



Visual determination of trace Cysteine based on promoted corrosion of triangular silver nanoplates by sodium thiosulfate



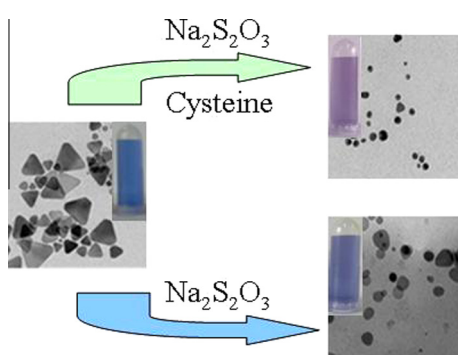
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HIGHLIGHTS

- A new colorimetric strategy for Cysteine detection is demonstrated.
- The $\text{Na}_2\text{S}_2\text{O}_3$ improved the sensitivity for Cysteine detection.
- $0.025 \mu\text{M}$ Cysteine could be detected by naked eye.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, triangular silver nanoplates (TAG-NPs) were used to detect trace Cysteine concentration in the presence of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$). Study showed that the TAG-NPs could be gently etched by Cysteine with the concentration of $1.0 \times 10^{-7} \text{ mol L}^{-1}$ through forming Ag–S covalent bond at the three corners. However, in the presence of $\text{Na}_2\text{S}_2\text{O}_3$ (only $3.0 \times 10^{-6} \text{ mol L}^{-1}$), the corrosion of Cysteine on TAG-NPs can be promoted significantly. It was also found that the color, morphology, and the maximum absorption wavelength of TAG-NPs change clearly with the concentrations of Cysteine as low as $2.5 \times 10^{-8} \text{ mol L}^{-1}$. Furthermore, the wavelength shift values ($\Delta\lambda$) of TAG-NPs solution were proportional to the concentrations of Cysteine in the range of 1.0×10^{-9} – $1.0 \times 10^{-7} \text{ mol L}^{-1}$, and the linear regression equation is $\Delta\lambda = -0.89 + 319.94 c$ (c , μM , $n = 5$) with the correlation coefficient of 0.990. At the same time, the color change of the TAG-NPs solution could be observed clearly by the naked eyes with increasing Cysteine concentrations in the range of 2.5×10^{-8} – $1.0 \times 10^{-7} \text{ mol L}^{-1}$. Thus, a novel method for the detection of Cysteine by either UV–vis spectrophotometry detection or naked eyes observation is established. It allows determination of Cysteine content in compound amino acid injection sample of 18AA-V.

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Introduction

So far, many silver nanomaterials have applied to the detection of Cysteine successfully [1–3]. Silver nanoparticles in different

shapes could display different optical properties and colors (like red, green, yellow, and blue respectively) [4,5]. Thus, the shape-controlled synthesis of silver nanoplates attracts many chemists attention. Recently, different morphologies and colors of silver nanomaterials with cubic [6], triangular [7,8], and hexagonal [9,10] shapes have been synthesized. In this study, the triangular silver nanoplates (TAG-NPs) with the color of blue was synthesized

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by the method of Zhang et al. [11], and it could be used to detect Cysteine either by spectra detection or by naked eyes.

Pawlukojc et al. have studied the neutron spectroscopy, raman and IR of Cysteine carefully in 2005 [12]. As an essential sulfhydryl-containing amino acid, Cysteine plays a pivotal role in biological systems, such as protein synthesis, detoxification and reversible redox reaction. For instance, it is a potential neurotoxin [13,14], a disease-associated physiological regulator [15] and a biomarker for various medical conditions [16,17]. Cysteine deficiency is involved in slowed growth, hair depigmentation, edema, lethargy, liver damage, muscle and fat loss, skin lesions, and weakness [18]. While many methods have been developed for the detection of Cysteine concentration in real samples, such as fluorescence [19–23], chromatography [24–26], electrochemical method [27–31], UV–vis spectrophotometry [32,33] and chemiluminescence [34]. Moreover, many visual methods for Cysteine detection have been developed and received great attention due to their simplicity [35–40]. Especially gold and silver nanomaterials have been considered as an aminothiols visual sensor due to they could provide strong affinity toward thiols [1–3,38,39]. For example, Wu et al. have reported a colorimetric method for detection of Cysteine using triangular silver nanoplates (TAg-NPs) as the probe [2]. However, this method requires to heating, and the detection limit is not low enough. Thus, developing a new visual method for sensitive and specific detection of Cysteine is significant.

Here, we report a new UV–vis spectrophotometry and visual detection method for sensitive and selective detection of Cysteine based on the UV–vis spectra and the color change of TAg-NPs. Studies have shown that, corners of TAg-NPs are poorly protected by PVP [41]. Thus, the TAg-NPs could react with $\text{Na}_2\text{S}_2\text{O}_3$ easier especially in the presence of trace Cysteine. Furthermore, the color, morphology, and the absorbance at the position of maximum absorption peak of TAg-NPs could be changed with the change of the concentrations of Cysteine. The shift values of the absorption peak of TAg-NPs were proportional to the concentrations of Cysteine in the range of 1.0×10^{-9} – 1.0×10^{-7} mol L⁻¹ in the presence of $\text{Na}_2\text{S}_2\text{O}_3$ with the concentration of 3.0×10^{-6} mol L⁻¹. Therefore, a simple, sensitive and visual method for detection of Cysteine was established.

Experiment

Apparatus

The experiments were carried out using a Lambda-35 UV–vis spectrophotometer (Perkin Elmer Instruments Inc., USA) and a quartz cell (1×1 cm²), which are used to measure the UV–vis absorption spectrum of the TAg-NPs solutions. Tecnai G20 transmission electron microscopy (FEI Company, USA) 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.

Reagents

Dissolving pure L-Cysteine with water to prepare the stock solution with the concentration of 1.0 mmol L⁻¹ and directly diluted with water to prepare Cysteine stock solutions for other concentrations. The Britton–Robinson buffer solutions with pH value of 1.81, 2.87, 3.78, 4.78, 5.72, 6.80, 7.96, 8.69, 9.62, and 10.88, were prepared by mixing appropriated volume of sodium hydroxide solution with the concentration of 0.2 mol L⁻¹ and the three acid solution, which is contained 0.2473 g boric acid, 0.228 mL acetic acid, and 0.274 mL 85% phosphate acid in the volume of 100 mL

solution. All chemicals are analytical reagents, and the water is redistilled water.

Synthesis of the TAg-NPs

TAg-NPs were synthesized by the method of Zhang et al. [11] Typically, 24.75 mL of twice-distilled water was added to a 50 mL Erlenmeyer flask and continuously magnetically stirred at room temperature. Subsequently, silver nitrate (0.05 mol L⁻¹, 50 μ L), trisodium citrate (75.0 mmol L⁻¹, 0.5 mL), H₂O₂ (30 wt%, 60.0 μ L), and 4.0 mL poly-vinylpyrrolidone solution with the concentration of 0.5 mg mL⁻¹ (PVP, average molecular weight $M_w \approx 58,000$ g mol⁻¹, manufacturer Aladdin Chemistry Co., Ltd., product number 22752, the concentration is 0.5 mg mL⁻¹, 4.0 mL) were successively added to the above solution. Next, sodium borohydride (NaBH_4 , 100.0 mmol L⁻¹, 250.0 μ L) was rapidly added into the above mixture; the color of the solution immediately turned to light-yellow. After 25 min, the colloidal solution turned to deep yellow because the quantity of the TAg-NPs products increased. Further, as the morphology of nanoparticles changed to TAg-NPs, the color of the mixture gradually changed from deep yellow to red, green, and blue within the next few seconds.

Spectra detection procedures and pretreatment of samples

1.4 mL TAg-NPs, appropriate concentrations of Cysteine or sample solution were added to a 2.0 mL Eppendorf tube, then the solution was mixed and kept reaction for 25 min, and then mixed with 100 μ L Britton–Robinson buffer solution (pH 5.72), 60.0 μ L $\text{Na}_2\text{S}_2\text{O}_3$ (1.0×10^{-4} mol L⁻¹), and diluted the mixture with water to 2.0 mL. After reacting 15 min, the mixture was transferred for UV–vis detection. The sample was prepared by diluting the compound amino acid injection of 18AA-V (Shandong, China) with water.

Results and discussion

The role of $\text{Na}_2\text{S}_2\text{O}_3$ in this system

The TAg-NPs could be reacted more readily with many substances owing to the corners of TAg-NPs are poorly protected by stabilized reagent. For instance, Wu et al. established the method for Cysteine detection using its reaction with TAg-NPs in aqueous solution under heating for 3 min. They found that the Cysteine can etch the three corners of TAg-NPs and forming the Ag–S covalent [2]. We found that higher concentrations of Cysteine ($\geq 10^{-6}$ mol L⁻¹) could cause the spectra of TAg-NPs changes obviously under room temperature. As Fig. S1 in the supporting information shown, the maximum absorption wavelength of TAg-NPs is 736 nm with the absorbance of 0.74, one of the mixture of TAg-NPs/Cysteine ($c_{\text{cysteine}} \geq 10^{-6}$ mol L⁻¹) shifted to the red band of 817 nm with the absorbance of 0.56. This phenomenon may be caused by interaction between Cysteine and TAg-NPs, which leded the aggregation of TAg-NPs. Yet, corrosion of Cysteine to TAg-NPs was not obvious when the concentration of Cysteine is lower as 1.0×10^{-7} mol L⁻¹. As Fig. 1a shows, the maximum absorption wavelength and the color of TAg-NPs hardly changed, the absorbance decreased only about 3.3% in the presence of Cysteine with the concentrations of 1.0×10^{-7} mol L⁻¹.

However, compared Fig. 1a and b, we concluded that the TAg-NPs were corroded in the presence of $\text{Na}_2\text{S}_2\text{O}_3$ with the concentration of 3.0 μ mol L⁻¹ and produced the $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ ions [42]. As Fig. 1 shown the maximum absorption wavelength of TAg-NPs is 737 nm (as the curve a in Fig. 1a), and yet one of the mixture of TAg-NPs/ $\text{Na}_2\text{S}_2\text{O}_3$ is 573 nm (as the curve a in Fig. 1b). But the maximum absorption wavelength of TAg-NPs was hardly changed

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