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 (HAuCl4·4H2O) were purchased from Sinopharm Group Chemical Regent Co., Ltd. (Shanghai, China). Trisodium citrate (Na3C6H5O7·2H2O) and HgCl2 were supplied by the Chemical Reagent Co., Ltd. (Shanghai, China). Sodium borohydride (NaBH4) 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/HNO3 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 HAuCl4 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 $1.4 \times 10^{-10}$ M according to molar extinction coefficient of $3.0 \times 10^9$ cm$^{-1}$ M$^{-1}$ at 530.0 nm for 30-nm particles as reported [2].

**Procedure**

First, 25 µL of $1.4 \times 10^{-10}$ M AuNPs, 110 µL of $1.0 \times 10^{-3}$ M TMB, 70µL of 5.0 M H$_2$O$_2$, 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 spectroscopy (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, $1 \times 10^5$; 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$_2$O$_2$ 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).
Fig. S1 Typical absorption profiles for the Hg$^{2+}$-stimulated peroxides-like catalytic activity of AuNPs: 1, $2.2 \times 10^{-4}$ M TMB + 0.70 M H$_2$O$_2$; 2, $2.2 \times 10^{-4}$ M TMB + 0.70 M H$_2$O$_2$ + $1.0 \times 10^{-5}$ M Hg$^{2+}$; 3, $2.2 \times 10^{-4}$ M TMB + 0.70 M H$_2$O$_2$ + $7.0 \times 10^{-12}$ M AuNPs; 4, $2.2 \times 10^{-4}$ M TMB + 0.70 M H$_2$O$_2$ + $7.0 \times 10^{-12}$ M AuNPs + $1.0 \times 10^{-6}$ M Hg$^{2+}$; pH, 4.1

Fig. S2 Optimization of AuNPs size. AuNPs, $5.6 \times 10^{-12}$ M; TMB, $2.2 \times 10^{-4}$ M; Hg$^{2+}$, $3.0 \times 10^{-7}$ 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, $1.4 \times 10^{-10}$ M.
**Fig. S4** TEM image of citrate-capped AuNPs and a histogram of the size distribution of AuNPs. The average particle size is $30.5 \pm 2.8$ nm and the total number of particles counted for the histogram is 116.

**Fig. S5** Decomposition of $\text{H}_2\text{O}_2$. 1, 0.70M $\text{H}_2\text{O}_2$; 2, 0.70 M $\text{H}_2\text{O}_2 + 7.0 \times 10^{-12}$ M AuNPs; 3, 0.70 M $\text{H}_2\text{O}_2 + 7.0 \times 10^{-12}$ M AuNPs + $4.0 \times 10^{-7}$ M Hg$^{2+}$. pH, 4.1. Incubation, 20 min. Addition of Hg$^{2+}$ into the mixture of $\text{H}_2\text{O}_2$ 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 (NaBH₄). AuNPs, $7.0 \times 10^{-12}$ M; TMB, $2.2 \times 10^{-4}$ M; H₂O₂, 0.70 M; Hg²⁺, $4.0 \times 10^{-7}$ M; NaBH₄, $1.0 \times 10^{-3}$ M; pH, 4.1.

**Fig. S9** Time-course of AuNPs/TMB/H₂O₂ in the absence (1) and presence (2) of Hg²⁺. AuNPs, $5.6 \times 10^{-12}$ M; TMB, $2.2 \times 10^{-4}$ M; H₂O₂, 0.40 M; Hg²⁺, $2.5 \times 10^{-7}$ M; pH, 4.1.
**Fig. S10** Effect of the concentration of $\text{H}_2\text{O}_2$ on the AuNPs/TMB/H$_2$O$_2$ absorbance in the absence (1) and presence (2) of Hg$^{2+}$. AuNPs, $5.6 \times 10^{-12}$ M; TMB, $2.2 \times 10^{-4}$ M; Hg$^{2+}$, $4.0 \times 10^{-7}$ M; pH, 4.1. incubation time, 20 min.

**Fig. S11** Effect of the concentration of TMB on the AuNPs/TMB/H$_2$O$_2$ absorbance in the absence (1) and presence (2) of Hg$^{2+}$. AuNPs, $5.6 \times 10^{-12}$ M; H$_2$O$_2$, 0.70 M; Hg$^{2+}$, $4.0 \times 10^{-7}$ M; pH, 4.1. incubation time, 20 min.
**Fig. S12** Effect of pH on the AuNPs/TMB/H$_2$O$_2$ absorbance in the absence (1) and presence (2) of Hg$^{2+}$. AuNPs, $5.6 \times 10^{-12}$ M; TMB, $2.2 \times 10^{-4}$ M; H$_2$O$_2$, 0.70 M; Hg$^{2+}$, $4.0 \times 10^{-7}$ M; incubation time, 20 min.

**Fig. S13** Effect of the volume of AuNPs on the AuNPs/TMB/H$_2$O$_2$ absorbance in the absence (1) and presence (2) of Hg$^{2+}$. TMB, $2.2 \times 10^{-4}$ M; H$_2$O$_2$, 0.70 M; Hg$^{2+}$, $4.0 \times 10^{-7}$ M; pH, 4.1; incubation time, 20 min.
Fig. S14 Effect of the ionic strength on the AuNPs/TMB/H$_2$O$_2$ absorbance in the absence (1) and presence (2) of Hg$^{2+}$. AuNPs, $7.0 \times 10^{-12}$ M; TMB, $2.2 \times 10^{-4}$ M; H$_2$O$_2$, 0.70 M; Hg$^{2+}$, $4.0 \times 10^{-7}$ M; pH, 4.1; incubation time, 20 min.

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

<table>
<thead>
<tr>
<th>samples</th>
<th>Results obtained by proposed method (n=3, P=0.90) (10$^{-8}$M)</th>
<th>Results obtained by AAS (n=3, P=0.90) (10$^{-8}$M)</th>
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<td>1</td>
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<td>4.82 $\pm$ 0.11</td>
<td>4.71$\pm$ 0.083</td>
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References

