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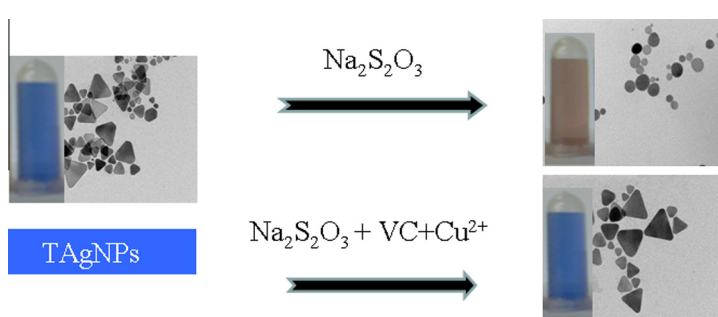
Visual detection of trace copper ions based on copper-catalyzed reaction of ascorbic acid with oxygen

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HIGHLIGHTS

- A new colorimetric method for copper ion detection is established.
- Copper ion could be detected by naked eye in the range of 0.075–0.50 μM .
- High selectivity and sensitivity allow the Cu^{2+} detection in human hair sample.

GRAPHICAL ABSTRACT



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ABSTRACT

A visual detection method for trace Cu^{2+} in aqueous solutions using triangular silver nanoplates (abbreviated as TAgNPs) as the probe was developed. The method is based on that TAgNPs could be corroded in sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solutions. The absorption spectrum of TAgNPs solution changed when it is corroded by $\text{Na}_2\text{S}_2\text{O}_3$. The reaction of oxygen with ascorbic acid (Vc) in the presence of a low concentration of Cu^{2+} generates hydrogen peroxide that reacts with $\text{Na}_2\text{S}_2\text{O}_3$, which leads the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ in the solution to be decreased. Therefore, the reaction between TAgNPs and the reacted mixture of $\text{Na}_2\text{S}_2\text{O}_3/\text{Vc}/\text{Cu}^{2+}$ was prevented efficiently. When the $\text{Na}_2\text{S}_2\text{O}_3$ concentration and reaction time are constant, the decrease in the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ is directly proportional to the Cu^{2+} concentration. Thus, morphology, color, and maximum absorption wavelength of TAgNPs changed with the change of Cu^{2+} concentration. The changed maximum absorption wavelength of TAgNPs ($\Delta\lambda$) is proportional to Cu^{2+} concentration in the range from 7.5×10^{-9} to 5.0×10^{-7} M with a correlation coefficient of $r = 0.9956$. Moreover, color change of TAgNP solution was observed clearly over a Cu^{2+} concentration range from 7.5×10^{-8} to 5.0×10^{-7} M. This method has been used to detect the Cu^{2+} content of a human hair sample, and the result is in agreement with that obtained by the atomic absorption spectroscopy (AAS) method.

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Introduction

Metallic nanostructures are able to application in many fields such as sensing, biological labeling, and other biological and

chemical fields [1–4]. However, the optical, physical, and chemical properties of metallic nanostructures depend on their size and shape, particularly for silver nanostructures [5,6]. In this study, triangular silver nanoplates (TAgNPs) were synthesized using the method of Zhang et al., [7] and it was used to detect trace Cu^{2+} . Studies have shown that the interaction between TAgNPs and other corrosion substances is easy at the three corners of the

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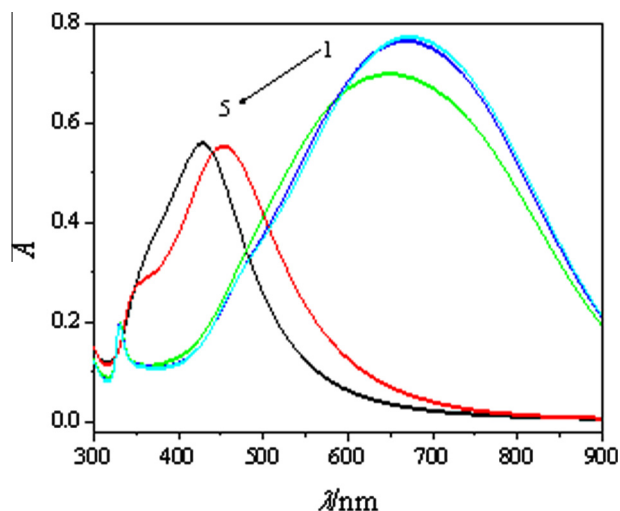


Fig. 1. UV-visible absorption spectra of TAGNPs/Na₂S₂O₃, spectra (curves 1–5) are shown for Na₂S₂O₃ concentration of 0, 0.1, 1.0, 10.0, and 50.0 μmol L⁻¹; pH, 5.72.

TAGNPs containing many active silver atoms [8]. When the above interaction happened, the morphology and color of TAGNPs changed. Therefore, TAGNPs have been widely utilized as the chromogenic components in colorimetric sensing systems [9–11].

Copper is a transition metal elemental that plays a key role in environmental, biological, and chemical systems [12]. Copper ion (Cu²⁺) is physiologically vital for various aspects such as bone formation and cellular respiration and serves as an important catalytic cofactor for several metalloenzymes [13,14]. The recommended daily allowances of Cu²⁺ by the National Research Council are 1.5–3.0 mg for adults, 1.5–2.5 mg for children, and 0.4–0.6 mg for infants [15]. Various methods such as atomic absorption spectroscopy (AAS) [16,17], inductively coupled plasma spectroscopy (ICP) [18,19], anodic stripping voltammetry [20], infrared absorption spectroscopy [21], and fluorescent sensors [22–24] have been developed for the detection of Cu²⁺ at trace levels; however, these methods suffer from harsh experimental conditions, time-consuming operations, etc. Colorimetric methods are extremely attractive because they can be easily visualized with the naked eye. Although many colorimetric sensors for Cu²⁺ detection have been reported [25–29], developing a visual method with high sensitivity and selectivity for Cu²⁺ detection is still a need.

Studies have shown that Na₂S₂O₃ could corrode the TAGNPs, as a consequence of altering their morphology and color in solutions. The reaction of oxygen (O₂) with ascorbic acid (Vc) in the presence of a low concentration of Cu²⁺ generates hydrogen peroxide (H₂O₂), which could be reacted with sodium thiosulfate (Na₂S₂O₃). As a result, corrosion of TAGNPs was prevented because of the

decreased concentration of Na₂S₂O₃. Furthermore, the color and UV-visible spectrum of TAGNPs changed with Cu²⁺ concentration in the range from 7.5 × 10⁻⁹ to 5.0 × 10⁻⁷ M. Thus, Cu²⁺ could be detected accurately by UV-visible spectrum determination. This method was used in determining the Cu²⁺ content in a human hair sample with satisfactory results.

Experimental

Apparatus

The UV-visible absorption spectra of the TAGNPs solutions were measured using a Lambda-35 UV-visible spectrophotometer (Perkin Elmer Instruments Inc., USA) and a quartz cell (1 × 1 cm²). Transmission electron microscopy (TEM) images were recorded using a Tecnai G20 TEM (FEI Co., USA). The pH values of the solutions were measured using a pH meter (Mettler-Toledo International Inc. Shanghai, China). A DF-101B magnetic stirrer (Yu Hua Instrument Inc. Gongyi, China) was used to blend the solutions in an Erlenmeyer flask to prepare the TAGNPs. Nikon Coolpix 4500 digital camera was used to record the images of the aqueous solutions. Analyst 100 atomic absorption spectrophotometer (Perkin Elmer, USA) was used to detect the Cu²⁺ contents in real samples for comparison with this method.

Synthesis of TAGNPs

TAGNPs were synthesized by the method of Zhang et al. [7]. First, 24.75 mL of redistilled water was added to a 50 mL Erlenmeyer flask and continuously magnetically stirred at room temperature. Then, silver nitrate (0.05 M, 50 μL), trisodium citrate (75.0 mM, 0.5 mL), H₂O₂ (30 wt%, 60.0 μL), and 4.0 mL polyvinylpyrrolidone (PVP, average molecular weight $M_w \approx 58,000$ g/mol) with a concentration of 0.5 mg/mL were added sequentially. Next, sodium borohydride (NaBH₄, 100.0 mM, 250.0 μL) was added quickly into the above mixture; the color of the solution immediately changed to light-yellow. After 25 min, the colloidal solution became deep yellow, because the quantity of the silver nanoparticles increased. Further, as morphology of the silver nanoparticles changed to that of TAGNPs, the color of the mixture gradually changed from deep yellow to red, green, and blue within the next few seconds.

Reagents

Cu²⁺ stock solution with a concentration of 1.0 × 10⁻² M was freshly prepared by dissolving pure CuSO₄·5H₂O (obtained from Hunan reagent factory) with redistilled water. Solutions of other Cu²⁺ concentrations were prepared by diluting the Cu²⁺ stock solution with water. The Britton–Robinson buffer solution was used to adjust the pH of the reaction system. Ascorbic acid (Vc) was

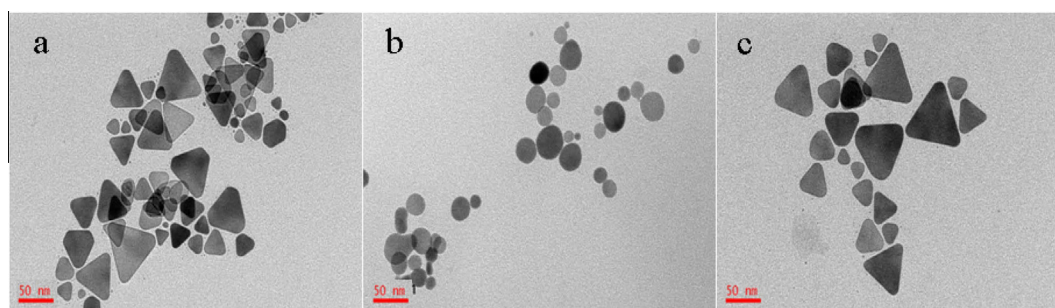


Fig. 2. TEM images of the TAGNPs (a), the mixture of TAGNPs/Na₂S₂O₃ (b), the mixture of TAGNPs/Na₂S₂O₃/Vc/Cu²⁺ (c). $c_{\text{Cu}^{2+}}$ (0.5 μmol L⁻¹), $c_{\text{Na}_2\text{S}_2\text{O}_3}$ (5.0 μmol L⁻¹), pH 5.72, c_{Vc} (1.0 mmol L⁻¹).

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