Electronic Supporting Information

for

Fluorescent sensing of mercury(II) based on formation of catalytic gold nanoparticles

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Experimental Section

Chemicals and apparatus

Hydrogen tetrachloroaurate(III) dehydrate, trisodium citrate, $HgCl_2$ and *o*-phenylenediamine were obtained from Sinopharm® Chemical Reagent (China). All other chemicals were analytical reagent grade or better. Solutions were prepared with deionized water (18.2 MΩ, Pall® Cascada). Fluorescence spectra were performed on Fluoromax-4® (Horiba Scientific). Absorption spectra of AuNPs were scanned by the UV/visible spectrophotometer (Beckman Coulter® DU-800, USA). Images of dispersed AuNPs were achieved by transmission electron microscopy (TEM, JEOL® JEM-1230, Japan) operated at 100 kV.

Gold nanoparticles synthesis

Citrate-capped gold nanoparticles were prepared by means of the chemical reduction

of $HAuCl_4$ by citrate in the liquid phase. Briefly, 200 mL aqueous solution of 0.25 mM $HAuCl_4$ was first brought to boil with vigorous stirring. Then 1.2 mL trisodium citrate with a concentration of 50 mM was added rapidly and the mixture was heated under reflux for another 15 min. During the process, the color changed from pale yellow to red. Thereafter, the solution was cooled to room temperature while being stirred continuously. The size of AuNPs, as determined by TEM imaging, was 30 nm (Fig. S1). The concentration of the synthesized AuNPs was estimated about 1.4×10^{-10} M.

Procedure

To 900 μL deionized water, 100 μL Britton-Robinson, 10μL $HgCl_2$ and 10 μL Polyethylene Glycol (PEG, M = 6000, 1%), 15 μL AuNPs were successively added. The solution was incubated for ~ 1 min at room temperature. After that, 10 μL *o*-phenylenediamine with a concentration of 0.21 M was added. The solution was then transferred for fluorescence spectra scanning after incubating for 25 min at room temperature.

Determination of Hg^{2+} in drinking water sample

Drinking water collected from our institute was first filtered through a 0.22 μm membrane. To the water sample, few drops of 0.5 M HNO_3 was added to adjust pH to 5.65. Then 900 μL of water sample was mixed with 100 μL BR buffer, PEG, AuNPs and *o*-phenylenediamine as described in procedure.

Evidence for formation of gold amalgam

In Long's work (Chem. Commun., 2011, 47, 11939), the author verified the formation of gold amalgam by XPS experiment. In this work, the experiment condition was almost consistent with that reported in Long's literature. Therefore, we deduced that gold amalgam also existed in our system. The deduction was further verified by ICP-MS. The ICP-MS intensities of Hg^{2+} (10^{-7} M) was examined to be 5019, while the intensities of Hg in supernatant and precipitation after addition of AuNPs to the solution containing 10^{-7} M Hg^{2+} followed by centrifugation were 530 and 4913, respectively. These results indicated that Hg was enriched on nanoparticles owing to

the formation of gold amalgam.

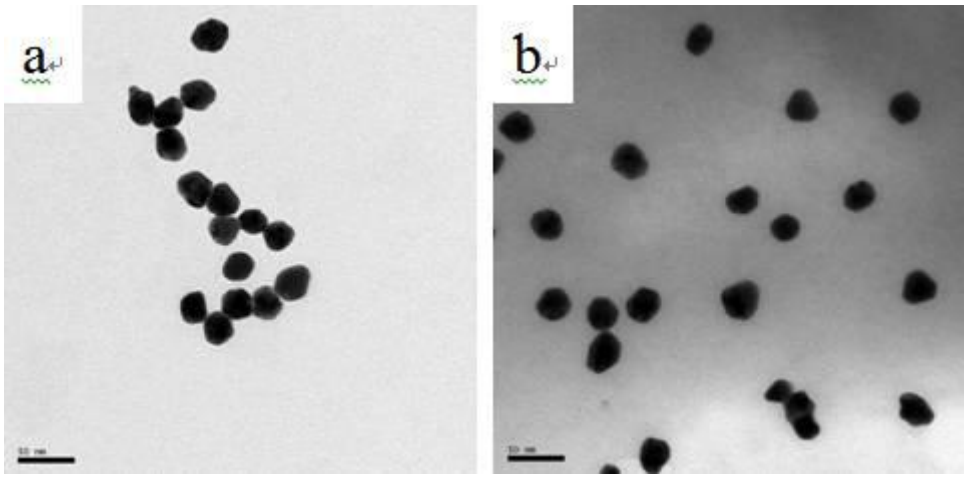

Fig. S1 TEM images of synthesized AuNPs (a) and Hg-Au alloys. There is no obvious difference between AuNPs and Hg-Au nanoparticles.

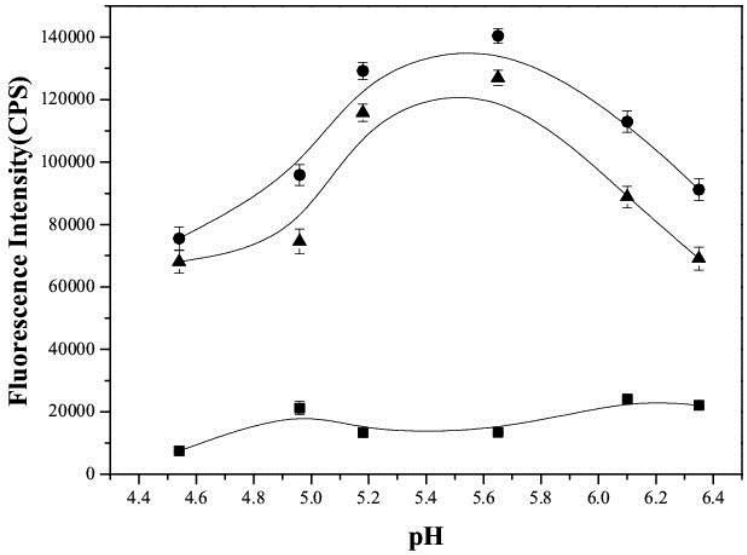

Fig. S2 Effect of pH on the fluorescence intensity at 562 nm in the absence (■) and presence (●) of 5.0×10^{-8} M Hg^{2+}. ▲ is the difference between the fluorescence intensity (F_{Hg} - F_{blank}). Other conditions: volume of AuNP 15 μL; PEG 0.01%; *o*-phenylenediamine 2.1 mM; incubation time 20 min.

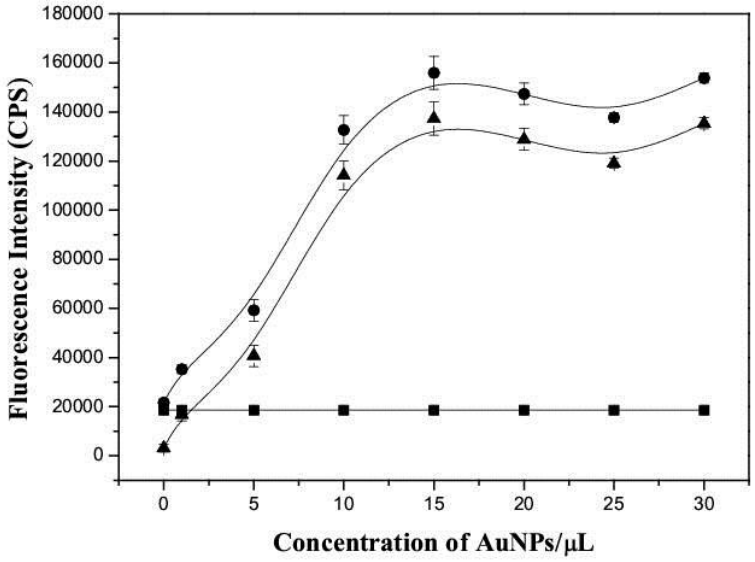

Fig. S3 Effect of the volume of AuNPs on the fluorescence intensity at 562 nm in the absence (■) and presence (●) of 5.0×10^{-8} M Hg^{2+} . ▲ is the difference between the fluorescence intensity (F_{Hg} - F_{blank}). Other conditions: pH 5.65; PEG 0.01%; *o*-phenylenediamine 2.1 mM; incubation time 20 min.

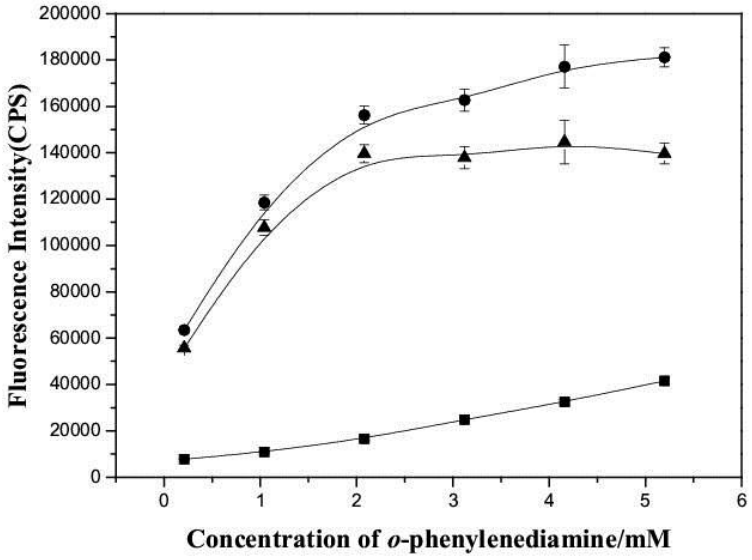

Fig. S4 Effect of the concentration of *o*-phenylenediamine on the fluorescence intensity at 562 nm in the absence (■) and presence (●) of 5.0×10^{-8} M Hg^{2+} . ▲ is the difference between the fluorescence intensity (F_{Hg} - F_{blank}). Other conditions: pH 5.65; PEG 0.01%; volume of AuNP 15μL; incubation time 20 min.

The signals of blank and sample both increased with the concentrations of o-phenylenediamine. The sensitivity depends on the signal-to-noise ratio. When the concentration of o-phenylenediamine was 2.1 mM, the difference of the signals

between the presence and the absence of Hg^{2+} was obvious, meanwhile, the signal-to-noise ratio was larger than what can be achieved by using 3 mM o-phenylenediamine. So 2.1 mM o-phenylenediamine was selected.

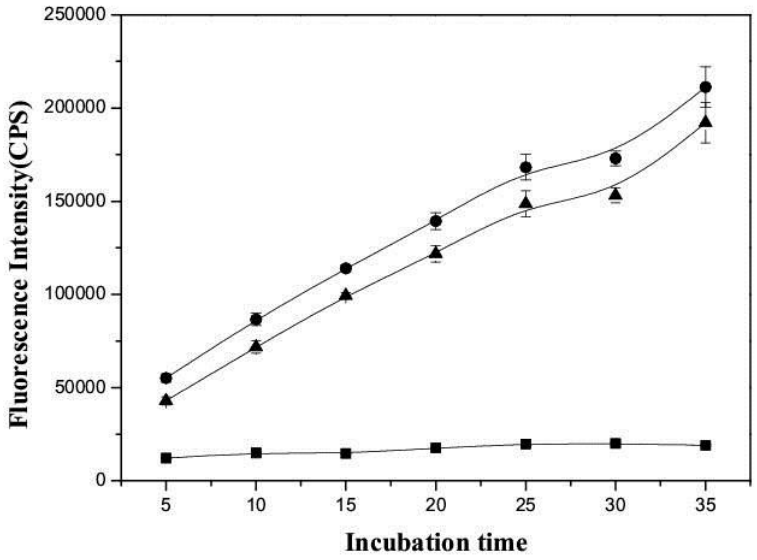

Fig. S5 Effect of incubation time on the fluorescence intensity at 562 nm in the absence (■) and presence (●) of 5.0×10^{-8} M Hg^{2+} . ▲ is the difference between the fluorescence intensity (F_{Hg} - F_{blank}). Other conditions: pH 5.65; PEG 0.01%; volume of AuNP 15μL; *o*-phenylenediamine 2.1 mM.

The signal value increased linearly with the incubation time. Theoretically, the sensitivity depends on the signal-to-noise ratio. For the signals of blank and sample both increased linearly with the incubation time, we can conclude that the increasing incubation time would not improve the sensitivity. We chose 20 min as the optimal incubation time because '20 min' was easy to be controlled accurately. Assumed that the whole incubation time error is 30 s, the detection error is 0.5/20×100% = 2.5%. Of course, less incubation time might result in more error, and more incubation time is time-consuming.

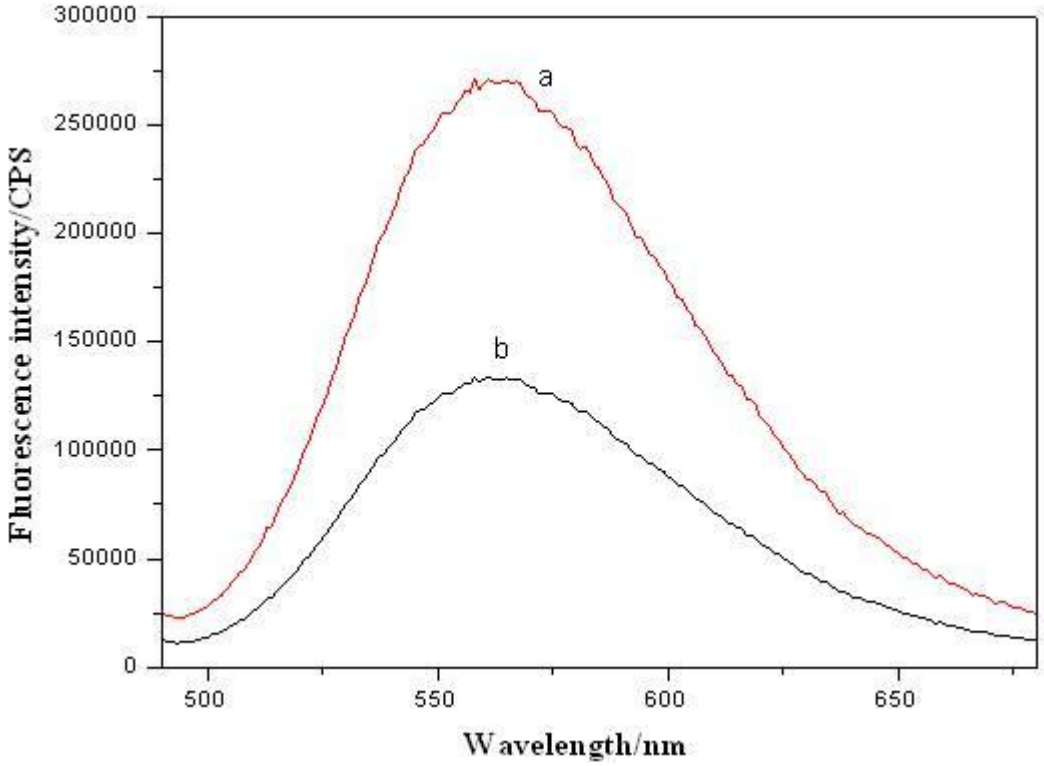

Fig. S6 Fluorescent emission spectra for sensing of 10^{-7} Hg^{2+} (a) and 1.04 μM 2,3-diaminophenazine (b). (using for illustrating the effect of the concentration of dissolved oxygen)

The fluorescence intensity at 562 nm recorded for the BR solution containing 1.04×10^{-6} M 2,3-diaminophenazine was about half of the intensity for the determination of 10^{-7} M Hg^{2+}. Assumed that the fluorescence intensity was linear with the concentration of 2,3-diaminophenazine, the 2,3-diaminophenazine produced in the determination of 10^{-7} M Hg^{2+} was about 2.08×10^{-6} M. For the saturation concentration of oxygen in water is about 2.58×10^{-4} M, These results meant that only 1.63% dissolved oxygen was consumed. We concluded that the concentration of dissolved oxygen was sufficient for determination of different concentration of Hg^{2+} less than 10^{-7} M and did not change in the whole sensing process. The conclusion was also supported by the effect of incubation time on the fluorescence intensity. That the fluorescence intensity was almost linear with the increase of incubation time indicated the catalytic reaction rate was steady, demonstrating all the concentration of substrates were almost unchanged.

Table S1 Fluorescence intensity before and after pumping oxygen to the sensing system in the presence of Hg^{2+} (0.1 μM) or not. the standard deviation of each sample was obtained by three measurements.

Samples	Fluorescence Intensity before addition of Hg^{2+}/CPS	Fluorescence Intensity after addition of 1×10^{-7} Hg^{2+}/CPS
Sample after pumping oxygen for 20 min	14798 ± 341.863	288680 ± 13113.45
Sample without pumping oxygen	14699 ± 262.981	270330 ± 10855.27

The fluorescence intensities at 562 nm before and after pumping oxygen to the test solution for 20 min were almost the same, indicating dissolved oxygen in samples was saturated before pumping of oxygen.

Fig. S6 and Table S1 indicated that need no approach to control the concentration of dissolved oxygen for sensing of Hg^{2+}.