HO•-induced DNA chain scission results in the restoration of fluorescence.

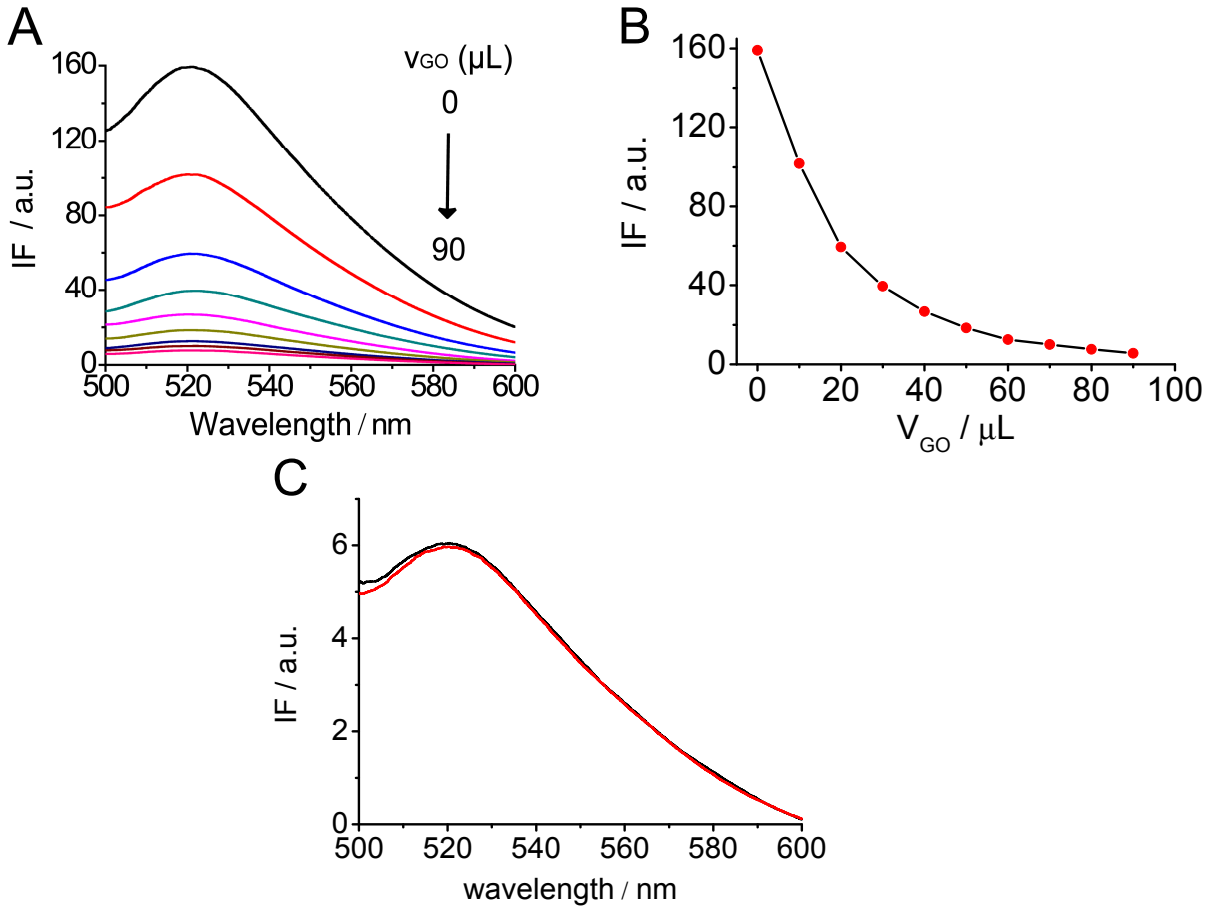

Figure S3. (A) Fluorescence emission spectra recorded during the process of titration of the fluorescein dyes aqueous solution (100 nM) with various volumes of 0.844 mg/mL GO dispersion. (B) Fluorescence quenching of the fluorescein dyes as a function of volumes of GO dispersion (V_{GO}). (C) Fluorescence emission spectra of the fluorescein dyes-GO in the absence (black line) and presence (red line) of HO•, respectively. Excitation wavelength: 480 nm; emission wavelength: 520 nm. Buffer: 10 mM HEPES, 0.2 M NaAc, pH = 7.4.

4. The Effect of pH on the Fluorescence Intensities of the FAM-Labeled P1 in the Absence and Presence of GO and the Kinetic Behavior of the Reaction

The kinetic behaviors of reactions between P1 and GO (in step a in Scheme 1, in the manuscript), as well as between the P1-GO complex and Fenton reagent (in step b in Scheme 1, in the manuscript), were studied by monitoring the fluorescence intensity as a function of time. In the present experiment, 400 μL of the resulting P1-GO bioconjugate solution (containing: 48 nM P1, 32.5 μg/mL GO, 10 mM HEPES, 0.2 M NaAc, pH = 7.4) was transferred to a quartz cuvette. To generate hydroxyl radicals, the simultaneous addition of Fe^{2+}-EDTA and H_2O_2 (Fe^{2+}-EDTA/H_2O_2 1:6 mol mol^{-1}) was limited to 5 μL so that the volume change was insignificant. Then the fluorescence intensity of the mixture solution (about 410 μL) was recorded every 5 min for a total time of 60 min at 25 °C to observe their restoration kinetics.

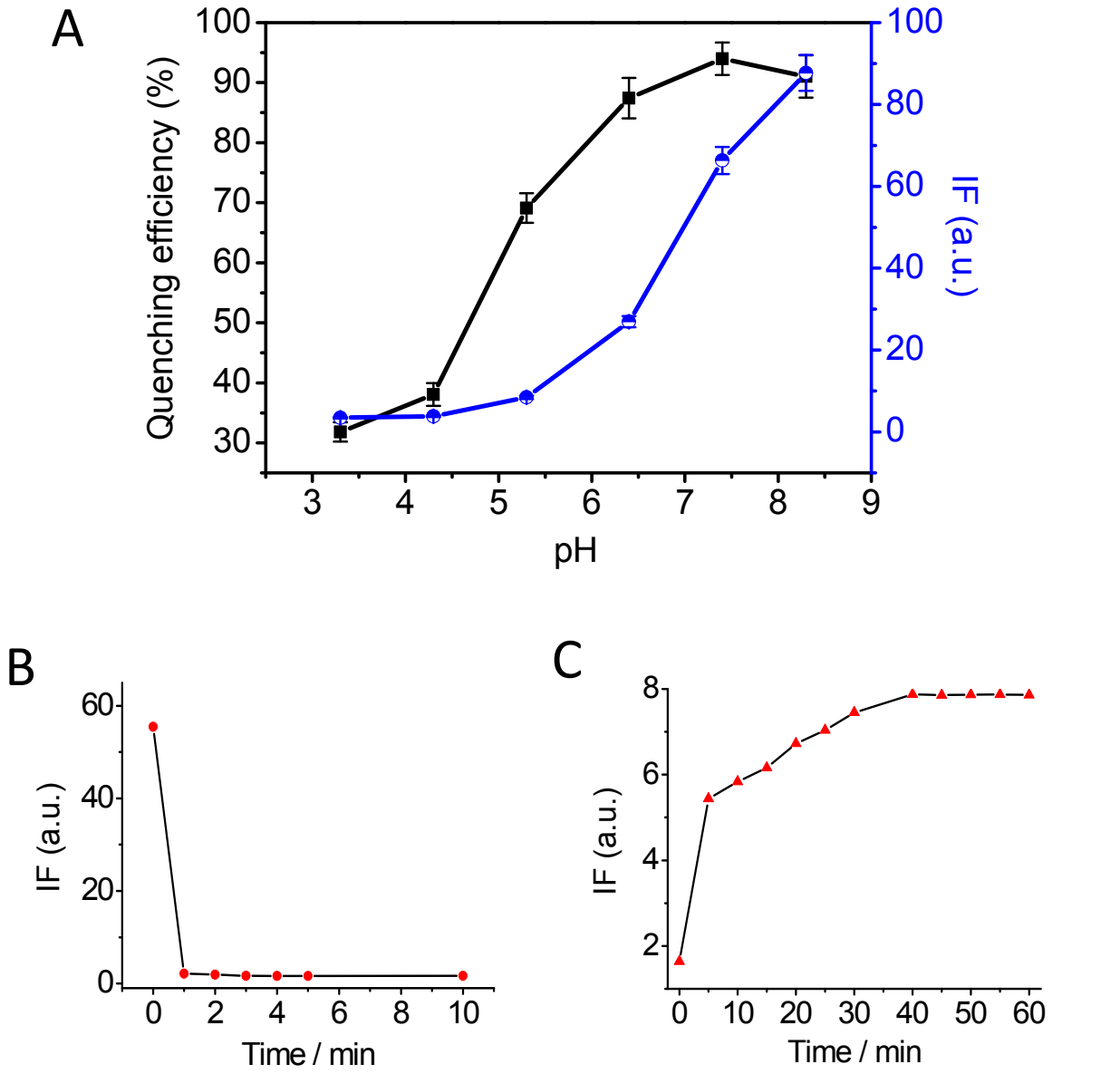

Figure S4. (A) pH-dependent fluorescence quenching (left) of P1 (50 nM) in the presence of GO (32.5 μg/mL); and fluorescence intensity evolution of P1 (50 nM) in the absence of GO. (B) Fluorescence quenching of P1 (50 nM) in HEPES buffer (pH 7.4, 10 mM) by GO as a function of time. (C) Fluorescence restoration of P1-GO in HEPES buffer by Fenton reagent (50 μM) as a function of time. Excitation: 480 nm, and emission: 530 nm.

5. The Detection of Iron(II) in Environmental Water Samples Using Solid Phase Extraction Followed by Spectrophotometric Determination according to Standard Examination Methods for Drinking Water–Metal Parameters (Chinese National Standard GB/T 5750.6-2006)[2]

One tap water and one pond water samples on our campus were collected, filtered through 0.45 μm membrane, and analyzed after sampling. Prior to use, Sep-Pak C18 cartridges were rinsed successively with 10 ml of 2 M hydrochloric acid, 10 ml of water, and 10 ml of methanol. The cartridges were connected to a filter holder with a 0.45 μm-Nuclepore filter (0.45 μm in pore size, 25 mm in diameter). A sample solution of 50 ml was taken into a 50-m1 graduated syringe, which had been equipped with a short polyvinyl chloride tube (3 mm in inside diameter, 10 mm in length) at its head for connection to the other syringes. A small glass ball was included inside for mixing of solution. To the sample in the syringe, 2.0 ml of phenanthroline solution and 10.0 ml of acetate solution were added through the tube with 5-ml graduated syringes, respectively. After 2 min, the resulting colored solution was passed through the cartridge via the filter. The iron(II) complex adsorbed was eluted from the cartridge with 5 ml of a mixture of acetone and 0.1 M hydrochloric acid solution (7:3, v/v). The absorbance of the eluent was measured at 510 nm.

Table S1. Analytical Results for the Detection of Fe^{2+} in Water Samples by a National Standard Procedure (GB/T 5750.6-2006) and the Present System

Sample	Found by this method (mean ± σ, n = 3) /μM	Recovery (mean ± σ, n = 3)[b] /%	Found by GB/T 5750.6-2006 (mean ± σ, n = 3) /μM
Tap water	0.121 ± 0.031	99 ± 3	0.134 ± 0.023
Pond water	nd[a]	102 ± 5	nd

[a] nd: not detectable. [b] For 0.20 μM Fe^{2+} spiked in the water samples.

References

1 (a) Z. Liu, J. T. Robinson, X. M. Sun and H. J. Dai, *J. Am. Chem. Soc.*, 2008, **130**, 10876–10877; (b) M. Zheng, A. Jagota, E. D. Semke, B. A. Diner, R. S. McLean, S. R. Lustig, R. E. Richardson and N. G. Tassi, *Nat. Mater.*, 2003, **2**, 338–342.

2 M. Okumura, Y. Seike, K. Fujinaga and K. Hirao, *Anal. Sci.*, 1997, **13**, 231–235.