Electronic Supporting Information

Crystal violet as a G-quadruplex-selective probe for sensitive amperometric sensing of lead

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Experimental Section

Materials. Oligonucleotide was synthesized by SBS Genetech. Co. Ltd. 2-mercaptoethanol (MCH) was purchased from Sigma-Aldrich. Crystal violet (CV) was supplied by New Public-Private Partnership in China Chemical Plant (Shanghai, China). Metal salts used in this study ($CoCl_2$, $CuCl_2$, $ZnCl_2$, $CaCl_2$, $MgCl_2$, $CdCl_2$, $NiCl_2$, $MnCl_2$, $AgNO_3$, $Hg(NO_3)_2$, KCl, $Pb(NO_3)_2$) were purchased from Sinopharm Chemical Reagent Co. Ltd.(shanghai, China). Tris–HCl buffers were prepared by mixing stock standard solutions of Tris and HCl to various pH values. All other reagents were of analytical reagent grade and were used without further purification or treatment. Double distilled water (DDW) was used throughout the measurements. The DNA sequence is list as follows:

T30695: 5'-GGGTGGGTGGGTGGGT-3'

Instruments. Cyclic voltammetric (CV), differential pulse voltammetric (DPV), and electrochemical impedance spectroscopy (EIS) measurements were performed with a CHI 660D electrochemical analyzer (Shanghai CH Instrument Company, China). A three-electrode system was employed with Pt wire as the auxiliary electrode, saturated calomel electrode as the reference electrode, and gold (Au) electrode or modified Au electrode as the working electrode, respectively. Circular dichroism (CD) spectra were measured on a Jasco J-715 spectropolarimeter.

Preparation of the probe DNA modified Au electrodes. Prior to modification, Au electrode was polished with 1.0, 0.3, and 0.05 μm alumina slurry, respectively. Then, the electrode was rinsed thoroughly with DDW between each polishing step and was cleaned by ultrasonication. Then the clean electrode was incubated in 1 μM T30695 solution (10 mM Tris–HCl, pH 8.0) overnight at 4 °C. After being thoroughly rinsed with DDW, the electrode was blocked by immersion in 1.0 mM MCH for 30 min. The electrode was thoroughly rinsed with DDW and denoted as S/Au.

Formation of Pb^{2+}-stabilized G-quadruplex (G4) and intercalation of CV. The S/Au was firstly incubated in solutions of different concentrations of Pb^{2+} (20 mM Tris–HCl, pH 7.0). The solutions were heated to 90 ^{o}C for 5 min, and allowed for slow cooling down to room temperature in 1 h. They were incubated at room temperature for another 1 h to ensure the formation of G4. Then the above electrode was carefully rinsed with Tris–HCl buffer and DDW, respectively, and denoted as Pb^{2+}–S/Au. Subsequently, it was transferred into 1.0 mM CV (20 mM Tris–HCl, pH 7.0) for 10 min at room temperature. The obtained electrode was then rinsed with the same buffer and denoted as CV/Pb^{2+}–S/Au.

Electrochemical characterization. The electrochemical properties of differently modified electrodes were characterized by CV and DPV, with 20 mM Tris–HCl (pH 7.0) containing 0.2 M NaCl as the supporting electrolyte. EIS measurement was performed in 0.1 M KCl containing 1.0 mM $Fe(CN)_6^{3-}$ and 1.0 mM $Fe(CN)_6^{4-}$, with the frequency ranging from 10^{-1} to 10^{4} Hz.

CD measurement. CD spectra were recorded on a spectropolarimeter at room temperature under an atmosphere of nitrogen. After T30695 (2 μM) being mixed with 50 μM Pb^{2+} (20 mM Tris–HCl, pH 7.0), the solution was heated to 90 ^{o}C for 5 min, and allowed for slow cooling down to room temperature in 1 h, followed by another 1-h incubation at room temperature. For intercalating CV, a certain amount of CV was added to the above solution, and then kept for 1 h at room temperature. The final concentration of CV is 15 μM. Spectra were recorded in the 200–320 nm range in 0.5 mm pathlength cuvettes after equilibration at room temperature for 20 min, using a scanning speed of 50 nm/min, a response time of 1 s and a bandwidth of 0.2 nm. Spectra were averaged from 3 scans.

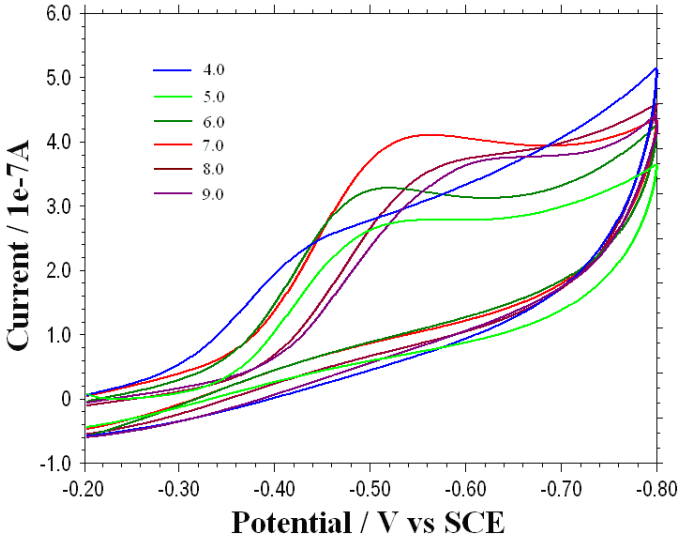

Fig. S1 Cyclic voltammograms of CV/Pb^{2+}–S/Au in 20 mM Tris–HCl (0.2 M NaCl) of different pH values from 4.0 to 9.0. The concentration of Pb^{2+} is 1.0×10^{-8} M.

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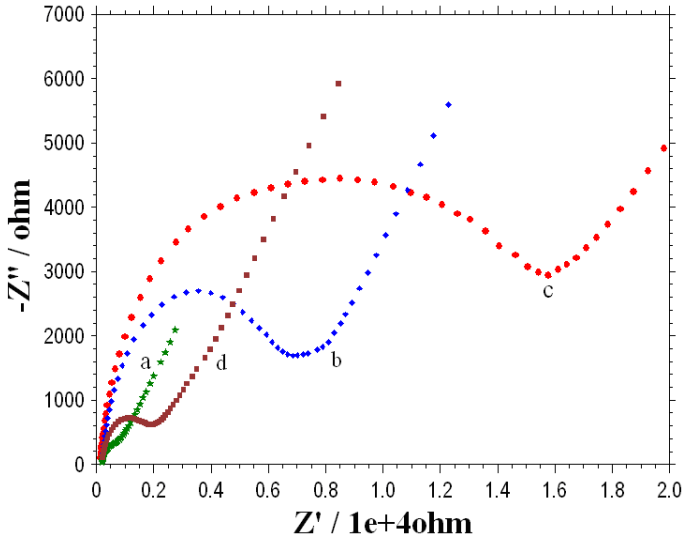

Fig. S2 Nyquist plots of the bare Au electrode (a), S/Au (b), Pb^{2+}–S/Au (c), and CV/Pb^{2+}–S/Au (d) in 0.1 M KCl containing 1.0 mM $Fe(CN)_6^{3-}$ and 1.0 mM $Fe(CN)_6^{4-}$. The concentration of Pb^{2+} is 1.0×10^{-8} M.

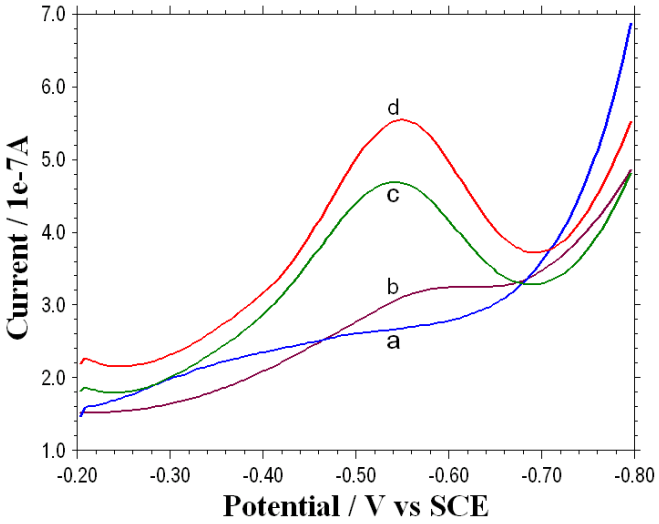

Fig. S3 DPVs of S/Au (a) and CV/Pb^{2+}–S/Au with analysis of Pb^{2+} in river water sample: river water (b), river water + 5.0×10^{-9} M Pb^{2+} (c), and river water + 5.0×10^{-8} M Pb^{2+} (d).

Table 1 Comparison of analytical performance of oligonucleotide-based Pb^{2+} biosensors

Probe	Technique	Method	Linear range	LOD	Ref.
G4/ZnPPIX[a]	Fluorescence	Driven-switch DNA molecules	10 nM – 2.0 μM	5.0 nM	1
G4/AUR[b]	Fluorescence	Induced enhancement of catalysis	0 – 1.0 μM	0.4 nM	2
8-17 DNAzyme/AuNPs[c]	Colorimetry	Induced release of the substrate strand	0.1 – 4.0 μM	–	3
8-17 DNAzyme/DNA–Au	Amperometry	Induced release of the substrate strand	5.0 nM – 0.1 μM	1.0 nM	4
G4	EIS	Induced-switch DNA molecules	0.5 nM – 50 μM	0.5 nM	5
G4/CV	Amperometry	Induced-switch DNA molecules	1.0 nM – 1.0 μM	0.4 nM	Proposed

[a] Zinc protoporphyric. [b] Amplex UltraRed. [c] Gold nanopartcles.

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