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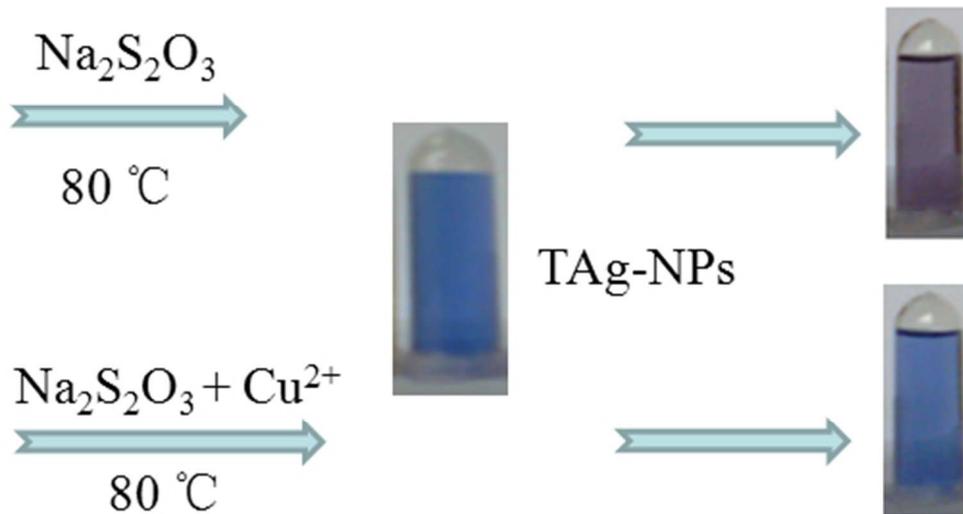
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Visual Trace Copper(II) Detection Based on Its Catalytic Action to the Disassociation of Thiosulfate

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In this study, we report a new method for the detection of Cu^{2+} based on triangular silver nanoplates (TAg-NPs), which could be corroded by sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$). TAg-NPs with the blue color can be changed to yellow color in the presence of a certain concentration of $\text{Na}_2\text{S}_2\text{O}_3$, however, its color change is unclearly when $\text{Na}_2\text{S}_2\text{O}_3$ was heated in the presence of Cu^{2+} . The reason may be that $\text{Na}_2\text{S}_2\text{O}_3$ is dissociated under heating in the presence of Cu^{2+} , which leads the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ to be decreased. Furthermore, when the heating time is fixed, the decreased concentration of $\text{Na}_2\text{S}_2\text{O}_3$ is proportion to the concentration of Cu^{2+} . As a result, the color of the mixture solution of TAg-NPs/ Cu^{2+} / $\text{Na}_2\text{S}_2\text{O}_3$ and the absorbance at the position of maximum absorption peak of TAg-NPs changed with the change of the concentrations of Cu^{2+} . The change values of the absorbance (ΔA , the absorbance of TAg-NPs/ Cu^{2+} / $\text{Na}_2\text{S}_2\text{O}_3$ subtracted by that of TAg-NPs/ $\text{Na}_2\text{S}_2\text{O}_3$ at the position of maximum absorption peak) were proportional to the concentrations of Cu^{2+} . Thus, a new method was established by UV-vis absorption spectrum or the naked eyes observation, which is simple, fast and low cost for copper ion detection. Using this method, the concentration of Cu^{2+} could be detected accurately in the range of 2.5×10^{-9} to $7.5 \times 10^{-7} \text{ mol L}^{-1}$ with the correlation coefficient of $r=0.9983$. Moreover, the color change of TAg-NPs could be observed in the Cu^{2+} concentration from 2.5×10^{-8} to $7.5 \times 10^{-7} \text{ mol L}^{-1}$.

1. Introduction

In recent years, metal nanomaterials have attracted many attentions due to their special properties[1-3] and potential application in many areas[4-6], furthermore, many of them have low toxicity[7], complex optical features spanning the visible and nearinfrared spectra[8], and exhibit facile surface functionalization chemistry[9]. These physical and chemical properties of metal nanomaterials depended on their shape and size [10,11] especially for silver nanostructures. So, shape-controlled synthesis of silver nanostructures has been attracting a

great number of attentions for scientists, and a large number of methods have been devoted to the synthesis of silver nanostructures with different shapes [12-15]. On the other hand, the applications of silver nanostructures mainly depends on its shape because the higher atomic fractions are located at corners, edges and defects of the silver nanostructures[16,17]. Recently, triangular silver nanoplates (TAg-NPs) have been widely used as chromogenic components in colorimetric sensing systems owing to their special optical properties[18,19].

Copper ion is one of the most abundant transition metal ion, and is commonly found as Cu^{2+} in natural water. However, the deficient or excessive amounts Cu^{2+} also brings serious environmental pollution and potential toxicity to living organisms. Such as microorganisms are affected by even submicromolar concentrations of Cu^{2+} [20], deficiency or excess of Cu^{2+} can bring on anemia, pancytopenia [21], gastrointestinal disturbance and/or damage to the liver and kidneys [22,23]. Various methods have been developed for the determination of Cu^{2+} at trace quantity levels in many kinds of samples, such as infrared absorption spectroscopic [24], anodic stripping voltammetry[25], atomic absorption spectroscopy (AAS) [26, 27], and inductively coupled plasma spectroscopy (ICP) [28, 29], moreover, many visual methods have been discovered for the detection of Cu^{2+} [30-34]. These visual detection methods are simple, because it could be achieved only by naked eyes. However, it need special reagent, and the sensitivity is still not very high. Thus, developing the visual method with high sensitivity for Cu^{2+} detection is still needed.

Herein, we reported a novel optical and visual method for detecting Cu^{2+} by UV-visible spectroscopy detection or naked eyes observation. The higher atomic fractions with higher activity atoms at the three corners of the TAg-NPs could react with $\text{Na}_2\text{S}_2\text{O}_3$ easily[17], as a result, the UV-visible spectra and the color of the solution changed clearly. $\text{Na}_2\text{S}_2\text{O}_3$ could be dissociated when it was heated especially in the presence of the catalysis Cu^{2+} . Thus, the morphology, the color and the change values of the absorbance (ΔA the absorbance of TAg-NPs/ Cu^{2+} / $\text{Na}_2\text{S}_2\text{O}_3$

subtracted by that of TAg-NPs/ $\text{Na}_2\text{S}_2\text{O}_3$ at the position of maximum absorption peak) changed with the increased concentration of Cu^{2+} . The ΔA was proportional to the concentration of Cu^{2+} in the range of 2.5×10^{-9} to 7.5×10^{-7} mol L^{-1} , with the correlation coefficient of $r=0.9983$. Furthermore, the color change of TAg-NPs could be observed clearly in the concentration of Cu^{2+} range of 2.5×10^{-8} to 7.5×10^{-7} mol L^{-1} . Thus, a new visual method with high sensitivity for trace Cu^{2+} detection has been established, and the Cu^{2+} content in human hair sample has been detected successfully.

2. Experiment

2.1 Apparatus.

The main experimental apparatus were a Lambda-35 UV-visible spectrophotometer (PerkinElmer Instruments Inc, American) and a quartz cell (1×1 cm²), which were used to measure the UV-visible absorption spectrum of TAg-NPs. Resonance light scattering (RLS) spectra were measured with a Hitachi F-4500 spectrofluorometer (Tokyo, Japan). Tecnai G20 transmission electron microscopy (TEM, FEI Company, U.S.A) was used to TEM measure. A DF-101B magnetic stirrer (Gongyi, China) was used to blend the solutions in an Erlenmeyer flask to prepare the TAg-NPs. Nikon coolpix-4500 digital camera was used to record the images of the aqueous solutions. An Analyst 100 atomic absorption spectrophotometer (Perkin Elmer, USA) was used to detect the Cu^{2+} contents in real samples for comparison with this method.

2.2 Reagents.

Cu^{2+} stock solution ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) was prepared by dissolving pure $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (obtained from Hunan reagent factory) with redistilled water, and then it could be diluted to different concentration with water. The Britton–Robinson buffer solutions were used to adjust the pH value of the reaction system. $\text{Na}_2\text{S}_2\text{O}_3$ stock solution with the different concentrations were prepared freshly by dissolving and diluting pure $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (obtained from Changsha the sub-intersection reagent chemical plant) with redistilled water. All other chemicals were analytical reagents and the water was redistilled water.

2.3 Synthesis of the triangular TAg-NPs.

TAg-NPs was synthesized by the method of Zhang et al.[35]. Firstly, 24.75 mL of redistilled water was added to a 50 mL Erlenmeyer flask and magnetically stirred at room temperature. Then, silver nitrate (0.05 M, 50 μL), trisodium citrate (75.0 mM, 0.5 mL), H_2O_2 (30 wt%, 60.0 μL), and 4.0 mL poly-vinylpyrrolidone solution with the concentration of 0.5 mg/mL (PVP, average molecular weight $M_w \approx 58,000 \text{ g/mol}$) were successively added. Next, sodium borohydride (NaBH_4 , 100.0 mM, 250.0 μL) was rapidly added into the above mixture; the color of the solution immediately turned to light-yellow. About 25 min later, the colloidal solution turned to deep yellow for the many of the TAg-NPs products forming. Further, as the morphology of nanoparticles changed to that of TAg-NPs gradually, the color of the mixture changed from deep yellow to red, green, and blue within the next few seconds.

2.4 Spectra Detection Procedures.

At first, an appropriate volume Cu^{2+} solution or sample solution were added to a 2.0 mL eppendorf tube, then, it was mixed with 100.0 μL $\text{Na}_2\text{S}_2\text{O}_3$ ($1.0 \times 10^{-4} \text{ M}$) and 100.0 μL Britton–Robinson buffer solutions (pH=6.8), finally, it was diluted by the appropriate volume of water to keep the total volume of 2.0 mL. Subsequently, the above solution was heated for 30 min to obtain the mixture solution. Then, 200.0 μL the above mixture solution was added to the TAg-NPs solution with the volume of 1.8 mL, and the final mixture was transferred for UV-vis spectra detection after reaction for 40 min. All RLS spectra were obtained by scanning the excitation and emission monochromators simultaneously (namely $\Delta\lambda = 0 \text{ nm}$) from 200.0 to 800.0 nm.

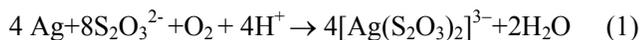
2.5 Pretreatment of Samples.

The hair sample was cut into patch with the length less than 1.0 cm using the stainless steel scissors firstly, and then it was immersed in detergent solution with the concentration of 1.0% for 0.5 h. After that, the samples washed four times with water, and dried 3h in oven under the temperature of 105 $^\circ\text{C}$. Then, 1.0 g of hair samples and 2.0 mL of $\text{HNO}_3/\text{HClO}_4$ ($v/v=3/1$) mixed solution were added into a quartz beaker, which was covered with a watch glass, and was placed for overnight. The next day, the reacted solution was heated until the sample was dissolved completely. Then, it was diluted to 50.0 mL with water as the stock solution. Informed consent was signed for relative human about the hair sample in this study, and all experiments have approved by the Joint Ethics Committee of the Xiangtan Health Authority and performed in accordance with national guidelines.

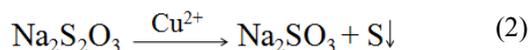
3. Results and discussion

3.1 Colorimetric sensing strategy

The curve a in Fig. 1 (A) is the UV-visible absorption spectrum of TAg-NPs, its absorption peak wavelength is about 730 nm. The curve d in Fig. 1 (A) is the UV-visible absorption spectrum of the TAg-NPs/ $\text{Na}_2\text{S}_2\text{O}_3$ mixture, its absorption peak wavelength is about 530 nm, blue shift about 200 nm compared with that of the TAg-NPs solution. These results show that $\text{Na}_2\text{S}_2\text{O}_3$ could etch the TAg-NPs and changed their morphology easily, because there are higher atomic fractions with higher reactivity for $\text{Na}_2\text{S}_2\text{O}_3$ on its three corners [17], and thereby produced $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ ions. Reaction 1 was proposed as the chemical reactions of the principle[36].



According to the phenomenon that the dissociation of $\text{Na}_2\text{S}_2\text{O}_3$ could be catalysed by Cu^{2+} especially under heated condition[37], which is described as the equation of (2). We assumed if the solution of $\text{Na}_2\text{S}_2\text{O}_3$ was treated with heating firstly in the presence of Cu^{2+} , the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ will be decreased effectively, and then it could not corroded the TAg-NPs easily. As curve b in Fig.1 (A) shown, the UV-visible absorption peak wavelength of TAg-NPs/ $\text{Na}_2\text{S}_2\text{O}_3$ / Cu^{2+} mixture solution is about 730 nm still when the $\text{Na}_2\text{S}_2\text{O}_3$ and Cu^{2+} concentrations are 5.0 μM and 0.75 μM respectively.



The morphology change of TAg-NPs could be identified by TEM detection further, as shown in Fig. 1(B), it changed from triangle (Fig. 1(B) a) to circular (Fig. 1(B)

b), and the size of the TAg-NPs clearly decreased in the presence of $\text{Na}_2\text{S}_2\text{O}_3$ (5.0 μM). The morphology of TAg-NPs hardly changed (Fig. 1(B) c) when the heated mixture of $\text{Na}_2\text{S}_2\text{O}_3$ (5.0 μM)/ Cu^{2+} (0.75 μM) was added to the TAg-NPs solution. Yet, the TAg-NPs were corroded seriously when the unheated mixture of Cu^{2+} / $\text{Na}_2\text{S}_2\text{O}_3$ was added to the TAg-NPs. As curve c in Fig. 1 (A) shown, the UV-visible absorption peak wavelength of the unheated mixture solution is about 530 nm, and the absorbance at the maximum absorption peak position of TAg-NPs is decreased to 0.530. That is to say, the catalysis effect of Cu^{2+} to the dissociation of $\text{Na}_2\text{S}_2\text{O}_3$ is not outstanding under room temperature.

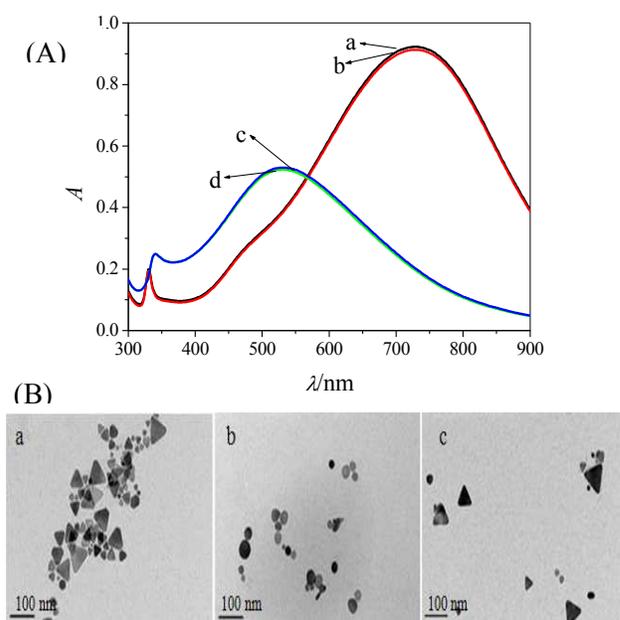


Fig. 1. (A) UV-visible absorption spectra of TAg-NPs (Curve a), TAg-NPs mixed with heated (Curve b) or unheated $\text{Na}_2\text{S}_2\text{O}_3$ (Curve c), and the Curve d was the UV-vis absorption spectra of TAg-NPs/ $\text{Na}_2\text{S}_2\text{O}_3$. (B) TEM images of the TAg-NPs (a), the mixture of TAg-NPs/ $\text{Na}_2\text{S}_2\text{O}_3$ (b), (c) the mixture of TAg-NPs/ Cu^{2+} / $\text{Na}_2\text{S}_2\text{O}_3$. $c_{\text{Cu}^{2+}}$ (0.75 μM), $c_{\text{Na}_2\text{S}_2\text{O}_3}$ (5.0 μM), pH 6.8, heating temperature 80 $^\circ\text{C}$, heating time 30 min and then reacted with TAg-NPs for 40 min at room temperature.

3.2 Optimization of reaction conditions.

The optimal heating temperature and heating time of the mixture of Cu^{2+} (0.75 μM)/ $\text{Na}_2\text{S}_2\text{O}_3$ (5.0 μM) was explored. The results were shown as the Fig. S1 and Fig. S2 in the supporting information. From the figures, we known that the reaction of Cu^{2+} and $\text{Na}_2\text{S}_2\text{O}_3$ was completed substantially after heated in water bath at 80 $^\circ\text{C}$ for 25 min under the $\text{Na}_2\text{S}_2\text{O}_3$ concentration of 5.0 μM and Cu^{2+} concentration of 0.75 μM , but in order to complete the reaction we chose 80 $^\circ\text{C}$ as the optimal heating temperature, and 30 min as the optimum heating time in this system.

To learn the influence of $\text{Na}_2\text{S}_2\text{O}_3$ on the detection, we detected the UV-visible absorption spectrum of the mixture TAg-Nps/ $\text{Na}_2\text{S}_2\text{O}_3$ / Cu^{2+} under different concentration of $\text{Na}_2\text{S}_2\text{O}_3$. As the Fig. S3 in the supporting information shown, the curve a and b respectively represented the absorbance at the maximum absorption peak of TAg-NPs absence or presence of Cu^{2+} under different concentration of $\text{Na}_2\text{S}_2\text{O}_3$. And curve c is the relationship of ΔA , which is the absorbance at the maximum absorption peak of TAg-Nps/ $\text{Na}_2\text{S}_2\text{O}_3$ / Cu^{2+} compared with that of TAg-Nps/ $\text{Na}_2\text{S}_2\text{O}_3$, with different concentration of $\text{Na}_2\text{S}_2\text{O}_3$ over the range of 1.0 μM to 10.0 μM . It can be seen that the ΔA is maximum when the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ reaches 5.0 μM . Thus, the $\text{Na}_2\text{S}_2\text{O}_3$ concentration of 5.0 μM was chosen as the optimal concentration in this study.

Fig. S4 in the supporting information shown the acidity of solution has a profound influence on the detection. Curve a and b in Fig. S4 represented the

absorbance at the maximum absorption peak of TAg-NPs/ $\text{Na}_2\text{S}_2\text{O}_3$ without and with Cu^{2+} respectively in the different acidity of solution. Curve c represented the relationship of ΔA with the pH over the range of 4.78 to 11.82, it shows that the ΔA is relatively high when the pH value is in the range of 6.8 to 8.69. However, Cu^{2+} would be deposited when its concentration is excess 1.0 μM under the acidity of solution greater than or equal 7.17[38], so the pH 6.8 is the best one in this method. Furthermore, the interference not only by Cr(VI) but also by Fe^{3+} could be avoided under this acidity to detect Cu^{2+} .

We also detected the optimum reaction time of TAg-NPs and the mixture of Cu^{2+} / $\text{Na}_2\text{S}_2\text{O}_3$. From Fig. S5 in the Supporting Information, we could find that when the reaction time of TAg-NPs and the mixture of Cu^{2+} / $\text{Na}_2\text{S}_2\text{O}_3$ is 40 min, the ΔA is no longer changed, so, in this study, 40 min is the optimal reaction time for detecting of Cu^{2+} .

3.2 The selectivity for Cu^{2+} detection.

Under the optimal conditions, the effects of foreign substances in this system were measured and the results were listed in Fig. 2, from which it was found that the signals response for a variety of foreign substances were lower the $\pm 10.0\%$ compared with the signals responded by Cu^{2+} . These results suggested that the selectivity of this method to detect Cu^{2+} is high. In the studied metal ions, the maximum absorption peak position had a relative greater change in the presence of Hg^{2+} , yet, the ΔA for the TAg-NPs/ $\text{Na}_2\text{S}_2\text{O}_3$ / Hg^{2+} is smaller than that of TAg-NPs/ $\text{Na}_2\text{S}_2\text{O}_3$ / Cu^{2+} . Thus, we detected Cu^{2+} through

detection the ΔA of the system to avoid the interference of Hg^{2+} .

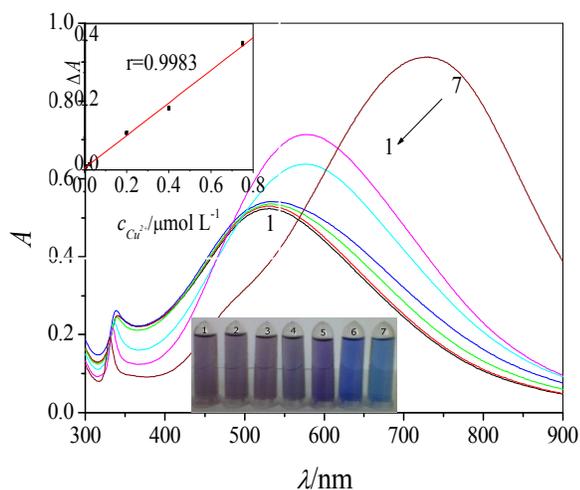


Fig. 2. The histogram of the ΔA of foreign substances and Cu^{2+} . $c_{\text{Cu}^{2+}}$ or foreign substances (0.75 μM), $c_{\text{Na}_2\text{S}_2\text{O}_3}$ (5.0 μM), pH 6.8, heating temperature 80 $^\circ\text{C}$, heating time 30 min and then reacted with TAG-NPs for 40 min at room temperature. The inserted picture displays the color changes corresponding to Cu^{2+} and foreign substances.

3.3 The application of TAG-NPs for Cu^{2+} detection in human hair sample.

Under optimum conditions, the UV-visible spectrometer was detected under the different concentrations of Cu^{2+} . As Fig. 3 shown, the UV-visible absorption peaks of the TAG-Nps/ $\text{Na}_2\text{S}_2\text{O}_3$ / Cu^{2+} red shifted gradually from 530 to 730 nm, and the absorbance at the maximum absorption peak of TAG-NPs increased gradually from 0.530 to 0.913 with the increase of Cu^{2+} concentrations. Furthermore, as the insert graph in Fig.3, the color of the TAG-NPs changed from violet to blue clearly with the increase of the concentrations of Cu^{2+} . It could be observed visually when the concentrations of Cu^{2+} were in the range of 2.5×10^{-8} to 7.5×10^{-7} mol/L. Thus, the visible detection could be achieved and semi-

quantitative detection of Cu^{2+} could be proposed using camera as a recorder.

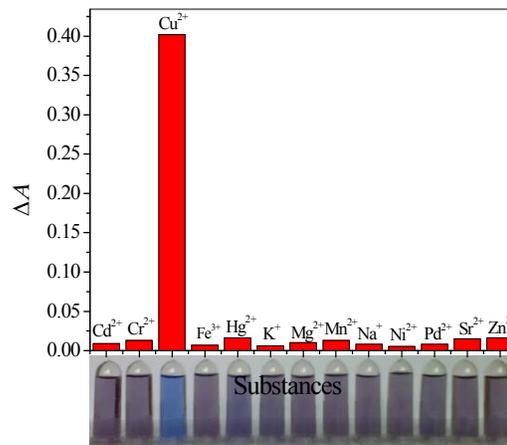


Fig. 3. UV-vis absorption spectra of TAG-NPs- Cu^{2+} - $\text{Na}_2\text{S}_2\text{O}_3$, spectra shown for Cu^{2+} concentrations of 0, 0.0025, 0.0075, 0.025, 0.2, 0.4 and 0.75 μM . $c_{\text{Na}_2\text{S}_2\text{O}_3}$ (5.0 μM), pH 6.8, heating 30 min at 80 $^\circ\text{C}$, and reacted 40 min at room temperature. The inserted graph displays the color changes corresponding to the curve 1-7.

In addition, as the insert graph in Fig.3 shown, the linear relationship of Cu^{2+} concentration with ΔA was obtained for Cu^{2+} concentrations in the range of 2.5×10^{-9} mol/L to 7.5×10^{-7} mol/L, which follows a linear equation of $\Delta A = 0.0050 + 0.5034 c$ (c , μM , $r = 0.9983$, $n = 6$). The detection limit is 1.0 nmol/L ($3\sigma/k$). Compared to the published visible detection for Cu^{2+} ion detection based silver or gold nanoparticles (Table S1 in the Supporting Information), the method has comparable sensitivity with the reported method [29,32,33,39]. According to the calibration curve, a hair sample was determined under the optimum condition, and the determination results were listed in Table 1, the results were satisfactory and had an excellent relative standard deviation (RSD, 1.63 %), and the average copper content of human hair was 10.60 μg

g^{-1} . Studies have shown that the copper content in human hair is 3.2–32.8 $\mu\text{g g}^{-1}$ [40]. So, the detection results were within the scope of the actual value, which is close to that obtained by the AAS method (9.65 $\mu\text{g g}^{-1}$, Table 1). This indicates that the developed method is reliable.

Table 1. The determination results of the actual samples

Sample	Detection value ($\mu\text{g g}^{-1}$)	Average ($\mu\text{g g}^{-1}$)	AAS ($\mu\text{g g}^{-1}$)	RSD
Human hair	10.50, 10.50, 10.80	10.60	9.65	1.63%

4. Conclusion

A new colorimetric method for Cu^{2+} detection in an aqueous solution has been developed based on the reaction of $\text{Na}_2\text{S}_2\text{O}_3$, Cu^{2+} and TAG-NPs. In this study, we found that the reaction of $\text{Na}_2\text{S}_2\text{O}_3$ and Cu^{2+} must be heated under the temperature of 80 °C for 30 min, furthermore, the best acidity of the reaction was pH 6.8. As the above experiment shown, the concentrations of Cu^{2+} could be detected in the range of 2.5×10^{-9} mol L^{-1} to 7.5×10^{-7} mol L^{-1} with the calibration equation of $\Delta A = 0.0050 + 0.5034 c$, under the optimum reaction conditions (pH 6.8, $c_{\text{Na}_2\text{S}_2\text{O}_3}$ with the concentration of 5.0 μM , reacted 40 min under room temperature). Based on the calibration curve, the Cu^{2+} content in human hair samples were detected with the satisfactory result. In addition, further work will be aimed at the application of the probe in other biological, environmental samples. This method is simple, rapid, low cost and high sensitivity.

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Notes and references

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