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Copper nanoparticles: A new colorimetric probe for quick, naked-eye detection of sulfide ions in water samples

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ABSTRACT

This study introduces a new method for the visual and spectrophotometric detection of chemical species using copper nanoparticles (Cu NPs). A simple method for the synthesis of Cu NPs for rapid colorimetric visual detection of sulfide ions (S^{2-}) in water samples is described. The Cu NPs sensor detects sensitive and selective color change in the presence of micromolar levels of S^{2-} that can be observed with the naked eye and monitored using a UV–vis spectrophotometer. The color change quantitatively correlates with the concentration of S^{2-} from 12.5×10^{-6} M to 50.0×10^{-6} M. Samples of tap water and river water were spiked and analyzed using the proposed system. The results showed that the sensor exhibited excellent detection for S^{2-} in the water samples. A main advantage of the new method is that it provides good selectivity for detecting S^{2-} without the need for complex readout equipment. The proposed method has a high potential for rapid environmental monitoring of sulfide ions.

1. Introduction

Nanoscience is the exploration of materials by fabricating nanometer scale materials with novel and improved properties that can affect all areas of physical and chemical science. Nanomaterials show unique properties. One important nanomaterial is metal nanoparticles [1,2]. Noble metal nanoparticles (NPs) are of interest for their physico-chemical properties and potential applications in fields such as catalysis, electronics, plasmonics, and biotechnology. These nanoparticles, gold, silver and copper have drawn attention for their promising properties. As the dimensions of the particles dispersed in liquid media decrease to nanometer size, a strong UV–vis band appears that does not exist on the bulk metal spectrum.

The properties of these nanoparticles give rise to increased localized surface plasmon resonance (LSPR) absorption and can be used in the development of analytical methods such as optical sensing. Surface plasmon resonance (SPR) results from surface electromagnetic waves that propagate in a direction parallel to the metal–dielectric interface. LSPR mode is responsible for the peaks observed in the absorption spectra of metallic nanoparticles. An extinction band appears when the incident photon frequency is resonant with the collective excitation of the conduction electrons. At resonant frequency, the incident light is absorbed by the nanostructure and some of these photons will be scattered at the same frequency in all directions [3,4].

For gold, silver, and copper nanoparticles over a range of 10–60 nm, the SPR peaks are positioned at about 520 nm, 400 nm, and 570 nm, respectively. When dispersed in aqueous media, the nanoparticles are responsible for the purple (gold), yellow (silver) and red (copper) color of the colloid solutions [5–8]. The SPR properties of gold and silver nanostructures have been useful for a variety of applications. Nanoparticles with well-controlled sizes have recently been used as suitable probes in colorimetric determinations [9–16].

Preparation of plasmonic nanostructures has been limited to the use of gold and silver nanoparticles. Cu is less expensive than Au and Ag, but displays a localized plasmon band in the visible part of the spectrum. Unfortunately, the preparation and application of copper nanostructures has not received as much attention as that of Ag and Au nanoparticles. The major difficulty in the use of Cu-based plasmonic nanostructures is their tendency to oxidize after preparation [17–19]. In this study, simple and efficient methods previously reported by Wu and Chen [7] and Sun [8] were used to synthesize Cu NPs. The experiments showed that the synthesized Cu NPs were relatively stable in aqueous solution and can be used as a colorimetric probe.

The drinking water for the province of Khuzestan in southwest Iran is mainly supplied by the Karun River. The quality of the river water has deteriorated in the past few years because of pollution loads from cities in Khuzestan and surrounding regions. The toxicity of S^{2-} in its liberated hydrogen sulfide form (H_2S) is

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well-known [20,21]; it is commonly found in natural water and wastewater samples and is an important pollution index for water. Sulfide detection is essential to environmental protection, biological research and other fields.

Determination of the presence of small amounts of sulfide requires sensitive methods. Various methods have been used for the determination of S^{2-} concentrations, including classical [22], optical, [13,16,23–26] electrochemical [20,21,27–29] and electrophoresis [30]. Some techniques, such as chromatography, have complex processes that require expensive apparatus and maintenance costs or are unsuitable for online analysis. Titrimetry is the only technique suitable for macro-analysis. Colorimetric methods have garnered attention because they can be easily monitored with the naked eye without special instrumentation.

No reports have been found on the spectrophotometric detection of chemical species using Cu NPs. The proposed method is a selective and sensitive colorimetric assay method for S^{2-} using Cu NPs LSPR. The results of this study demonstrate that the proposed optical sensor can be applied to determine micromolar concentrations of S^{2-} in water samples in just a few minutes. Moreover, this colorimetric probe is faster for online analysis of S^{2-} than other methods.

2. Experimental

2.1. Materials and reagents

All chemicals were of analytical reagent grade purity. Stock solutions of sulfide ions were prepared daily at a concentration of 100 mg L^{-1} by appropriate dissolution of $Na_2S \cdot 9H_2O$ (98%; Sigma Aldrich) salt in basic medium (0.1 mol L^{-1} NaOH). They were stored in a tightly capped bottle. The solution remained stable for a few days if stored in a refrigerator.

The solutions were alkaline because of the NaOH supply and volatile H_2S exhaust into the gas atmosphere was negligible. The stock solution was standardized using the common iodimetric titration method. Hydrazine hydrate (80%), cetyltrimethylammonium bromide (CTAB), NaOH and copper (II) nitrate were purchased from Merck (Darmstadt, Germany) and phosphoric acid (84–85%) from Fluka (Buchs, Switzerland). All solutions were prepared with doubly distilled water and all experiments were performed at ambient temperature (25 ± 2 °C).

2.2. Apparatus

Spectrophotometric measurements were carried out using a Cintra 101 spectrophotometer (GBC Scientific Equipment, Australia) with a 1 cm polymeric cell. A pH meter (model 632 Metrohm, Herisau, Switzerland) and a transmission electron microscope (TEM; 906E, LEO, Germany) were employed.

2.3. Synthesis of Cu nanoparticles

The current procedure for synthesis is a modified version of methods developed by Wu and Chen [7] and Sun [8] for Cu nanoparticles. The synthesis of Cu NPs was achieved in a capped bottle (200 mL) by mixing 4 mL of 0.1 mol L^{-1} solution of Cu^{2+}, 5 mL of 1% CTAB solution as a stabilizing agent, and 5 mL NaOH (0.005 mol L^{-1}) to increase the pH of the solution. The mixture was stirred at 80 °C for 5 min. Then 2 mL of hydrazine hydrate (99.9%) was added and the reaction solution was vigorously stirred at 80 °C for 45 min.

At this stage, the reduction of copper ions to metallic copper could proceed. After addition of hydrazine hydrate solution, the solution changed from colorless to red within 20 min, which indicated the formation of Cu NPs. The resulting product was then cooled to room temperature and used for the next determinations.

In most synthesis protocols, N_2 gas is passed to avoid the oxidation of Cu NPs [7,8]. In the present method, this was not necessary. The reduction of copper ions by hydrazine has some advantages. Nitrogen evolution occurred slowly, which maintains homogeneity of the reaction solution and also produces an inert atmosphere. Furthermore, hydrazine can increase the pH of the solution. The overall reaction is represented as

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_{2(S)}$$

$$Cu(OH)_{2(S)} + 2OH^- \rightarrow [Cu(OH)_4]^{2-}_{(aq)}$$

$$4[Cu(OH)4]^{2-}_{(aq)} + N_2H_4 \rightarrow 2Cu_2O_{(s)}\ (\text{yellow}) + N_{2(g)} + 8OH^- + 6H_2O$$

$$2Cu_2O + N_2H_4 \rightarrow 4Cu^0\ (\text{red}) + N_{2(gas)} + 2H_2O\ (\text{pH} \sim 10 \text{ at } 80\ ^\circ\text{C})$$

The colloidal dispersion of the metal exhibits absorption bands in the ultra-violet visible region at about 570 nm. It has been reported that Cu NPs less than 100 nm in size typically exhibit a surface plasmon peak at around 570 nm [7,8,31,32]. Previous research has shown that the Cu NPs does not change in inert atmosphere. In the presence of oxygen dissolved in the aqueous solution, the Cu NPs concentration and the intensity of the LSPR peak gradually decreased as a result of oxidation [7,31]. In the present study, however, absorption intensity remained unchanged for a few days after formation and no precipitation and oxidation occurred. This indicates that the Cu NPs were very stable in aqueous solution in the presence of CTAB and extra hydrazine in a capped bottle.

2.4. Procedure

To evaluate the optical characteristics of the Cu NPs solution as a LSPR-based sulfide sensor, 2 mL prepared Cu NPs solution was added to 5 mL volumetric flasks with 1 mL NaOH (0.005 mol L^{-1}) solution to adjust pH and different concentrations of sulfide ions. After the addition of the analyte, the solution was mixed slowly and a portion was transferred within 5–6 min into a 1 cm spectrophotometric cell to record absorbance. Absorbance was measured at 570 nm, which is λ_{max} of the Cu NPs SPR peak at room temperature against a blank

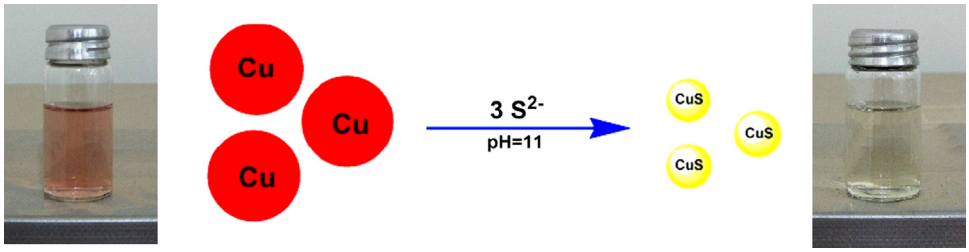

Fig. 1. Schematic illustration for the colorimetric sensing of S^{2-} based on etching of Cu NPs. [Condition of 10 mL: Cu NPs solution = 2 mL, $[OH^-] = 5 \times 10^{-4}$ mol L^{-1}, $[S^{2-}] = 30 \times 10^{-6}$ mol L^{-1}, and reaction time: 5–6 min]. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)