



# A new simple and reliable Hg<sup>2+</sup> detection system based on anti-aggregation of unmodified gold nanoparticles in the presence of O-phenylenediamine



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## ABSTRACT

A simple and reliable colorimetric detection system based on anti-aggregation of gold nanoparticles (AuNPs) is proposed for rapid detection of Hg<sup>2+</sup> with high selectivity and sensitivity. O-phenylenediamine (OPD) can cause the aggregation of AuNPs due to formation of the strong covalent NH—Au bond, and then induce color change of the AuNPs solution from red to blue. However, in the presence of Hg<sup>2+</sup>, OPD prefers to combine with Hg<sup>2+</sup> rather than AuNPs resulting in inhibition of the color change. Based on the anti-aggregation mechanism, Hg<sup>2+</sup> can be detected by observing the color change of AuNPs solution containing OPD. After optimization, the selectivity of this Hg<sup>2+</sup> detection system by the naked eyes and UV–vis spectra is excellent comparing with other ions. The limit of the detection (LOD) is 0.1 μM by the naked eyes and 5.0 nM by UV–vis spectroscopy, which is lower than the mercury toxic level (10 nM) defined by US Environmental Protection Agency. It's a good linear relationship between A<sub>520</sub>/A<sub>680</sub> and Hg<sup>2+</sup> concentration from 0.01 μM to 2.0 μM, which is used for the quantitative assay of Hg<sup>2+</sup>. The applicability of our detection system is also verified by analysis of Hg<sup>2+</sup> in tap water and lake water.

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## 1. Introduction

As we all know, mercury is widely used in thermometers, blood-pressure cuffs, batteries, switches, and fluorescent light bulbs [1]. It has aroused wide public concerns because: (1) mercury, which may exist in metallic, organic and inorganic materials, can contaminate the eco-environment through abusing of anthropogenic sources, for instance gold mine, solid waste, fossil fuel, etc. [2]; (2) mercury is one of the highly toxic environmental contaminants, and may bring extremely adverse influence on the brain, kidney, nervous system and endocrine system in humans and animals [1,3–6]. Therefore, it is very important to establish a highly selective and efficient sensor for the detection of Hg<sup>2+</sup> to control the spread of damage [6]. Currently, a variety of instrumental techniques with high sensitivity can be used to detect Hg<sup>2+</sup>, such as atomic

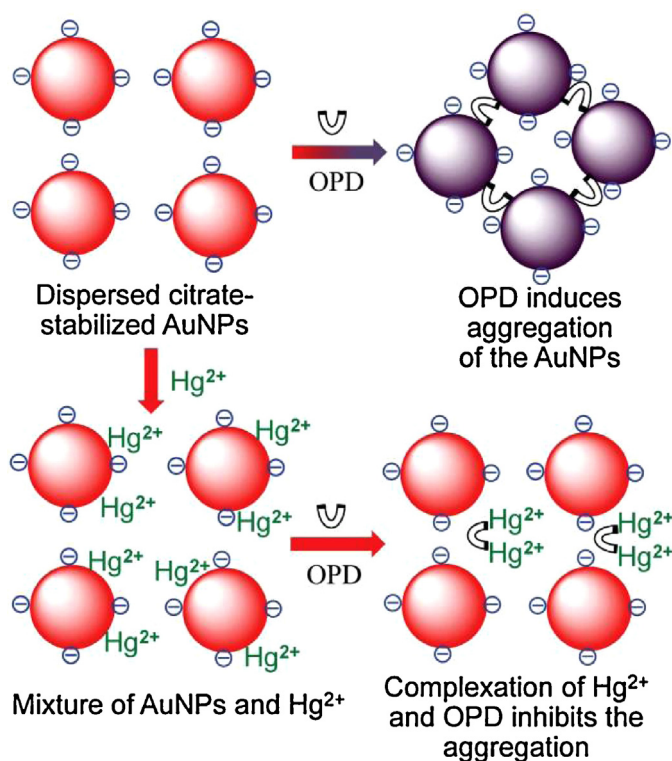
absorption spectroscopy (AAS) [7,8], inductively coupled plasma mass spectrometry (ICP–MS) [9,10], and atomic fluorescence spectrometry (AFS) [11]. However, they also have disadvantages, such as high operating costs and complicated sample preparation process, which limit their applications for on-site analysis.

The fluorescent and colorimetric sensors have aroused wide public concern in the past two decades [5,12–14]. With the advantage of visualization, simplicity, on-site analysis, sensitivity, and real-time detection, colorimetric sensors have attracted more and more attentions [15,16]. Owing to their strong surface plasma resonance, AuNPs-based colorimetric sensors exhibits powerful optical properties [17,18] and large absorption coefficients [19]. However, a majority of the colorimetric sensors based on AuNPs need modification of the AuNP surface with specific ligands, which are designed to combine with targets triggering the aggregation of AuNPs accompanied with visible color change [6,17–21]. But many other external factors in real applications can also trigger the aggregation of AuNPs. In order to increase the reliability, recently the colorimetric sensors based on anti-aggregation of AuNPs have been designed for Hg<sup>2+</sup> sensing through deactivation of the aggregation agent [22–25]. However, most of them revealed poor selectivity

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**Scheme 1.** Schematic illustration of the sensing mechanism based on citrate-stabilized AuNPs.

and/or poor limit of detection (LOD) compared with the high sanitary standard of  $\text{Hg}^{2+}$  concentration in drinkable water of China (5 nM) [26].

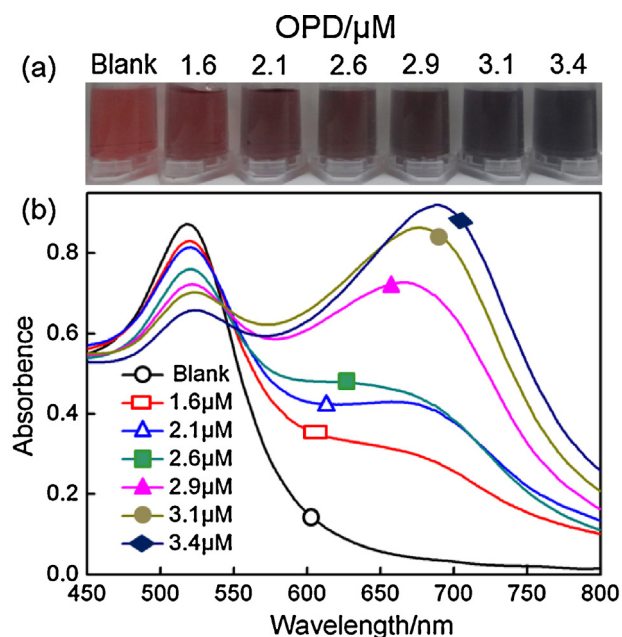
With these insights, we propose a new simple and reliable detection system, which is based on anti-aggregation mechanism and composed of AuNPs and *O*-phenylenediamine (OPD), for rapid detection of  $\text{Hg}^{2+}$  at room temperature with high selectivity and sensitivity. OPD can cause the aggregation of AuNPs due to formation of the strong covalent NH–Au bond, and then induce color change of the AuNP solution from red to blue. However, in the presence of  $\text{Hg}^{2+}$ , OPD prefer to combine with  $\text{Hg}^{2+}$  rather than AuNPs resulting in inhibition of the color change. Based on the anti-aggregation mechanism,  $\text{Hg}^{2+}$  can be detected by observing the color change of AuNP solution containing OPD. Furthermore,  $\text{Hg}^{2+}$  can also be quantitatively measured by UV–vis spectroscopy.

## 2. Experimental

### 2.1. Materials and apparatuses

*O*-phenylenediamine (OPD), *P*-phenylenediamine (PPD), *M*-phenylenediamine (MPD),  $\text{MgCl}_2$ ,  $\text{NaNO}_3$  and NaF were purchased from Aladdin-reagent Co., Ltd. (Shanghai, China).  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (>99%), Risodium citrate dehydrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ ,  $\geq 99.0\%$ ) and the other fundamental reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). All the chemical reagents were used as received without further purification. The glasswares were washed by using aqua regia ( $\text{HCl}/\text{HNO}_3 = 3:1$  (v/v)), then cleaned with Milli-Q water.

Transmission electron microscopy (TEM) images were performed using a JEOL2100 instrument operated at an accelerating voltage of 200 kV. UV–vis spectra were measured by using a T10CS instrument (PERSEE, China) and the dynamic light scattering (DLS) data were obtained on Zetasizer Nano ZS instrumentation (Malvern Instruments Ltd.). Fourier transform infra-red spectroscopy



**Fig. 1.** Photographic image (a) and UV–vis spectra (b) of the citrate-stabilized AuNPs incubated with various concentrations of OPD ranging from 1.6 to 3.4  $\mu\text{M}$ .

(FT-IR) analyses were performed using a Nicolet 6700 spectrometer. The inductively coupled plasma–atomic emission spectrometry (ICP–AES) data were recorded on an Optima 2100DV ICP instrument.

### 2.2. Synthesis of AuNPs

AuNPs were synthesized according to the reported method by the reduction of  $\text{HAuCl}_4$  in the aqueous media using trisodium citrate [18]. Briefly, 5.0 mL of  $\text{HAuCl}_4$  aqueous solution (5.0 mM) was added to 91 mL of Milli-Q water. The solution was heated to be boiling and then 4.0 mL of 1.0 wt% trisodium citrate dehydrate was added into the boiling solution under vigorously stirring. After 30 min of reaction (the color of the solution changed from light yellow to ruby red), the nanoparticle dispersion was cooled naturally at room temperature and stored at ambient condition.

### 2.3. Sensing detection of $\text{Hg}^{2+}$

The color sensing of  $\text{Hg}^{2+}$  at room temperature was carried out in aqueous solution. First, the pH value of the prepared AuNP dispersion was respectively adjusted to 4.6–9.0. Then, 100  $\mu\text{L}$  of different concentration of  $\text{Hg}^{2+}$  solutions were respectively added into 800  $\mu\text{L}$  of the AuNP dispersions. Immediately, 60  $\mu\text{L}$  of MPD, OPD or PPD (50  $\mu\text{M}$ ) solution was successively added into each mixture, and the mixtures were shaken and stored at ambient condition for 3.0–40 min. Finally, the color change and the corresponding UV–vis absorption spectra were observed.

### 2.4. Selective detection of $\text{Hg}^{2+}$

To verify the selectivity of our proposed detection system based on AuNPs, other ions including  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CH}_3\text{COO}^-$  ( $\text{Ac}^-$ ) and  $\text{NO}_3^-$  (The initial  $\text{Hg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  aqueous solutions were prepared by dissolving  $\text{Hg}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$ , and  $\text{AlCl}_3$  powders into diluted  $\text{HNO}_3$  solution, respectively. Simultaneously, these various concentrations of solutions' acidity were adjusted by using the various concentrations of  $\text{HNO}_3$

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