Supporting information

EXPERIMENTAL SECTION

Materials and chemicals. DNA oligonudeotides (1) and (2) were synthesized by Sangon Inc. (Shanghai, China). Their sequences are shown below:

5'-HS-$(CH_2)_6$-TTTCATTCCTTTGTTGTTC-3' (1)

5'-NH_2-GTTCTTCTTTGGTTTGATT-3' (2)

$Ru(bpy)_3^{2+}$, tetraethyl orthosilicate (TEOS), Triton X-100 (TX-100), n-hexanol, cyclohexane, 2-(Dibutylamino)ethanol (DBAE) and 6-mercaptohexano (MCH) were purchased from Sigma, USA. All other chemicals were of analytical grade.

All solutions were prepared with using Milli-Q reagent water (Milli-Q, Millipore, 18.2-MΩ resistivity. DNA buffer solutions (the concentration of oligonudeotide is 10μmol/L) were obtained by dissolving oligonudeotides with a 40mmol/L Tris-HCl buffer solution (pH 7.6) containing 0.1mol/L NaCl. Metal ion solutions were prepared from nitrate salts. All work solutions were prepared with Tris-HCl buffer solution.

The waste water samples were taken from the sewerage network near Fuzhou University, Fujian, China. Before experiment the samples collected was first filtered by a filter membrane (0.20 μm) to remove insoluble substance.

Apparatus. The ECL detection system consisted of a BPCL ultra-weak luminescence analyzer (Institute of Biophysics, Chinese Academy of Science, Beijing, China) and a CHI 660a electrochemical system (CH Instruments, Shanghai, China). A three-electrode electrochemical cell with an optically flat bottom was used. Gold

electrodes (2 mm in diameter, CH Instruments, Shanghai, China) were used as the work electrode. Platinum wire and Ag/AgCl (saturated with KCl) were used as counter and reference electrodes, respectively (shown in Fig. S1). Buffer solutions were purged with highly purified nitrogen for 20 min before measurement and kept in the cell during determinations. The electrochemical cell was placed directly in front of a photomultiplier (PMT, operated at -800 V) and the PMT window was only opened to the working electrode to reduce the interference of ECL from the counter electrode.

The TAS-986 Atomic Absorption Spectrometry (Beijing Purkinje General Instrument Co.LTD. Beijing, China) had been applied to test the mercury in the waste water.

Ru-SNPs synthesis and surface modification. (1) Nanoparticle synthesis. Ru-SNPs were prepared by the water-in-oil (W/O) microemulsion in the previous literature [39]. The mixture of 1.77 mL of TritonX-100, 7.5 mL of cyclohexane, 1.8 mL of n-hexanol, 340 μL of $Ru(bpy)_3^{2+}$ solution were stirred for 30 min at room temperature, forming a uniform W/O microemulsion. The water-surfactant molar ratio was kept constant at 10. Above mixture polymerizate reacted with TEOS by initiation of NH_4OH for 24 h at the room temperature. After reaction, the Ru-SNPs were isolated by acetone, followed by centrifuging, ultrasonicating and washing with ethanol and deioned water several times to remove residual molecules and physically absorbed $Ru(bpy)_3^{2+}$ from the surface of the partciles. Then Ru-SNPs were suspended in 2mL Tris-HCl buffer solution by ultrasonication for the following experiments.

(2) Surface modification of Ru-SNPs and covalent conjugation of

oligonucleotides onto the nanoparticle surface. According to the literature [40], we performed to functionalization of surface of Ru-SNPs. Above Ru-SNPs were immersed in freshly prepared 1% solution of DETA containing 1 mmol/L acetic acid for 30 min at room temperature and rinsed with deioned water several times to remove excess DETA.

The above Ru-SNPs were reacted with 5% glutaraldehyde solution in 37 °C water bath for 2 h with shaking and washed with deioned water to remove the excess glutaraldehyde thoroughly. The oligonucleotides solution was added to the functionalized SNPs solution and stirred for 120 min. Oligonucleotides conjugated nanoparticles were treated with glycine solution. At last, the product was washed and centrifuged, resuspended in Tris-HCl buffer solution (pH 7.6) and stored at 4 °C.

(3) Sensor Preparation. Gold electrodes were polished with aqueous slurries of 1.0 μm, 0.3 μm and 0.05 μm α-Al_2O_3 powders on a polishing microcloth and sonicated with deioned water, ethanol for 3 min, respectively. Finally, the electrodes were rinsed with deioned water. Then they were electrochemically activated in 0.5 mol/L sulfuric acid. The activeted gold electrodes were interacted with 10 nmol/L oligonudeotides(1) solution for 90min, and oligonudeotides (1) can be immobilized on the gold electrode by thiol-Au interactions. And the surfaces of the electrodes were passivated with 1mmol/L MCH. The electrodes modified oligonudeotides (1) were immersed into the 10nmol/L oligonudeotides (2) solution containing different concentrations of Hg^{2+} for 2h in 37 °C water bath. The biosensors are obtained to determinate content of Hg^{2+}.

(4) ECL measurements. The above treated gold electrodes, as the work electrode, were ringed with water thoroughly and then immersed into an ECL cell containing 2 mL of Tris-HCl buffer solution (pH 7.6), 10 μL 1.0 mol/L DBAE and 0.1 mol/L NaCl. The cell was laid in the dark chamber without stirring. In this work, we chose cyclic voltammetry (CV) as scan mode. A pulse potential exerted on the work electrode ranged from +0.8 V (versus Ag/AgCl) to +1.6 V. The scan rate was 50 mV/s. The height of ECL signal was used for quantification.

Fig. S 1

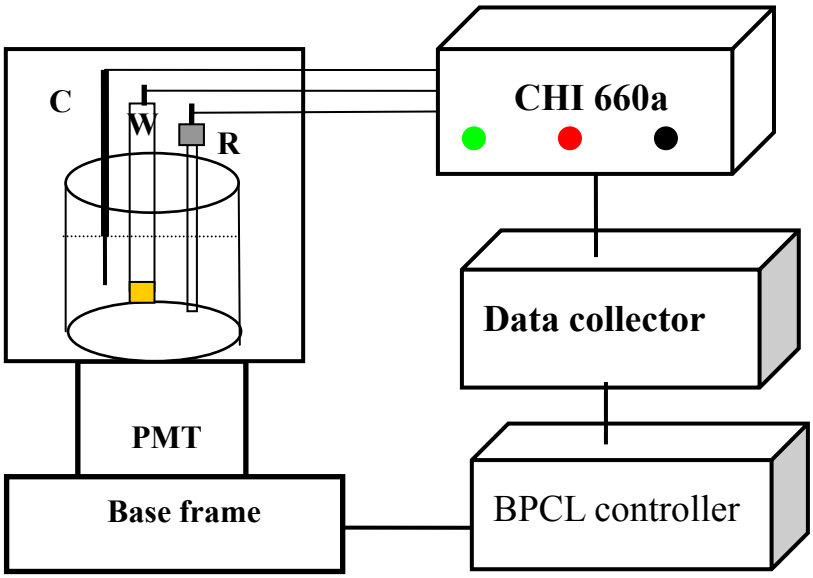

Fig. S 1 The scheme of the ECL detection system.

C: counter electrode; W:working electrode; R: reference electrode