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A simple colorimetric sensor based on anti-aggregation of gold nanoparticles for Hg^{2+} detection

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ABSTRACT

A new method has been proposed to realize the visual detection of Hg^{2+} *via* anti-aggregation of gold nanoparticles (Au NPs). The positively charged Au NPs were prepared using poly(diallyldimethylammonium) chloride (PDDA) as reducer and stabilizer. In the presence of cysteine, the color of Au NPs solution turned from ruby red to royal purple, indicating the aggregation of Au NPs. Owing to the high stability constant of cysteine with Hg^{2+}, the pre-incubation of Hg^{2+} with cysteine would form Hg^{2+}–cysteine complexes and significantly reduce the concentration of free cysteine molecules, thus the aggregation of Au NPs was interrupted since there was not enough inducer. With the increase of Hg^{2+} concentration, the color of the Au NPs solution would progress from purple to red, allowing the visual detection of Hg^{2+} ranging from 5.0×10^{-8} to 1.0×10^{-5} M, with a detection limit of 2.5×10^{-8}M. The proposed method is convenient, low-cost and free of complex equipment, making it possible to analyze Hg^{2+} in drinking water, rain water or water extracted air samples.

1. Introduction

Mercury, one of the most hazardous environmental toxins, is ubiquitous in the environment. It is generally used in thermometers and blood-pressure cuffs and commercially in batteries, switches, and fluorescent light bulbs [1]. It can contaminate the ecosystems through atmospheric transport and deposition in watersheds. Therefore, the mercury biogeochemical cycle in atmospheric environments and water bodies need to be better constrained. Mercury is unique among the heavy metals in that it can exist in several physical and chemical forms, including metallic, inorganic, and organic forms. Due to the high water solubility, mercury ions (Hg^{2+}) are easily ingested by human beings through water or the food chain. This stable inorganic mercury form passes easily through biological membranes and causes a wide variety of diseases to the brain, nervous system, kidneys, and endocrine system [2,3].

Currently, several methods and techniques have been established to monitor concentration levels of mercury in water samples. The traditional techniques, such as atomic absorption spectroscopy (AAS) [4,5], inductively coupled plasma mass spectrometry (ICP-MS) [6], atomic fluorescence spectrometry (AFS) [7,8] and reversed-phase high-performance liquid chromatography [9], provide limits of detection at ppb (parts-per-billion) level. Although these methods are sensitive, they usually require expensive and sophisticated instrumentation and/or complicated sample preparation processes.

In response to these shortcomings, several techniques, for example, using organic fluorophores [10–12] or chromophores [13,14], semiconductor nanocrystals [15,16], DNAzymes [17–19], and polymer-oligonucleotide composites [20], have been reported for the detection of Hg^{2+} in aqueous solution. Unfortunately, these strategies still display drawbacks and have limited practical use owing to the poor aqueous solubility, cross-sensitivity toward other metal ions, high cost and the need for designing molecules such as fluorophores or DNAzymes.

Due to the unique chemical and physical properties, gold nanoparticles (Au NPs) have been used for developing the colorimetric sensors, which can be easily monitored with the naked eye, without any advanced instruments. One of the most interesting properties is their strong surface plasmon resonance (SPR) absorption in the visible wavelength range which depends on their size, shape, interparticle distances, and surrounding medium. These visual methods have been employed for the detection of melamine [21,22], TNT [23], and heavy metal ions such as Pb^{2+}, and Cu^{2+}

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[24–28], with a high sensitivity. Therefore, Au NPs sensors offer a promising approach for facile tracking of metal ions in aqueous solution. Hg^{2+} is capable of interacting with thymines and forming stable T–Hg^{2+}–T complexes. Thus, some DNA oligonucleotides bearing T–T mismatches have been designed for the colorimetric detection of mercuric ions [29–31]. Because of the intrinsic specific interaction between Hg^{2+} and thymine, this strategy could offer a high selectivity toward Hg^{2+} over other related environmental heavy metal ions. To overcome the cost issue of using DNA, a cheap ligand, mercaptopropionic acid, was employed for Hg^{2+} monitoring, based on the coordination between Hg^{2+} and carboxylic groups of MPA [32–34]. However, some additional chelating ligand or fluorescent indicator must be used to improve selectivity and/or sensitivity. An alternative strategy has been developed to detect Hg^{2+} with the use of fluorescent Au nanoclusters (NCs) [35,36]. Hg^{2+} could interact with as-prepared protein-modified Au NCs and therefore quench the fluorescence. The high selectivity was attributed to the specific metallophilic interactions between Hg^{2+} and Au^{+} [36]. Based on a similar Hg–Au interaction mechanism, citrate-modified gold nanoparticles can be also used for Hg^{2+} detection. Hg^{2+} was reduced to Hg(0) by citrate and then directly deposited onto the surface of Au NPs through the formation of Hg–Au alloys [37]. Thus, the stabilizing molecules were desorbed from gold nanoparticles and led to aggregation.

Cysteine is a common amino acid and plays a key role in structure direction and activity of biological processes. Cysteine possesses a terminal thiol moiety, thus it can bind onto the surface of Au NPs through the Au—S bond and form the cysteine functionalized gold nanoparticles (Cys-Au NPs). Su et al. exploited a simple method based on Cys-Au NPs to detect Hg^{2+} in aqueous solution [38]. They found that the Cys-Au NPs can be induced agglomeration in the presence of Hg^{2+}. It is well known that mercury has a high thiophilicity [39], thus mercury ions (Hg^{2+}) can combine with cysteine through Hg—S bond and form Hg–Cys complexes. The binding affinity of the thiol in cysteine for the Hg^{2+} is substantially greater than that for other metal ions [40]. Taking advantage of this unique attribute of Hg^{2+}, we devised a new, facile and colorimetric sensor to detect Hg^{2+} based on the anti-aggregation of Au NPs, through the competing combination with cysteine between Hg^{2+} and Au NPs. We prepared positively charged gold nanoparticles and used cysteine as aggregation agent. Most of previous methods were based on the fact that Au NPs are induced to aggregate by inter-particle crosslinking in the presence of Hg^{2+}, then the color of Au NPs solution changes from red to purple or blue. However, in our method, the detection of Hg^{2+} was realized through interrupting the aggregation of gold nanoparticles induced by cysteine, which can be observed by the naked eye according to the color changing from purple to red. Up to now there are few reports on the colorimetric detection of Hg^{2+} based on anti-aggregation of Au NPs. In addition, it is much simpler and more cost-effective than the other existing methods for Hg^{2+} assay by using a common molecule cysteine in this method, without designing and synthesizing DNA or fluorophore molecules as mentioned before. In this simple way, 2.5×10^{-8} M Hg^{2+} was detected only by the naked eye.

2. Experimental

2.1. Chemicals

Poly(diallyldimethylammonium) chloride (PDDA, 25 wt% in water, molecular weight 20,000) was obtained from Sigma–Aldrich (USA). Tetrachloroauric acid ($HAuCl_4{\cdot}4H_2O$) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). L-Cysteine was purchased from North Ringer Biotechnology Co., Ltd. (Beijing, China). $HgCl_2$ and other metal ions were bought from Beijing Chemical Company (Beijing, China). HAc–NaAc buffer solution (pH 4.2) was used to control the acidity of the aqueous solutions, and 0.1 M NaCl was employed to adjust the ionic strength of the solutions. All reagents were of analytical grade and prepared using ultrapure water with a resistivity of 18 MΩ cm. Stock solution of cysteine at 7 μg/mL in water was freshly prepared every day. Working solutions were obtained by serially diluting the stock solution immediately prior to use.

2.2. Apparatus

The UV–vis spectra were recorded by a UV-2550 spectrophotometer (Shimadzu, Japan), using 1-cm path length quartz cuvettes for measurements. The pH of the solution was measured with a PB-10 pH meter (Sartorius, Germany). Transmission electron microscopy (TEM) measurements were made on an Tecnai G2 Transmission Electron Microscope (FEI, Netherlands); the samples for TEM characterization were prepared by adding a drop of colloidal solution on a carbon-coated copper grid and drying at room temperature. The particle size was determined by dynamic light scattering (DLS) measurements (Nano ZS). Flame atomic absorption spectroscopy (FAAS) experiment was implemented by using an AA-6800 spectrometer (Shimadzu, Japan).

2.3. Preparation of Au NPs

PDDA coated gold nanoparticles were prepared according to the method in the literature [41]. Gold nanoparticles were synthesized by reducing $HAuCl_4$ with an ordinary and water-soluble cationic polyelectrolyte, namely, poly(diallyldimethylammonium) chloride (PDDA) to act as both the reducing and stabilizing agents. Typically, 1 mL PDDA, 160 mL water, 0.2 mL 2.5 M NaOH and 0.4 mL 50 mg/mL $HAuCl_4$ were added into a beaker. After being stirred for 2 min, the mixed solution was heated at 100 °C for several minutes until the solution color changed to ruby red, an inverted culture dish was covered on the beaker to avoid the reaction liquid from evaporating rapidly. The solution was cooled to room temperature while being stirred continuously. Thus, positively charged gold nanoparticles were formed. The stock solution of Au NPs was stored in a refrigerator at 4 °C. The size of the gold nanoparticles was verified by TEM (Tecnai G2, FEI) and DLS (Nano ZS).

2.4. Detection of Hg^{2+}

The colorimetric detection of Hg^{2+} in aqueous solution was performed at room temperature. 200 μL of 1.0 M NaCl, 200 μL of 7 μg/mL cysteine, 580 μL of ultrapure water, 20 μL of Hg^{2+} with different concentrations and 800 μL of gold nanoparticles were added into 200 μL HAc–NaAc buffer sequentially. The absorption spectra of the resulting solutions were measured with UV–vis spectrophotometry, and the color of the final solutions was recorded by photographs. Common metal ions were chosen to investigate their interference in Hg^{2+} detection, and the concentration of each metal ion studied was 1.0×10^{-5} M.

The feasibility of our method to detect Hg^{2+} in drinking water was verified. Water samples were from our own laboratory and no pretreatment was made. We spiked the samples with standard solution containing 1.0×10^{-5}–1.0×10^{-3} M Hg^{2+}. FAAS was then conducted to calculate recovery rate. To solve the discrepancy between the detection limits of traditional FAAS and our method, each sample was diluted 100-fold and the recovery rate recalculated using the proposed method.