

Colorimetric Detection of Trace Copper Ions Based on Catalytic Leaching of Silver-Coated Gold Nanoparticles

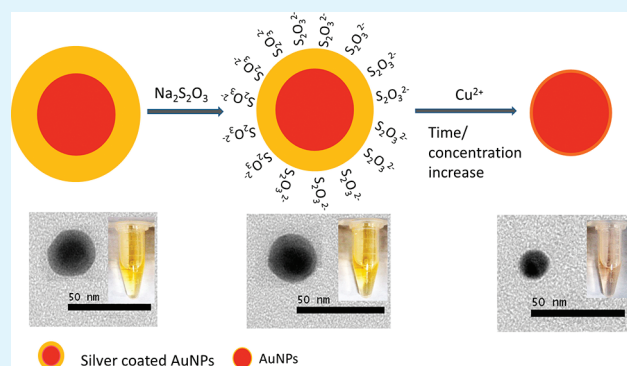
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ABSTRACT: A colorimetric, label-free, and nonaggregation-based silver coated gold nanoparticles (Ag/Au NPs) probe has been developed for detection of trace Cu^{2+} in aqueous solution, based on the fact that Cu^{2+} can accelerate the leaching rate of Ag/Au NPs by thiosulfate ($\text{S}_2\text{O}_3^{2-}$). The leaching of Ag/Au NPs would lead to dramatic decrease in the surface plasmon resonance (SPR) absorption as the size of Ag/Au NPs decreased. This colorimetric strategy based on size-dependence of nanoparticles during their leaching process provided a highly sensitive (1.0 nM) and selective detection toward Cu^{2+} , with a wide linear detection range (5–800 nM) over nearly 3 orders of magnitude. The cost-effective probe allows rapid and sensitive detection of trace Cu^{2+} ions in water samples, indicating its potential applicability for the determination of copper in real samples.

KEYWORDS: copper ions, colorimetric detection, silver-coated gold nanoparticles, catalytic leaching



INTRODUCTION

Copper, as a widely used metal, is an essential trace element in the human body and an indispensable component of many enzyme systems.¹ However, it may cause adverse health effects at elevated concentrations in humans.² Copper ions (Cu^{2+}) can accumulate in human and animal livers through bioaccumulation. Under overloading conditions, copper exhibits high toxicity and can cause oxidative stress and disorders associated with neurodegenerative diseases (e.g., Wilson's diseases).³ The U.S. Environmental Protection Agency (EPA) issued the revised national water quality criteria for copper in 2007 and provided detailed recommendations on the Cu^{2+} concentration limits for the protection of aquatic life in freshwater. For example, under 100 mg/L hardness, the Cu^{2+} concentration limits are 13 ng/mL (acute) and 9 ng/mL (chronic), respectively.⁴ Naturally occurring concentrations of Cu^{2+} are generally from 0.20 to 30 ng/mL in fresh waters.⁵ Therefore, the identification and measurement of copper ions (Cu^{2+}) in water has become increasingly important. Currently, various techniques^{6–14} are available for the determination of trace Cu^{2+} in aqueous samples. Colorimetric methods, in particular, are extremely attractive because they can be easily read out with the naked eyes or low-cost portable instruments.^{15–17}

Many reported colorimetric sensors for Cu^{2+} usually employ organic dyes for both Cu^{2+} recognition and signal generation.^{17–21} However, most of them are applied in mixed solvent (water/organic solvent), while only a few of them are appropriate for neat aqueous solution, which greatly limits their applications. For color

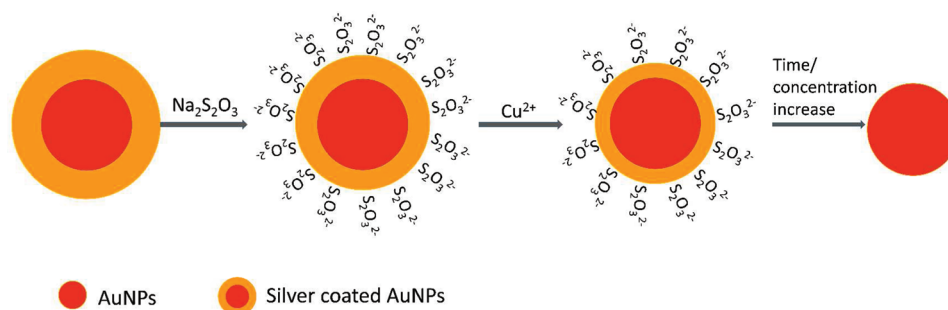
signal generation, gold nanoparticles (Au NPs) are particularly attractive as they possess much higher absorption coefficients compared to organic dyes, allowing sensitive colorimetric detections with minimal material consumption. More importantly, they display distance-dependent optical properties.²² Recently, the color changes associated with the dispersion-aggregation state of Au NPs have led to the rapid development of a number of assays.^{23–25} There are also some other detection methods for Cu^{2+} based on Au NPs.^{26–28} He et al. reported a new and homogeneous assay method to detect the Cu^{2+} ion based on the modulation of photoluminescent quenching efficiency between the perylene bisimide chromophore and Au NPs in the presence of Cu^{2+} .²⁶ Choi et al. presented a nanospectroscopic metal-ion detection technology based on metal–ligand coordination chemistry as well as plasmonic resonance energy transfer for detection Cu^{2+} .²⁷ Jiang et al. reported the visual detection of Cu^{2+} by azide- and terminal alkyne-functionalized Au NPs using click chemistry.²⁸ To improve the sensitivity and selectivity, we can incorporate new elements such as catalysis and conjugated polymers to amplify the sensing processes. Yang et al. found that DNAzyme could be cleaved into ssDNA in the presence of ascorbic acid and Cu^{2+} , which enhanced stabilization of Au NPs against salt-induced aggregation.²⁹ They successfully utilized this protocol for colorimetric detection of Cu^{2+} .

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Scheme 1. Schematic Representation of the Sensing Mechanism of the $S_2O_3^{2-}$ -Ag/AuNPs for the Colorimetric Detection of Cu^{2+} Based on Catalytic Leaching of Ag-Coated Au NPs^a



^a For clarity, the cross-sections of the NPs and the colors of their respective colloid solutions are given.

It is known that the absorption cross-sections of spherical Au NPs are proportional to the third power of their diameters (R^3), however there are only a few reports describing label-free optical detection methods based on the size dependence of single Au NPs during their leaching processes.^{31,32} Recently, Huang and co-workers designed a method based on the leaching of Au NPs by thiosulfate in the presence of 2-mercaptoethanol (2-ME) which led to dramatic decrease in the surface plasmon resonance (SPR) absorption for colorimetric assay of Pb^{2+} .³² It can be easily exploited using simple chemistries to develop the desired components and subsequent devices based on the trait of colorimetry and size-dependent properties of Au NPs. In fact, in hydrometallurgy, the thiosulfate leaching system has been applied for extraction of gold or silver from ores for many years in the presence of Cu^{2+} as one of the most promising nontoxic alternatives to cyanide.^{33–35} Inspired by this idea, a sensing platform for Cu^{2+} based on catalytic leaching of metal NPs was designed. Herein, silver-coated Au NPs (Ag/Au NPs) were chosen for monitoring changes in the SPR absorptions to investigate the $S_2O_3^{2-}$ -leaching system in the presence of Cu^{2+} . In the system, Au NPs were more difficult to leach than silver NPs, because they are more inert. Moreover, as is known that silver NPs are not stable for synthesis and storage, also the colloid solution is not uniform and not well-distributed. To overcome these problems, Ag/Au NPs were employed, and much brighter color was exhibited which is quite suitable for colorimetric detection. Thus, a label-free, simple, and low-cost assay was developed, employing Ag/Au NPs and $S_2O_3^{2-}$ for highly selective and sensitive detection of trace Cu^{2+} in aqueous samples.

EXPERIMENTAL SECTION

Chemicals. Sodium thiosulfate, trisodium citrate, hydrogen tetrachloroaurate (III) trihydrate, Tween 20, Tris, LiCl, KCl, NaCl, $MgCl_2$, $CaCl_2$, $CrCl_3$, $MnCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, $Cd(NO_3)_2 \cdot 4H_2O$, $AlCl_3$, $Pb(NO_3)_2$, $HgCl_2$, and $AgNO_3$ were ordered from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All other chemicals used in this work were analytical reagent grade or better. All solutions were prepared with deionized water (18.2 M Ω cm specific resistance) obtained with a Pall Cascada laboratory water system (Millipore, Bedford, MA, USA).

Instrumentation. TEM measurements were performed on a JEM-1230 electron microscope (JEOL, Ltd., Japan) operating at 100 kV. Colloid samples were prepared by placing 10 μ L of solution on carbon Formvar coated copper grids purchased from Beijing Zhongjingkeyi

Technology Co., Ltd. (China). The samples were allowed to dry in drying oven under 40–50 $^{\circ}C$.

UV–vis spectra were collected on a μ -Quant microplate reader (Nanodrop 2000C, Thermo Scientific, USA) using a 1 cm quartz cell.

Synthesis of Ag/Au NPs. Silver coated gold nanoparticles (Ag/Au NPs) were prepared following seeding growth approach as Natan's group with slight modifications.^{36,37} Au particles with ca. 13 nm diameters were first prepared according to the citrate reduction method, and then were used as seed.

A 200 mL aqueous solution consisting of 1 mM $H AuCl_4$ was brought to a vigorous boil with 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. The solution was heated under reflux for another 15 min, and during the 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 Au NPs determined by TEM images was ca. 13 nm. The particle concentration of the Au NPs (ca. 15 nM) was determined according to Beer's law using an extinction coefficient of ca. $2.7 \times 10^8 M^{-1} cm^{-1}$ at 520 nm. And then, trisodium citrate reduction of $AgNO_3$ was carried out in the presence of the 13 nm gold seed. Ten milliliters of 13 nm Au NPs was diluted to 100 mL solution and reheated under reflux by addition of 1 mL of 38.8 mM sodium citrate with vigorous stirring, and then 5 mL of $10^{-2} M AgNO_3$ was added and the boiling was continued for 1 h. Finally, the Ag/Au NP colloidal solution was cooled to room temperature and stored at 4 $^{\circ}C$ and protected from light.

All glassware was washed with freshly prepared aqua regia (HCl: HNO_3 , 3:1, v/v) followed by extensive rinsing with deionized water. Double-distilled deionized water was used for all experiments.

$S_2O_3^{2-}$ -Ag/Au NP-Based Sensor for Cu^{2+} . For Cu^{2+} sensing, aliquots (800 μ L) of 50 mM tris-HCl (pH 8.5) solutions containing 0.1% Tween 20 and Ag/Au NPs (1.5 nM), $Na_2S_2O_3$ (1.0 mM), and Cu^{2+} ions were equilibrated at room temperature for 60 min. The mixtures were then transferred separately and their UV–vis absorption spectra were recorded.

Analysis of Water Samples. Tap water sample obtained from our institute and pond water sample collected from a pond in the campus of Yantai University (Yantai, China) were filtered through a 0.2 μ m membrane. Aliquots (100 μ L) of the pond water were spiked with standard Cu^{2+} solutions (10 μ L) at concentrations over the range 0–10 μ M. The spiked samples were then diluted to 1000 μ L with the standard solutions containing the $S_2O_3^{2-}$ -Ag/Au NPs probe and 50 mM tris-HCl (pH 8.5).

Safety Considerations. Considering Cu^{2+} 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 Strategy. The leaching of silver in thiosulfate solutions has been used for the recovery of silver from its ores. There have been numerous studies of gold/silver extraction from ores by the thiosulfate leaching system.^{33–35} Here we utilize the leaching of Ag/Au NPs by $S_2O_3^{2-}$ to sense aqueous Cu^{2+} . Scheme 1 outlines the sensing mechanism employed. Depending on the nature of metal–S complexation, when Ag/Au NPs reacted with $S_2O_3^{2-}$ ions in solution, $Ag(S_2O_3)_2^{3-}$ complexes were formed immediately on the Ag/Au NP surfaces in the presence of dissolved oxygen, leading to part dissolving of NPs and a little

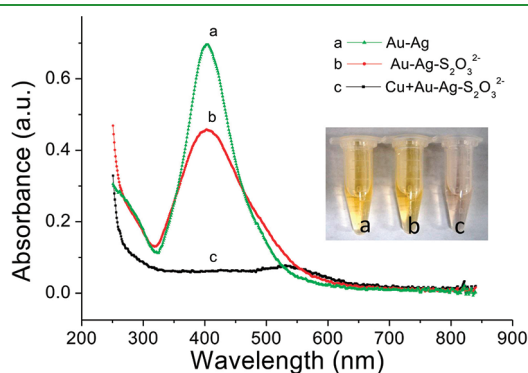
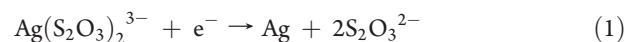
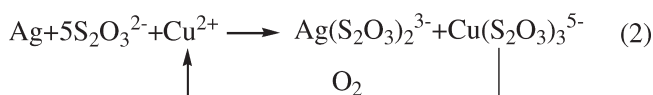


Figure 1. UV–vis absorption responses and photographs of solutions of (a) Tween 20-Ag/AuNPs, and Tween 20-Ag/AuNPs with the addition of $Na_2S_2O_3$ (b) before and (c) after the addition of $1 \mu M$ Cu^{2+} . Tween 20-Ag/AuNPs were prepared in Tris-HCl buffer at pH 8.5. The incubation time was 1 h.

decrease in their SPR absorption.



The standard potential of $Ag(S_2O_3)_2^{3-}/Ag$ is 0.01 V in eq 1, and the conditional potential of O_2/H_2O is 0.729 V calculated according to Nernst equation at pH 8.5 under room temperature. So Ag can be easily oxidized by dissolved oxygen (O_2) and form $Ag(S_2O_3)_2^{3-}$ complexes in solution. However, it has been found that this reaction is very slow if the surface of Ag is oxidized due to the formation of sulfur-like film as a result of decomposition of thiosulfate on the silver surface.^{38,39} Cu^{2+} has been found to have a strong catalytic effect on the leaching rate of gold and silver.^{40,41} Cu^{2+} can oxidize gold and silver in the presence of $S_2O_3^{2-}$ forming $Cu(S_2O_3)_3^{5-}$. And then the latter can also be oxidized to Cu^{2+} by dissolved oxygen. The overall reaction for the dissolution of Ag/Au NPs in aqueous solutions in the presence of O_2 was shown in eq 2.



As a result of adding Cu^{2+} into the $S_2O_3^{2-}$ -Ag/Au NP solution, the size of the particles was decreased and the SPR absorption decreased dramatically, at the end, the absorbance of Au NPs was observed, allowing quantitation of the Cu^{2+} in aqueous solution.

To verify the roles that $Na_2S_2O_3$ and Cu^{2+} played in accelerating the leaching rate of Ag/Au NPs, the SPR absorption was monitored as shown in Figure 1; meanwhile, TEM images revealed the corresponding average nanoparticle size as shown in Figure 2. As seen from Figure 1, curve (c) displays the absorption

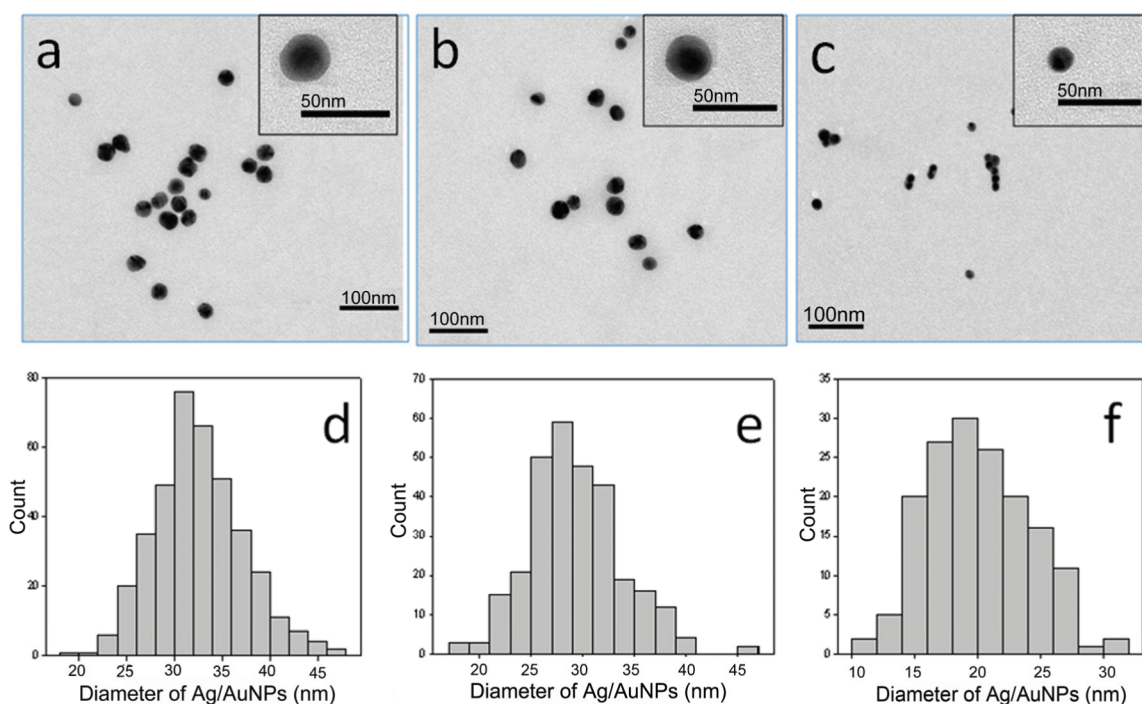


Figure 2. TEM images of nanoparticles (top) and their corresponding size distribution histograms (bottom). (a, d) Ag/AuNPs; (b, e) $Na_2S_2O_3$ -modified Ag/AuNPs; (c, f) $Na_2S_2O_3$ -modified Ag/AuNPs together with $5.0 \mu M$ Cu^{2+} . The incubation time was 1 h.

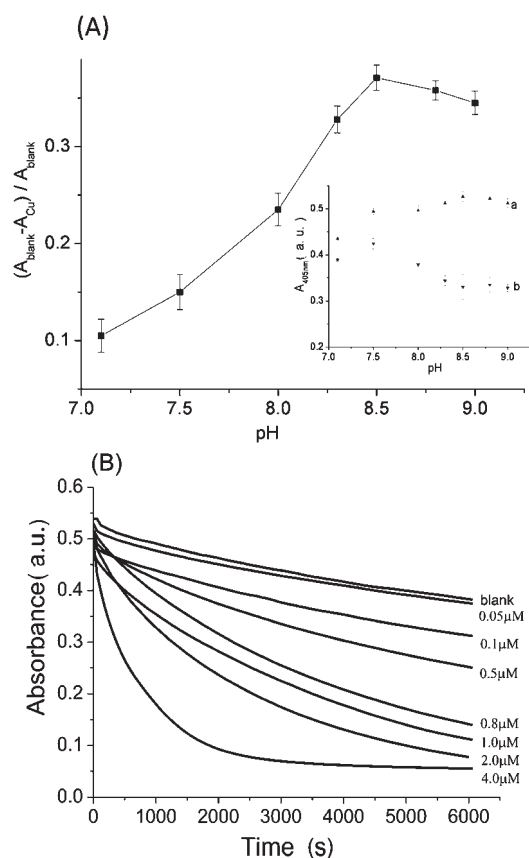


Figure 3. (A) Effect of the pH on the values of $(A_{\text{blank}} - A_{\text{Cu}}) / A_{\text{blank}}$ (at 405 nm) of the $\text{S}_2\text{O}_3^{2-}$ -Ag/AuNP solutions in the presence of 1.0 μM Cu^{2+} . Inset: effect of the pH on the values of $A_{405\text{nm}}$ in the (a) absence and (b) presence of 1.0 μM Cu^{2+} . Error bars represent standard deviations from three repeated experiments. (B) Time-dependence of absorption of the solutions after different concentrations (blank, 0.05, 0.1, 0.5, 0.8, 1.0, 2.0, and 4.0 μM) of Cu^{2+} were added. Other conditions were the same as those described in Figure 1.

spectrum of Ag/Au NPs (diameter about 30 nm, Figure 2a,d) in 50 mM Tris-HCl solution (pH 8.5); a strong SPR absorption appears at 405 nm. After addition of 1.0 mM $\text{Na}_2\text{S}_2\text{O}_3$, the absorption at 405 nm decreased (curve b). This is because it can react with Ag/Au NPs and further form $\text{S}_2\text{O}_3^{2-}$ -Ag/Au NPs complexes that would induce decreasing of the SPR absorption of the solution and partly dissolving of NPs, which can be seen from the TEM image (Figure 2b,e). With the existence of Cu^{2+} , the Ag/Au NPs would be catalytically oxidized and leached into the solution. After about 1 h in room temperature, the SPR absorption was changed to 520 nm and intensity was decreased (Figure 1c) due to the smaller particle size (diameter about 20 nm, Figure 2c and 2f). This illustrated that Ag coatings on the surface were dissolved gradually and Au NPs were left in the solution. This could be proved by both the color change of the solution from yellow to pink (inset of Figure 1) and the TEM image (Figure 2c,f). If reaction time was long enough, the solution containing Cu^{2+} would become colorless, which illustrated that Au NPs could also dissolve into the solution. It is notable that when particles were leached away, there could be a higher chance for them to aggregate, which can be seen in TEM image that the particles aggregate slightly in some extent (Figure 2c). Fortunately, the slight aggregation did not

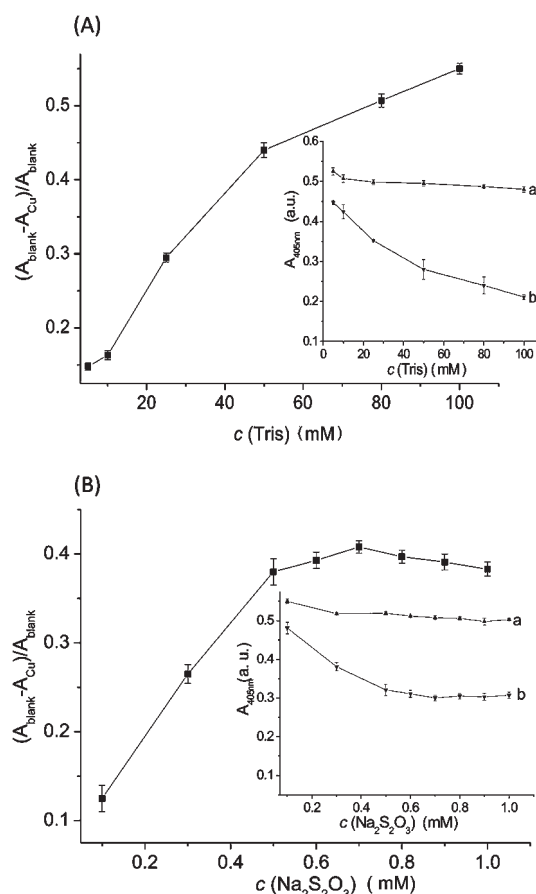


Figure 4. Effect of the concentration of (A) Tris and (B) $\text{Na}_2\text{S}_2\text{O}_3$ on the values of $(A_{\text{blank}} - A_{\text{Cu}}) / A_{\text{blank}}$ (at 405 nm) of the $\text{S}_2\text{O}_3^{2-}$ -Ag/AuNP solutions. Inset: effect of the concentration of (A) Tris and (B) $\text{Na}_2\text{S}_2\text{O}_3$ in the (a) absence and (b) presence of 1.0 μM Cu^{2+} . Error bars represent standard deviations from three repeated experiments. Other conditions were the same as those described in Figure 1.

significantly affect the detection results.³² In this system, Tween 20 and $\text{S}_2\text{O}_3^{2-}$ were employed to minimize the possible aggregation of Ag/Au NPs. The sensing strategy for Cu^{2+} was based on the catalytic effect of Cu^{2+} on the $\text{S}_2\text{O}_3^{2-}$ -Ag/Au NPs leaching system.

Effect of pH, Time. The effect of pH on the leaching of Ag/Au NPs was investigated in the $\text{S}_2\text{O}_3^{2-}$ -Ag/Au NPs system in the absence and presence of Cu^{2+} (1.0 μM). As shown in Figure 3A, the effect of pH was obvious for solutions containing Cu^{2+} in the range of 7.1–9.0, with the optimum pH at 8.5. In acidic media, $\text{S}_2\text{O}_3^{2-}$ can break down to form sulfide, sulfite, sulfate, trithionate, tetrathionate, polythionates ($\text{S}_x\text{O}_y^{2-}$) and polysulfides (S_x^{2-}).^{35,42} Therefore, increasing the pH may increase the stability of $\text{S}_2\text{O}_3^{2-}$, and consequently, the stability of $\text{S}_2\text{O}_3^{2-}$ -Ag/Au NPs. However, if pH was higher than 9.0, the NPs would aggregate in the solution. In this system, 0.1% Tween 20 was used as stabilized reagent not only to stabilize $\text{S}_2\text{O}_3^{2-}$ but also to block the influence of complex matrix such as high pH solution, and therefore the rate of Ag/Au NPs dissolution was maximized at pH 8.5. So, the Tris-HCl system at pH 8.5 was used to buffer the sensing solution.

The leaching of Ag/Au NPs was a chemical kinetics process. They were leached into solutions gradually as the reaction time and Cu^{2+} concentrations increased. The effect of incubating time

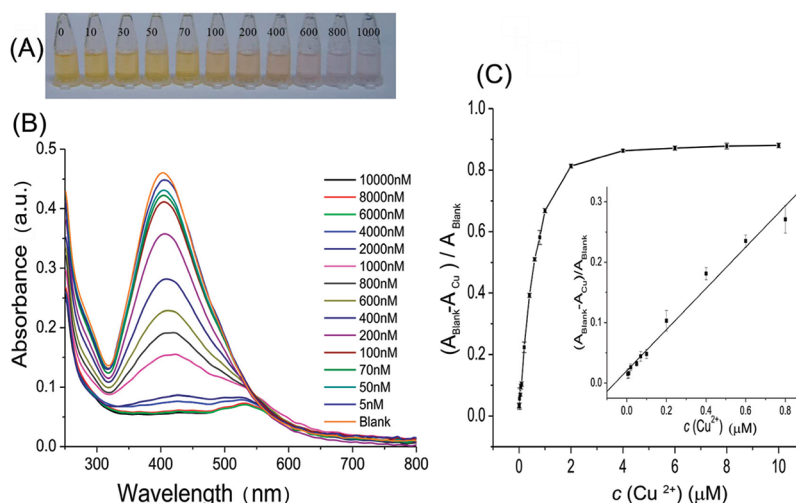


Figure 5. (A) Photographs and (B) absorption responses of the $\text{S}_2\text{O}_3^{2-}$ -Ag/AuNP solution addition of Cu^{2+} , and (C) plot of $(A_{\text{blank}} - A_{\text{Cu}})/A_{\text{blank}}$ (at 405 nm) values versus Cu^{2+} concentration. Inset: the enlarged portion of the plot in the Cu^{2+} concentration range of 5–800 nM; the regression equation is $(A_{\text{blank}} - A_{\text{Cu}})/A_{\text{blank}} = 0.0202 + 0.341c$ (μM) ($r = 0.991$).

under the optimized pH was also investigated after certain concentration of Cu^{2+} was present in the solution (Figure 3B). It was noticed that the absorbance of solutions became constant in the high concentration of Cu^{2+} ($>2 \mu\text{M}$) after 1 h. Therefore, the absorption of solutions was all tested within 1 h after adding $\text{Na}_2\text{S}_2\text{O}_3$ and Cu^{2+} .

Effect of Concentrations of Tris and $\text{Na}_2\text{S}_2\text{O}_3$. Next, we investigated the optimum concentrations of Tris and $\text{Na}_2\text{S}_2\text{O}_3$ in the system. Figure 4 displays the change of extinction in various concentrations of Tris and $\text{Na}_2\text{S}_2\text{O}_3$ solutions with and without $1 \mu\text{M}$ Cu^{2+} . As seen from Figure 4A, the concentration of Tris could affect the extinction of NPs. This is because the high concentration of Tris would affect the stability of the Ag/Au NPs. In the presence of Cu^{2+} , the extinction of solution is decreased obviously while the concentration of Tris is high. Combining the practical consideration, the concentration of Tris is selected as 50 mM. The effect of concentration of $\text{S}_2\text{O}_3^{2-}$ was also recorded. As seen from Figure 4B, the leaching rates of NPs were all accelerated during absence and presence of Cu^{2+} (inset a and b). However, at a concentration of 0.7 mM, the value of ratio is the biggest (Figure 4B). So, 0.7 mM $\text{S}_2\text{O}_3^{2-}$ ions were selected.

Sensitivity and Selectivity. To determine the sensitivity of the sensor, we recorded the UV–vis spectra of the Ag/Au NPs solution in the presence of various concentrations of Cu^{2+} after the addition of $\text{Na}_2\text{S}_2\text{O}_3$ under the optimized conditions. The absorption value versus the concentration of Cu^{2+} was plotted in Figure 5. It was clearly observed that the $A_{405 \text{ nm}}$ value gradually decreased with the increase of the concentration of Cu^{2+} . The absorption ratio could be fitted as the equation of $(A_{\text{blank}} - A_{\text{Cu}})/A_{\text{blank}} = 0.0202 + 0.341c$ (μM) over the range of 5–800 nM (inset of Figure 5C) with the correlation coefficient of 0.991 (Here A_{blank} means absorbance of solution without Cu^{2+} and A_{Cu} means absorbance of solution after Cu^{2+} have been added.). The limit of detection was determined to be 1 nM ($3\sigma/\text{slope}$), which is comparable to those of other sensitive analytical methods including fluorescent measurements.^{20,21}

To test the selectivity of the developed method, we added various environmentally relevant metal ions to the solution separately. The results indicated that the existence of about

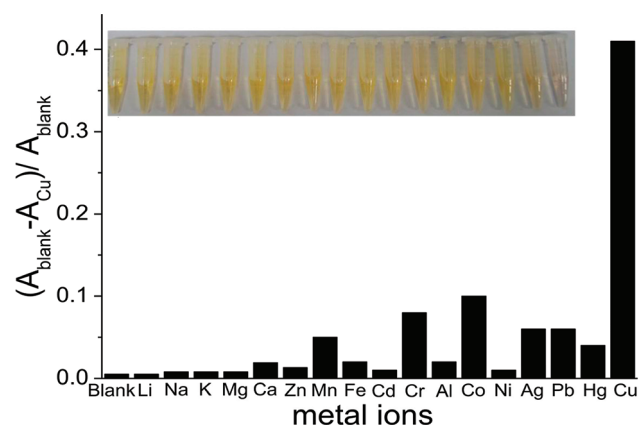


Figure 6. Relative absorption decrease (values of $(A_{\text{blank}} - A_{\text{Cu}})/A_{\text{blank}}$ (at 405 nm)) of the $\text{S}_2\text{O}_3^{2-}$ -Ag/AuNP solutions upon the addition of various metal ions, respectively. Concentrations: $1.0 \mu\text{M}$ Cu^{2+} ; $100 \mu\text{M}$ K^+ , Li^+ , Na^+ , Mg^{2+} , Ag^+ , Ca^{2+} , Mn^{2+} , Al^{3+} , Hg^{2+} , Cd^{2+} , and Zn^{2+} ; $20 \mu\text{M}$ Cr^{3+} and Co^{2+} ; $10 \mu\text{M}$ Pb^{2+} and Ni^+ . Inset: corresponding photographs of the solutions upon the addition of various metal ions, respectively. Other conditions were the same as those described in Figure 1.

100-fold excess of K^+ , Li^+ , Na^+ , Mg^{2+} , Ag^+ , Ca^{2+} , Mn^{2+} , Al^{3+} , Hg^{2+} , Cd^{2+} , and Zn^{2+} , 20-fold of Cr^{3+} and Co^{2+} , and 10-fold of Pb^{2+} and Ni^+ , did not affect the determination of $1 \mu\text{M}$ Cu^{2+} , as shown in Figure 6. The absorption ratio values ($A_{405 \text{ nm}}$) upon the addition of various other metal ions were similar to that given by the blank, and $A_{405 \text{ nm}}$ values in the presence of various metal ions caused less than 5% variations. However, excitedly, Cu^{2+} gave a remarkably enhanced absorption ratio at an identical concentration with other metal ions, demonstrating that the system had excellent selectivity toward Cu^{2+} .

Application. Additionally, practical applications were successfully carried out by using the $\text{S}_2\text{O}_3^{2-}$ -Ag/Au NPs for sensing Cu^{2+} in real samples such as tap water and pond water samples. As shown in Table 1, satisfactory recoveries of Cu^{2+} were obtained, 82–115% with the relative standard deviation (RSD) of 0.66–1.47% for tap water, and 81–119% with the RSD of 1.01–1.68% for pond water, respectively. This demonstrated the developed sensing

Table 1. Recoveries for the Determination of Cu²⁺ in Water Samples (n = 3)

samples	added (μM)	found (μM)	recovery (%)	RSD (%)
tap water		ND ^a		
	0.050	0.047	94.0	1.26
	0.100	0.820	82.0	0.66
	0.200	0.230	115.0	1.47
pond water	0.400	0.389	97.2	1.16
		ND		
	0.100	0.081	81.0	1.03
	0.200	0.237	118.5	1.68
	0.400	0.448	112.0	1.02
	0.600	0.620	103.3	1.01

^a ND = not detected.

method was potentially applicable for the determination of Cu²⁺ ions in drinking and environmental water samples.

CONCLUSIONS

In summary, a new and rapid assay was developed for the sensitive and selective detection of Cu²⁺ ions based on the catalytic leaching of Ag/Au NPs. The changes in the SPR absorptions of Ag/Au NPs allowed readily detecting Cu²⁺ in aqueous solution. Under the optimized conditions, the Cu²⁺-specific probe exhibited high sensitivity of nM level and high selectivity over other possible interference ions, and offered a wide linear detection range and satisfactory recoveries for several water samples. This sensing method avoided the need of complicated/sophisticated equipments or procedures and provided a simple and quick sensing system for the detection of heavy metal ions. This assay strategy set an excellent example of catalytic leaching in analytical chemistry for the analysis of heavy metal ions using nanotechnology, which also provided potential applications in the biological and environmental fields.

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