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Colorimetric detection of Hg^{2+} ions in aqueous media using CA–Au NPs

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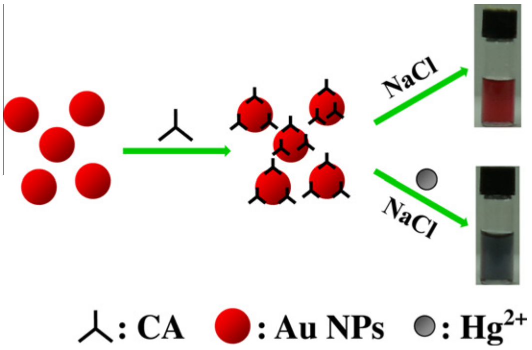
HIGHLIGHTS

- We developed a colorimetric method for detecting Hg^{2+} ions using Au NPs and CA.
- The experiment validated the selective interaction between CA and Hg^{2+} ions.
- The experiment validated the anti-aggregation of CA–Au NPs induced by NaCl.
- We also evaluated the sensitivity and selectivity of the sensor of Hg^{2+} ions.
- The use of a highly stable and commercially available CA as Hg^{2+} acceptor avoids any other labeling or modification steps.

GRAPHICAL ABSTRACT



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ABSTRACT

Based on the selective interaction between Hg^{2+} ions and cyanuric acid (CA) and the anti-aggregation of CA stabilized gold nanoparticles (CA–Au NPs), a simple colorimetric method was developed for detecting Hg^{2+} ions. In a medium of pH 7.4 tris–HCl buffer containing 8×10^{-3} M NaCl, the CA–Au NPs solution was red, which was due to CA adsorbed onto the surface of Au NPs, stabilizing Au NPs against aggregation. When CA–Hg^{II}–CA complex was formed in the presence of Hg^{2+}, the stability of CA–Au NPs reduced, and then aggregation of Au NPs occurred. Consequently, the color of the solution changed from red to blue and could easily be measured with a common spectrophotometer. The aggregation of Au NPs was also validated using transmission electron microscopy (TEM). The controlled experiment showed that other ions including Ba^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Cu^{2+}, Mg^{2+}, and Ni^{2+} ions did not induce any distinct spectral changes, which constituted a Hg^{2+}-selective sensor. A dynamic range of 1.6–16 $\times 10^{-6}$ M Hg^{2+} ions was observed at the optimized reaction condition. This method provides a potentially useful tool for Hg^{2+} detection.

1. Introduction

Heavy-metal pollution (e.g. mercury) is an important environmental concern because it can cause serious human health problems [1,2]. It has been reported that mercury could cause permanent harmful effects in living organisms even at relatively low dose, such as memory loss, neuronal, hepatic, and nephritic damage, decrease in the rate of fertility, as well as birth defects in offspring [2]. Thus, there is a pressing need to develop specific ion sensors for the rapid detection of mercury ions (Hg^{2+}).

Many methods have been developed for the determination of Hg^{2+} ions in different biological, industrial and food samples. Traditional quantitative approaches to Hg^{II} analysis (e.g. atomic absorption spectroscopy, cold vapor atomic fluorescence spectrometry, and gas chromatography) require complicated, multistep sample preparation and/or sophisticated instrumentation [3–7]. Compared with conventional techniques, chemical sensors based

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on optical signal measurement are considered as the advanced techniques because of its simplicity, reasonable selectivity, improved sensitivity, and fieldwork applicability. Despite the above strongpoint, the use of chemical sensors suffers from several drawbacks, such as the complicated organic synthesis procedure involved [8]. As such, there has still been a growing need or desire for constructing optical chemical sensors for fast and economical monitoring of Hg^{2+} ions.

The highly selective determination of Hg^{2+} ions is usually accomplished by spectroscopic methods upon binding to the specific receptors. It has recently been found that Hg^{2+} ions can bind with two thymine (T) residues of DNA to form the T–Hg^{II}–T complex [9,10]. The stability of this T–Hg^{II}–T base pair is higher than that of a T–A Watson–Crick pair, and this interaction is highly specific (only Hg^{2+} ions can stabilize the T–T base pair) [10]. It provides a rationale for applying T-containing oligonucleotide sequences for specifically sensing aqueous Hg^{2+} in diverse ways [11–15]. Moreover, Au NPs-based sensing methods have attracted more and more attention due to their intrinsically high sensitivity and easy colorimetric read-out [16–18]. Hence, a variety of colorimetric sensors based on T-containing DNA/Au NPs have been developed for the selective detection of Hg^{2+} ions [19–25]. However, the design and synthesis of various sophisticated DNA oligomer probes is tedious and expensive, and the enzymatic DNA degradation is unavoidable when detecting Hg^{2+} from environmental water samples. The structure of CA with high stability was similar as that of thymine (diimide groups), so it is possible to replace T or DNA by using CA as the specific receptors for determining Hg^{2+} ions.

Herein, we demonstrated that Hg^{2+} ions could be recognized selectively in aqueous solution by the colorimetry based on cyanuric acid stabilized Au NPs (CA–Au NPs). In our experiment, the addition of Hg^{2+} ions reduced the stability of CA–Au NPs, and then aggregation of Au NPs occurred after adding NaCl, which induced visible colorimetric response of CA–Au NPs solution from red to purple. The sensitivity and selectivity of the colorimetric assay were also investigated.

2. Experimental

2.1 Reagents and apparatus

$HAuCl_4 \cdot 4H_2O$, $Na_3(C_6H_5O_7) \cdot 2H_2O$, $Hg(NO_3)_2$, NaCl, concentrated HCl, and concentrated HNO_3 were purchased from Sinopharm Group, Shanghai, China. All chemicals were of analytical-reagent grade. Deionized water produced by a Milli-Q system (Millipore, USA) was used for preparing solutions. All glassware used in these preparations was thoroughly cleaned in aqua regia (3 parts HCl, 1 part HNO_3), rinsed in triply distilled H_2O, and oven-dried prior to use. Unless otherwise noted, the experiments were carried out at room temperature (20–25 °C).

UV/vis absorption spectra were recorded with an Evolution 300 UV/vis spectrophotometer (Thermo Scientific, USA). TEM images were acquired by using Hitachi-7650 (HITACHI, Japan) transmission electron microscopes operated at 120 kV.

2.2 Colloidal gold preparation [26]

Colloidal gold were prepared following the described method. 50 milliliters of 1 mM $HAuCl_4$ was brought to a round-bottomed flask under vigorous stirring. 5 millilters of 38.8 mM trisodium citrate was rapidly added to the vortex of the boiling solution, resulting in a color change from pale yellow to burgundy. Boiling was prolonged for 10 min. The heating mantle was then removed, while the stirring was continued for an additional 15 min. The resulting solution of colloidal Au NPs was characterized by absorption spectroscopy and transmission electron microscopy (TEM). The spherical Au NPs obtained were characterized by a maximum absorption at 520 nm and had uniform size ∼14 nm (Figure S1).

2.3 Procedure of detecting Hg^{2+} ions

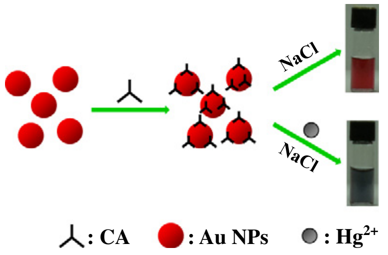
In a 10 mL test tube, 300 μL Au NPs was mixed with 5.0 mL of Tris–HCl buffer. 25 μL of 10^{-3} mol L^{-1} of CA and 4 mL of distilled H_2O was added, and equilibrated for 10 min at room temperature. Different concentrations of Hg^{2+} solution were added into this mixture, and then, 100 μL of NaCl (0.4 mol L^{-1}) was added to the resulted solution before being incubated for another 5 min. The absorbance of solution was measured in the range of 400–1000 nm. All reported concentrations of reagents or samples were the initial values in reaction mixtures.

3. Results and discussion

3.1 The sensing mechanism and feasibility for detecting Hg^{2+} ions

Our basic idea of the present work is on the basis of the adsorption of CA on the surface of Au NPs, and the addition of Hg^{2+} ions, which could react with CA through CA–Hg^{II}–CA coordination, reduces the stability of CA–Au NPs so that NaCl could readily induce the aggregation of Au NPs, resulting in shifting surface plasmon resonance (SPR) signals owing to the distance changes between Au NPs [17,18]. The detailed sensing mechanism of CA–Au NPs sensor for Hg^{2+} ions is shown in Scheme 1.

In order to study the feasibility of our approach, two below experiments were conducted: the anti-aggregation of CA–Au NPs, and the interaction between CA and Hg^{2+}. In Turkevich method, citrate ions act as both a reducing agent and a capping agent, which sticks to Au NP surface to prevent them from aggregating [16,17]. However, the interaction force between citrate ions and Au NPs is weak, so it is easy to replace citrate ions by other molecules with heterocyclic N and SH groups [16–18,23,27,28]. It is shown from Figure S2 that adding 0.3 ml NaCl to colloidal Au NPs led to their aggregation, which increased the relative absorption at longer wavelength region. However, in the presence of CA, the addition of 0.3 ml NaCl did not change the relative absorption of Au NPs solution. It is said that the anti-aggregation ability of Au NPs was enhanced because CA was absorbed on the surface of Au NPs via its heterocyclic N [16,17]. Then, we explored whether CA could reacted with Hg^{2+} for the structure of CA was similar as that of thymine (diimide groups) [9–15]. After different amount of Hg^{2+} ions was added to the solution of 10^{-4} mol L CA, the absorption increased in the UV range (Figure S3). The above change resulted from the interaction between CA and Hg^{2+} ions, so CA could be used as functional group for detecting Hg^{2+}. From the above experiments, it is possible to develop the sensor for Hg^{2+} by CA and Au NPs.



Scheme 1. Detection of Hg^{2+} ions using Au NPs coated with CA.