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Short communication

A non-aggregation spectrometric determination for mercury ions based on gold nanoparticles and thiocyanuric acid

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ABSTRACT

We provide a highly sensitive and selective colorimetric assay to detect mercury ions (Hg^{2+}) in aqueous environment using thiocyanuric acid (TCA) molecule-functionalized gold nanoparticles (AuNPs). This method is based on the thiophilicity of Hg^{2+} and AuNPs as well as the unique optical properties of TCA-functionalized AuNPs. In the presence of TCA, AuNPs aggregate due to the strong attraction between thiol groups of TCA and surface-bounded $AuCl_4^-$/$AuCl_2^-$ ions, which induces the visible color change from red to blue. With the addition of Hg^{2+}, Hg^{2+} is more apt to interact with thiols than AuNPs. Thus, Hg^{2+} can remove the AuNPs of the TCA-functionalized AuNPs and trigger AuNP aggregation redisperse again. This assay can selectively detect Hg^{2+} with the detection limits as low as 0.5 nM in aqueous solution.

1. Introduction

Mercury is highly toxic element in the environment [1,2]. Mercury accumulation even in low concentration in the human body can cause diseases such as prenatal brain damage, serious cognitive and movement disorders, and Minamata disease [1,2]. Thus, it is highly desirable to develop facile, economical and rapid methodologies with favorable sensitivity and selectivity for real time Hg^{2+} detection in biological samples or in human bodies.

The detection of Hg^{2+} has become an increasing demand in recent years. Many efforts have been exerted to detect Hg^{2+} using various detection techniques, such as optical spectroscopy [3–6], electrochemical methods [7,8], high-performance liquid chromatography [9,10], and inductively coupled plasma mass spectrometry [10,11]. However, most of these methods require expensive instrumentation and complicated sample preparation, which make them inappropriate for in-situ applications. To overcome these drawbacks, a variety of colorimetric sensors based on gold nanoparticles (AuNPs) have been designed for the simple, rapid detection of Hg^{2+} [12–15].

Spectrometric determination based on AuNP aggregation have recently attracted considerable interests in diagnostic applications mainly due to their simplicity, versatility, and comparable sensitivity with the aforementioned methods. The aggregation of AuNPs can induce a rapid visible color change from wine-red to blue due to the coupling of interparticle surface Plasmon [16,17]. Thus, the color change of AuNPs induced by aggregation or redispersion of AuNPs provides a platform for the colorimetric detection of analyte. In most cases, AuNPs are modified with oligonucleotide- or thiol-containing organic molecules to indicate color change. For example, Jiang et al. provided a highly sensitive and selective method to detect Hg^{2+} through quaternary ammonium group-terminated thiols modified AuNPs [18]. Liu et al. demonstrated a novel and practical system for colorimetric detection of mercury based on DNA/nanoparticle conjugates [13]. However, these sensors are cost- or pollution-consuming. Therefore, it is vital to develop a facile, low cost, rapid, and eco-friendly method for Hg^{2+} detection.

Herein, by taking advantage of the formation of Au-S bonds between thiocyanuric acid (TCA) and AuNPs and higher affinity of TCA toward Hg^{2+} over AuNPs, a very simple colorimetric sensor was designed for Hg^{2+} detection based on the TCA and AuNPs. This reliable sensing platform allows direct analysis of the samples by the naked eye or simple instruments. Furthermore, the limit of detection (0.5 nM) of this method is also lower than that of the other colorimetric sensors. Therefore, the developed colorimetric sensor was reliable, inexpensive, and sensitive.

2. Experimental

2.1. Reagents and apparatus

Chloroauric acid trihydrate and sodium citrate were purchased from Sigma-Aldrich (USA). Thiocyanuric acid was obtained from the Alfa Aesar (Tianjing, China) company. Standard mercuric ion in

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2–5% nitric acid was purchased from AccuStandard (Beijing, China). All other reagents were of analytical grade. All solutions were prepared with Milli-Q water from a Millipore system.

Ultraviolet-visible (UV–vis) absorption spectra were recorded on an UV-2550 Spectrophotometer (Shimadzu Corporation). Transmission electron microscope (TEM) images were obtained on a Hitachi (H-7650, 80 kV) transmission electron microscope.

2.2. Preparation of AuNPs

The 15-nm diameter AuNPs were prepared according to the literature [19]. First, an aqueous solution (100 mL) containing $HAuCl_4$ (0.25 mM) under stirring and brought to a boil in a conical flask (250 mL). Upon boiling, 1% sodium citrate (3 mL) was added quickly and left to continue boiling for another 30 min under stirring, until the solution turned red. The final product was stored at 4 °C. The size of 15 nm and concentration (10 nM) of AuNPs were obtained from UV–vis data according to reference [20].

2.3. Colorimetric detection of Hg^{2+}

In order to demonstrate the detection of Hg^{2+}, first, 20 μM TCA solution in 500 μL Tris–HCl buffer solution (10 mM, pH=7.0) was added into a 1.5 mL plastic vial containing 500 μL AuNP solution (10 nM) under stirring. And then a series of Hg^{2+} with various concentrations was added into the mixture. The solution was mixed thoroughly, which ensured that Hg^{2+} completely bound onto the TCA-AuNPs. After that, the resulting solution was transferred to a 1 cm path length quartz cuvette for spectral recording. The UV–vis absorption spectra were measured over the wavelength range from 300 nm to 800 nm. All assays were performed at room temperature.

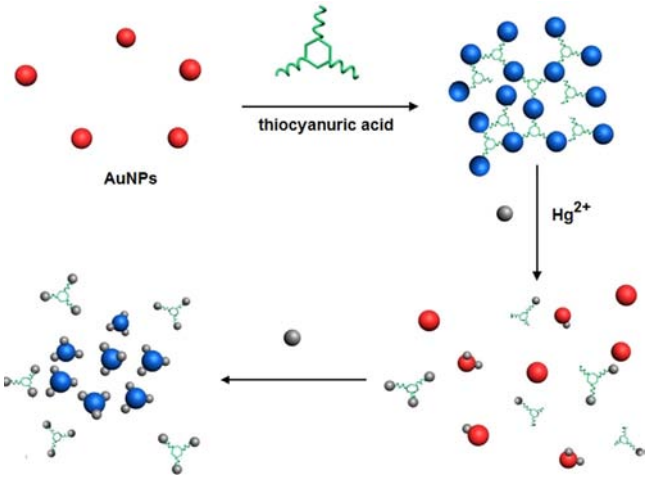

Fig. 1. Schematic of the colorimetric detection strategy for Hg^{2+} based on AuNPs and TCA.

3. Results and discussion

3.1. Sensing strategy

Fig. 1 outlines the sensing mechanism employed in this work. The AuNPs in solution remain dispersed and the solution shows wine-red color because the AuNPs are capped by negatively charged citrate ions and the electrostatic repulsion between them keeps them separate from aggregation. The thiol group of TCA can be easily attached to the surface of the AuNPs by the formation of Au-S bonds. Accordingly, the AuNPs in the presence of TCA are crosslinked and the solution color changes to blue. While the addition of Hg^{2+} into AuNPs-TCA solution, a significant color change from blue to red is observed because Hg^{2+} is more apt to interact with thiols than AuNPs. Thus, it can remove the AuNPs and closely combine with thiols. When the content of Hg^{2+} combined with thiols of TCA reaches saturation, with the further addition of Hg^{2+}, Hg^{2+} can absorb on the surface of AuNPs, decreases the negative charge density on the surface of AuNPs and diminishes the stability of AuNPs, resulting in the aggregation of AuNPs and a corresponding red-to-white color change.

3.2. Sensitivity of TCA-AuNPs to Hg^{2+}

It is well known that Hg^{2+} is apt to interact with thiols and amino groups such as cysteine [21] and melamine [22]. Thus, a rational strategy to detect Hg^{2+} is to combine TCA-AuNPs and Hg^{2+}. Inspired by this theory and under the optimized detection condition (C_{TCA}=20 μM, pH=7, real time detection (less than 30 s), Fig. S1), the sensitivity of the sensor to Hg^{2+} was investigated. As shown in Fig. 2A, with the increase of Hg^{2+} concentration, an increase in the intensity of the absorbance at 530 nm can be observed. It indicated that the TCA-AuNPs aggregation induced redispersion with the increase of Hg^{2+} concentration, and a progressive color change from blue to red was observed (inset of Fig. 2B). When Hg^{2+} interacted

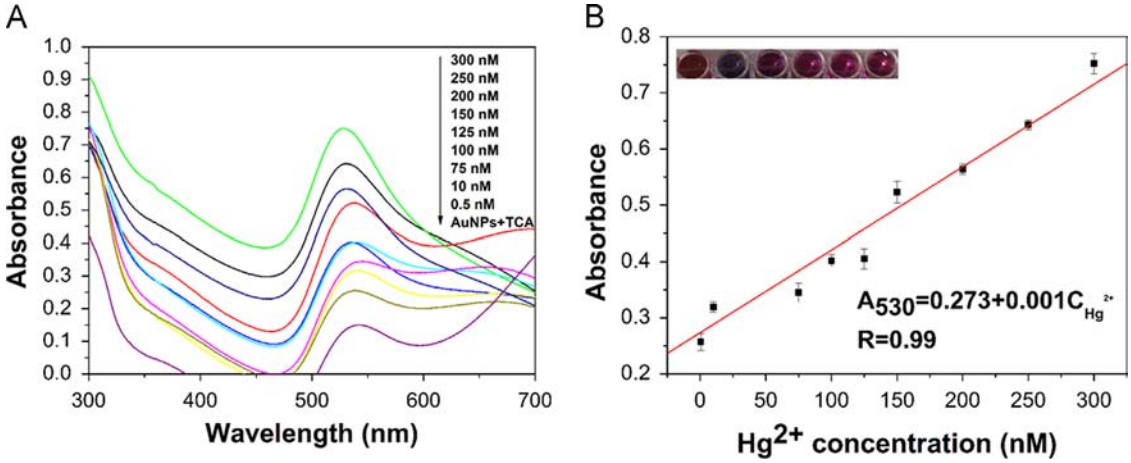

Fig. 2. (A) Absorbance response for different concentrations of Hg^{2+}. (B) The peak absorbance value at 530 nm is linear with Hg^{2+} concentration over the range from 0.5 to 300 nM. **Inset of** Fig.2**(B):** The photographic images of TCA-AuNPs with various concentrations of Hg^{2+}, from left to right: (a) AuNPs, (b) AuNPs-TCA, (c) 0.5 nM Hg^{2+}, (d) 100 nM Hg^{2+}, (e) 200 nM Hg^{2+}, and (f) 300 nM Hg^{2+}.

with thiols of TCA reaches saturation, the further increase of Hg^{2+} concentration induces a monotonous decrease of the absorbance at 530 nm (Fig. S2), resulting in the aggregation of AuNPs and a corresponding red-to-white color change (inset of Fig. S2). This is mainly because that the positively charged Hg^{2+} can absorb on the surface of AuNPs, decreases the negative charge density on the surface of AuNPs and diminishes the stability of AuNPs. The peak absorbance value at 530 nm is linearly related to the Hg^{2+} concentration with the linear range 0.5–300 nM (Fig. 2B). The calibration equation is $A_{530}= 0.001\ C_{Hg}^{2+} +0.273$ with a correlation coefficient of 0.99, and the detection limit is 0.5 nM as calculated in terms of the 3 σ rule [30], which is much better than previously reported optical Hg^{2+} assays, as shown in Table 1. The formations of aggregates on addition of the TCA to the AuNP solution and 300 nM Hg^{2+}/TCA/AuNPs were confirmed by the TEM images, as shown in Fig. 3(A,B), respectively. They indicated that AuNPs underwent an aggregation-redispersion process.

3.3. The selectivity

The above results indicate that the colorimetric sensor is sensitive to the detection of Hg^{2+}. In this case, the selectivity, the most important factor for a sensor, needs to be explored. To evaluate the selectivity of the sensor for Hg^{2+}, various competitors such as Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Na^{+}, Cu^{2+}, Fe^{3+}, Zn^{2+}, Mg^{2+}, Cd^{2+}, and Pb^{2+} were examined. As shown in Fig. 4 (Fig. S3), except for Hg^{2+}, none of these metal ions could prevent the TCA-induced aggregation of AuNPs, because the sulfydryl in TCA preferentially bind to Hg^{2+} compared to other metal ions in chemical affinity.

Table 1
Comparison between the proposed colorimetric method and other optical techniques for Hg^{2+} detection.

Method	Technique	LOD	References
Optical	Colorimetry	0.5 nM	This work
Optical	Fluorescence	10 μM	[23]
Optical	FRET[a]	0.249 μM	[24]
Optical	Colorimetry	40 nM	[21]
Optical	Colorimetry	10 nM	[25]
Optical	Colorimetry	30 nM	[26]
Optical	Fluorescence	16 nM	[27]
Optical	Fluorescence	0.92 nM	[28]
Optical	Fluorescence	2.1 nM	[29]

[a] Fluorescence resonance energy transfer

3.4. Recovery examination

In order to investigate the practical application of the proposed approach, the method has been applied to the determination of trace Hg^{2+} in the certified reference materials (GBW (E) 080392 sample). The analytical results were listed in Table 2. As can be seen, a good agreement between determined values and the certified values could be obtained. The method was also applied to the determination of Hg^{2+} in tap water and lake water. First, we filtered the water samples through 0.2 mm membrane. Then, we used tap water and lake water spiked with standard Hg^{2+} solutions (5 and 10 nM), respectively, the recovery of standard addition was 88.9, 92.7, 102.2, and 106.0%, respectively, as shown in Table 3. Considering that some organic matter existing in tap water could react with Hg^{2+} to form an organic complex [31], the results were still satisfactory.

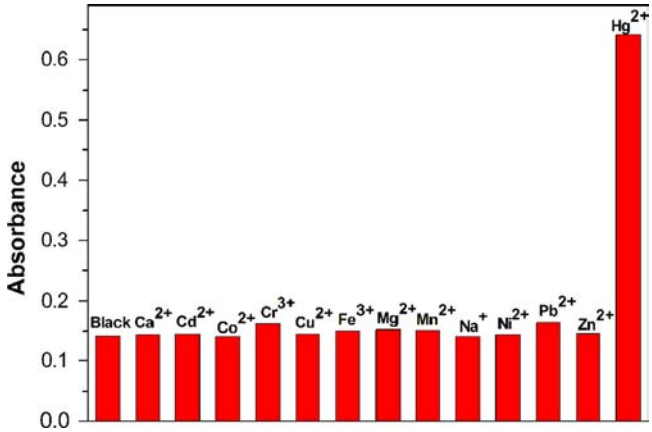

Fig. 4. Selectivity of the colorimetric sensing system toward Hg^{2+} over various metal ions (all at 0.1 μM).

Table 2
Analytical results for Hg^{2+} in the certified reference material (GBW (E) 080392).

Species	Founded (nM)	Certified (nM)	Recovery (%)
Hg^{2+}	10.21	10.00	102.1

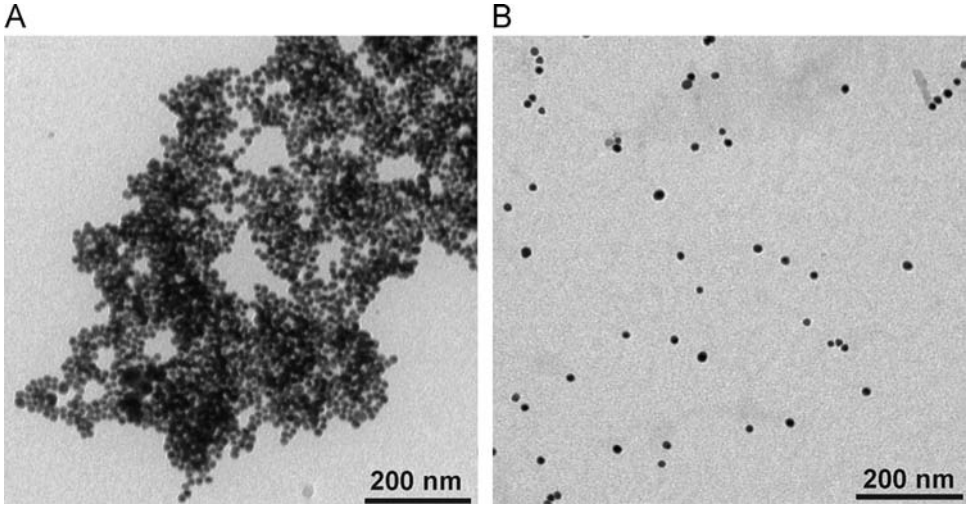

Fig. 3. (D) and (E) TEM images of AuNPs with TCA in the absence and presence of Hg^{2+} (300 nM).

Table 3
Analytical results for Hg^{2+} in tap water and lake water.

Sample	Added Hg^{2+} (nM)	Founded Hg^{2+} (nM)	Recovery (%)	R.S.D (%)
Tap water	–	Not detected	–	–
S1in tap water	5.00	4.45	88.9	4.04
S2 in tap water	10.0	9.27	92.7	2.08
Lake water	–	Not detected	–	–
S3 in lake water	5.00	5.11	102.2	2.59
S4 in lake water	10.0	10.6	106.0	3.83

4. Conclusions

In summary, the study proposes, citrate anions-protected AuNPs as a facile, label free colorimetric probe for the sensitive detection of Hg^{2+} in aqueous systems, based upon Hg^{2+}-specific binding TCA. The selective binding of the TCA with Hg^{2+} prohibits the TCA-mediated AuNP aggregation, switching the solution color from blue to red as a visualized read-out. The sensitivity for the method with 0.5 nM detection limit was sufficient without resorting to advanced, complex readout equipment. The novelty of non-aggregation colorimetric assay lies in its simplicity, convenience, lower cost, speed and multiplicity.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.11.065.

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