ACS APPLIED MATERIALS & INTERFACES

RESEARCH ARTICLE

www.acsami.org

Blue-to-Red Colorimetric Sensing Strategy for Hg^{2+} and Ag^{+} via Redox-Regulated Surface Chemistry of Gold Nanoparticles

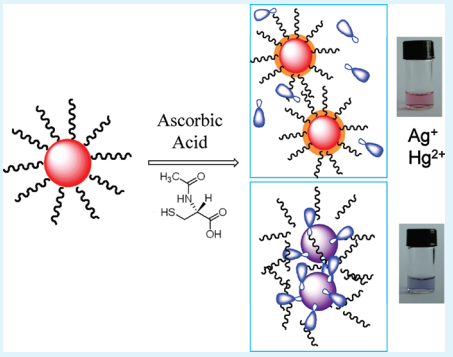
Tingting Lou,[†,‡] Zhaopeng Chen,[†] Yunqing Wang,[†] and Lingxin Chen*[,†]

[†]Key Laboratory of Coastal Environmental Processes, CAS; Shandong Provincial Key Laboratory of Coastal Zone Environmental Processes; Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China

[‡]Graduate University of Chinese Academy of Sciences, Beijing 100049, China

Supporting Information

ABSTRACT: Here we report a "blue-to-red" colorimetric method for determination of mercury ions (Hg^{2+}) and silver ions (Ag^{+}) based on stabilization of gold nanoparticles (AuNPs) by redox formed metal coating in the presence of ascorbic acid (AA). AuNPs were first stabilized by Tween 20 in phosphate buffer solution with high ionic strength. In a target ion-free system, the addition of N-acetyl-L-cysteine resulted in the aggregation of Tween 20 stabilized AuNPs for mercapto ligand self-assembled on the surface of AuNPs, which induced the AuNPs to be unstable. This would lead to a color change from red to blue. By contrast, in an aqueous solution with Hg^{2+} or Ag^{+}, the ions could be reduced with the aid of AA to form Hg—Au alloy or Ag coating on the surface of AuNPs. This metal coating blocked mercapto ligand assembly and AuNPs kept monodispersed after addition of N-acetyl-L-cysteine, exhibiting a red color. Therefore, taking advantage of this mechanism, a "blue-to-red" colorimetric sensing strategy could be established for Hg^{2+} and Ag^{+} detection. Compare with the commonly reported aggregation-based method ('red-to-blue'), the color change from blue to red seems more eye-sensitive, especial in low concentration of target. Moreover, selective analysis of Hg^{2+} and Ag^{+} was simply achieved by the redox nature of target ions and the application of classic ion masking agents, avoiding the design and selection of ion chelating moieties and complicated gold surface modification procedure. This method could selectively detect Hg^{2+} and Ag^{+} as low as 5 nM and 10 nM in pure water with a linear range of 5×10^{-7} to 1×10^{-5} M for Hg^{2+} and 1×10^{-6} to 8×10^{-6} M for Ag^{+}, respectively. It was successfully applied to determination of Hg^{2+} and Ag^{+} in tap water and drinking water.



KEYWORDS: gold nanopartilces, colorimetric detection, "blue-to-red" strategy, mercury ion, silver ion

INTRODUCTION

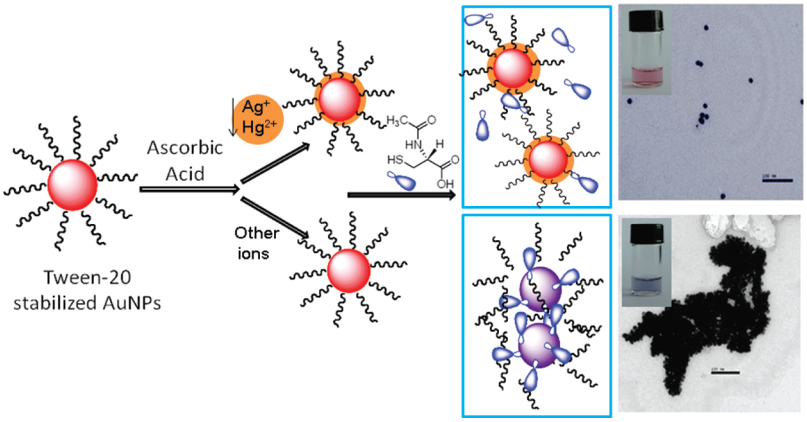
Monitoring of heavy metal ions in aquatic ecosystems is always an important issue because these ions exert adverse effects on the environment and also on human health.[1] Mercury ions (Hg^{2+}) and silver ions (Ag^{+}) are two of the toxic heavy metal pollutants which wildly exist in water, soil and even in food. Mercury ions can damage the brain, heart, stomach, intestine, and kidney,[2,3] while silver ions can inactivate sulfhydryl enzymes and accumulate in the body.[4] Increasing concerns over monitoring mercury ions and silver ions in aqueous solution have motivated the development of new methods with high selectivity and sensitivity. The techniques usually adopted for detecting these two metal ions include atomic absorption spectrometry (AAS),[5] atomic emittion spectrometry (AES),[6] inductively coupled plasma mass spectrometry (ICP-MS),[7] electrochemical method,[8,9] and so on.

Colorimetric methods, in particular, are extremely attractive because the detection results can be easily read out with the naked eyes. Moreover, they offer advantages of simplicity, rapidity, cost effectiveness and no requirement of any sophisticated instrumentation. Procedures using small molecules,[10−12] DNAzymes,[13−15] oligonucleotides,[16] polymers,[17] and functional nanoparticles[18] have all been developed for the selective detection of Hg^{2+} and Ag^{+} in aqueous solutions. However, most of these methods suffer from low water solubility, complex synthesis procedure, or time-consuming DNA probe preparation.

Recently, gold nanoparticles (AuNPs) have attracted much attention in colorimetric detection because of its high extinction coefficient in the visible region and color-tunable behavior that depends on the interparticle distance.[19−22] In recent years, several groups proposed colorimetric detection methods based on AuNPs for the assay of heavy metal ions. The first strategy is based on manipulating AuNPs with different recognition units such as oligonucleotides, DNAzymes, peptides, protein, and small thiolate ligand to induce aggregation.[23] For instances, Hg^{2+} could be selectively and sensitively detected based on thymidine—Hg—thymidine coordination chemistry.[24−28] When two cDNA—AuNPs are combined by the introduction of Hg^{2+}, the linked DNA would aggregate through thymidine—Hg^{2+}—thymidine coordination,[29−36] which resulted in the color change of the colloid. Sharing the same principle, T-rich single strands DNA (ssDNA) modified AuNPs were also developed into Hg^{2+}

Received: January 30, 2011
Accepted: April 6, 2011
Published: April 06, 2011

Scheme 1. Illustration of Colorimetric Sensing Mechanism Based on Redox Reaction Modulated Surface Chemistry of AuNPs; TEM Image of Aggregated AuNPs in Hg^{2+}-free PBS Solution and the Monodispersed AuNPs Obtained after Addition of 10 μM Hg^{2+}



sensors. The ssDNA can protect unmodified AuNPs from aggregation in a high salt solution;[37−39] however, they would aggregate in the presence of Hg^{2+} because of the formation of folded DNA structure that lost the protection ability for the AuNPs. Similarly, thiol-capped AuNPs for colorimetric detection Hg^{2+} and other metal ions were proposed. The coordination between the carboxyl groups of thiols and metal ions[40,41] resulted in the aggregation of AuNPs and the red colloidal gold changed to blue. Tseng and co-workers[42] reported a colorimetric detection method for Hg^{2+} by using 3-mercaptopropionate acid (MPA) and adenosine monophosphate (AMP)-functionalized AuNPs. AMP could protect the AuNPs from aggregation in the presence of a given high concentration of salt. Through the coordination between the carboxylic group of MPA and Hg^{2+}, it could capture Hg^{2+} in aqueous solution, which resulted in the aggregation of AuNPs.

The methods above relied on the ion chelating agent induced color change of gold colloid. More recently, researchers found that the change of AuNPs surface state would not only influence the surface plasmon resonance (SPR) property but also the surface molecular conjugation feature and therefore the resultant colloid stability. On the basis of the surface chemistry modification of AuNPs, a novel strategy for colorimetric detection was explored. For instance, it is reported that AuNPs surface exhibits a strong affinity for mercury,[43−45] with the reduction of Hg^{2+}, the Hg(0) would deposit on the surface of AuNPs and form a solid amalgam-like structure. This would result in the decrease of SPR band intensity of AuNPs.[46−48] In addition, Tseng and co-workers used Tween 20-modified AuNPs to detect Hg^{2+} and Ag^{+} based on reduction of Hg^{2+} and Ag^{+} by citrate to form Hg−Au alloys and Ag on the surface of the AuNPs. For citrate was oxidized, Tween 20 was removed from the AuNP surface, resulting in aggregation and a red-to-blue change of the colloid.[19]

Inspired by ion redox-modulated surface chemistry of AuNPs, we proposed a novel "blue-to-red" colorimetric strategy for Hg^{2+} and Ag^{+} detection based on stabilization of colloidal gold by redox formed metal coating. In the presence of ascorbic acid (AA), Hg^{2+} or Ag^{+} was reduced to Hg(0) and Ag(0) deposited onto the surface of AuNPs. When N-acetyl-L-cysteine was added, it could not access to the surface of AuNPs and cause Tween 20 stabilized AuNPs aggregation. Thus the color of AuNPs still kept red. In contrast, when Hg^{2+} was absence in the solution, the N-acetyl-L-cysteine would induce the AuNPs aggregate immediately with a concomitant red-to-blue color change. Comparing with the as proposed colorimetric method, this strategy had several advantages: (i) the color of the gold colloid changed from light blue to red with increasing amount of sensing ions. For red is more sensitive to eyes than purple and blue, the color change from blue to red can easily be observed by eyes, especially when the color change is very slight. (ii) The selectivity was simply achieved by the redox nature of target ions and the application of classic ion masking agents, avoiding the design and selection of ion chelating moieties and complicated gold surface modification procedure. (iii) The sensitivity of the method is satisfactory. The minimum detectable concentration of the method was up to 5 nM for Hg^{2+} and 10 nM for Ag^{+}, respectively, which was comparable or even lower than other reported method.[13,19,40,41] We further demonstrated the analytical potential of this method for monitoring Hg^{2+} and Ag^{+} in water samples. The outstanding selectivity and sensitivity provided a unique way to determine metal ion pollutants in water samples without previous separation or preconcentration of the original sample.

EXPERIMENTAL SECTION

Chemicals and Apparatus. Hydrogen tetrachloroaurate (III) dehydrate ($HAuCl_4$), trisodium citrate, ascorbic acid (AA), ethylenediaminetetraacetic acid (EDTA), Tween 20, Na_2HPO_4, Na_3PO_4, $NaBH_4$, LiCl, KCl, $MgCl_2$, $CaCl_2$, $SrCl_2$, $CrCl_3$, $MnCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, $Cd(ClO_4)_2$, $AlCl_3$, $Pb(NO_3)_2$, $HgCl_2$, $AgNO_3$ and NaCl were obtained from Sinopharm Chemical Reagent (China). N-acetyl-L-cysteine was purchased from Sigma-Aldrich. All other chemicals were analytical reagent grade or better. All solutions were prepared with deionized water (18.2 MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system.

Transmission electron microscopy (TEM) analyses were performed on a JEM-1230 electron microscope (Japan) operating at 100 kV. Absorption spectra were measured on a Beckman coulter DU-800 UV/visible spectrophotometer (USA). ICP-MS analyses were performed on PerkinElmer Elan DRC II (USA).

Nanoparticle Synthesis. Citrate-capped AuNPs were prepared by means of the chemical reduction of $HAuCl_4$ in the liquid phase.[49] A

200 mL aqueous solution of 1 mM $HAuCl_4$ was brought to boil with vigorous stirring in a round-bottom flask fitted with a reflux condenser. 38.8 mM trisodium citrate (20 mL) was then added rapidly to the solution, and the mixture was heated under reflux for another 15 min, during which time its color changed from pale yellow to deep red. The solution was cooled to room temperature while being stirred continuously. The size of citrate-capped AuNPs determined by TEM image was about 13 nm. The particle concentration of the AuNPs (ca. 15 nM) was determined according to Beer's Law using an extinction coefficient of ca. $2.43 \times 10^8\ M^{-1}\ cm^{-1}$ at 520 nm.[50]

Sample Preparation. The detection was performed in 100−1000 mM phosphate buffer solution (PBS) with different pH. For Hg^{2+} sensing, the ions were added to a PBS solution (900 μL) containing 0.1% Tween 20 and AuNPs (100 μL, 15 nM), ascorbic acid (0.01 mM-2 mM) and NaCl (100 μL, 1 M). For Ag^+ sensing, the ions were added to a PBS solution containing AuNPs (100 μL, 15 nM), ascorbic acid (1 mM) and EDTA (0.1 M). Then N-acetyl-L-cysteine (0.5 mM-5 mM) was added. After equilibrating at ambient temperature for the optimum incubation time, the resulting solutions were subjected to record the absorption spectra.

Analysis of Real Samples. A series of samples were prepared by spiking standard solutions of Hg^{2+} or Ag^+ to the drinking water and tap water obtained locally. These spiked samples were added to a solution containing 100 μL AuNPs and 10 μL ascorbic acid (1 mM) in pH 7.2. After incubation for 30 min, 100 μL N-acetyl-L-cysteine (2 mM) was added to the solution and the solution was incubated for another 3 min before spectra measurement.

Safety Considerations. As Hg^{2+}, Ag^+, and most of tested metal ions are highly toxic and have adverse effects on human health, all experiments involving heavy metal ions and other toxic chemicals should be performed with protective gloves. The waste solutions containing heavy metal ions should be collectively reclaimed to avoid polluting the environment.

RESULTS AND DISCUSSION

Sensing Mechanism. As indicated in Scheme 1, AuNPs were first stabilized with Tween 20 in PBS solution containing 0.1 mM AA. When Hg^{2+} and Ag^+ were absent, the addition of N-acetyl-L-cysteine resulted in the aggregation of AuNPs for the thiols were readily accessed the surfaces of the AuNPs, displacing citrate ions and Tween 20 through the formation of stronger Au−S linkages[51] (Bond energy: ca. 184 kJ mol^{-1}). The negatively surface charged density of the AuNPs was then reduced, and aggregation occurred in the high ionic strength solution. However, when Hg^{2+} was presented in the solution, AA would reduce it to Hg(0). Because of the high affinity between Au and Hg, the reduced Hg(0) could directly deposit onto the gold surface through the formation of Hg−Au alloys.[52] Similarly, the AA could reduce Ag^+, forming and Ag-coated AuNPs. ICP-MS was used to provide a further evidence for the Hg−Au alloys and Ag-coated AuNPs, which were obtained by five cycles of centrifugation of a solution of Tween 20-AuNPs and after metal ions and AA were added into the solution (see Figure S1 in the Supporting Information). The surface chemistry modification would block the aggregation of AuNPs in a high ionic-strength solution. The TEM images of the aggregated AuNPs in Hg^{2+}-free PBS solution and the monodispersed AuNPs obtained after addition of Hg^{2+} are also shown in Scheme 1.

Both N-acetyl-L-cysteine and AA played important roles in the colorimetric sensing system. N-acetyl-L-cysteine was used to regulate the dispersed-aggregated state of the AuNPs while AA offered a reduction circumstance for the target ions. As illustrated in Curve a of Figure 1, the maximum absorbance of Tween 20 stabilized AuNPs appeared at 520 nm and the solution was still red (Picture a), indicating AuNPs were well dispersed in the redox media of 50 mM PBS solution containing 1 mM AA. This phenomenon was in accordance with the report that Tween 20 could protect AuNPs against aggregation in high ionic strength solution.[19,53] After N-acetyl-L-cysteine was added, the surface protective Tween 20 would be displaced, which resulted in the absorbance of the solution at 520 nm decreased and the absorption band was red shift to 620 nm (Curve b) with a concomitant red-to-blue color change (Picture b), illustrating the AuNPs aggregation. On the other hand, AA used for the reduction of target ions was a key factor to change the surface chemistry of AuNPs. Curve c showed the absorption spectrum of the AuNPs solution in the presence of 1 μM Hg^{2+} without AA. The addition of N-acetyl-L-cysteine still resulted in maximum absorbance at 520 nm decreasing and the absorption band at 620 nm growing (Curve c), as well as a color change from red to blue of the colloid (Picture c). This is similar to Curve b obtained without metal ions. However, if 1 μM Hg^{2+} was present in the PBS solution containing 1 mM AA, the addition of N-acetyl-L-cysteine would not cause any aggregation, but only a slight blue shift of absorption band, suggesting interaction between Hg^{2+} and AA formed Hg−Au alloy[19] (Curve d). The formation of Hg−Au alloy protected AuNPs against aggregation in the presence of N-acetyl-L-cysteine in high ionic strength solution. This would also be easily distinguished by eye observation for the colloid kept red (Picture d). The results illustrated that without AA, the Hg^{2+} would not be reduced. So in the system the AA was crucial to make sure the Hg was reacted completely and formed Hg(0) depositing on the surface of AuNPs. Similar phenomenon was also observed in the system of sensing Ag^+.

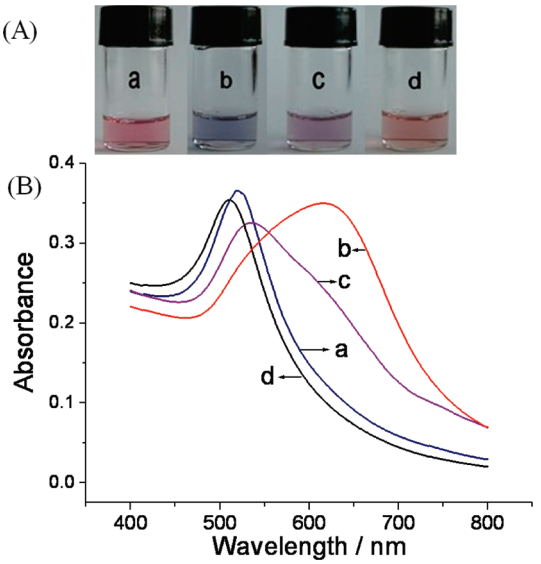


Figure 1. (A) Color changes and (B) absorption spectra of (a) Tween 20-AuNPs in 50 mM PBS solution (solution A); (b) after the addition of 100 μL 20 mM N-acetyl-L-cysteine into solution A with 1 mM AA (in the absence of Hg^{2+}); (c) after 100 μL 20 mM N-acetyl-L-cysteine was added into solution A in the presence of 10 μM Hg^{2+} (in the absence of AA); (d) 100 μL 20 mM N-acetyl-L-cysteine was added into solution A with 1 mM AA in the presence of 10 μM Hg^{2+}.

Effect of pH and Phosphate Concentration. The effect of pH on the aggregation of AuNPs in the PBS system in the absence and

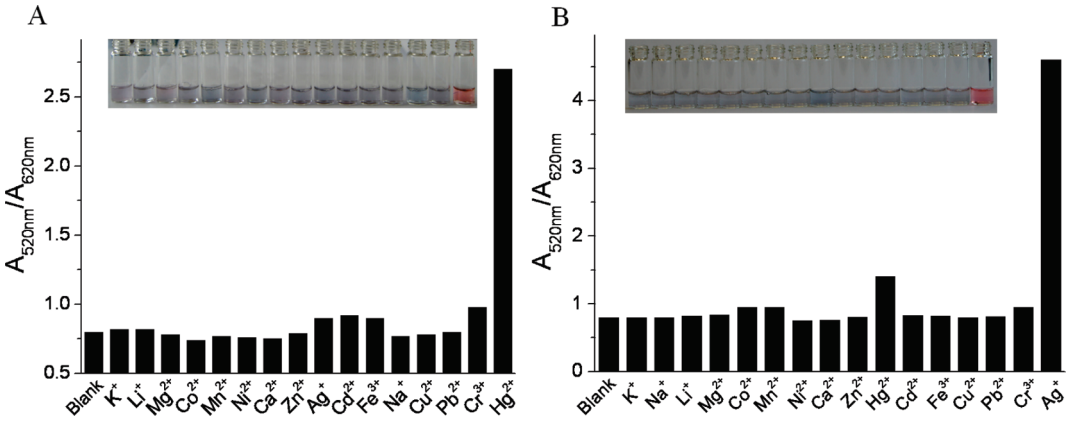


Figure 2. (A) Value of $A_{520\ nm}/A_{620\ nm}$ of 50 mM PBS containing Tween 20-AuNPs with 1 mM AA and 0.1 M NaCl upon the addition of 5 μM Hg^{2+} and 500 μM other metal ions. (B) Value of $A_{520\ nm}/A_{620\ nm}$ of 50 mM PBS containing Tween 20-AuNPs with 1 mM AA and 0.01 M EDTA upon the addition of 5 μM Ag^+ and 100 μM of Hg^{2+} and 500 μM other metal ions. The incubation time was 3 min.

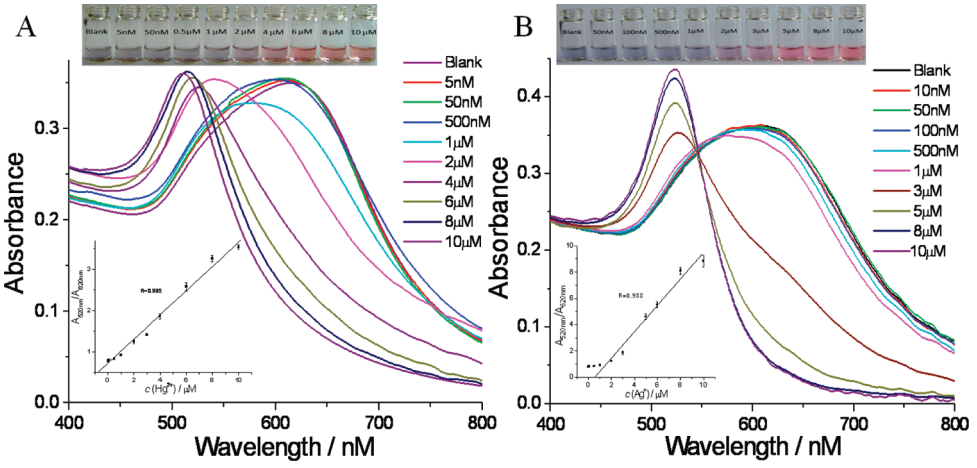


Figure 3. Digital photographs, absorption spectra, and plots of $A_{520\ nm}/A_{620\ nm}$ versus the concentration (inset) in 50 mM PBS (pH 7.2) containing Tween 20-AuNPs, 1 mM AA, and 0.1 M NaCl (0.01 M EDTA) upon addition of (A) 0−10 μM Hg^{2+} and (B) Ag^{2+}. The incubation time was 3 min. The error bars represented standard deviations based on three independent measurements.

presence of Hg^{2+} (5 μM) was investigated (see Figure S2A in the Supporting Information).The absorption values of the solution at 620 and 520 nm corresponded to the quantities of dispersed and aggregated AuNPs, respectively. Thus, the molar ratio of dispersed to aggregated AuNPs can be expressed by the ratio of the absorption value at 520 nm to that at 620 nm ($A_{520\ nm}/A_{620\ nm}$). The addition of both Hg^{2+} and Ag^+ to a solution resulted in an increasing value of $A_{520\ nm}/A_{620\ nm}$. The effect of the pH is important for the system. As shown in Figure S2A, the ratio of absorption ($A_{520\ nm}/A_{620\ nm}$) in the presence and in the absence of Hg^{2+} was maximized at pH 7.2. In acidic media, the value of pH was close to the isoelectric point of N-acetyl-L-cysteine (pI = 5.02), so they would not cause the aggregation of AuNPs and the presence of Hg^{2+} and Ag^+ in the media could not significantly change the value of $A_{520\ nm}/A_{620\ nm}$. However, in alkaline media, the Hg or Ag coated AuNPs were found to aggregate easily, so the absorption value ratio in the presence and in the absence of Hg^{2+} also had no great difference. Therefore, in the following experiments, pH of 7.2 was selected.

Phosphate concentration affects the ion strength of the solution. The ratio of $A_{520\ nm}/A_{620\ nm}$ in the presence (5 μM) and absence of Hg^{2+} was shown in Figure S2B (Supporting Information). It was can be seen that below the concentration of 100 mM, the ratio of $A_{520\ nm}/A_{620\ nm}$ was small. This was because at low ionic strength, the N-acetyl-L-cysteine could not make AuNPs aggregate in the absence of Hg^{2+}. After the concentration of phosphate was more than 100 mM, the ratio of $A_{520\ nm}/A_{620\ nm}$ in the presence and absence of Hg ions was nearly constant. Here the concentration of 100 mM was selected throughout the experiments.

Effect of the Concentration of AA and N-Acetyl-L-cysteine. We further investigated the effect of the AA concentration (0−2 mM) on the aggregating of AuNPs in the absence and presence of 5.0 μM Hg^{2+} ions (see Figure S2C in the Supporting Information). In the system, AA played an important role in the selected conditions. If there was no AA, when N-acetyl-L-cysteine was added to the solution in the presence of Hg^{2+}, the red solution became blue rapidly. This is because in the selected conditions, Hg^{2+} could exist in the solution and had not been reduced. The concentration of 1 mM AA could reduce Hg^{2+} completely from Figure S2C in the Supportng Information. So, 1 mM AA was selected in the system.

The effect of the concentration of N-acetyl-L-cysteine was also explored. At different concentration of N-acetyl-L-cysteine (from

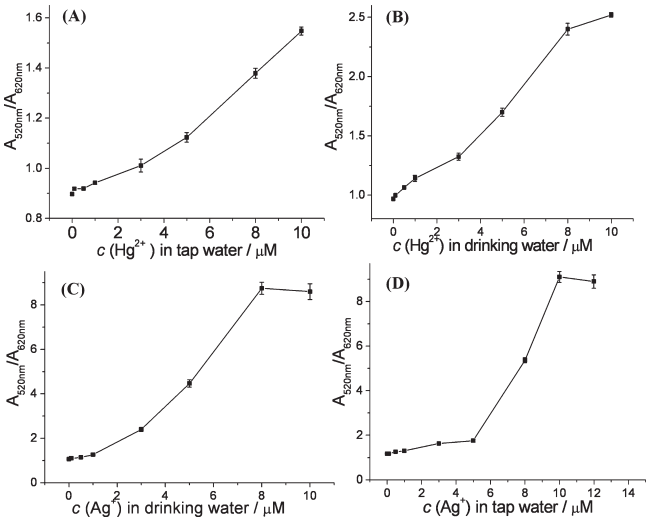


Figure 4. Plots of $A_{520\ nm}/A_{620\ nm}$ versus concentrations of Hg^{2+} and Ag^{+} in drinking water samples and tap water samples. Other conditions were the same as those described for Figure 3.

0.5 mM to 5 mM), the ratio of $A_{520\ nm}/A_{620\ nm}$ in the presence and absence of Hg^{2+} was performed in Figure S2D (see the Supporting Information). At relatively high concentrations, the solution with some concentration of Hg^{2+} would induce the aggregation of AuNPs. However, after a low concentration of N-Acetyl-L-Cysteine added, the solution without Hg^{2+} was still red. To obtain a high value of $A_{520\ nm}/A_{620\ nm}$, we selected 2 mM N-acetyl-L-cysteine for colorimetric detection of Hg^{2+} and Ag^{+}.

Sensitivity and Selectivity for Determination of Hg^{2+} and Ag^{+}. To realize the selectivity of the system based on redox activity on the surface of Tween 20 protected AuNPs toward Hg^{2+} and Ag^{+}, respectively, other metal ions including Li^{+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, and Pb^{2+} were tested under the same conditions as in the case of Hg^{2+} and Ag^{+}. The results showed that Hg^{2+}, Ag^{+}, and higher concentration of Cu^{2+} could protect Tween 20-AuNPs against aggregation in the presence of AA. Among those metal ions, Hg^{2+}, Ag^{+}, and Cu^{2+} could be reduced by AA and form metal deposited on the surface of AuNPs. This can be seen from the standard electrode potentials: $E^{o}(Hg^{2+}/Hg) = 0.852$ V; $E^{o}(Ag^{2+}/Ag) = 0.799$ V; $E^{o}(Cu^{2+}/Cu) = 0.339$ V, and the electrode potentials of AA is 0.050 V at pH 7.2. So, Cu^{2+} would interfere with the detection. Here, acetyl acetone was selected for mask Cu^{2+} for formation of acetyl acetone−copper complexes ($lg\beta_1$= 8.27; $lg\beta_2$ = 16.34).[54] For selective determination of Hg^{2+}, both 0.1 M NaCl and 1 mM acetyl acetone were added to the solution to mask Ag^{+} and Cu^{2+} since the formation of AgCl and Cu^{2+}−acetyl acetone complex. As shown in Figure 2A, the addition of 5 μM Hg^{2+} to a solution resulted in a value of $A_{520\ nm}/A_{620\ nm}$ as 2.7, whereas the addition of other metal ions (100-fold toward Hg^{2+}) resulted in a value nearly the same as blank, illustrating 100-fold other metal ions did not interfere the determination of Hg^{2+}. For Ag^{+} sensing, EDTA was chose as a masking agent because it could form more stable complexes with Hg^{2+} and Cu^{2+} than that with Ag^{+}. The system performed high selectivity toward Ag^{+}. Over 20-fold of Hg^{2+} and 100-fold of other tested metals ions had no influence on the assay of Ag^{+} (Figure 2B).

Under the optimum conditions, the sensitivity of the system was evaluated toward Hg^{2+} and Ag^{+}. When the concentration of Hg^{2+} increased from 0 to 10 μM, the absorption peak at 520 nm increased while that at 620 nm decreased, induced the value of $A_{520\ nm}/A_{620\ nm}$ of the system increasing gradually, along with the color of the solutions changing from blue to red gradually (Figure 3A). The solution containing 0.01 M EDTA showed a similar response to Ag^{+}, the color of the colloid also changed from blue to red gradually (Figure 3B).The inset of Figure 3A and B showed $A_{520\ nm}/A_{620\ nm}$ increased linearly with increasing Hg^{2+} and Ag^{+} concentration over the range of 0.5 to 10 μM (R = 0.994) and 1 to 8 μM (R = 0.988), respectively. The difference in linearity between the two metal ions was probably due to these two kinds of metal had different block effects to N-acetyl-L-cysteine. For Hg^{2+} sensing, the $A_{520\ nm}/A_{620\ nm}$ value of 0 nM and 5 nM Hg^{2+} is 0.771 ± 0.002 and 0.791 ± 0.006, respectively. For Ag^{+} sensing, the $A_{520\ nm}/A_{620\ nm}$ value of 0 nM and 10 nM, Ag^{+} is 0.791 ± 0.005 and 0.804 ± 0.009, respectively. So the system could detect Hg^{2+} and Ag^{+} at concentration as low as 5 and 10 nM, easily.

Application in Real Water Samples. To test the application of the proposed approach, we applied the method to determination of Hg^{2+} and Ag^{+} in drinking water and tap water. As shown in Figure 4, the value of $A_{520\ nm}/A_{620\ nm}$ increased linearly with increasing the spiked concentration of Hg^{2+} in drinking water over the range of 1×10^{-7} to 8×10^{-6} M and in tap water over the range of 5×10^{-7} to 1×10^{-5} M. The lowest detectable concentration of Hg^{2+} in drinking water and tap water were estimated to be 5×10^{-8} and 1×10^{-7} M, respectively. For analysis of Ag^{+}, the linear ranges are 1×10^{-6} to 8×10^{-6} M in drinking water and 3×10^{-6} to 8×10^{-6} M in tap water. The lowest detectable concentration in drinking water and tap water were both 5×10^{-7} M. The responses to Hg^{2+} and Ag^{+} in drinking water and tap water were different from that in pure water, which may because some organic matter existed in these solutions that could reacted with Hg^{2+} and Ag^{+} and formed organic complex.

CONCLUSIONS

A new colorimetric method for the sensitive and selective detection of Hg^{2+} and Ag^{+} was developed based on the redox reaction occurred on the surface of AuNPs. The color change from blue to red is different from that of usual analyte-induced aggregation methods. For red is more sensitive to eyes than blue, the proposed method allows us to detect Hg^{2+} and Ag^{+} by naked eyes conveniently. Under the optimal conditions, the method showed highly sensitivity (5 nM for Hg^{2+} and 10 nM for Ag^{+}, respectively) and good selectivity toward Hg^{2+} ions with linear detection range from 5×10^{-7} to 1×10^{-5} M for Hg^{2+} and 1×10^{-6} to 8×10^{-6} M for Ag^{+}. This approach abrogated the need for complicated chemosensors or sophisticated equipment. We validated the practicality of this method through the analyses of drinking water and tap water samples. This simple, rapid and cost-effective sensing system appears to hold great practicality for the detection of heavy metal ions in real samples.

ASSOCIATED CONTENT

Supporting Information. The ICP-MS intensities of Hg and Ag in the precipitates of obtained from (a) the solution of Tween 20-AuNPs, after addition of (b) 10 μM Hg^{2+} and (c) Ag^{+} to a solution of Tween 20-AuNPs prepared in phosphate at pH 7.2. The precipitates were obtained by five cycles of centrifugation of the

resulting solution (Figure S1); Effects of the pH (A), and the concentration of phosphate (B), AA (C), N-acetyl-L-cysteine (D) of the sensing system on the ratio of $A_{520\ nm}/A_{620\ nm}$ in the presence and absence of 1 μM Hg^{2+}. The incubation time is 3 min (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: lxchen@yic.ac.cn.

ACKNOWLEDGMENT

This work was financially supported by the National Natural Science Foundation of China (20975089), the Innovation Projects of the Chinese Academy of Sciences (KZCX2-EW-206), the Department of Science and Technology of Shandong Province (2008GG20005005, BS2009DX006), the Department of Science and Technology of Yantai City of China (2007156) and the 100 Talents Program of the Chinese Academy of Sciences.

REFERENCES

(1) Campbell, L. M.; Dixon, D. G.; Hecky, R. E. *J. Toxicol. Environ. Health, B* **2003**, *6*, 325–356.
(2) Hoyle, I.; Handy, R. D. *Aquat. Toxicol.* **2005**, *72*, 147–159.
(3) Zalups, R. K. *Pharmacol. Rev.* **2000**, *52*, 113–143.
(4) Ratte, H. T. *Environ. Toxicol. Chem.* **1999**, *18*, 89–108.
(5) Gomez-Ariza, J.; Lorenzo, F.; Garcia-Barrera, T. *Anal. Bioanal. Chem.* **2005**, *382*, 485–492.
(6) Han, F. X.; Dean Patterson, W.; Xia, Y. J.; Maruthi Sridhar, B. B.; Su, Y. *J. Water, Air, Soil Pollut.* **2006**, *170*, 161–171.
(7) Fong, B.; Mei, W.; Siu, T. S.; Lee, J.; Sai, K.; Tam, S. *J. Anal. Toxicol.* **2007**, *31*, 281–287.
(8) Gholivand, M. B.; Parvin, M. H. *Electroanalysis* **2010**, *22* (19), 2291–2296.
(9) Deng, W.; Tan, Y.; Li, Y.; Wen, Y.; Su, Z.; Huang, Z.; Huang, S.; Meng, Y.; Xie, Q.; Luo, Y.; Yao, S. *Microchim. Acta* **2010**, *169*, 367–373.
(10) Tatay, S.; Gaviña, P.; Coronado, E.; Palomares, E. *Org. Lett.* **2006**, *8*, 3857–3860.
(11) Paramjit, K.; Divya, S. *Dyes Pigm.* **2011**, *88*, 296–300.
(12) Lee, M. H.; Cho, B. K.; Yoon, J.; Kim, J. S. *Org. Lett.* **2007**, *9* (22), 4515–4518.
(13) Liu, J.; Lu, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 7587–7590.
(14) Wang, G.; Wang, Y.; Chen, L.; Choo, J. *Biosens. Bioelectron.* **2010**, *25*, 1859–1868.
(15) Liu, J.; Lu, Y. *J. Am. Chem. Soc.* **2003**, *125*, 6642–6643.
(16) Lin, Y. H.; Tseng, W. L. *Chem. Commun.* **2009**, *43*, 6619–6621.
(17) Liu, X.; Tang, Y.; Wang, L.; Zhang, J.; Song, S.; Fan, C.; Wang, S. *Adv. Mater.* **2007**, *19*, 1471–1474.
(18) Freeman, R.; Finder, T.; Willner, I. *Angew. Chem., Int. Ed.* **2009**, *48* (42), 7818–7821.
(19) Lin, C. Y.; Yu, C. J.; Lin, Y. H.; Tseng, W. L. *Anal. Chem.* **2010**, *82*, 6830–6837.
(20) Wang, G; Chen, Z; Chen, L. *Nanoscale*, **2011**, DOI: 10.1039/C0NR00863J.
(21) Zhang, J. F; Lim, C. S; Cho, B. R; Kim, J. S. *Talanta* **2010**, *83*, 658–662.
(22) Zhang, J. F; Kim, J. S. *Anal. Sci.* **2009**, *25*, 1271–1281.
(23) Wang, Z.; Ma, L. *Coord. Chem. Rev.* **2009**, *253*, 1607–1618.
(24) Katz, S. *J. Am. Chem. Soc.* **1952**, *74* (9), 2238–2245.
(25) Kosturko, L. D.; Folzer, C.; Stewart, R. F. *Biochemistry* **1974**, *13*, 3949–3952.
(26) Thomas, C. A. *J. Am. Chem. Soc.* **1954**, *76* (23), 6032–6034.
(27) Miyake, Y.; Togashi, H.; Tashiro, M.; Yamaguchi, H.; Oda, S.; Kudo, M.; Tanaka, Y.; Kondo, Y.; Sawa, R.; Fujimoto, T.; Machinami, T.; Ono, A. *J. Am. Chem. Soc.* **2006**, *128* (7), 2172–2173.
(28) Tanaka, Y.; Oda, S.; Yamaguchi, H.; Kondo, Y.; Kojima, C.; Ono, A. *J. Am. Chem. Soc.* **2007**, *129* (2), 244–245.
(29) Lee, J. S.; Han, M. S.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 4093–4096.
(30) Han, M. S.; Lytton-Jean, A. K. R.; Oh, B. K.; Heo, J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2006**, *118*, 1839–1842.
(31) Han, M. S.; Lytton-Jean, A. K. R.; Oh, B. K.; Heo, J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 1807–1810.
(32) Lee, J. S.; Stoeva, S. I.; Mirkin, C. A. *J. Am. Chem. Soc.* **2006**, *128* (27), 8899–8903.
(33) Xue, X.; Wang, F.; Liu, X. *J. Am. Chem. Soc.* **2008**, *130* (11), 3244–3245.
(34) Li, H. X; Rothberg, L. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101* (39), 14036–14039.
(35) Li, H. X.; Rothberg, L. *J. Am. Chem. Soc.* **2004**, *126* (35), 10958–10961.
(36) Wang, L. H.; Liu, X. F.; Hu, X. F.; Song, S. P.; Fan, C. F. *Chem. Commun.* **2006**, *36*, 3780–3782.
(37) Huang, C. C.; Chang, H. T. *Anal. Chem.* **2006**, *78* (24), 8332–8338.
(38) Wang, Y.; Wang, J.; Yang, F.; Yang, X. *Anal. Sci.* **2010**, *26*, 545–549.
(39) Darbha, G. K.; Singh, A. K.; Rai, U. S.; Yu, E.; Yu, H.; Chandra Ray, P. *J. Am. Chem. Soc.* **2008**, *130* (25), 8038–8043.
(40) Hung, Y. L.; Hsiung, T. M.; Chen, Y. Y.; Huang, Y. F.; Huang, C. C. *J. Phys. Chem. C* **2010**, *114* (39), 16329–16334.
(41) Huang, C. C.; Chang, H. T. *Chem. Commun.* **2007**, *12*, 1215–1217.
(42) Yu, C. J.; Tseng, W. L. *Langmuir* **2008**, *24* (21), 12717–12722.
(43) Rex, M.; Hernandez, F. E.; Campiglia, A. D. *Anal. Chem.* **2006**, *78* (2), 445–451.
(44) Leopold, K.; Foulkes, M.; Worsfold, P. J. *Anal. Chem.* **2009**, *81* (9), 3421–3428.
(45) Lisha, K. P.; Anshup; Pradeep, T. *Gold Bull.* **2009**, *42* (2), 144–152.
(46) Xiao, Y.; Pavlov, V.; Niazov, T.; Dishon, A.; Kotler, M.; Willner, I. *J. Am. Chem. Soc.* **2004**, *126* (24), 7430–7431.
(47) Shlyahovsky, B.; Li, D.; Katz, E.; Willner, I. *Biosens. Bioelectron.* **2007**, *22*, 2570–2576.
(48) Wang, G.; Chen, Z.; Wang, W.; Yan, B.; Chen., L. *Analyst* **2011**, *136*, 174–178.
(49) Frens, G. *Nat. Phys. Sci.* **1973**, *241*, 20–22.
(50) Link, S.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 8410–8426.
(51) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437–463.
(52) Rex, M.; Hernandez, F. E.; Campiglia, A. D. *Anal. Chem.* **2006**, *78*, 445–451.
(53) Shen, C. C.; Tseng, W. L.; Hsieh, M. M. *J. Chromatogr., A* **2009**, *1216*, 288–293.
(54) Danie, C. H. *Quantitative Chemical Analysis*, Sixth ed.; W. H. Freeman and Company: New York, 2003; AP23.