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# Synthesis of 3,4-Diaminobenzenethiol and Its Application in Gold Nanoparticle-based Colorimetric Determination of Copper Ions

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An improved synthetic method for synthesis of 3,4-diaminobenzenethiol is presented. The practical application of this reagent as a new ligand for gold nanoparticles for the rapid detection of  $Cu^{2+}$  in water is demonstrated. The method is shown to have high sensitivity and selectivity. Well-defined peaks, proportional to the concentration of the corresponding  $Cu^{2+}$ , were observed from 0.5  $\mu$ M to 2  $\mu$ M, and the recovery was in the range of 92~109%. This method provides a facile route for  $Cu^{2+}$  analysis.

# Introduction

In recent years, the development of economy has led to serious environmental pollution. Especially, a large quantity of waste water that contains a huge number of heavy metal ions, has been poured into rivers, lakes and other water sources. Heavy metal contamination is known to be very difficult to degrade and be easily accumulated. Additionally, heavy metals can enter the food chain readily and thereby harm the health of animals, plants and humans via biological enrichment.

Copper is an essential nutrient for organism, but the high  $Cu^{2+}$  concentration can cause metabolic disorders, developmental stagnation and even death.<sup>1-3</sup> It is therefore important to monitor concentration of  $Cu^{2+}$  in environment.

At present, methods for the detection of  $Cu^{2+}$  mainly include atomic absorption spectrometry,<sup>4,5</sup> inductively coupled plasma emission spectrometry,<sup>6,7</sup> inductively coupled plasma mass spectrometry<sup>8</sup> and Spectrophotometry.<sup>9</sup> However, some of these methods may not be highly sensitive, or some of them are too complex and expensive. Therefore, a simple, sensitive and rapid  $Cu^{2+}$  detection method would be of great benefit to the wastewater monitoring industry.

In recent years, gold nanoparticles (AuNPs) have been widely used in various research fields because of their high extinction coefficient and unique optical properties.<sup>10-17</sup> Gold nanoparticlesbased colorimetric assay is one of these applications and has recently gained much interest because of its low cost, simple sample 3,4-Diaminobenzenethiol, which has two amino groups and a thiol group, was reported by first.<sup>33</sup> Its mercapto functional group can react with AuNPs via a strong covalent Au-S bond. The exposed amino functional groups on the benzene ring from neighboring AuNPs can bind copper ions, resulting in AuNPs aggregatings (Scheme1). 3,4-Diaminobenzenethiol can therefore be used as a ligand to modify gold nanoparticles for the colorimetric detection of copper ions that can be quantitatively monitored by UV/Vis spectrophotometry.

In this paper, a simply and optimalizing approach to synthesis of 3,4-diaminobenzenethiol using a three-step synthetic process with onitroaniline as a starting material was developed. The intermediates and final products were characterized by FTIR, NMR and GC-MS. A gold nanoparticle-based colorimetric method to detect copper ions using 3,4-diaminobenzenethiol as functioning ligand was established. The experimental conditions were optimized and the test results were compared with ICP-OES, and the feasibility of this method was verified.

processing procedures and sufficient sensitivity.<sup>18-27</sup> Recently, a colorimetric approach for sensing Cu<sup>2+</sup> was reported using bare AuNPs.<sup>28</sup> This method can be used without complicated pretreatment but it has relatively high limits of detection. Moreover, some rapid visual methods were reported for the detection of Cu<sup>2+</sup> based on modified AuNPs <sup>29, 30</sup> or gold nanorods (AuNRs) <sup>31, 32</sup>. These methods could be sensitive. However, the reagents required could be expensive or difficult to obtain, it is necessary to find ligands that are inexpensive and technically easy to synthesize.

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<sup>†</sup> Electronic supplementary information (ESI) available: FTIR, <sup>1</sup>H NMR and GC-MS spectra.

Scheme 1 Schematic representation of the sensing mechanism of the AuNPs-based colorimetric determination of  $Cu^{2+}$ .

# **Experimental section**

# Chemicals and materials

Ligand: 3,4-Diaminobenzenethiol was synthesized in a three-step procedure, sealed in a brown reagent bottle at  $5^{\circ}$ C.

10 mM  $Cu^{2+}$  solution: 0.4262 g of copper(II) chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O) is accurately weighed and dissolved with ddH<sub>2</sub>O, and then stored at 5 °C. The stock solution was then diluted to the desired concentrations with ddH<sub>2</sub>O.

Buffers: Phthalate buffer, mixed phosphate buffer and sodium tetraborate buffer were purchased from Shanghai Leici Instrument Co., Ltd. All buffers were stored at  $5^{\circ}$ C. Prior to use, pH of the buffers were adjusted again.

Sodium chloride, tri-sodium citrate and other chemical agents were of analytical reagent grade (Sinopharm Chemical Reagent Co., Ltd.). All solutions were prepared by  $ddH_2O$  (18 Mohm cm resistance), unless noted specially. All glasswares were cleaned with aqua regia (3:1 (v/v) HCl-HNO<sub>3</sub>) thoroughly and rinsed with  $ddH_2O$  prior to use.

### Apparatus

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ACY-600-U ultra-pure water system (Chongqing Yi Yang Enterprise Development Co., Ltd., China); TU-1901 double beams UV-Vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China); CM12 transmission electron microscope (Philips Ltd., Netherlands); UB-7 digital pH meter (Denver Instrument, USA); ME204E analytical balance (Mettler Toledo Ltd., Switzerland); ICP-5000 inductively coupled plasma emission spectrometer (Hangzhou Juguang Technology Co., Ltd., China); Agilent 7890-5975C gas chromatography-mass spectrometer (Agilent Co., Ltd., USA); Nicolet 6700 Fourier transform infrared spectrometer (Thermo Fisher Co., Ltd., USA); and VNMR 400 nuclear magnetic resonance spectrometer (Varian Co., Ltd., USA).

# Synthesis of AuNPs

Citrate-capped AuNPs were prepared by method of the chemical reduction of  $HAuCl_4$  in the liquid phase.<sup>34</sup> Briefly, 35 ml of deionized water and 0.6 ml of  $HAuCl_4$  (25 mM) were mixed in a conical flask. After boiling for several minutes, 1 ml of tri-sodium citrate solution (38.8 mM) was added quickly with vigorous stirring. The color of the solution changed into red in a few seconds. After boiling for 5 min, the solution was cooled to room temperature and then stored at 5°C.

# Synthesis and purification of 3,4-diaminobenzenethiol<sup>33, 35-39</sup>

(1) Synthesis of 2-nitro-4-thiocyanoaniline

O-nitroaniline (8.25 g, 60 mmol) and sodium thiocyanate (18 g, 0.22 mol) were dissolved in 100 ml glacial acetic acid (98%) and then cooled to 5°C. Bromine (9.6 g, 60 mmol) was dropped into 10 mL glacial acetic acid (98%) and then cooled to 5°C. Above two kinds of solution were mixed and reacted for 72 h, then the mixture was warmed to  $15^{\circ}$ C and poured into 500 ml ddH<sub>2</sub>O, resulting in an orange turbid solution. The solution was filtered. The solid material acquired was washed with ddH<sub>2</sub>O, and then dissolved in 100 ml acetone. The resulting solution was filtered and evaporated. A yellow solid product was gained.

# (2) Synthesis of 4-amino-3-nitrobenzenethiol

The first step product was added multiple times to 100 ml potassium hydroxide (6 g) ethanol solution, stirred for 1 h at 5°C. Sulfuric acid ethanol solution (5%) was added slowly until the color of the mixture changed from dark violet to orange. The orange mixture was then poured into 400 ml ddH<sub>2</sub>O and extracted three times by 100 ml ethyl acetate. The combined organic extracts were washed with brine, dried over magnesium sulfate, and evaporated. In the end, red solid was obtained.

(3) Synthesis of 3,4-diaminobenzenethiol

The product of the second step was dissolved in ethanol-water solution (300 ml, 1:1) and then sodium dithionite (13.4 g, 80 mmol) was added over a period of 20 min. After that, the pH was adjusted to 3.0 by adding sodium hydroxide. The stirred solution was refluxed for 1 h at 105°C and then extracted with chloroform after cooled to room temperature. A crude solid resulting from vacuum drying, was subjected to silica gel column chromatography using MeOH–EtOAc (1:5) to acquire a yellow solid product.

# Colorimetric detection of Cu<sup>2+</sup>

A volume of 1 ml of 3,4-diaminobenzenethiol solution (0.2 mg/L) and 0.1 ml of  $Cu^{2+}$  with different concentrations were added to 0.9 ml phosphate buffer solution (pH 6.0). The reaction proceeded at room temperature for 5 min, then 1 ml of AuNPs suspension were added and the mixture was incubated for 15 min. The UV measurements were carried out by UV/Vis photometer (TU-1901) in Faculty of Materials Science and Chemistry, China University of Geosciences.

# Fourier transform infrared spectroscopy (FTIR)

After vacuum drying, the sample with dry KBr was ground. The FTIR measurements were carried out by Nicolet 6700 in Faculty of Materials Science and Chemistry, China University of Geosciences.

## Nuclear magnetic resonance spectroscopy (NMR)

These samples were dissolved with chloroform-d solution, and the nuclear magnetic resonance measurements were carried out by VNMR 400 at Central China Normal University.

# Gas chromatographic mass spectrometry (GC-MS)

The samples were dissolved with ethyl acetate, and the GC-MS measurements were carried out by full scanning (Agilent 7890-5975C) at the Hubei Environmental Monitoring Center.

#### Transmission electron microscope characterization (TEM)

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The samples were prepared on copper grids. The TEM characterization was carried out in Faculty of Materials Science and Chemistry, China University of Geosciences.

# **Results and discussion**

# Chemical structure confirmation of synthetic products

Fig. S1 shows the FTIR spectra of synthetic products. In the spectrum of 2-nitro-4-thiocyanoaniline (Fig. S1A), the characteristic bands of primary amine (NH<sub>2</sub>) are 3475 cm<sup>-1</sup> and 3357 cm<sup>-1</sup> for asymmetric and symmetric stretching, respectively, the thiocyano moiety's symmetric stretching shows an absorption band at 2150 cm<sup>-1</sup> (C=N), and the nitro aromatic moiety's symmetric stretching band appears at 1552 cm<sup>-1</sup> (N-O), confirming the presence of expected functional groups in the synthesized 2-nitro-4-thiocyanoaniline. The <sup>1</sup>H NMR spectrum of 2-nitro-4-thiocyanoaniline (Fig. S2A) also indicates the presence of -NH, where the signal at  $\delta = 6.2$  ppm is attributed to the protons of -NH.

In the FTIR spectrum of 4-amino-3-nitrobenzenethiol (Fig. S1B), while the NH<sub>2</sub> asymmetric and symmetric stretching bands (3463 cm<sup>-1</sup> and 3350 cm<sup>-1</sup>, respectively) and the N-O symmetric stretching band (1554 cm<sup>-1</sup>) appear, there is no absorption band at 2150 cm<sup>-1</sup>, indicating that the thiocyano moiety has been hydrolyzed. The <sup>1</sup>H NMR spectrum of 4-amino-3-nitrobenzenethiol (Fig. S2B) confirms the presence of -SH, where the signal at  $\delta$  = 3.4 ppm is attributed to the protons of -SH.

The FTIR spectrum of 3,4-diaminobenzenethiol presented in Fig. S1C shows that the characteristic bands of NH<sub>2</sub> are at 3476 cm<sup>-1</sup> and 3361 cm<sup>-1</sup> for asymmetric and symmetric stretching, respectively, and at 1619 cm<sup>-1</sup> for N-H, and the primary aromatic amine symmetric stretching band appears at 1247 cm<sup>-1</sup> (C-N). These results show that a portion of nitro groups in the sample was reduced to amino groups.

GC-MS measurements were further performed to confirm the chemical structure of synthetic products. The total ion flow chromatogram of 2-nitro-4-thiocyanoaniline (Fig. S3A) shows that 2-nitro-4-thiocyanoaniline (molecular weight 195) is eluted at 39.75 min, other peaks were fragment ions whose corresponding molecular weights are 149, 122, 105, 95, 63 and 52. These characteristic peaks were consistent with those of 2-nitro-4-thiocyanoaniline in the NIST library.

Fig. S3B shows the total ion flow chromatogram of 4-amino-3nitrobenzenethiol. The NIST library does not contain this material, therefore there is no direct standard. Despite this, some thiol compound is detected at 34.61 min, and its m/z is close to molecular weight of 4-amino-3-nitrobenzenethiol. Fragment ions of m/z 149, 122, 105, 95, 63 and 52 are also detected. The characteristic peaks indicate that thiocyano group has been hydrolyzed to thiol group, which is consistent with the reported 4-amino-3-nitrobenzenethiol.<sup>33</sup>

The total ion flow chromatogram of 3,4-diaminobenzenethiol is depicted in Fig. S3C. Because the NIST library does not contain this material, it cannot be directly matched. However, some compound which has same relative molecular weight as target product is detected at 38.46 min. Besides m/z 95, 80 and 52, fragment ion of m/z 107 that could be  $-C_6H_3NH_2NH_2$  is detected, suggesting that nitro group has been reduced to amino group. The result is consistent with the reported 3,4-diaminobenzenethiol.<sup>33</sup>

#### **Detection mechanism**

AuNPs could be capped by 3,4-diaminobenzenethiol via thiol groups due to their strong binding ability to sulphur. The Au-S bond is stable in high concentration salt solutions and can resist the attack of amino groups. The amino groups on the 3,4-diaminobenzenethiol have strong binding ability to copper ions, and the stability constant of the amino-Cu complex is higher than most of other interfering ions. Therefore, the 3,4-diaminobenzenethiol-capped AuNPs could bind copper ions to form stable complexes, and subsequently aggregate, resulting in a color change. This mechanism is consistent with some previous reports.<sup>40-42</sup> This color change can be quantitatively analyzed by UV-Vis spectrophotometry.

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As shown in Fig. 1, AuNPs show a strong SPR peak at 520 nm (black line). When the ligand 3,4-diaminobenzenethiol was added, this characteristic peak only slightly decreased (red line) and the color of the solution remained red (left inset). However, upon the addition of  $Cu^{2+}$ , the color of the solution changed from red to blue (right inset). While the original SPR peak at 520 nm significantly decreased, a new distinct SPR peak at 700 nm appeared (blue line), indicating the  $Cu^{2+}$ -induced aggregation of 3,4-diaminobenzenethiol-capped AuNPs.



**Fig. 1** UV-Vis spectra of AuNPs in the absence and presence of the ligand 3,4-diaminobenzenethiol and  $Cu^{2+}$ . The insets show the optical photographs of AuNPs solutions in the absence (left) and presence (right) of  $Cu^{2+}$ .

The dispersed and aggregated AuNPs were also confirmed by TEM images (Fig. 2). While Fig. 2A shows that AuNPs have nearly spherical shape and uniformly disperse, Fig. 2B displays significant aggregation of AuNPs after the addition of the ligand and Cu<sup>2+</sup>.



Fig. 2 TEM images of AuNPs in the (A) absence and (B) presence of 3,4-diaminobenzenethiol and  $Cu^{2+}$ .

#### Optimum concentration of ligand for the aggregation of AuNPs

Ligand concentration has a high impact on the efficacy of this system. The citrate-stabilized surface of AuNPs is negatively charged and a high concentration of positively charged ligand can cause aggregation of the AuNPs. Alternatively, a low concentration of ligand can lead to isolated AuNPs, but this latter condition may not be conducive to highly sensitive detection of  $Cu^{2+}$ . The ligand was therefore diluted to different concentrations and the absorption spectra were recorded.

As shown in Fig. 3, when the ligand concentration was 2 mg/L, the absorption peak of AuNPs at 520 nm was significantly lower than the absorption peak with no ligand added (0 mg/L) and a new absorption peak at 670 nm appeared, demonstrating that high concentration of the ligand causes AuNPs aggregation. When the concentration of ligands was 0.2 mg/L, ligands did not induce significant aggregation of AuNPs as evidenced by the absorption peak being not dramatically decreased and the absence of AuNP solution color change. Therefore, to gain highest sensitivity, 0.2 mg/L of 3,4-diaminobenzenethiol was chosen for subsequent experiments.



Fig. 3 Effect of ligand concentration on the aggregation of AuNPs

# **Optimum reaction time**

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A concentration of 10  $\mu$ M of Cu<sup>2+</sup> was reacted with ligand modified AuNPs at room temperature and the absorbance of the solution was determined at different times. The effect of reaction time is shown in Fig. 4, where the ordinate denotes  $A_{650}/A_{520}$ , the ratio of the extinction coefficients at 650 nm and 520 nm, which is on the behalf of the molar ratio of the aggregated to the dispersed AuNPs. It is shown that the ratio of  $A_{650}/A_{520}$  was stable when reacting after 15 min, and therefore in order to ensure the convenience of experimental operation, these experimental parameters were chosen as optimum for analysis.



Fig. 4 Effect of reaction time on the determination

# Optimum pH

The pH value of solution not only has influence on the stability of AuNPs probes, it also affects the stability of the amine-Cu complex. According to previous experimental methods, a range of pH values from 4 to 9 of buffer solution was tested without changing other conditions, and the absorbance ratio  $(A_{650}/A_{520})$  was determined. Fig. 5 depicts how the pH of solution influences aggregation of AuNPs. At pH values ranging from 4 to 8, the ratio of  $A_{650}/A_{520}$  remains stable, indicating this pH region can be chosen for subsequent experiments. When the pH was greater than 8, the ratio of  $A_{650}/A_{520}$ decreased dramatically. This indicates that pH value influences the stability of the complexes likely through the formation of metal hydroxides at higher pH. The formation pH of copper hydroxide for micro molarity of Cu<sup>2+</sup> estimated from the corresponding solubility product ( $K_{sp} = 2.2 \times 10^{-20}$ ) is about 6.8. Considering the coordination of the ligand, the actual formation pH would be higher than 6.8. Based on these results, a pH of 6 was chosen as the optimum pH condition in our experiments.



Fig. 5 Effect of pH on the determination

# Detection of Cu<sup>2+</sup>

Under the optimized conditions, different concentrations of Cu<sup>2+</sup> were mixed with 0.2 mg/L 3,4-diaminobenzenethiol ligand and AuNPs for 15 min, and then UV-Vis spectroscopy was used to quantitatively determine the content of Cu<sup>2+</sup> in aqueous solution. As shown in Fig. 6A, when Cu<sup>2+</sup> concentration increased, more ligands would bond to Cu<sup>2+</sup>, and AuNPs were aggregated. Concentration of Cu<sup>2+</sup> was determined by measuring  $A_{650}/A_{520}$ . Linear equation,  $A = 0.296 \ C$ -0.127 ( $R^2 = 0.998$ ), was generated over the range of 0.5-2  $\mu$ M Cu<sup>2+</sup> (Fig. 6B).

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Fig. 6 (A) UV-Vis spectra of different concentration gradient of  $Cu^{2+}$  and (B) Working curve

# Selectivity of the method

To evaluate the selectivity of the colorimetric detection of  $Cu^{2+}$ , some other environmentally related metal ions were chosen for the investigation, including Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>6+</sup>, Mn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup>. Fig. 7 shows that only Cu<sup>2+</sup> lead to a significant increase in the value of  $A_{650}/A_{520}$  compared to blank, while that of other metal ions exhibited no significant changes. Additionally, the color of the solution in the presence of Cu<sup>2+</sup> changed into blue (inset), while that of solutions containing other metal ions remained red, also indicating that this colorimetric assay method exhibits high selectivity for Cu<sup>2+</sup> detection.



Fig. 7 Influence of various cations on the determination of Cu<sup>2+</sup>. Cu<sup>2+</sup> (2  $\mu$ M); K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup> (100  $\mu$ M); Mn<sup>2+</sup>, Cr<sup>6+</sup> (40  $\mu$ M); Pb<sup>2+</sup>, Cd<sup>2+</sup> (20  $\mu$ M); Zn<sup>2+</sup>(10  $\mu$ M). The insets are the corresponding optical photographs.

# Real water samples analysis

To demonstrate the viability of the assay in measuring  $Cu^{2+}$  in real water samples, we measured the amount of  $Cu^{2+}$  in electroplating wastewater. As shown in Table 1, the method provided recoveries of 92 to 109% of  $Cu^{2+}$  in electroplating wastewater samples. The concentration of  $Cu^{2+}$  in electroplating wastewater was found to be 49  $\mu$ M. To compare the data with well-established techniques, we also measured the  $Cu^{2+}$  content using ICP-OES. The amount of  $Cu^{2+}$  in electroplating wastewater was found to be 52  $\mu$ M.

# Conclusions

In summary, we adopted an improved three-steps synthesis method for synthesis of 3,4-diaminobenzenethiol, a novel ligand for modifying AuNPs. Further, we established a sensitive and selective colorimetric assay for  $Cu^{2+}$  in water. And satisfied results were obtained in detecting the actual samples. The operational simplicity of the method may facilitate the analysis of  $Cu^{2+}$  in industrial waste water. This method would be valuable for colorimetric detection in environmental monitoring.

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Table 1 Results of detection and recovery of $Cu^{2+}$ in electroplating wastewater (n=3)				
Sample	Added (µg/L)	Detected (µg/L)	Recovery (%)	RSD (%, n=3)
1	3.2	13.18	92	3.2
2	6.4	16.38	95	2.8
3	12.8	22.78	109	2.3

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# **Graphic Abstract**



3,4-Diaminobenzenethiol can react with AuNPs via a strong covalent Au-S bond. The exposed amino functional groups on the benzene ring from neighboring AuNPs can bind copper ions, resulting in AuNPs aggregating.