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Supporting Information for

An ultrasensitive electrochemical sensor for mercuric ion via controlled assembly of SWCNTs

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Experimental Section

Chemicals. Hg^{2+} ion standard solution (1000 μg ml^{-1}) was purchased from General Research Institute for Nonferrous Metals of China. 3-(N-morpholino) propanesulfonic acid (MOPS) was bought from Sinopharm Group Co. Ltd (Shanghai, China). 16-Mercaptohexadecanoic acid (MHA) and ferrocenecarboxylic acid (FcCOOH) were obtained from Sigma Aldrich Chemical Co. Single-walled carbon nanotubes (SWCNTs) with an average diameter of 1~2 nm was provided by Beijing Nachen S&T Ltd. of China. All other chemicals were of analytical grade and used without further purification. The solutions were prepared using ultrapure water which was purified by Millipore Milli-Q (18 MΩ·cm). The HPLC-purified oligonucleotides P1 and P2 used in this work were synthesized by Shanghai Sangon Biological Engineering Technology & Services Co., Ltd (Shanghai, China). The oligonucleotide solutions were prepared and diluted with ultrapure water. Hg^{2+} ion standard solution was diluted to applicable concentration step by step with ultrapure water. Other metal ion solutions for selective assay were prepared from nitrate salts.

Preparation of SWCNTs-DNA complex. Two milliliters of aqueous containing 1.0 mg/mL SWCNTs and 20.0 μM ssDNA P1 was sonicated (200 W) for 2 hours in ice bath using a KQ5200DE model ultrasonic cleaner to obtain a black dispersed solution. Then the resulting suspension was centrifuged at 12000 g for 70 min to remove possible SWCNTs aggregates. The SWCNTs in the supernatant was collected and filtered through a centrifugal filter with a molecular weight cutoff of 100 Kda (Dingguo, Beijing) to remove excessive ssDNA which were not wrapped around the SWCNTs. After washing with water 10 times, the SWCNTs-DNA complex was redispersed in ultrapure water. The suspension of SWCNTs-DNA complex was stored at 4 °C before use.

Electrochemical measurements. All electrochemical measurements were performed with a CHI660d electrochemical analyzer (CH Instruments, Shanghai, China). A conventional three-electrode cell assembly was employed all through the experiment, which involved a working gold electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode. All potentials are reported versus Ag/AgCl reference at room temperature. All electrochemical measurements were conducted in 20 mM MOPS buffer (pH 7.4) containing 0.2 mM FcCOOH. Cyclic voltammetry (CV) measurements were recorded using a step potential of 1 mV within the potential range from -0.2 V to + 0.8 V at a scan rate of 100 mV/s. Differential pulse voltammetry (DPV) was performed at a pulse amplitude of 50 mV and a pulse width of 0.2 s between 0 V and + 0.6 V. The reported DPV curves were background subtracted through extrapolation to the baseline in the regions far from the peaks. Electrochemical impedance spectroscopy (EIS) was

performed in the frequency range from 0.1 Hz to 100 kHz with 10 mV as the frequency modulation at a bias potential of 0.19 V.

Gold electrode treatment and modification. Gold disk electrodes (99.99% polycrystalline, ~2 mm diameter, CH Instrument Inc.) were polished on a microcloth (Buehler) with 0.05 μm γ-alumina suspension (CH Instrument Inc.) and rinsed with ultrapure water and ethanol. The electrodes were then sonicated in ultrapure water for 2 min to remove adsorbed particles, rinsed thoroughly with ultrapure water, and dried under mild nitrogen stream. The electrodes were cleaned further by electrochemical oxidation and reduction in 0.5 M H_2SO_4 by applying a positive potential of +2.0 V to the electrodes for 5 s, followed by a negative potential of -0.35 V for 10 s. They were then electrochemical etched in 0.5 M H_2SO_4 by cycling the electrode potential between -0.35 V and +1.6 V with a scan rate of 4 V s^{-1} until a reproducible cyclic voltammogram was achieved. Finally, the electrodes were checked for cleanness by running a CV cycle in a fresh 0.5 M H_2SO_4 solution with a scan rate of 100 mV s^{-1} between -0.35 V and +1.6 V. The characteristic single sharp reduction peak located at +0.9 V and multiple overlapping peaks in the range of ca. +1.2 ~ +1.4 V were visible. The pretreated electrodes were immersed into an ethanol solution of MHA (20 mM) for ~2 h at 25 °C to allow formation of a dense SAM. The electrodes (denoted as MHA/SAM-modified electrodes, hereafter) were then thoroughly rinsed using ethanol to remove MHA adsorbed on the electrode surface and followed by drying under mild N_2 stream. These gold electrodes could be used for assay of the next sample via polishing to remove the adsorbates followed by the aforementioned treatments.

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Electrochemical measurements of Hg^{2+}. Fifteen microliter of MOPS buffer (10 mM, pH 7.1) containing 100 mM $NaNO_3$ was added to the mixture of 2 μL suspension of SWCNTs-DNA complex, 1 μL ssDNA P2 and 2μL Hg^{2+} solution of a given concentration. The resulting solution (3μL) was dropped on the surface of MHA/SAM-modified electrodes and incubated in a humid atmosphere at room temperature for 55 min. Subsequently, the electrode was thoroughly rinsed with ethanol and ultrapure water to remove SWCNTs weakly adsorbed on the electrode surface. The electrodes (denoted as SWCNTs/MHA/SAM-modified electrodes, hereafter) were dried under N_2 stream before electrochemical measurements.

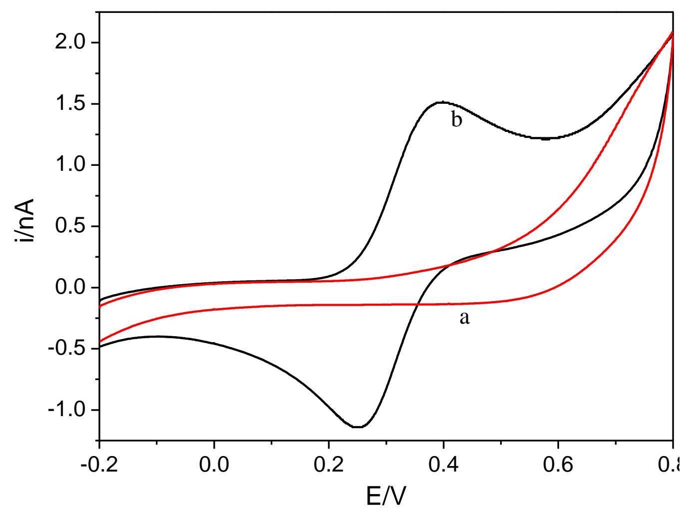

Fig. S1 Cyclic voltammograms of MHA/SAM-modified electrode after incubation with 0.05 μM ssDNA2 and 1.0 μM Hg^{2+} ion (a); SWCNTs-DNA complex, 0.05 μM ssDNA P2 and 1.0 μM Hg^{2+} ion (b). Electrolyte: 20 mM MOPS buffer (pH 7.4) containing 0.2 mM FcCOOH; Scan rate: 100 mV s^{-1}.

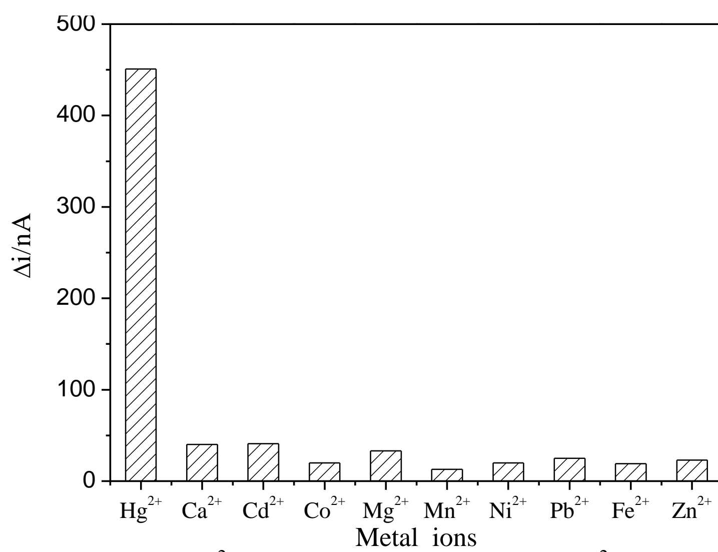

Fig. S2 Selectivity of the Hg^{2+} ion electrochemical sensor. Hg^{2+} ion was 10 nM, all competing ion solutions were 500 nM.

Table S1. Comparison of the sensitivity of different oligonucleotide-based Hg^{2+} sensors

Detection method	Limit of detection	Reference
colorimetric and fluorescent method based on conjugated polymer	2.5 μM and 42 nM	S1
colorimetric detection using DNA–Au NPs	100 nM	S2
visual detection based on gold nanoprobe	5 μM	S3
colorimetric method based on DNA–Au NP probe	250 nM	S4
colorimetric method using DNA/nanoparticle conjugates	3 μM	S5
colorimetric detection using gold nanoparticle and DNA-Based machines	10 nM and 1 nM	S6
visual detection based on TMB-H_2O_2 system	100 nM	S7
colorimetric method based on ABTS-H_2O_2 system	50 nM	S8
colorimetrical detection based on TMB-H_2O_2 system	0.1 nM	S9
colorimetric detection based on Hg^{2+}-induced aggregation of mononucleotides-stabilized gold nanoparticles	0.05 μM	S10
colorimetric detection by double-stranded DNA-carrying gold	0.5 μM	S11
visual and fluorescent method based on gold nanoparticles	40 nm	S12
fluorescence method based on FRET	40 nM	S13
Fluorescent method based on allosteric DNAzyme catalytic beacons	2.4 nM	S14
fluorescence method with mercury-specific DNA and Sybr Green I	1.33 nM	S15
fluorescent method based on structure-switching DNA	3.2 nM	S16
fluorescent method based on TOTO-3 and T_{33}	3 nM	S17
fluorescent method by using oligonucleotides, DNA intercalators, and conjugated polymers	0.27 nM	S18
fluorescent method based on photoinduced charge transfer between fluorophore and π-stacked T-Hg(II)- T base pairs	20 nM	S19
fluorescence method with SWCNTs as quencher	14.5	S20
fluorescent method using carbon nanotubes to reduce background signal	7.9 nM	S21
fluorescence microscopy method by PDA liposome-based microarrays	5 μM	S22
fluorescence polarization assay (FPA) with gold nanoparticle enhancement	1.0 nM	S23
localized surface plasmon resonance light-scattering method based on Hg^{2+}-DNA complex induced aggregation of gold nanoparticles	1.0 nM	S24
resonance scattering method using aptamer-modified nanogold	0.03 nM	S25
resonance scattering assay by malachite green	1.7 nM	S26
chip-based scanometric method	10 nM	S27
flow cytometry with magnetic microparticles based enrichment	5 nM	S28
SERS method based on gold microshell	50 nM	S29
electrochemical method with Au nanoparticles-based signal amplification	0.5 nM	S30
electrochemical method with Au nanoparticles-based signal amplification	0.5 nM	S31
electrochemical sensor based on ferrocene-labeled DNA	0.1 μM	S32
electrochemical sensor based on the cooperativity of proximate poly-T oligonucleotides	0.5 nM	S33
electrochemical impedance spectroscopy	100 pM	S34
electrochemiluminescent method with $Ru(phen)_3^{2+}$ as ECL probe	20 pM	S35
electrochemical sensor based on target-induced structure-switching DNA	0.060 nM	S36
electrochemiluminescent biosensor using $Ru(bpy)_3^{2+}$-doped silica nanoparticles	2.3 nM	S37

electrochemical method using an electrically contacted relay/enzyme structure as a transducing element	100pM	S38
electrochemical method based on HRP enzymatic signal amplification	0.3 nM	S39
electrochemical method via controlled assembly of SWCNTs	16.3fM	This work

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