Electronic Supporting Information

for

Visual observation on the mercury-stimulated peroxidaes mimetic activity of gold nanoparticles

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Experimental Section

Materials

Hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4·4H_2O$) were purchased from Sinopharm Group Chemical Regent Co.,Ltd (Shanghai, China). Trisodium citrate ($Na_3C_6H_5O_7·2H_2O$) and $HgCl_2$ were supplied by the Chemical Reagent Co., Ltd. (Shanghai, China). Sodium borohydride ($NaBH_4$) was purchased from Huanwei Fine Chemical Co., Ltd, Tianjin, China). 3, 3, 5, 5-tetramethylbenzidine (TMB) was supplied by Sigma-Aldrich (St. Louis, MO). All of the reagents used were of analytical grade without further purification. Ultra-pure water prepared with a Milli-Q Pure system (18.2 MΩ) was used throughout.

Preparation of citrate capped AuNPs

Gold nanoparticles (AuNPs) were synthesized as reported [1]. All glassware used was thoroughly cleaned using aqua regia solution (HCl/HNO_3 in volume = 3: 1) and oven-dried prior to use. Briefly, in a flask with a condenser, 50 ml Ultra-pure water containing 0.25 mM $HAuCl_4$ was brought to a boil with rigorous stirring. Then 300 μL of 50 mM trisodium citrate was added quickly. The solution turned dark-blue within 2 minutes and about 30 s latter, the color change to be red. Kept boiling for about 15 min and removed the heating source. Stopped stirring when the colloid solution reached room temperature.

And the concentration was estimated about 1.4 × 10^{-10} M according to molar extinction coefficient of 3.0 × 10^{9} cm^{-1} M^{-1} at 530.0 nm for 30-nm particles as reported [2].

Procedure

First, 25 µL of 1.4 × 10^{-10} M AuNPs, 110 µL of 1.0 × 10^{-3} M TMB, 70µL of 5.0 M H_2O_2, 50 µL of Britton-Robinson buffer (pH 4.1) were pipetted into a 1.5 mL vial, and then an appropriate volume of $HgCl_2$ working solution was added. After that, the mixture was diluted to 500 µL and vortex mixed thoroughly. The solution was then transferred for UV-vis scanning after incubating for 20 minutes.

TEM

The size of the AuNPs was characterized by TEM on a Tecnai G^2 20 transmission electron microscopy (FEI, Netherlands).

XPS

X-ray photoelectron spectroscopy (XPS) spectra were measured by a Thermo ESCALAB250 X-ray photoelectron spectroscope (Thermo, UK). Citrate capped AuNPs solution containing Hg^{2+} was dropped on a Pt substrate and oven-dried before measurement.

UV-Vis detection

UV-Vis spectra were recorded using a UV-3600 UV-Vis spectrophotometer (Shimadzu, Japan). Absorbance at 652 nm were monitored for quantitative analysis.

EPR

EPR signal was measured by a Bruker ESP 300E (X-band) spectrometer (Bruker, Rheinstetten, Germany) with microwave bridge (receiver gain, 1 × 105; modulation amplitude, 2 Gauss; microwave power, 10 mW; modulation frequency, 100 kHz). A sample containing 0.1 M DMPO was transferred to a quartz capillary tube and placed in the EPR cavity. Under the UV-irradiation at 355 nm, EPR signal was detected.

Determination of Hg^{2+} in the lake water samples.

Water samples were obtained from different locations in Chongde Lake on the campus of our University. The samples collected were first filtered through a 0.22 μm membrane and a column (packed with an anionic-exchange resin) to remove oils and other organic impurities [3]. After boiled for 5 min, 50 ml water sample was concentrated to 5 ml by rotary evaporation. 2M HNO_3 was used to adjust the sample's pH to about 4. Then, 150 μL of the water sample was mixed with buffer, AuNPs, TMB and H_2O_2 as described in **procedure**.

To estimate the accuracy of this method, we measured the mercury concentration in the concentrated sample and compared our results with the hydride generator -AAS method.

AAS assay.

AAS signals were recorded by a TAS-986 Atomic Absorption Spectrophotometers (Beijing Purkinje General Instrument Co. Ltd, Beijing, China).

Figures

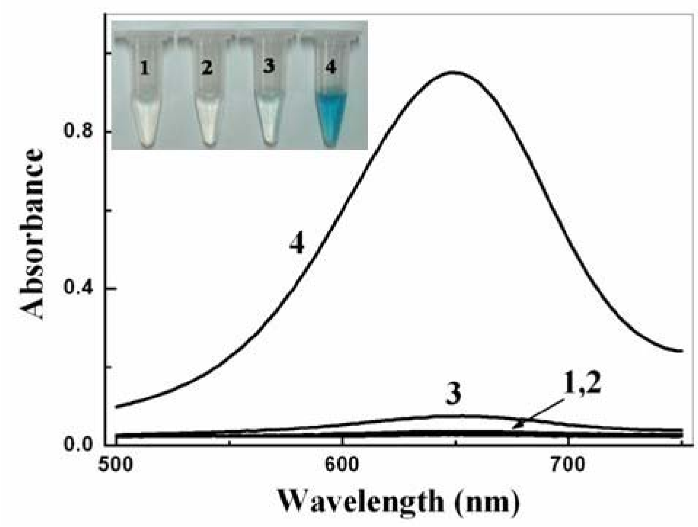

Fig.S1 Typical absorption profiles for the Hg^{2+}-stimulated peroxides-like catalytic activity of AuNPs.1, 2.2 × 10^{-4} M TMB + 0.70 M H_2O_2; 2, 2.2 ×10^{-4} M TMB + 0.70 M H_2O_2 + 1.0 × 10^{-5} M Hg^{2+}; 3, 2.2 × 10^{-4} M TMB + 0.70 M H_2O_2 + 7.0 × 10^{-12} M AuNPs; 4, 2.2 × 10^{-4} M TMB + 0.70 M H_2O_2 + 7.0 × 10^{-12} M AuNPs +1.0 × 10^{-6} M Hg^{2+}; pH, 4.1

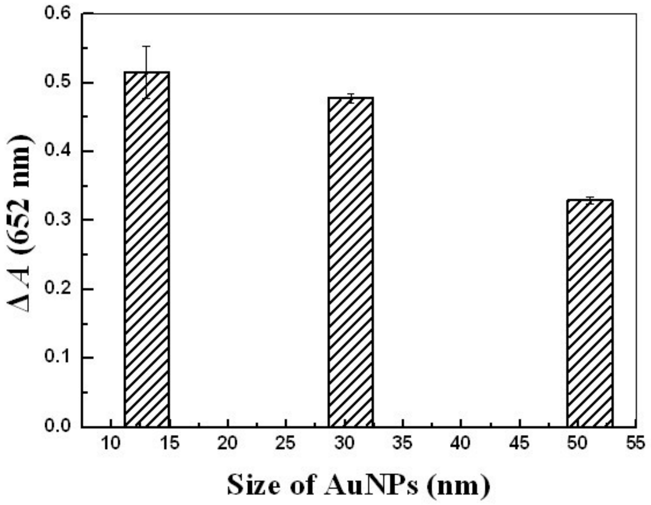

Fig. S2 Optimization of AuNPs size. AuNPs, 5.6 × 10^{-12} M; TMB, 2.2 × 10^{-4} M; Hg^{2+}, 3.0 × 10^{-7} M; pH, 4.1. incubation time, 20 min. RSD: 7.4%, 1.5%, 1.6% (from left to right, n = 5)

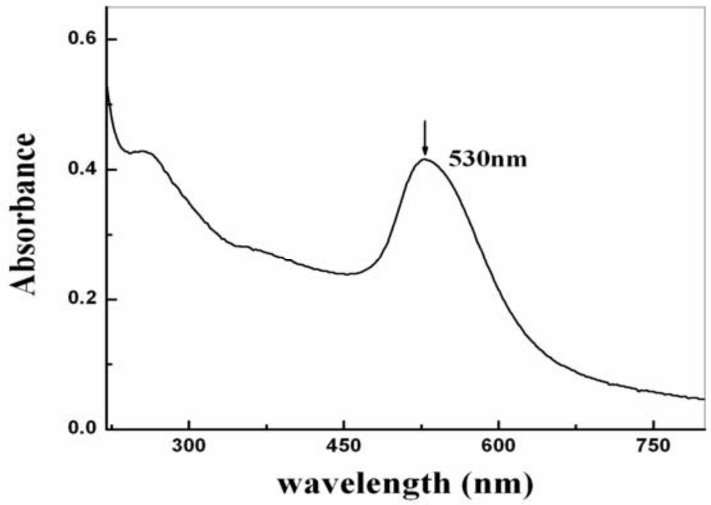

Fig. S3 Absorption of citrate-capped AuNPs. AuNPs, 1.4 × 10^{-10} M.

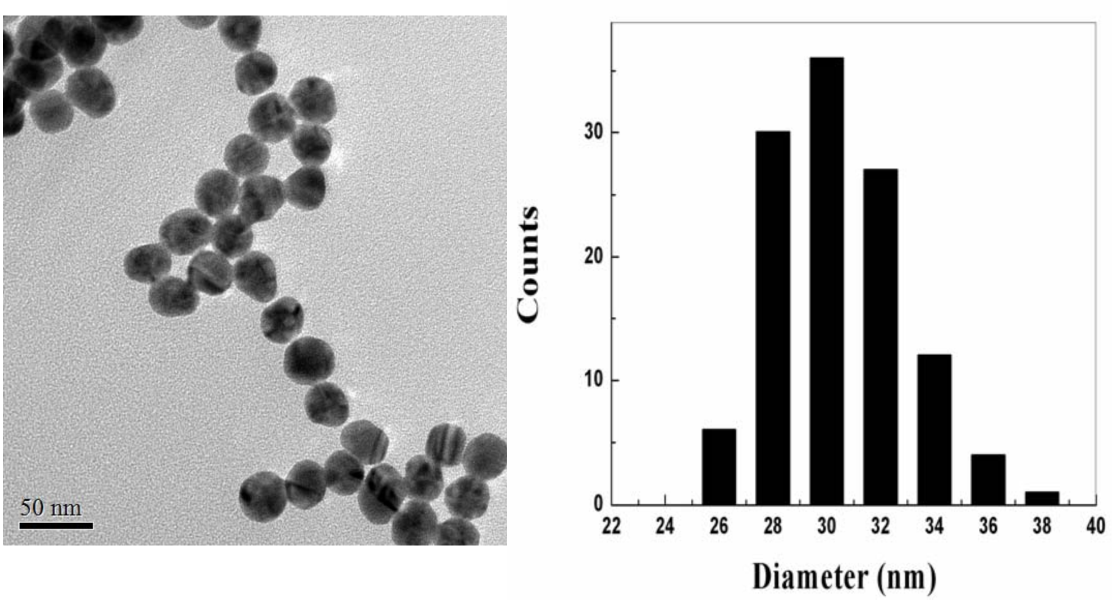

Fig. S4 TEM image of citrate-capped AuNPs and a histogram of the size distribution of AuNPs. The average particle size is 30.5 ± 2.8 nm and the total number of particles counted for the histogram is 116.

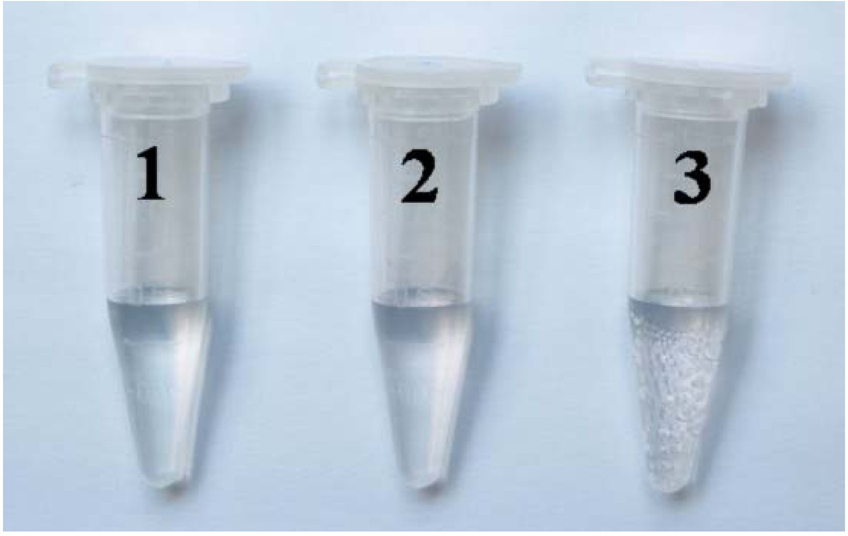

Fig. S5 Decomposition of H_2O_2. 1, 0.70M H_2O_2; 2, 0.70 M $H_2O_2 + 7.0 \times 10^{-12}$ M AuNPs; 3, 0.70 M H_2O_2 + 7.0×10^{-12} M AuNPs + 4.0×10^{-7} M Hg^{2+}. pH, 4.1. Incubation, 20 min. Addition of Hg^{2+} into the mixture of H_2O_2 and AuNPs (Vial 2) results in a lot of bubbles (Vial 3).

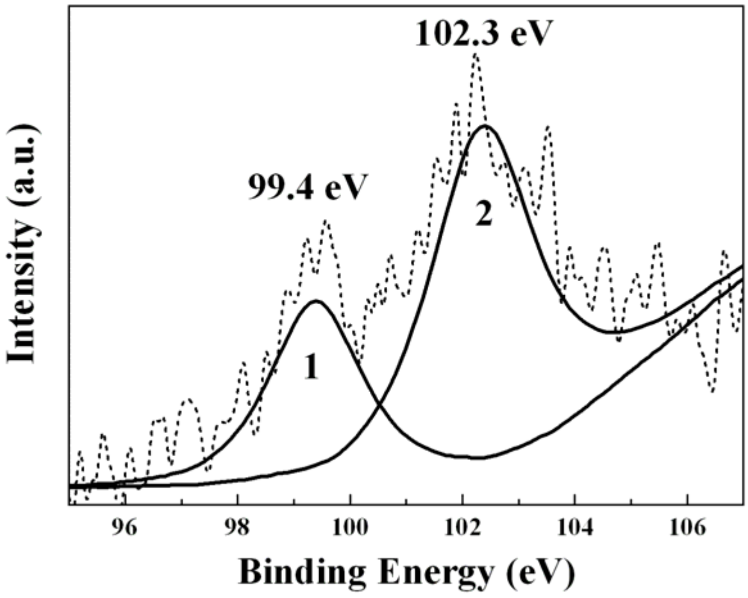

Fig. S6 XPS of mercury on the surface of the citrate capped AuNPs. 1, Hg^0; 2, Hg^{2+}.

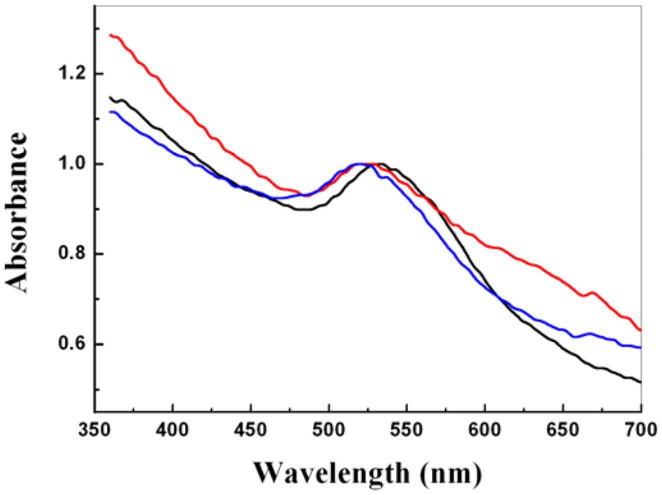

Fig. S7 Normalized absorption spectra of AuNPs. black: citrate capped AuNPs; red: citrate capped AuNPs + Hg^{2+}; blue: citrate capped AuNPs + Hg^{2+} + $NaBH_4$; AuNPs, 7.0×10^{-12} M; Hg^{2+}, 4.0×10^{-7} M; $NaBH_4$, 1.0×10^{-3} M; pH, 4.1. The blue-shifted surface plasmon absorption peak implicates that much more Hg^0 was reduced onto the surface of AuNPs.

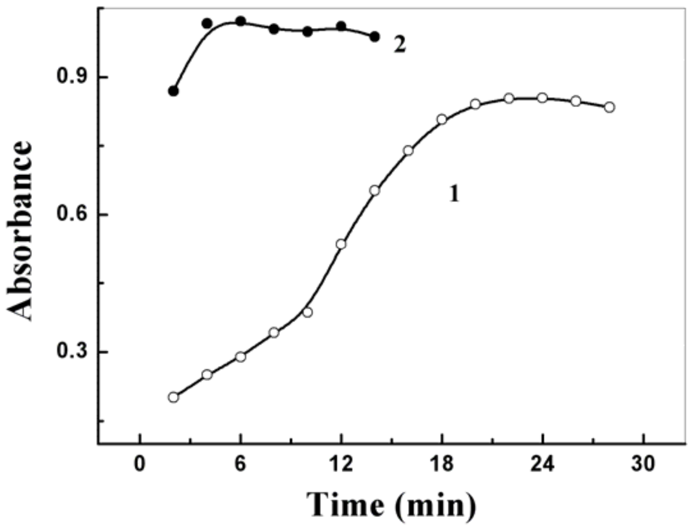

Fig. S8 Enhancing effects of mercury ions on the citrate-capped AuNPs catalytic activity in the absence (1) and presence (2) of sodium borohydride ($NaBH_4$). AuNPs, 7.0 × 10^{-12} M; TMB, 2.2 × 10^{-4} M; H_2O_2, 0.70 M; Hg^{2+}, 4.0 × 10^{-7} M; $NaBH_4$, 1.0 × 10^{-3} M; pH, 4.1.

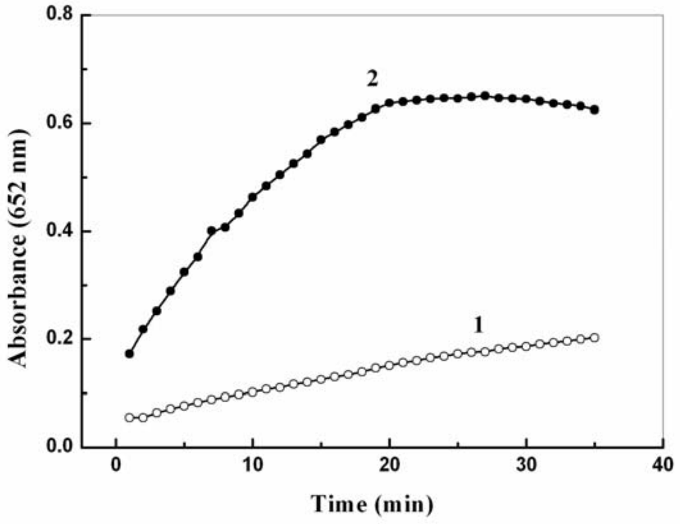

Fig. S9 Time-course of AuNPs/TMB/H_2O_2 in the absence (1) and presence (2) of Hg^{2+}. AuNPs, 5.6 × 10^{-12} M; TMB, 2.2 × 10^{-4} M; H_2O_2, 0.40 M; Hg^{2+}, 2.5 × 10^{-7} M; pH, 4.1.

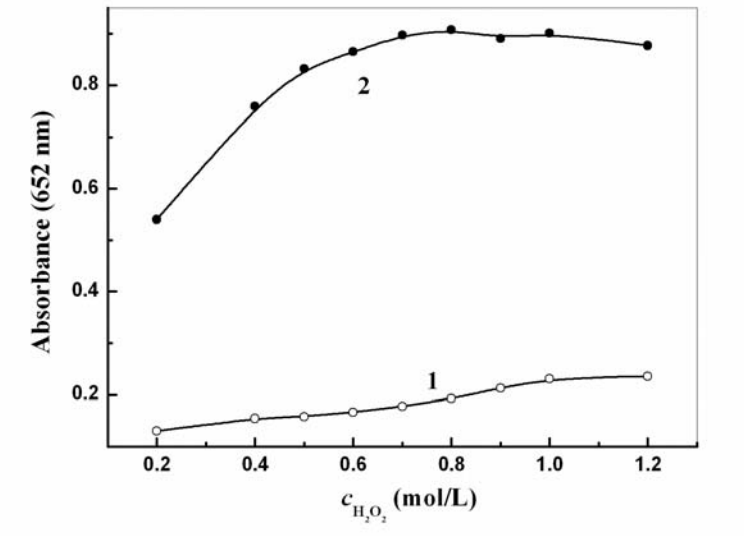

Fig. S10 Effect of the concentration of H_2O_2 on the AuNPs/TMB/H_2O_2 absorbance in the absence (1) and presence (2) of Hg^{2+}. AuNPs, 5.6×10^{-12} M; TMB, 2.2×10^{-4} M; Hg^{2+}, 4.0×10^{-7} M; pH, 4.1. incubation time, 20 min.

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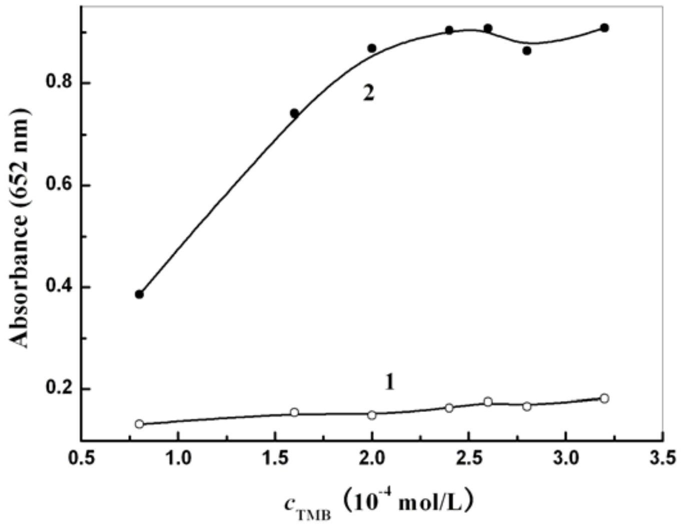

Fig. S11 Effect of the concentration of TMB on the AuNPs/TMB/H_2O_2 absorbance in the absence (1) and presence (2) of Hg^{2+}. AuNPs, 5.6×10^{-12} M; H_2O_2, 0.70 M; Hg^{2+}, 4.0×10^{-7} M; pH, 4.1. incubation time, 20 min.

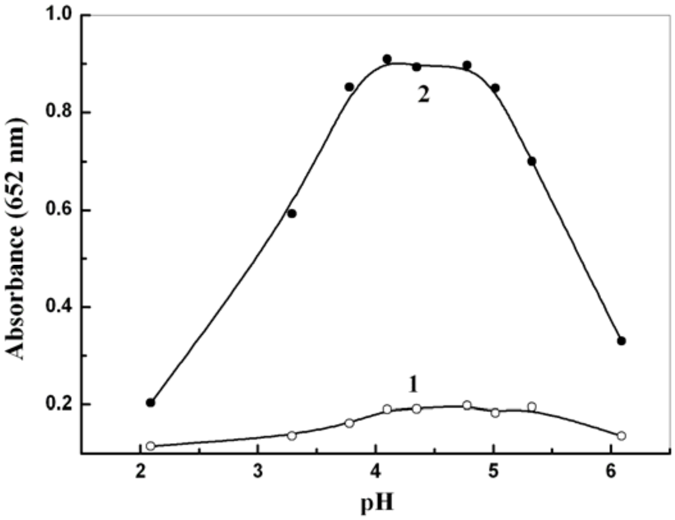

Fig. S12 Effect of pH on the AuNPs/TMB/H_2O_2 absorbance in the absence (1) and presence (2) of Hg^{2+}. AuNPs, 5.6 × 10^{-12} M; TMB, 2.2 × 10^{-4} M; H_2O_2, 0.70 M; Hg^{2+}, 4.0 × 10^{-7} M; incubation time, 20 min.

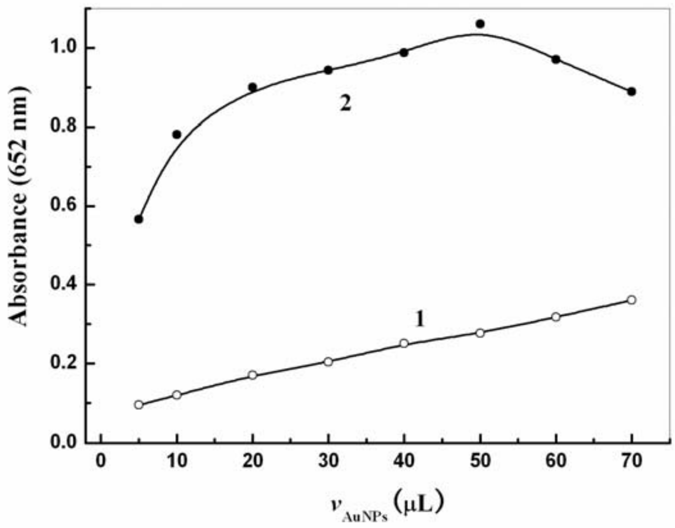

Fig. S13 Effect of the volume of AuNPs on the AuNPs/TMB/H_2O_2 absorbance in the absence (1) and presence (2) of Hg^{2+}. TMB, 2.2 × 10^{-4} M; H_2O_2, 0.70 M; Hg^{2+}, 4.0 × 10^{-7} M; pH, 4.1; incubation time, 20 min.

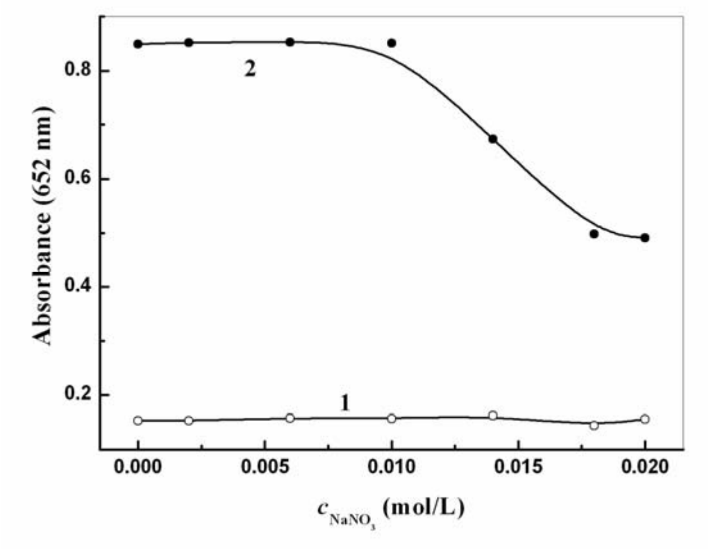

Fig. S14 Effect of the ionic strength on the AuNPs/TMB/H_2O_2 absorbance in the absence (1) and presence (2) of Hg^{2+}. AuNPs, 7.0 × 10^{-12} M; TMB, 2.2 × 10^{-4} M; H_2O_2, 0.70 M; Hg^{2+}, 4.0 × 10^{-7} M; pH, 4.1; incubation time, 20 min.

Table S1 Determination of Hg^{2+} in water samples.

samples	**Results obtained by proposed method (n=3, P=0.90)(** 10^{-8}M**)**	**Results obtained by AAS (n=3, P=0.90) (** 10^{-8}M**)**
1	4.06 ± 0.096	4.13 ± 0.079
2	4.82 ± 0.11	4.71± 0.083

References

1. K. C. Gradar, R. G. Freeman, M. B. Hommer, M. J. Natan, ***Anal. Chem***. 1995, **67**, 735-743.
2. G. K. Darbha, A. K. Singh, U. S. Rai, E. Yu, H. Yu and P. Chandra Ray; ***J. Am. Chem. Soc.*** 2008, **130**, 8038.
3. H. Wang, Y. X. Wang, J. Y. Jin and R. H. Yang, ***Anal. Chem***. 2008, **80**, 9021.