



## Detection of pollutants using gold nanoparticles as environmental sensor

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### Abstract:

*Environmental monitoring needs quick and credible analytical devices that can perform sample analysis with minimal sample handling. Environmental sensors that are based on gold nanoparticles have the capability to analyze toxins, heavy metals, and inorganic and organic pollutants in water, soil, and air and are expected to play highly significant role in environmental monitoring. Gold nanoparticles-based sensors have higher selectivity, stability and higher sensitivity and they are low in cost. Citrate-capped gold nanoparticles with amino-acid is very selective to the detection of  $Hg^{+2}$  in drinking water. Sensitive colorimetric assay based on citrate-capped gold nanoparticles is used to detect  $Hg^{+2}$  in drinking water. The colorimetric assay is very fast, and all analysis can be completed within a few minutes.*

**Keywords:** Environmental monitoring, Pollutants

### 1. Introduction

Mercury is one of the toxic heavy metal in environment and has harmful effect on human health [1]. One of the most usual and stable forms of mercury pollution is mercury ions ( $Hg^{+2}$ ). So, monitoring  $Hg^{+2}$  in aqueous environment has obtained more interest. Due to their constitutionally high sensitivity and easy colorimetric read-out, AuNps based sensing methods have attracted more and more attention. Hence, various colorimetric detection methods based on surface modifications of AuNPs have been developed to selectively recognize  $Hg^{+2}$  in aqueous solutions [7]. As the sensing element many are constructed with thymine (T) containing oligonucleotides in these sensors.  $Hg^{+2}$  can bind with two T residues of DNA to form the T–Hg–T complex [8]. Only  $Hg^{+2}$  ions has been found to bind with the T–T mismatch in duplex DNA. No other metal ions have been found.  $Hg^{2+}$  ions bind with two T residues to form T–Hg–T which can stabilize the duplex with the T–T mismatched base pairs and be able to direct the folding of single stranded DNAs into duplexes [9]. It provides T-containing oligonucleotide sequences for sensing aqueous  $Hg^{+2}$  in different ways. Hence, for the selective detection of  $Hg^{+2}$  a variety of colorimetric sensors based on T-containing DNA/AuNPs have been developed. Although the developed sensors based on DNA/AuNPs have good sensitivity and selectivity, the chemical synthesis and modification of DNA are relatively expensive and difficult. The low stability against nuclease, and the nonspecific interaction end in from the negatively charged backbone also limit the appeal of DNA-based sensors in real complex samples. Liu and co-workers making a colorimetric sensor based on thymine derivatives (thymine acetamidoethanethiol) modified AuNPs for  $Hg^{+2}$  detection with high selectivity [15]. The above methods still need molecular modification of thymine and involve synthetic steps.

Here, we present a very easy and sensitive method based on the thymine molecule without any modification for the colorimetric detection of  $Hg^{+2}$ . Thymine can be bind to the surface of AuNPs via Au–N bonds and exchange citrate ions in  $Hg^{+2}$  free solution, thus inducing the aggregation of the AuNPs occur by a color change from red to blue [13]. In the presence of  $Hg^{+2}$ , thymine can bind with  $Hg^{+2}$  and form T–Hg complexes in the solution, thus thymine cannot insert the surface of the AuNPs

and the color of solution is still red. This type of unmodified AuNPs-based sensor for  $\text{Hg}^{+2}$  ions in aqueous media have high selectivity and sensitivity. This unmodified method has many advantages: first, does not require any modification of the AuNPs and the sensing platform is label-free; second, to get a color change or aggregation of AuNPs, the sensing system does not need any additional salt; moreover, the method involves the use of small organic molecules that are stable and cheap thereby avoiding the use of oligonucleotides (DNA or RNA) or other derivatives which are relatively expensive or complicated. The sensitivity and selectivity of the method were also analyzed. The application of the method for the detection  $\text{Hg}^{+2}$  in practical water samples was indicated.

## Experiment section

### 1. Chemicals and materials

Chloroauric acid ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ), thymine (T), and the used metal salts, including  $\text{Hg}(\text{NO}_3)_2$ ,  $\text{CdCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{Pb}(\text{Ac})_2$ ,  $\text{ZnCl}_2$ ,  $\text{NiSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{CuSO}_4$  and  $\text{Ba}(\text{NO}_3)_2$ .

AuNPs with a diameter of 13 nm were prepared using the trisodium citrate reduction method.

### 2. Methods

#### 2.1 Nanoparticle synthesis

Citrate-capped AuNPs were prepared. The Turkevich method is one of the most commonly used methods for synthesis of spherical AuNPs in the size range of 10nm-20nm. The principle of this method involves reduction of gold ions ( $\text{Au}^{+3}$ ) to gold atoms ( $\text{Au}^0$ ) in the presence of reducing agents like citrate, amino acids, ascorbic acid or UV light. Size of AuNPs is further stabilized using capping/stabilizing agents. The narrow range of AuNPs that could be generated by this method.

#### Preparation

Gold stock solution is made by mixing 0.03 g of gold salt ( $\text{HAuCl}_4$ ) with 100 ml of Millipore. 10 ml of gold stock solution added into three flasks. Glass condenser is connected to central neck of the flask and stopper on the side neck flask and whole assembly is placed on the magnetic stirrer for 20 minutes at 600 c temp. With continuous stirring gold chloride solution is heated up to boiling. Trisodium solution made by mixing of 1 g trisodium citrate with 100 ml of milipour water is added drop wise. Boiling is further continued with continuous stirring. Change in color of gold chloride solution from pale yellow to red. One minute after addition of trisodium citrate dehydrate solution the formation of colloidal GNPs. Mixture allow to reflux for another 20 minutes. Heating is turned off and allow to cool up to 23-25<sup>0</sup>c at room temp with continuous stirring. Synthesized AuNPs are collected in a clean amber- colored glass container (wash with acetone/Aquaregia).

#### 2.2. Sample preparation

The detection was carried in 1 mM Tris-HCl buffer solution at different pH. The ions were added to a buffer solution (800 mL) containing AuNPs (100 mL, 15 nM) for  $\text{Hg}^{+2}$  sensing and then thymine (100 mL, 0.05–0.8 mM) was added to the solution. After equilibrating at ambient temperature for the optimum incubation time, the absorption spectra of the resulting solutions were recorded.

#### 2.3 Analysis of samples

A series of samples were prepared by spiking standard solutions of  $\text{Hg}^{+2}$  to tap water obtained locally. These spiked samples were added to a buffer solution containing AuNPs, then different concentrations of thymine were added into the solutions and the solutions were incubated for some time before spectral measurement.

Safety considerations. As  $\text{Hg}^{+2}$  and most of the tested metal ions are highly toxic and have reverse effects on human health, all experiments containing heavy metal ions and other toxic chemicals should

be performed with protective gloves. To avoid polluting the environment, the waste solutions containing heavy metal ions should be collectively regained.

### 3. Results and discussion

#### 1. Sensing mechanism

The citrate ions on the surfaces which keep AuNPs from aggregation are easily removed by other ligands with heterocyclic N and SH groups [17-18]. The N donors have a stronger affinity with AuNPs than the carboxyl group [19] because electron-rich nitrogen atoms easily bind via coordinating interactions between nitrogen atoms with the electron-deficient surface of the metal nanoparticles. The citrate ions on the surface which protects them from aggregation were replaced by thymine, this occurs only when thymine was added into the AuNPs solution. The AuNPs could not stabilize and the color turned blue. The  $\text{Hg}^{2+}$  reacted with thymine and formed a T–Hg complex through N–Hg bonds like T–Hg–T in  $\text{Hg}^{2+}$  containing solution. In that case, the solution remains red because thymine does not attach to the surface of AuNPs.

The  $\text{Hg}^{2+}$  induced anti-aggregation of AuNPs was confirmed by UV-vis absorption. In the absence of  $\text{Hg}^{2+}$  ions resulted from the replacement of citrate to thymine from the surface of the citrate capped AuNPs. In the presence of  $\text{Hg}^{2+}$  ions, AuNPs were well dispersed because the thymine could form complexes with  $\text{Hg}^{2+}$  ions and could not access the surface of the AuNPs. The color change of the solution in the absence and presence of  $\text{Hg}^{2+}$  ions as well as the UV-vis absorption spectra, thus the designed sensing system was suitable for  $\text{Hg}^{2+}$  detection.

#### 4. Feasibility for the detection of $\text{Hg}^{2+}$

The feasibility of using the sensing platform for the colorimetric detection of  $\text{Hg}^{2+}$ . The citrate on the surface of AuNPs was replaced by thymine and AuNPs aggregated and the color changed to blue when a certain concentration of thymine was added into the solution. A significant red shift was observed due to the aggregation of the AuNPs. At about 670 nm, an absorbance peak was observed. If 5 mM  $\text{Hg}^{2+}$  was present in the solution, with the subsequent addition of thymine, the solution was still red, and an absorbance peak was still present at about 520nm.

#### 5. Sensitivity of the sensor

To examine the sensitivity of the assay different concentrations of  $\text{Hg}^{2+}$  from one stock solution were tested. The absorbance value at 520 and 670 nm is related to the quantities of dispersed and aggregated AuNPs, respectively.

Thus, to reflect the ratio of dispersed and aggregated AuNPs, the absorption ratio at 520 nm and 670 nm ( $A_{520\text{nm}}/A_{670\text{nm}}$ ) was used here. Along with an increase in the  $\text{Hg}^{2+}$  the absorption ratio increase.

#### 6. Selectivity of the sensor

To realize the selectivity of the system, some commonly coexisting metal ions were chosen for the investigation, including  $\text{K}^+$ ,  $\text{Ca}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Mn}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Pb}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Fe}^{+3}$ ,  $\text{Cd}^{+2}$  and  $\text{Cr}^{+3}$ .

#### 7. Determination of $\text{Hg}^{2+}$ in water samples

Considering the alkaline earth and alkali metals, the tap water is more complex than other soft natural water matrices including river water and lake water (fresh). Thus, tap water sample spiked with  $\text{Hg}^{2+}$  was used to mimic the  $\text{Hg}^{2+}$  contaminated water for testing of this sensor. Concentrations of  $\text{Hg}^{2+}$  to AuNPs solution increased after the addition of tap water containing  $\text{Hg}^{2+}$ , color changed from blue to red and the absorption ratio also increased gradually. The results indicated the high potential of this anti-aggregation of AuNPs based colorimetric method for  $\text{Hg}^{2+}$  quantification in aqueous solutions.

## 8. Conclusions

In summary, a very simple and cost-effective method based on the specific interaction of  $\text{Hg}^{+2}$  and thymine for the colorimetric detection of  $\text{Hg}^{+2}$  in aqueous solution was developed. Besides the advantages of AuNPs-based assays such as simplicity and high selectivity, this method has other advantages:

(1) The use of a simple and commercially available thymine as a  $\text{Hg}^{+2}$  acceptor avoids any design or molecular modification or optimization of the  $\text{Hg}^{+2}$ -binding oligonucleotide. (2) Without any other labeling or modification steps this sensing platform is easily constructed in solution. (3) The detection procedure is very simple: after the addition of samples to the sensing system, it takes recording the absorption spectrum or observing the color change. For the visual detection of  $\text{Hg}^{2+}$  in complex samples, this colorimetric sensor shows good potential.

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