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Electronic Supplementary Information

Masking agent-free and channel-switch-mode simultaneous sensing of Fe^{3+} and Hg^{2+} using dual-excitation graphene quantum dots

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EXPERIMENTAL SECTION

Materials and Reagents.

Citric acid and sodium hydrate were purchased from China Pharmaceutical (Group) Shanghai Chemical Reagent Company. Ferric chloride ($FeCl_3$), potassium chloride (KCl), magnesium chloride ($MgCl_2 \cdot 6H_2O$), calcium chloride ($CaCl_2$), manganese chloride ($MnCl_2 \cdot 4H_2O$), zinc acetate ($ZnAc_2 \cdot 2H_2O$), cupric sulfate ($CuSO_4 \cdot 5H_2O$), lead nitrate ($Pb(NO_3)_2$), cadmium sulfate ($CdSO_4 \cdot 8H_2O$), silver nitrate ($AgNO_3$), mercuric perchlorate ($HgClO_4 \cdot 3H_2O$), and mercury nitrate ($Hg(NO_3)_2$) were obtained from Sinopharm chemical reagent Co., Ltd. (Shanghai, China). All other chemicals were of the highest grade available. All stock and buffer solutions were prepared using ultrapure water (18.2 MΩ·cm from Millpore purification system).

Synthesis of GQDs

GQDs were prepared using a modified citric acid pyrolysis method.[1] Briefly, 2 g of citric acid (CA) was put into a 100 mL round-bottom flask, which was heated with an electric heating jacket. About 5 min later, the temperature reached to 200 ℃ and CA was liquated gradually. After about 25 min, the color of the liquid melt was changed from colorless to deep orange, and the liquid melt was

transferred into a beaker containing 100 mL of 10 mg mL^{-1} NaOH aqueous solution with continuous stirring. With the completely dissolved, the above solution was neutralized to pH 7.0 with HCl. The orange GQDs solution was stored away from light at 4 ℃ for 3~4 days to age, and the color of GQD solution will be slip away to faint yellow. The stock solution without any further treatment was used for the following characterization and detection.

Characterization of GQDs.

Transmission electron microscopy (TEM) measurements were performed on a Tecnai G^2 20ST transmission electron microscope operated at 200 kV. TEM samples were prepared by spin coating 10 μL of GQDs onto carbon-coated copper grid substrates, which were then baked in an oven at 60 ℃. UV-vis absorption spectra were recorded on a Beckman Coulter DU-800 UV-vis spectrophotometer. FTIR spectra were obtained with a Tensor 27 Fourier transform infrared spectrometer (Bruker, Germany).

GQDs-based fluorescent sensing.

Fluorescent measurements were performed on an F-7000 fluorescence spectrophotometer (Hitachi, Japan) with a 1 mm×10 mm quartz cuvette containing 50 μL of solution at room temperature (25 ℃). The excitation wavelength was set at 310 nm and 420 nm in Channel-310 and Channel-420, respectively. Ex slit and Em slit width were 2.5 nm (950 V PMT).

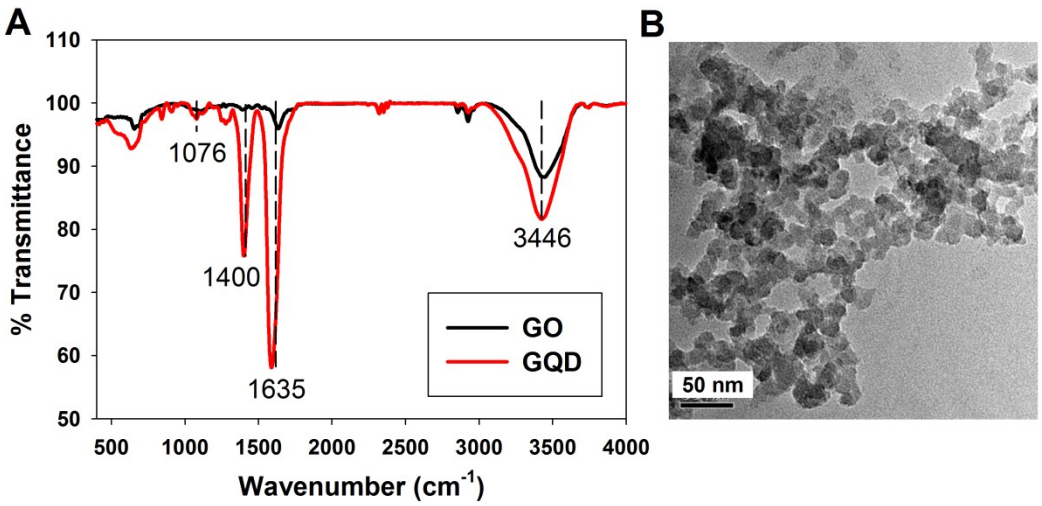

Figure S1. Characterization of GQDs. (A) FTIR spectra of GQDs and purchased graphene oxide (GO). (B) TEM images of GQDs.

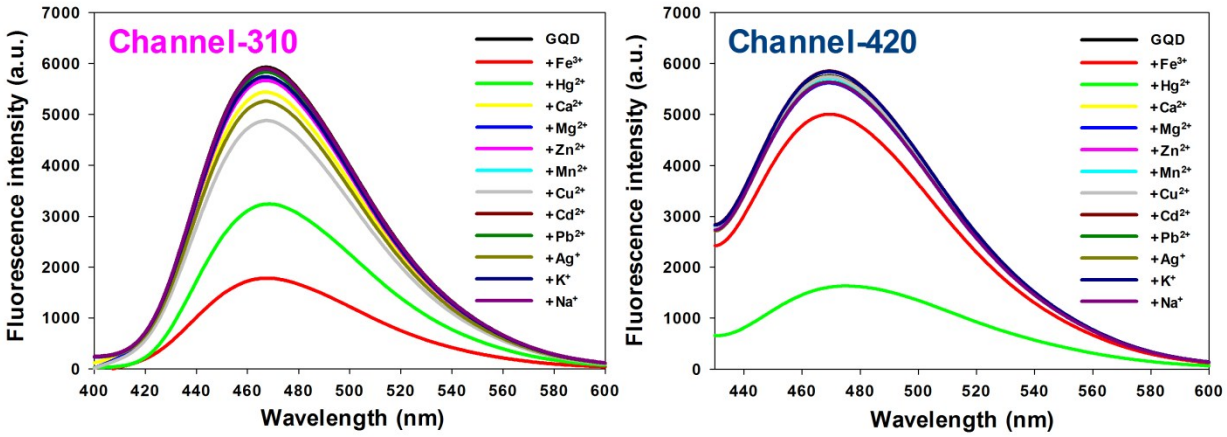

Figure S2. Fluorescence emission spectra of GQDs in the presence of different metal ions (500 μM), measured through Channel-310 and Channel-420 respectively.

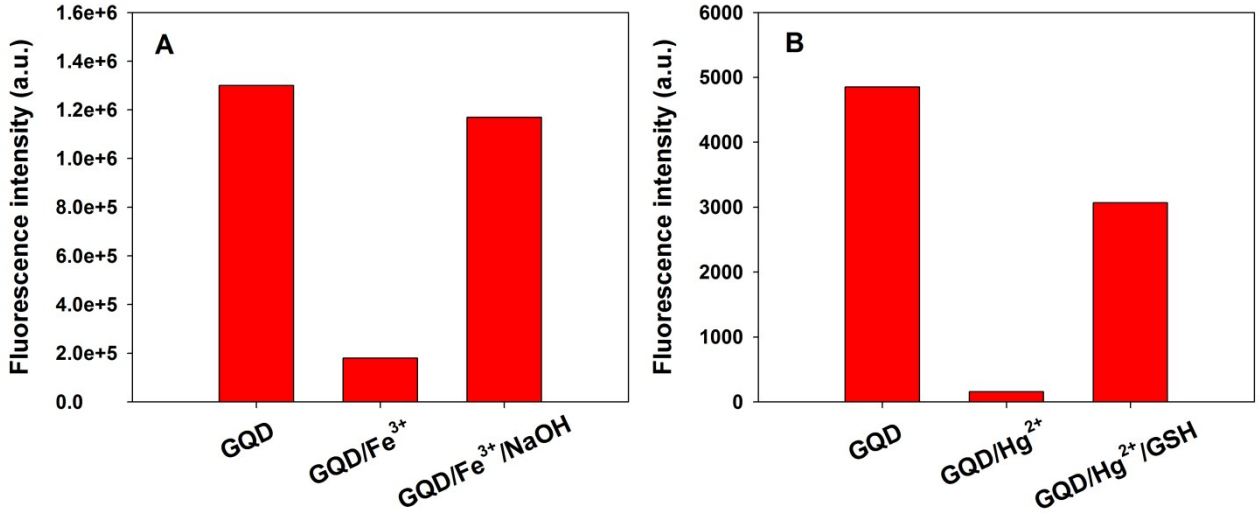

Figure S3. Fluorescence responses of GQD/Fe^{3+} (A) and GQD/Hg^{2+} (B) in the absence and presence of NaOH (10 mM) or GSH (5 mM) respectively. (The concentration of Fe^{3+} and Hg^{2+} were 1 mM.)

Table S1. Comparison of different fluorescent carbon nanomaterials, including GQDs[a], CQDs[b], CDs[c], CNP[d], CP[e], and CNS[f], for detection of Fe^{3+} or Hg^{2+}.

Target Ion(s)	Probe-Synthesis Method	Detection Limit	Selectivity (Interferent)	Ref.
Fe^{3+}	**GQDs**-Hydrothermal method (polycyclic aromatic hydrocarbon)	5 nM	Cu^{2+}, Fe^{2+}, Hg^{2+}	2
	GQDs-Electrochemical etching 3D graphene	≈7.22 μM	—	3
	N-GQDs-Hydrothermal method (pyrolyzing citric acid+hydrazine)	90 nM	Cu^{2+}, Hg^{2+}	4
	S-GQDs-Electrolysis of graphite in sodium *p*-toluenesulfonate	4.2 nM	Hg^{2+}	5
	CQDs-Electrochemical ablation of graphite electrodes	2 nM	Cu^{2+}	6
	CDs-Hydrothermal method (grape peel)	1 μM	Hg^{2+}	7
	CDs-Hydrothermal method (citric acid+ethylenediamine)	≈18 μM	Fe^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+}, Hg^{2+}	8
	CDs-Calcination β-cyclodextrin	0.8 μM	Oxidative ions	9
	N-CDs-Hydrothermal method (PEG diamine+citric acid)	2.5 nM	Fe^{2+}	10
	N-CDs-Microwave assisted hydrothermal method (histidine)	10 nM	Co^{2+}, Cu^{2+}, Ni^{2+}, Hg^{2+}, Zn^{2+}	11
	CNPs-Light induced glucose	≈10 μM	Cu^{2+}	12
Hg^{2+}	**CNPs**-Microwave assisted hydrothermal method (melamine and trisodium citrate dehydrate)	45 nM	—	13
	GQDs-Pyrolyzing citric acid	3.36 μM	Fe^{3+}	14
	CPs-Hydrothermal method (pomelo peel)	0.23 nM	—	15
Fe^{3+} & Hg^{2+}	**CNSs**-Hydrothermal method (cocoon silk)	50 μM Hg^{2+}, 50 μM Fe^{3+} Non-simultaneous detection	Cu^{2+}	16
	GQDs-Pyrolyzing citric acid	10 μM Hg^{2+}, 10 μM Fe^{3+} Masking agent-free simultaneous detection	Cu^{2+}	Our work

[a] GQDs: graphene quantum dots; [b] CQDs: carbon quantum dots; [c] CDs: carbon dots; [d] CNPs: carbon nanoparticles; [e] CPs: carbon particles; [f] CNSs: carbon nanospheres.

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