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Electronic Supplementary Information

A simply visual and highly selective colorimetric detection of Hg^{2+} based on gold nanoparticles modified with 8-hydroxyquinolines and oxalates

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Experimental Section

Materials

chloroauric acid ($HAuCl_4 \cdot 3H_2O$, >99.0%), sodium oxalate ($Na_2C_2O_4$, >99.0%), polyvinylpyrrolidone (PVP-K30), 8-hydroxyquinoline (8-HQ), and other reagents (metal salts) were all purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All of the chemicals were used as received without further purification.

Methods

Transmission electronmicroscopy (TEM) images and the energy dispersive X-ray spectra (EDS) data were recorded from a JEOL2100 instrument and were operated at 200 kV. UV-vis spectroscopy was performed using a Lambda 950 instrument. X-ray photoelectron spec-troscopy (XPS) testing was performed on an AXIS Ultra DLD instrument with Mg Kα radiation as the X-ray source. The dynamic light scattering (DLS) data of the AuNPs and AuNPs with different concentration of Hg^{2+} were obtained on Zetasizer Nano ZS instrumentation (Malvern Instruments Ltd.). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed with an Optima 2100DV instrument from Perkin Elmer. MilliQ water was used for all experiments.

Preparation of 8-HQ modified AuNPs

AuNPs were firstly prepared by reducing $HAuCl_4 \cdot 3H_2O$ with sodium oxalate in the presence of PVP. All the glassware was thoroughly washed with aquaregia (HCl/HNO_3 (v/v) = 3:1) and rinsed with Milli-Q water. Typically, 8.0 mL of 0.5 mM $HAuCl_4 \cdot 3H_2O$ was added to 72 mL Milli-Q water, the solution was heated to 90 ºC and kept for 10 min. The mixture of 20 mL of 0.02 M $Na_2C_2O_4$ and 7.0 mg PVP (pH = 4~5) was heated to boiling, to which was rapidly added the $HAuCl_4 \cdot 3H_2O$ solution with vigorous stirring and kept at 90 ºC for 30 min. The color of the mixture turned from blueviolet to wine red with the proceeding of the reaction. The prepared AuNPs was stored at room temperature for 24 hours at last for ageing.

The pH of the ageing AuNPs colloid was adjust to 4 and diluted with ethanol (volume ratio of AuNPs colloidal and ethanol, 2 : 3), and then modified by adding 0.1 mol/L 8-HQ (dissolved in ethanol) slowly with vigorous stirring for 2 hours. The modified AuNPs were kept for detection.

Detection of Hg^{2+}

50 μL of Hg^{2+} aqueous solutions with different concentration were respectively added into 950 μL the modified AuNPs dispersion, and the mixtures were maintained at room temperature for several minutes, the color of which changed from wine red to gray.

Some detail information about the mercury determination by ICP-AES system is as follows:

(1) Preparation of real water samples.

Firstly we got the real water samples from lake and tap water, the lake water was filtered by filter paper while the tap water was without further processing. And then Hg^{2+} standard solution which was prepared by deionized water was added to the lake water samples and tap water samples, thus the final real water samples were obtained.

(2) Preparation of standard samples.

The standard samples were prepared for 5 points (unit: mg/L): 0, 0.05, 0.10, 1.0, 10. The solvent was 2% saltpeter solution.

(3) Detection by ICP-AES system.

We detected the real water samples and got the data by ICP-AES of an Optima 2100DV instrument from Perkin Elmer. Detailed measuring parameters are shown in the Table as follows.

Parameter	Value
Observed ray	axial
RF power	1300W
Reflected power	＜5W
Plasma gas flow	15L/min
Auxiliary gas flow	0.2L/min
Carrier gas flow	0.8L/min
Hg emission line	253.652nm

(4) Detection results were obtained under the above parameters, and the unit of detection value was mg/L, then was converted to μmol/L (μM) as shown in Table S1.

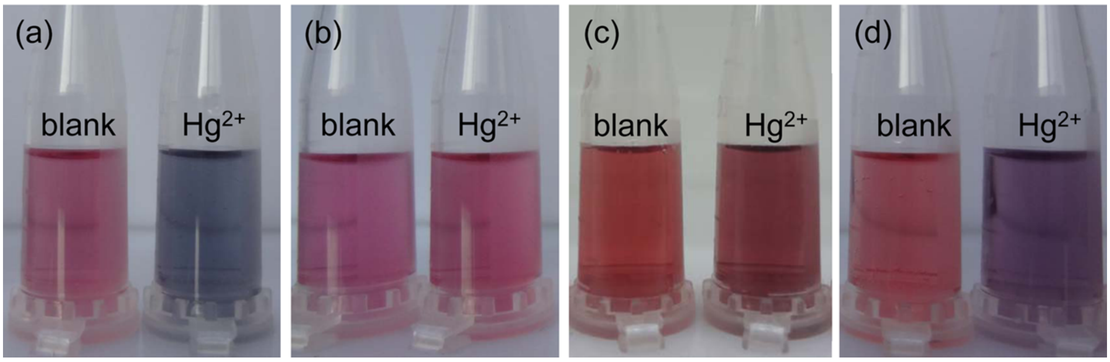

Fig. S1 Photographic images of contrast experiments under different conditions: (a) with 8-HQ and oxalate; (b) without 8-HQ; (c)without oxalate; (d) ascorbic acid replacing oxalate.

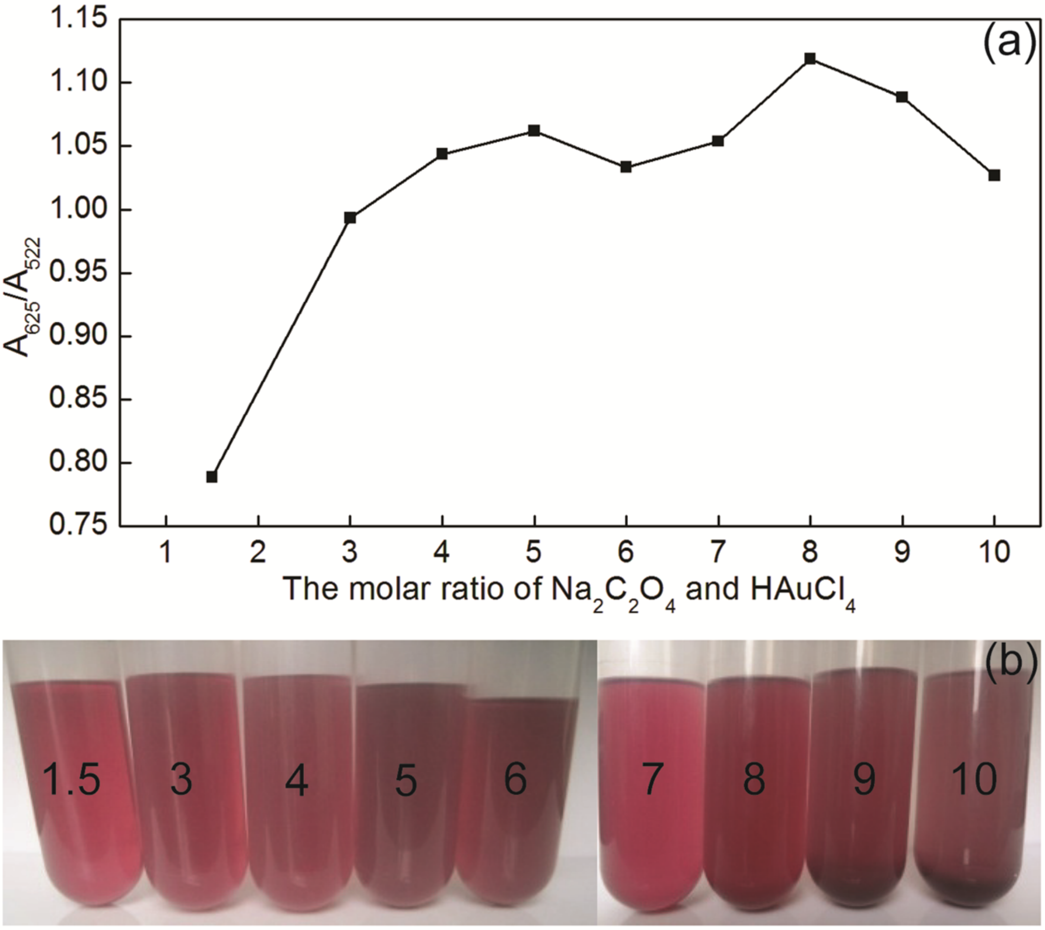

Fig.S2 A_{625}/A_{522} values of the modified AuNPs dispersion at different $Na_2C_2O_4$ concentration. A_{625} is the absorbance of the new appeared peak of modified AuNPs dispersion with Hg^{2+} and A_{522} is the absorbance of primary peak of modified AuNPs dispersion with 10μM Hg^{2+}.

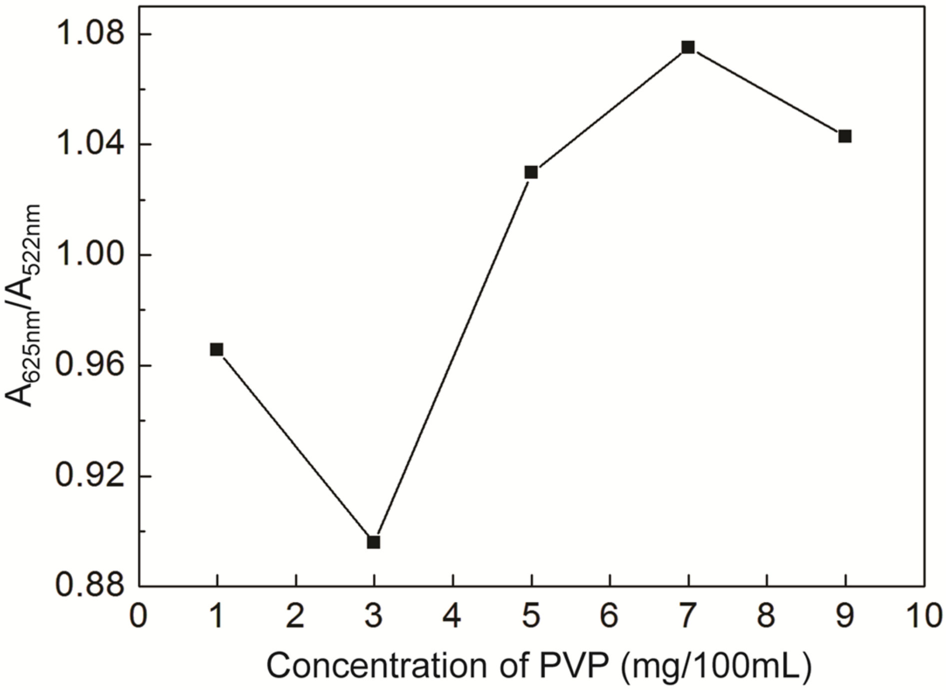

Fig.S3 A_{625}/A_{522} values of the modified AuNPs dispersion at different PVP concentration. A_{625} is the absorbance of the new appeared peak of modified AuNPs dispersion with Hg^{2+} and A_{522} is the absorbance of primary peak of modified AuNPs dispersion with 10μM Hg^{2+}.

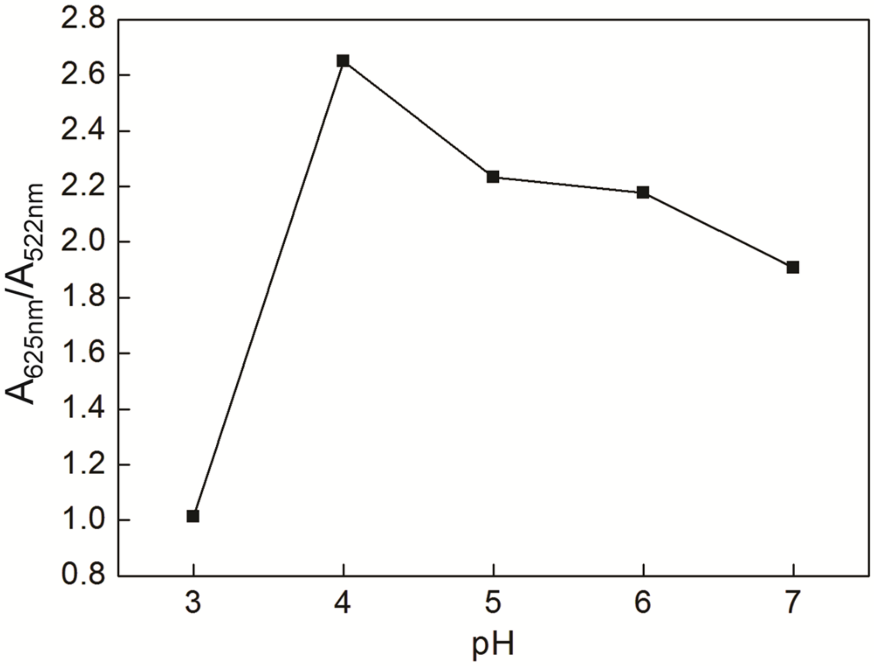

Fig.S4 A_{625}/A_{522} values of the modified AuNPs dispersion at different pH. A_{625} is the absorbance of the new appeared peak of modified AuNPs dispersion with Hg^{2+} and A_{522} is the absorbance of primary peak of modified AuNPs dispersion with 10μM Hg^{2+}.

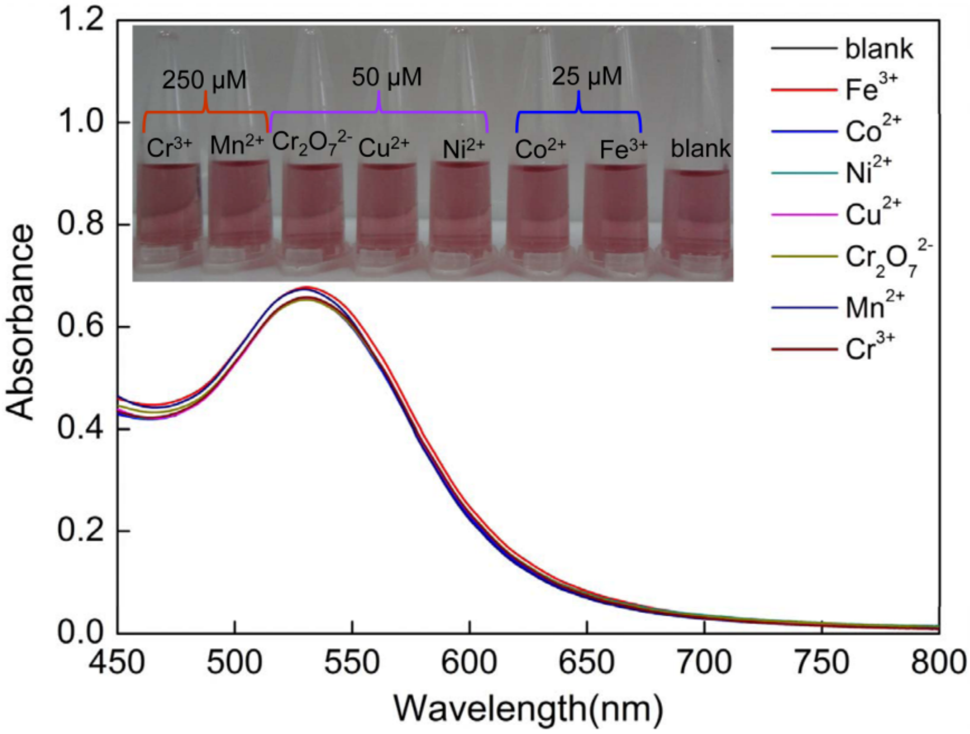

Fig. S5 UV-vis spectra of modified AuNPs dispersion in the presence of some metal ions with color of different high concentrations (Inset: images of relevant metal ions).

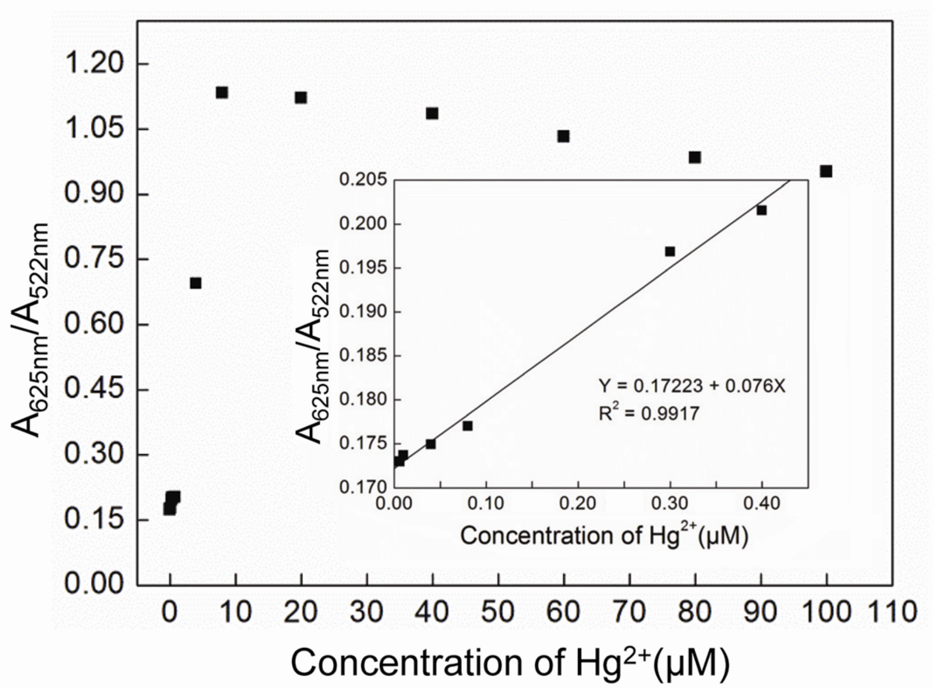

Fig. S6 The calibration curve for the detection of Hg^{2+} by the the modified AuNPs dispersions. The ratio (A_{625nm}/A_{522nm}) was plotted against different concentrations of Hg^{2+}. Where A_{625nm} is the new absorption peak in the present of Hg^{2+} in the wavelength of 625nm and A_{522nm} is the original absorption peak in the wavelength of 522nm.

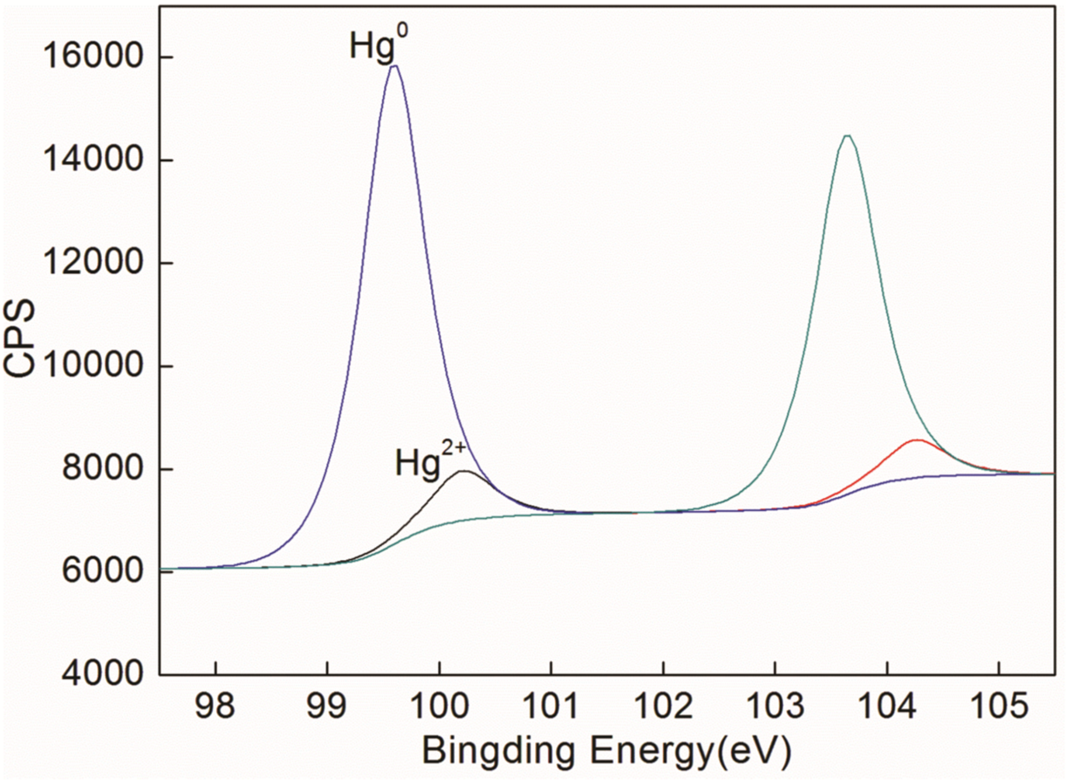

Fig.S7 The XPS characterization of modified AuNPs in the presence of Hg^{2+}.

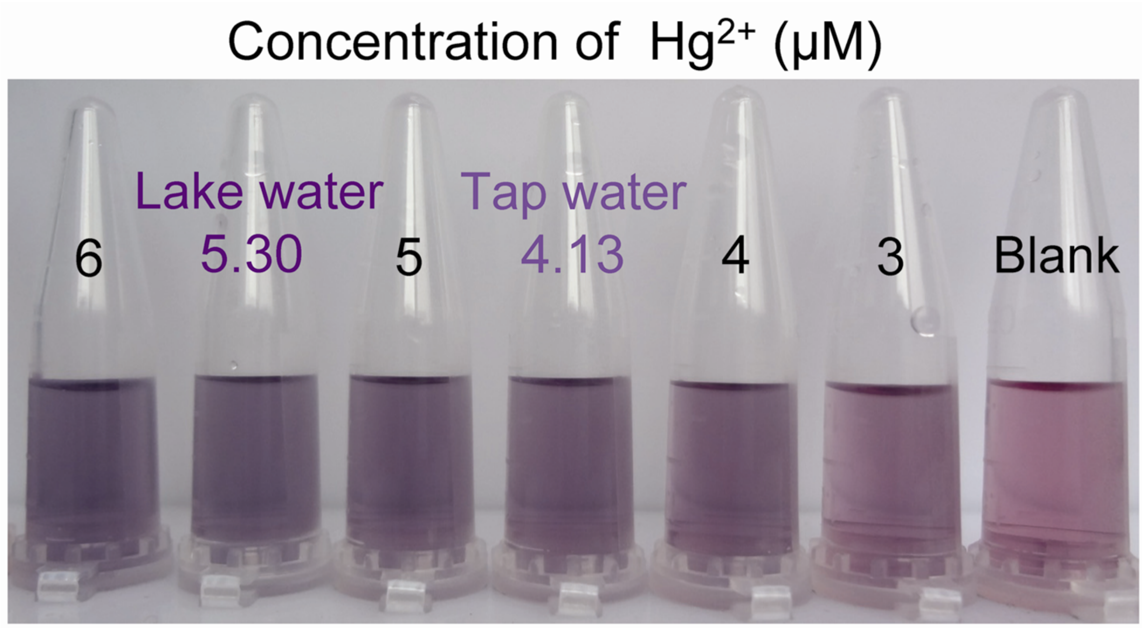

Fig. S8 Image of colorimetric detection of real water samples.

Table S1. Influence of potentially interfering ions

Potentially interfering ions	Tolerance ratios (compared to 4×10^{-7}M)
Na^+, K^+, Ca^{2+}, NO_3^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-} Cl^-	15000
Ba^{2+}, Mg^{2+}	7500
Mn^{2+}, Cd^{2+}, Cr^{3+}	750
Zn^{2+}, Ni^{2+}, Pb^{2+}, Al^{3+}, $Cr_2O_7^{2-}$	150
Fe^{3+}, Co^{2+}	75

Table S2. Determination of Hg^{2+} in real water samples

Samples	Hg^{2+}added (µM)	Hg^{2+} observed (µM) (Mean±E, n=3)	ICP-AES observed (µM)
Lake water	0.5	0.62±0.181	0.85
Tap water	0.5	0.65±0.066	0.33