

Electronic Supporting Information

for

High-throughput and ultratrace naked-eye colorimetric detection of Au^{3+} based on the gold amalgam-stimulated peroxidase mimetic activity in aqueous solutions

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Experimental Section

Materials

Hydrogen tetrachloroaurate (III) tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) were purchased from Sinopharm Group Chemical Reagent Co., Ltd (Shanghai, China). Hydrogen peroxide (H_2O_2 , 30%), citric acid ($\text{C}_6\text{H}_8\text{O}_7$), dibasic sodium phosphate (Na_2HPO_4), and other nitrate salts including (Na^+ , K^+ , NH_4^+ , Ag^+ , Ca^{2+} , Ba^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Fe^{2+} , Mg^{2+} , Al^{3+} , Co^{2+} , Mn^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , Fe^{3+} , Cr^{3+} and Hg^{2+}) were purchased from Tianjin Med.Co.Ltd. 3, 3', 5, 5'-tetramethylbenzidine ($\text{TMB} \cdot \text{HCl}$) 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 M Ω) was used throughout.

Instruments

The TEM measurements were carried out with a JEM-2100 (200 kV) instrument. The Hg NPs were dispersed in ultrapure water before deposited on copper grids.

Synthesis and characterization of citrate capped Hg NPs

Hg NPs were prepared according to previous literatures. Briefly, 150 μL Hg^{2+} was

added into 2 mL of citric acid–phosphate buffer solution (25 mM, pH 4.0) with stirring for 30 min.

Colorimetric analysis

Colorimetric investigations of peroxidase-like catalysis activities of the Au-Hg thin amalgam layer in the absence and presence of Au^{3+} were conducted using commercially-available TMB- H_2O_2 substrate and citric acid–phosphate buffer solution in quartz absorption cell. The colorimetric detection of Au^{3+} in aqueous solutions was performed at room temperature. Stock solutions (1 mM) of metal ions (Na^+ , K^+ , NH_4^+ , Ag^+ , Ca^{2+} , Ba^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Fe^{2+} , Mg^{2+} , Co^{2+} , Mn^{2+} , Cd^{2+} , Pb^{2+} , Al^{3+} , Fe^{3+} , Cr^{3+} and Hg^{2+}) were prepared in dd H_2O . Aqueous citric acid– phosphate buffer (25 mM, pH = 3, 4, 4.5, 5, 5.5, 6, 6.5, 7, 8, 9.38) was used to maintain the pH value of all the solutions used in the experiments.

In a typical test, chemicals were added into 1940 μL buffer solution (25 mM citric acid– phosphate, pH 4.0) in an order of certain amounts of 5.0 μL Hg^{2+} , 6.0 μL Au^{3+} (1.0 mM), 10 μL TMB (0.10 mM) and 40 μL H_2O_2 (30%) (0.40 M). The concentrations ranging from 1 mM to 1 μM of Au^{3+} solution were prepared using serial dilution of the stock solution. The color change was recorded instantly and the photographs were taken using Nikon j5 digital camera.

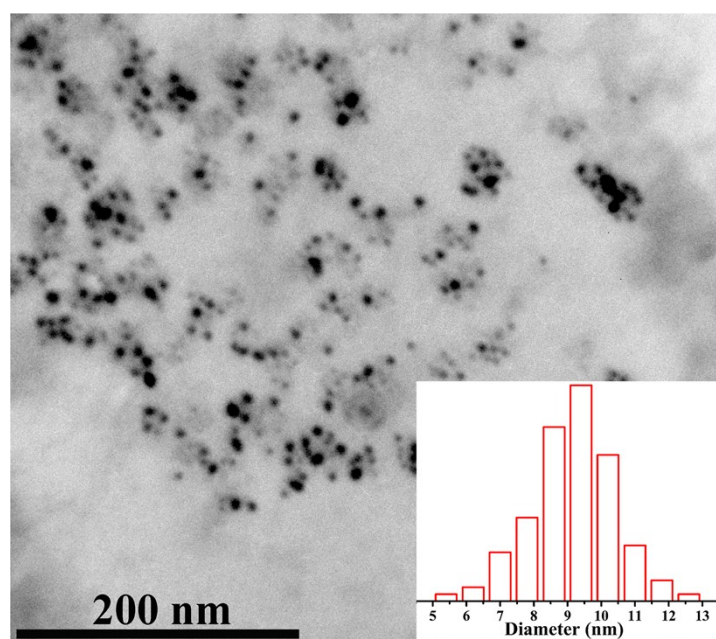


Figure S1. TEM images of Hg NPs, Insert: inset: the nanoparticle size distribution of Hg NPs.

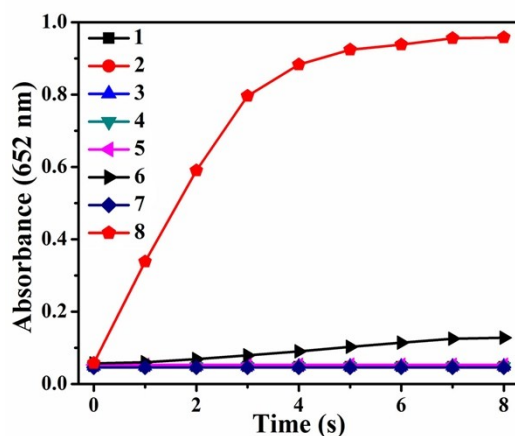


Figure S2. Time-dependent absorbance changes at 652 nm of the reaction solutions (1) black, (2) buffer + TMB, (3) buffer + H_2O_2 , (4) buffer + Hg^{2+} , (5) buffer + TMB + Hg^{2+} , (6) buffer + TMB + H_2O_2 + Hg^{2+} , (7) buffer + H_2O_2 + Hg^{2+} , (8) buffer + TMB + H_2O_2 + Hg^{2+} + Au^{3+} under the optimal experiment conditions.

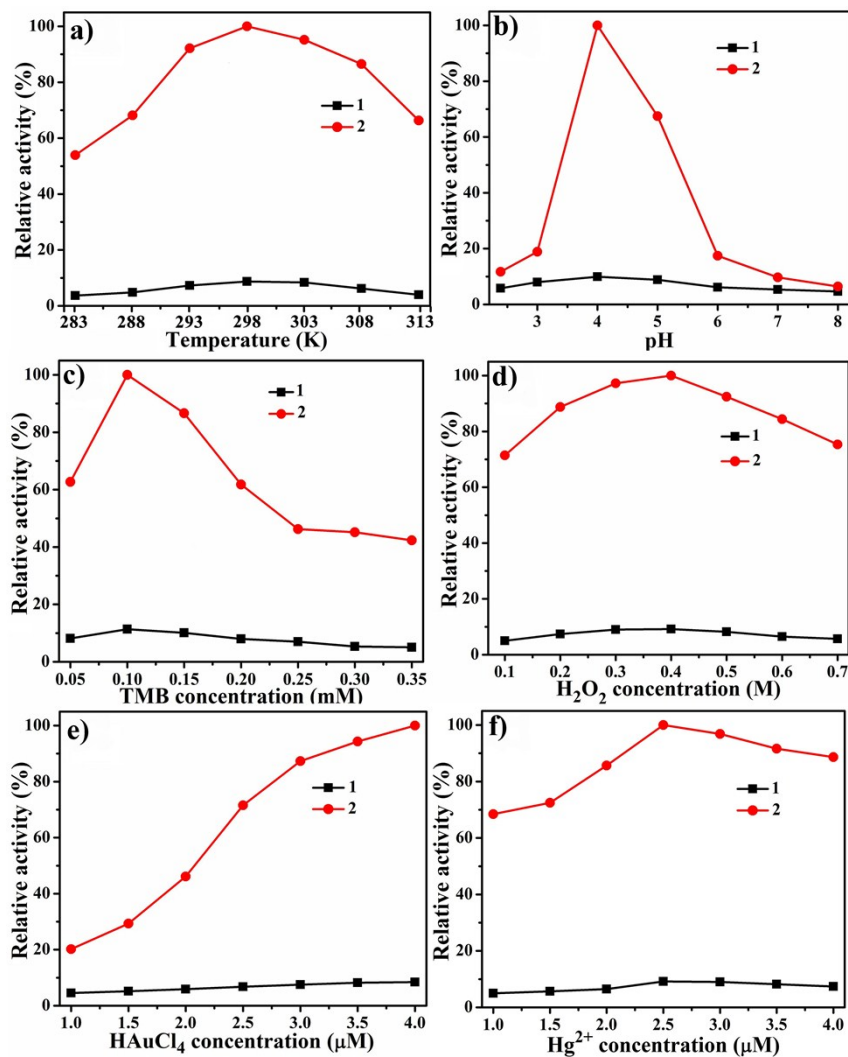
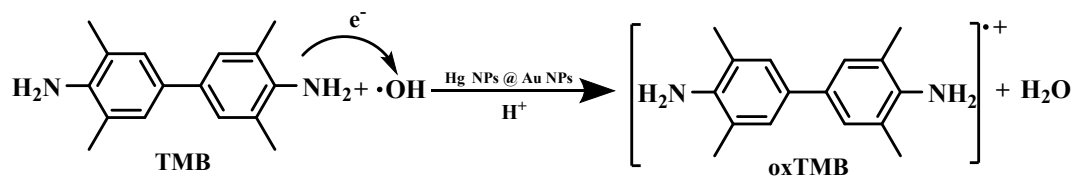


Figure S3. The mercury-stimulated peroxides-like catalytic activity of the Au-Hg thin amalgam layer in the absence (black) and presence (red) of Au^{3+} is dependent on (a) temperature, (b) pH, (c) TMB concentration, (d) H_2O_2 concentration, (e) Au^{3+} and (f) Hg^{2+} concentration.



This reaction equation is the key point of this manuscript. Under acid conditions, TMB (3, 3', 5, 5'-tetramethylbenzidine) can be oxidized by hydroxyl radical and obtain a blue color product (oxTMB) along with a color change from colorless to dark blue in solution that was detected by naked-eyes and absorption spectroscopic method. In the presence of gold ions, the peroxidase mimetic activity of Hg NPs was found to be stimulated and enhanced significantly. In this work, we used the citric acid-phosphate buffer not only as a pH adjustment but also as a reductant.

For temperature, because the Hg NPs @ Au NPs is a kind of catalyst possessing peroxidase mimetic activity, the temperature can affect the efficiency of catalyst. Thus, the analytical response increases or decreases when increasing the temperature.

For pH, we use the citric acid-phosphate buffer acting as a pH adjustment. On the one hand, the buffer can provide an acid environment to the reaction of the TMB oxidation. So the analytical response increases or decreases when increasing the pH. On the other hand, the efficiency of catalyst may rest with the reduction of Au^{3+} to Au^0 . When the pH value is 4.0, Au^{3+} maybe more easily reduced to Au^0 than other pH values.

For the concentration of TMB, H_2O_2 , TMB and H_2O_2 are the substrates of the catalytic reaction. As the concentration of substrates reach to saturation, the efficiency of catalytic reaction reaches to the maximum.

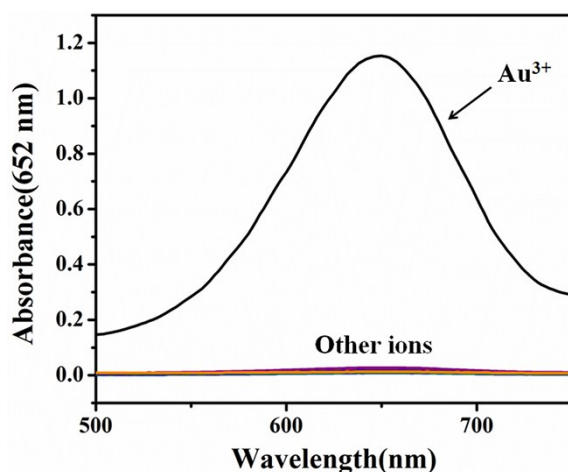


Figure S4. The UV-Vis absorption spectra of peroxidase mimetic activity of the Au-Hg thin amalgam layer in the presence of other metal ions and Au^{3+} .

Under acid conditions, generally, TMB (3, 3', 5, 5'-tetramethylbenzidine) can be oxidized by hydroxyl radical and obtain a blue color product (oxTMB) along with a color change from colorless to dark blue in solution which can be detected by naked-eyes. In the presence of gold ions, the peroxidase mimetic activity of Hg NPs was found to be stimulated and enhanced significantly. In this work, we used the citric acid-phosphate buffer not only as a pH adjustment but also as a reductant. Firstly, Hg^{2+} ions were reduced by citrate in the citric acid-phosphate buffer solution to form Hg^0 which was used as precursors to produce Hg NPs. Then, Au^{3+} ions were reduced by citrate to form Au^0 which can deposit on the surface of Hg NPs by forming gold amalgam which could greatly change the physico-chemical property of the nanoparticle surface, at which H_2O_2 molecules were decomposed efficiently to form highly reactive hydroxyl radicals that oxidized TMB to a dark blue.