Electronic supplementary information

A label-free fluorescent sensor for Pb^{2+} based on G-quadruplex and graphene oxide

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Experimental Section

Materials and reagents

Graphene oxide dispersion (2 mg/mL) was purchased from XF Nano (Nanjing, China). G-rich oligonucleotide (AGRO100: 5'-GGT GGT GGT GGT TGT GGT GGT GGT GG-3') was synthesized and HPLC purified by Shanghai Sangon Biotechnology Co. Ltd (Shanghai, China). Tris(hydroxymethyl)aminomethane (Tris) and AO were purchased from Sigma-Aldrich (St. Louis, MO, USA). All other chemicals were of analytical grade and used without further purification. All work solutions were prepared with 10 mM Tris-HAc buffer (pH 7.4). Deionized water was used for the preparation of aqueous solution.

Apparatus

F-2500 fluorescence spectrophotometer (Hitachi, Japan) was used to collect the fluorescence spectra with a scan rate of 1500 nm/min. The excitation wavelength was 490 nm, and the photomultiplier tube (PMT) voltage was 400 V. The slit widths for excitation and emission were both set at 10 nm. The optical path length of a quartz fluorescence cell was 1.0 cm. Fluorescence anisotropy was measured by a LS 55 fluorescence spectrometer (PerkinElmer, American) with an excitation wavelength at 490 nm and an emission wavelength at 524 nm.

Fluorescence determination of Pb^{2+}

The AGRO100 solution was heated at 90℃ for 10 min to dissociate any intermolecular interaction, and gradually cooled to room temperature. A solution containing 200 nM of AGRO100, 200 nM of AO and different concentrations of Pb^{2+} was incubated for 1 h at room temperature, then GO was added into the solution to make the final volume 1 ml. The final concentration of GO was 5 μg/ml. After the mixture was incubated for 10 min, the fluorescence emission spectra were recorded with an excitation wavelength of 490 nm. The same procedures were repeated in the presence of other metal ions instead of Pb^{2+} to assess the selectivity.

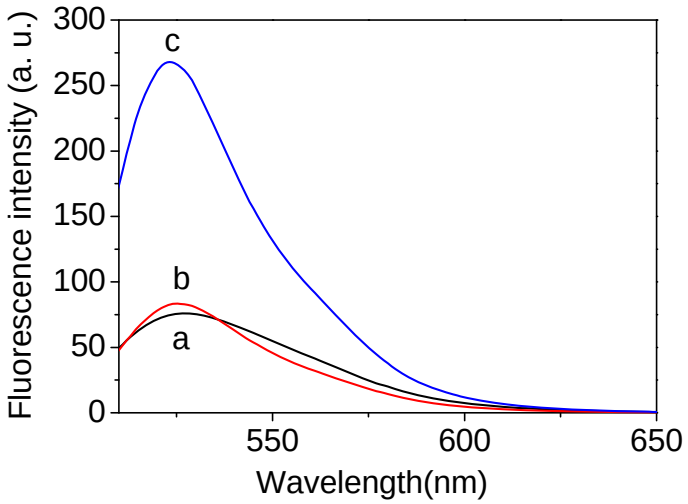

Fig. s1 Fluorescence emission spectra of AO under different conditions: (a) AO; (b) AO + AGRO100; (c) AO + AGRO100 + Pb^{2+}. Concentrations of AO, AGRO100 and Pb^{2+} are 200 nM, 200 nM and 1 μM, respectively. The excitation wavelength is 490 nm.

Table s1 Performance comparison of this work with other oligonucleotide-based sensors for Pb^{2+} detection.

Analytical method	**Sensor strategy**	**Linear range**	**Detection limit**	**Real sample**	**Ref.**
Fluorescence	G-quadruplex/ GO/ AO	5 – 300 nM	3 nM	Lake water Tap water	This work
Fluorescence	G-quadruplex/ ZnPPIX	20 – 1000 nM	20 nM	Not reported	1
Fluorescence	G-quadruplex/ PMNT	0 – 120 nM	6 nM	Tap water	2
Fluorescence	Single labeled G-quadruplex/ GO	2 – 50 nM	0.4 nM	Tap water	3
Fluorescence	Single labeled G-quadruplex/ GO	0.1 – 10 nM	90 pM	River water	4
Fluorescence	G-quadruplex/ SYBR Green 1	10 – 100 nM	3 nM	Hair sample	5
Fluorescence	G-quadruplex DNAzyme/ AUR	0 – 1000 nM	0.4 nM	Soil sample	6
Fluorescence	Double labeled G-quadruplex	0.5 – 30 nM	0.3 nM	Soil sample	7
Fluorescence	G-quadruplex/ DSA derivate/ Nuclease S1	0 – 600 nM	60 nM	Not reported	8
Fluorescence	G-quadruplex/ NMM	10 – 100 nM	5 nM	Tap water	9
Fluorescence	Single labeled G-quadruplex	0.5 – 500 nM	0.4 nM	Tap water	10
Fluorescence	G-quadruplex/ NMM	5 – 1000 nM	1 nM	Lake water	11
Fluorescence	G-quadruplex/ Tb^{3+}	3 – 50 nM	1 nM	Soil sample Pond water	12

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