

Research Article

Synthesis of Fluorescent Copper Nanoparticles and Ultrasensitive Free Label Detection of Ag^+

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In recent years, the application of fluorescent copper nanomaterials in environmental detection has attracted much attention. This paper mainly introduces the synthesis of copper nanomaterials and the detection of Ag^+ . A simple method for the determination of Ag^+ in water was established by using fluorescent copper nanoparticles synthesized by using glucose (Glc) as a reducing agent as a fluorescent probe. The experimental mechanism of this experiment is that silver ions can rapidly and effectively quench the fluorescence of Glc-CuNPs. A good linear relationship was observed in the range of Ag^+ at 100 mol/L–600 mol/L ($R = 0.9845$); the color is gradually enhanced under visible light and visual colorimetric detection. Moreover, the Glc-CuNP sensor selectively selected Ag^+ , which was not affected by other metal ions, indicating that Glc-CuNPs had good selectivity for the detection of Ag^+ . Based on this, Glc-CuNP completes the detection of heavy metal silver ions and has a good application prospect in environmental detection.

1. Introduction

In recent years, with the continuous development of industry and agriculture, more and more heavy metal silver ion wastes are discharged into the ecosphere. A large number of heavy metal silver ions beyond the standard not only destroy the soil, water, animal, and plant survival but also destroy protein, DNA, and other heavy metal ions to modify it; this will cause a variety of diseases to people's lives and health hazards. Therefore, developing a simple and rapid method for detecting heavy metal silver ions is of great practical significance.

As a novel fluorescent probe, high fluorescent nanomaterials have been widely used in many fields, including the detection of metal anions and cations [1, 2], bioimaging [3], protein [4], DNA [5], picric acid [6], and small molecules [7]. Nowadays, especially copper nanomaterials have the same properties as precious metal nanomaterials, such as ultrasmall size, strong fluorescence, good stability, low toxicity, good biocompatibility, and cheaper than precious metal nanomaterials. Therefore, copper nanomaterials have

attracted more and more attention. Lijuan et al. [8] synthesized fluorescent copper nanoclusters using T30DNA as a template, used Cu^{2+} to form a complex with melamine, which caused fluorescence quenching of copper nanoparticles, and realized the recovery and detection of melamine in milk samples. The following year, Lijuan et al. [9] synthesized fluorescent copper nanoclusters using double-stranded DNA as templates. It was speculated that the possible mechanism was based on the interaction between metals. Pb^{2+} was prone to metallophilic interaction, which destroyed the structure of copper nanoclusters and caused fluorescence quenching. A method for detecting lead ions was established. Han et al. [10] synthesized weak fluorescent copper nanoclusters using glutathione as a protectant and established a fluorescence analysis method for rapid detection of lead ions by using the mechanism of aggregation-induced luminescence. The linear range of Pb^{2+} detection is 200 $\mu\text{mol/L}$ –700 $\mu\text{mol/L}$. Huang et al. [11] synthesized fluorescent copper nanoclusters using glutathione as a protective agent and sodium citrate as a weak reducing agent. The fluorescence quenching of copper nanoclusters was caused by the interaction between Fe^{3+}

and Cu^{2+} . So as to achieve the application of iron ion detection. Hu et al. [12] synthesized high fluorescent copper nanomaterials using glutathione as a protectant and reductant. Similarly, mercury ions were detected by a fluorescence quenching mechanism. At the same time, the standard addition and recovery of water and rice samples were realized. Hu et al. [13] synthesized copper nanomaterials using dithiothreitol (DTT) at room temperature within 30 min. The DTT-CuNCs-based fluorescent probe has been successfully used to assay the content of aluminum in real food samples such as the fried food and pasta.

However, there is less focus on copper nanomaterials and less on visual colorimetric detection [14]. In this paper, glucose is used as a weak reducing agent to synthesize high fluorescent copper nanoparticles. Copper nanomaterials were used as probes to detect Ag^+ . When different concentrations of silver ions were added, the color of copper nanomaterials changed obviously. The detection of silver ions was completed based on visual colorimetry. This method can be applied to the detection of actual water samples. The greatest advantage of this method is to realize visual detection, and the preparation of materials is cheap and easy to obtain; the detection method is simple and fast, saving expensive instrument detection costs [14].

2. Experimental Part

2.1. Instruments and Reagents. An F-4600 fluorescence spectrophotometer (Hitachi High-Tech Company) and a JEM-2100F transmission electron microscope (Japan Electronics Corporation) are the instruments used.

$\text{C}_6\text{H}_{12}\text{O}_6$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Tianjin Fenghuang Chemical Reagent Technology Co. Ltd.), $\text{Bi}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, NaCl , KCl (Tianjin Beilian Fine Chemicals Development Co. Ltd.), AgNO_3 (Beijing Fuchen Chemical Reagent Co. Ltd.), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Beijing Shangle Chemical Factory), $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Beijing Shangle Chemical Reagent Co. Ltd.), Chaoyang Fourth Chemical Plant, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Beijing 5671 Chemical Plant), NaOH (Tianjin Sheng'ao Chemical Reagent Co. Ltd.), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Tianjin Bodi Chemical Co. Ltd.), $\text{Cd}(\text{NO}_3)_2$ (Beijing Chemical Plant), and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Shanghai Public-Private Joint Venture China Trade Factory) are the reagents used in this study; all chemicals are analytical, pure, and experimental solution. They are all configured with ultrapure water (resistance of about 18.25 M Ω).

2.2. Synthesis of Glc-CuNPs. Copper nanoparticles were synthesized by mixing 0.25 mL of 1 mmol/L $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with 2.5 mL of 0.1 mol/L glucose (containing 0.4 mol/L NaOH solution, pH = 12) for 30 minutes, then transferring to 55°C constant temperature water bath for 4 h. After centrifugation at room temperature, for 30 min, Glc-CuNPs were obtained and stored at the last 4 degrees to prepare for subsequent experiments.

2.3. Ag^+ Detection. The prepared 450 μL Glc-CuNPs were placed in a 1.5 mL centrifugal tube and then added with 50 μL different concentrations AgNO_3 . The fluorescence

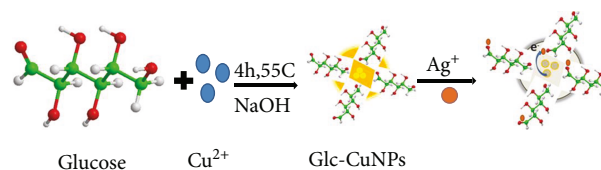


FIGURE 1: Schematic illustration of the Ag^+ sensing strategy based on Glc-CuNPs.

intensity at 541 nm was measured at room temperature for 30 minutes.

3. Results and Discussion

3.1. Glc-CuNP Synthesis and Ag^+ Detection Principle. The synthesis method of Glc-CuNPs and the detection of Ag^+ in this experiment are shown in Figure 1. Glc-CuNPs with high fluorescence can be synthesized by the reaction of glucose in a constant temperature water bath at 55°C for 4 h. When Ag^+ is added to the Glc-CuNP system, Ag^+ will destroy Glc-CuNPs and cause the aggregation of Glc-CuNPs, leading to fluorescence decay [11, 15, 16]. Therefore, the fluorescence of Glc-CuNPs can be effectively quenched by heavy metal silver ions, and the detection of silver ions can be realized.

3.2. Spectral Characteristics of Glc-CuNPs. As shown in Figure 2(a), the excitation and emission of Glc-CuNPs are at 471 nm and 541 nm, respectively. Figure 2(a) is an inside illustration which shows Glc-CuNPs in sunlight and 365 nm ultraviolet light. Figure 2(b) is a transmission electron microscopy (TEM) diagram of Glc-CuNPs. Figure 2(d) is a particle size distribution of Glc-CuNPs; the mean diameter of Glc-CuNPs is 5.0 ± 0.2 nm. The HRTEM image showed that the crystal lattice fringe was 3.70 Å (Figure 2(c)), which corresponded to the (110) plane of cubic-structured copper. It is shown that the synthesized Glc-CuNPs have smaller particle size, better dispersion, and smaller size. The highly fluorescent Glc-CuNPs were successfully synthesized. As shown in Figure 3(a), with the extension of time, the fluorescence intensity of CuNPs will not change at all. It can be seen that the synthesized Glc-CuNPs can be kept for about 1 month at 4°C. At the consecutive 60 min irradiation of a Xe lamp, Figure 3(b) demonstrates the good storage stability and good photostability of the Glc-CuNPs. Figure 3(c) shows the EDs image of Glc-CuNPs and the content of each element. The above data fully prove that CuNPs have been successfully synthesized.

3.3. Glc-CuNP Sensor Performance Analysis. A series of 18 metal ions (such as Mg^{2+} , Na^+ , K^+ , Fe^{3+} , Al^{3+} , Pb^{2+} , Bi^{3+} , Co^{2+} , Cd^{2+} , and Hg^{2+}) with the same concentration (100 $\mu\text{mol/L}$) were selected and detected. As shown in Figure 4(a), only Ag^+ can inhibit the fluorescence of Glc-CuNPs and other metal ions have a positive correlation with the fluorescence of Glc-CuNPs. As shown in Figures 4(b) and 4(c), only by adding silver ions, the color of copper nanomaterials has changed. It shows that this method has high selectivity for the detection of Ag^+ .

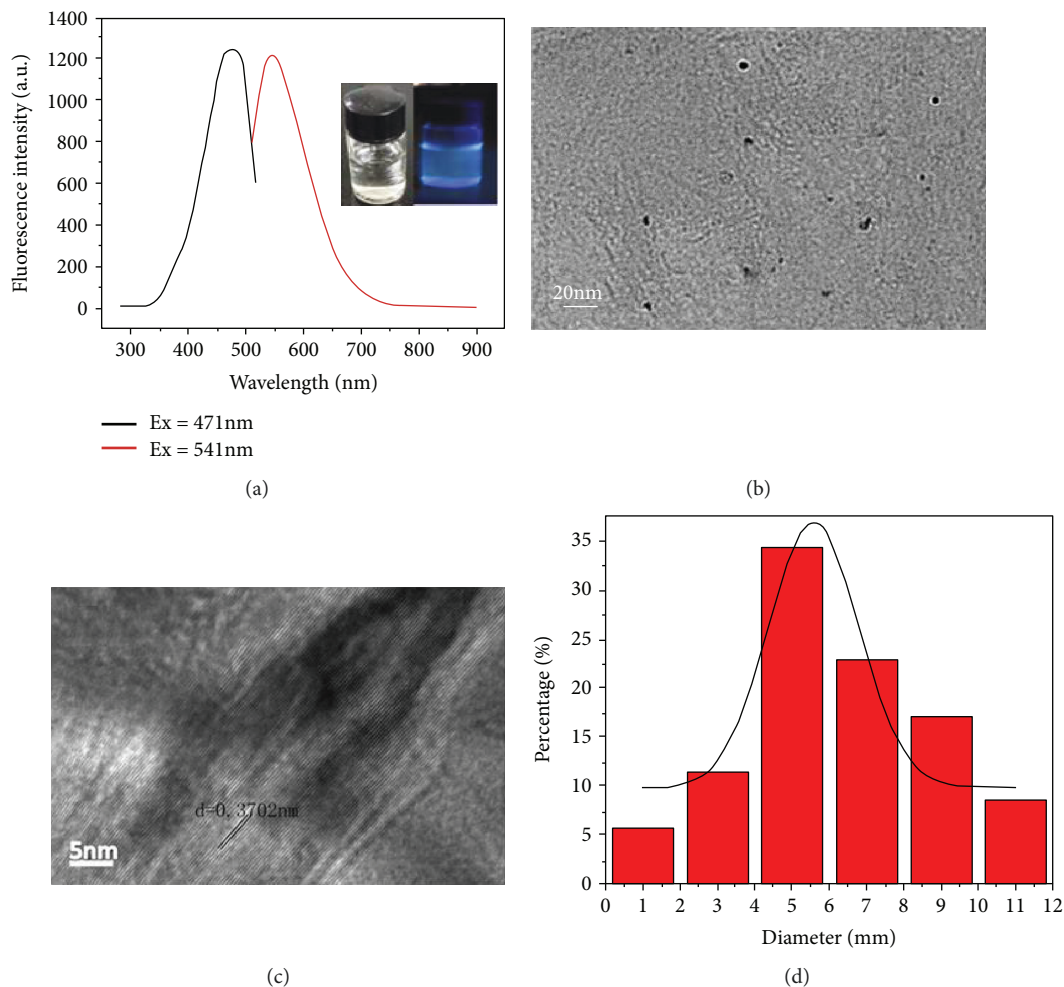


FIGURE 2: (a) Fluorescence spectra of Glc-CuNPs. (b) TEM image of Glc-CuNPs. (c) HRTEM image of Glc-CuNPs. (d) Size distribution histogram of Glc-CuNPs.

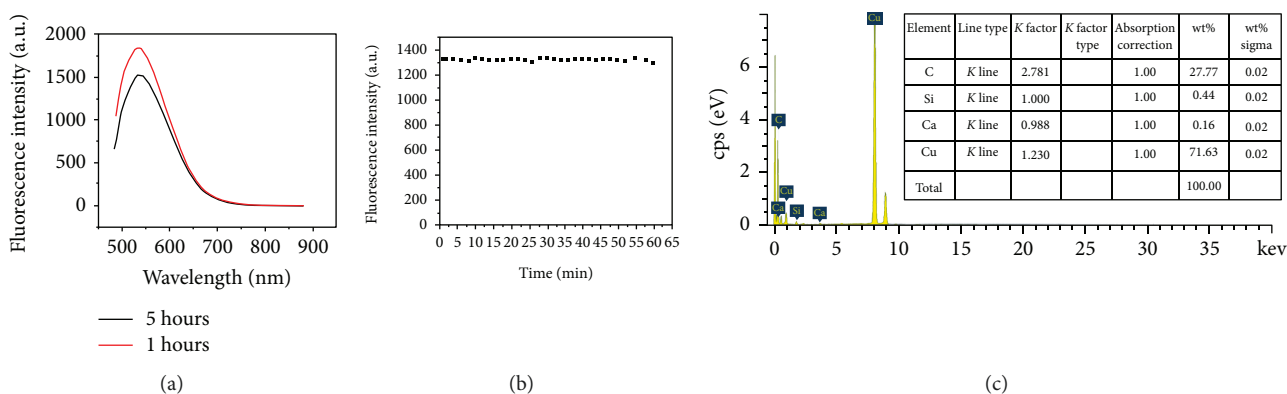


FIGURE 3: (a) The fluorescence intensity of the Glc-CuNPs after one-month storage at 4°C. (b) The fluorescence intensity of the Glc-CuNPs at the consecutive irradiation of a Xe lamp in different times. (c) EDs image of Glc-CuNPs.

In this experiment, a series of silver ions with different concentrations were used for sensing analysis. As shown in Figure 5(a), the fluorescence of Glc-CuNPs is quenched gradually with the increase of silver ion concentration (100 μmol/L–600 μmol/L). As shown in Figure 5(b), the

concentration of Ag⁺ in the range of 100 μmol/L–600 μmol/L has a good linear relationship ($R=0.9845$) and the linear regression equation is $F=-1.355C+1028.92$. The detection limit of 100 μmol/L was determined by 3 times blank standard deviation. As shown in

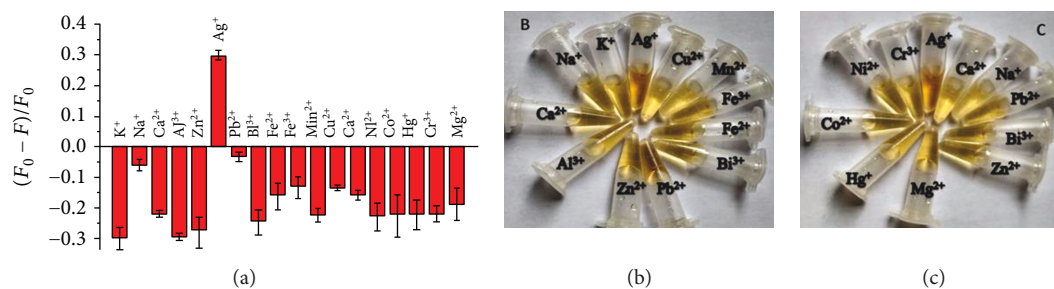


FIGURE 4: (a) Fluorescence intensities at 541 nm of as-synthesized Glc-CuNP solutions in the presence of different metal cations and (b) digital photographs of as-synthesized Glc-CuNPs in the presence of Ag^+ ($100 \mu\text{mol/L}$) or 18 kinds of other metal cations (1 mmol/L) under visible light.

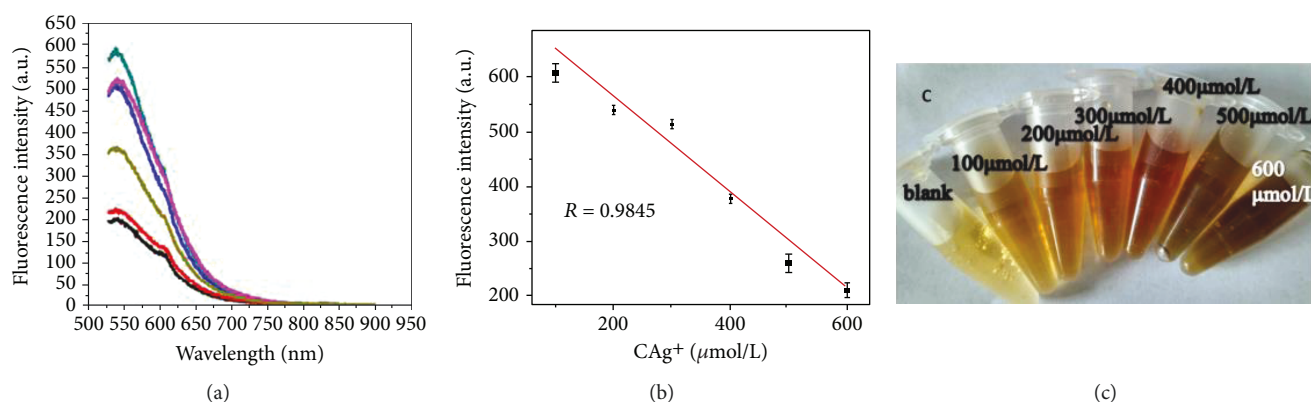


FIGURE 5: (a) Glc-CuNP fluorescence spectra with different concentrations of silver. (b) Linear relationship between fluorescence intensity of Glc-CuNPs and concentration of Ag^+ . (c) Digital photographs of Glc-CuNPs in the presence of different concentrations of Ag^+ under visible light.

TABLE 1: Analytical results for Ag^+ spiked in the Yellow River water sample.

Sample	Ag^+ supplemented ($\mu\text{mol/L}$)	Ag^+ measured ($\mu\text{mol/L}$)	Recovery (%)	RSD ($n = 3$)
1	100	94.6	94.6	5.4
	400	407.1	101.8	7.6
	600	589.7	98.3	3.4

Figure 5(c), when different concentrations of silver ions were added, the color of copper nanomaterials changed obviously. The detection of silver ions was completed based on visual colorimetry.

The feasibility of this method for detecting water in nature was also investigated. The Yellow River water was taken from the Baotou section of Inner Mongolia water for a few weeks and filtered with a $0.22 \mu\text{m}$ filter membrane. The silver ion in the Yellow River water could not be detected by this method. After that, silver ions were added to the water samples of the Yellow River by an internal standard addition method. The experimental results show that the recovery of silver ions in the Yellow River water is in the range as shown in Table 1. It shows that this method can be used to detect the actual water samples.

4. Conclusion

Based on the fluorescence quenching mechanism, a fluorescence analysis method for detecting Ag^+ was developed by using the prepared Glc-CuNPs as a fluorescence probe and the heavy metal Ag^+ as a quenching agent. The method shows a good fluorescence quenching linear relationship ($R = 0.9845$) in the range of $100 \mu\text{mol/L}$ – $600 \mu\text{mol/L}$ for silver ion and visual colorimetric detection. The recovery of environmental water samples is 94.6%–101.8%, and the relative standard deviation is less than 7.6%. Glc-CuNPs are cheap and easy to get, and the analysis method is fast and simple. It has a potential application value in environmental detection.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

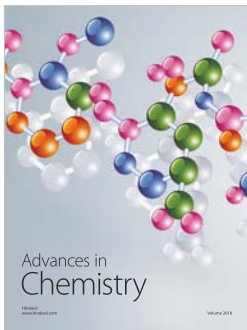
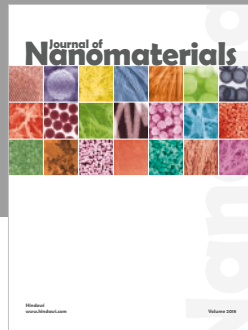
The authors declare that they have no conflicts of interest.

Acknowledgments

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