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A sensitive and selective colorimetric sensor for reduced glutathione detection based on silver triangular nanoplates conjugated with gallic acid

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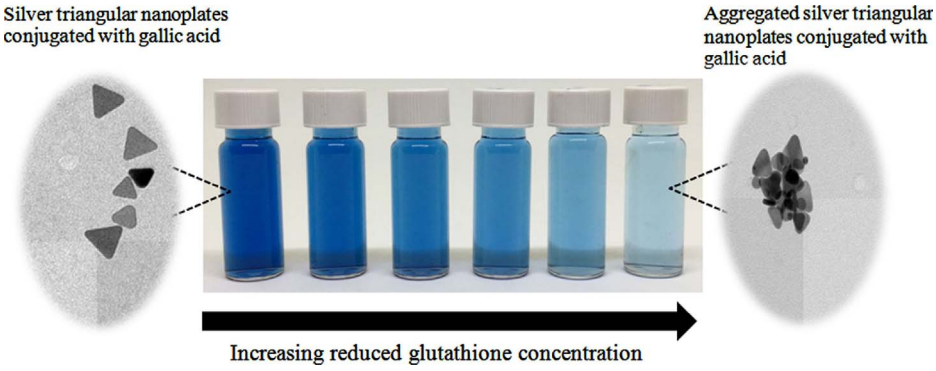
GRAPHICAL ABSTRACT



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ABSTRACT

Silver triangular nanoplates conjugated with gallic acid (AgTNPs·GA) was designed and synthesized for colorimetric detection of reduced glutathione (GSH). The surface plasmon resonance (SPR) properties of AgTNPs·GA were strongly influenced by the addition of GSH. The detection principle was based on the aggregation of AgTNPs·GA, which leads to the significant bathochromic shift of the SPR spectra from 602 nm to 650 nm. The dramatic color changes from the initial dark blue to light blue can be observed, which allowed simple monitoring of GSH ether by naked eye and UV–vis spectrophotometer. With UV–vis spectrophotometer measurements, a quantitative linearity was established in the range of 0.5–5.0 nM (R^2 = 0.9919) and with a limit of detection (LOD) of 0.12 ± 0.02 nM. Relative standard deviation (RSD) of 3.46% and 1.82% (n = 10) were achieved for the determination of 1.0 and 3.0 nM, respectively. No interfering substances such as ascorbic acid, glucose, sucrose, citric acid, cysteine, Ca^{2+}, Mg^{2+}, Fe^{3+} and K^{+} were revealed in the AgTNPs·GA based assay. The proposed colorimetric strategy could be extended as the general platform for detection of GSH in dietary supplements and no significant differences in accuracy and precision were observed compared to HPLC standard method.

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1. Introduction

Nowadays, reduced glutathione (GSH) supplements are attracting much attention from the teenagers in Bangkok of Thailand. Many teenagers have come to believe that, GSH is one of the great ways to whiten the skin tone in short span of time. GSH has a skin-whitening effect in humans through its tyrosinase inhibitory activity. The skin whitening benefits of GSH are a result from its ability to significantly lower the melanin index [1]. Therefore, there is a large array of GSH containing supplements currently on the drugstore or even the market. GSH supplements are available in several forms such as powdered, capsules, pills and liquid with varying the amount of GSH. The recommended dosage of GSH that should be obtained is between 60 and 250 mg/day [2]. If the dosage is greater than the recommended dose, can cause allergic to shock and death [3]. Therefore, the improvement of sensitive, selective, rapid, simple and inexpensive detection method of GSH in dietary supplements is highly desired. Although some analytical techniques such as capillary electrophoresis (CE) [4], spectrofluorometry [5], hi-performance liquid chromatography (HPLC) [6] and gas chromatography with flame photometric detection [7] have also been used for quantitative analysis of GSH, some problems still occur due to labor-intensive, time consuming and sophisticated instrumentation [8,9].

Recently, colorimetric sensor based on silver nanoparticles (AgNPs) have been attracting much attention because they can provide convenience of visual observation, simple operations, rapid and inexpensive [10–12]. Due to their fascinating optical properties of AgNPs, construction of perceptual devices for colorimetric detection based on AgNPs have been extensively utilized for both biological and chemical analyzes [13,14]. The differentiation of various analyses detection based on AgNPs is dependent upon the phenomenon of size [15], morphology [16], dielectric constant of the surrounding medium [17] as well as interparticles distance of AgNPs [18]. Among colorimetric sensor, AgNPs have the excellent SPR properties in the visible region (400–700 nm) of the spectrum, which makes the detection of biological and chemical easier [19]. In this sense, the surface modifications of AgNPs were played the crucial roles in improving of the optical properties of AgNPs and enhance its sensitivity as a sensor. For examples, He et al. [20] developed a colorimetric detection of Mn^{2+} using AgNPs cofunctionalized with 4-mercaptobenzoic acid and melamine. The detection limit for Mn^{2+} ion was approximately to 5×10^{-8} mol L^{-1}. Khayatian et al. [21] used chitosan to modify AgNPs for detection of cysteine in urine and plasma. Under optimum conditions, the calibration curve was linear over a concentration range of 0.1–10 μM with detection limit of 15.0 nM. Zhang et al. [22] developed a colorimetric detection of uric acid in human serum using uricase-stimulated etching of silver nanoprism. The detection limit of uric acid was 0.7 μM.

Consequently, the quantitative analysis of GSH in dietary supplements using gallic acid modified the surface of silver triangular nanoplates (AgTNPs) was developed. The dark blue color of AgTNPs·GA solution changed to light blue in accordance with the GSH level added as the aggregation of AgTNPs·GA induced by GSH lead to a bathochromic shift of the SPR spectra from 602 nm to 650 nm. The effect of various parameters, including such as concentration of AgTNPs·GA, incubation times and pH have been explored to establish the optimized conditions. Under the optimal conditions, the colorimetric detection of GSH using AgTNPs·GA was found in the concentration range of 0.5–5.0 nM with the limit of detection of 0.12 ± 0.02 nM. The results confirmed that our colorimetric method is sensitive, selective, simple, rapid, and quantitative for colorimetric detection of GSH in dietary supplements.

2. Experimental

2.1. Chemicals

Silver nitrate ($AgNO_3$, 99.99%), sodium borohydride ($NaBH_4$, 99%), gallic acid ($C_6H_2(OH)_3COOH$), cysteine ($C_3H_7NO_2S$) and reduced glutathione ($C_{10}H_{17}N_3O_6S$) were purchased from Sigma–Aldrich, Co., Ltd USA. Hydrogen peroxide (H_2O_2, 30 wt%.), acetic acid (CH_3COOH), sodium acetate (CH_3COONa), potassium chloride (KCl), magnesium sulfate ($MgSO_4$), calcium carbonate ($CaCO_3$), sodium chloride (NaCl) and potassium nitrate (KNO_3) were purchased from Carlo Erba Co., Ltd USA. All reagents obtained commercially were of analytical reagent grade (AR grade) and used without purification. All solutions were prepared using ultrapure water with a resistivity of 18.2 MΩ cm at 25 °C (Milli-Q®, Millipore system).

2.2. Synthesis of AgTNPs·GA

AgTNPs·GA was prepared following the literature [23] with some modifications, in which sodium citrate was removed from the preparation. Briefly, 50 mL of 1 mM silver nitrate was mixed with 3 mL of 20 mM gallic acid in the presence of 0.12 mL of 30 wt.% H_2O_2. Then, an aliquot of 0.33 mL $NaBH_4$ (100 mmol/L) was rapidly added to a mixture solution under stirring for 10 min at 25 °C. During this time, the initial colorless of the mixture solution was changed gradually to yellow, orange, red, purple and blue, respectively.

Blue color of the colloidal solution was indicated the formation of silver triangular nanoplates. Finally, the blue solution of AgTNPs·GA was stored at 4 °C in the refrigerator for further use. To estimate the concentration of AgTNPs·GA, the stock colloidal AgTNPs·GA solution was diluted 3 times using ultrapure water. The SPR spectra of AgTNPs·GA were recorded by UV–vis spectrophotometer for five repetitive measurements. According to Beer's law [24], the concentration of AgTNPs·GA was estimated to be 0.014 ± 0.001 nM according to extinction coefficient on particle diameter. For references, the extinction coefficient (ε) and mean diameter of AgTNPs·GA were calculated to 5.56×10^{10} M^{-1} cm^{-1} and 55.4 ± 1.2 nm, respectively.

In addition, the stability of the as-synthesized AgTNPs stabilized with GA was evaluated by keeping them in 4 °C refrigerator over 2 months (Fig. S1, Supporting material). The SPR spectra shows the minimal peak shift of AgTNPs in the presence of GA stabilizer, indicating that the as-synthesized AgTNPs·GA were intact and more stable than those prepared in the previous works [23,25].

2.3. Characterizations

The SPR spectra of AgTNPs·GA were recorded on UV1800 Ultraviolet–visible (UV–vis) spectrophotometer (Shimadzu Co. Ltd., China) with a matched pair of 10 mm quartz cuvette.

The zeta potential (surface charges) and size distribution of colloidal solutions were acquired using Zeta-sizer Nano, ZS with 633 nm Helium-Neon lazer (Malvern instrument, England). Transmission electron microscope (TEM, JEM-2001 model, JEOL Co., Ltd Japan) was used to evaluate the morphology of AgTNPs·GA. For TEM analysis, samples have been prepared by spotting diluted solution of AgTNPs·GA onto carbon coated 200 mesh copper grids and it were allowed to dry before imaging.

2.4. Colorimetric detection of GSH

To detection of GSH, 2 mL of different concentrations from 0.5 nM to 6.0 nM of GSH were mixed with 2 mL of AgTNPs·GA. The mixture solutions were incubated for 10 min at room temperature (25 °C) until instant coloration. Following this, UV–vis spectrophotometer was used to record the SPR of the mixture solutions. From the spectral results, calibration curve was constructed. The quantification of GSH in the