



## Research Paper

# Colorimetric detection of glutathione based on phthalic acid assisted synthesis of silver nanoparticles

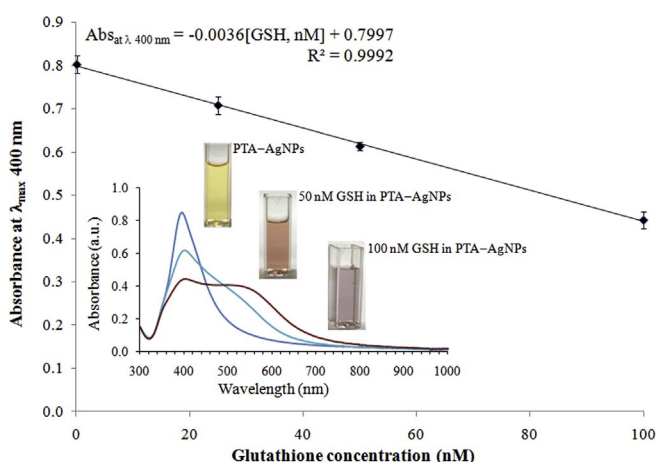


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## GRAPHICAL ABSTRACT



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## ABSTRACT

A new rapid, sensitive and selective colorimetric sensing platform for the detection of glutathione (GSH) in dietary supplements was developed by phthalic acid (PTA) assisted synthesis of silver nanoparticles (AgNPs). The di-carboxylic functional groups of PTA were used to modify the surface of AgNPs. The resulting AgNPs product was characterized by surface plasmon resonance (SPR) Ultraviolet–visible spectroscopy (UV–vis), Zeta potential analyzer, Fouriertransform infrared spectroscopy (FT-IR), Transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD) techniques, demonstrated that PTA is an effective capping agent to stabilize AgNPs. AgNPs stabilized with PTA could cause the strong affinity to GSH. As the GSH concentration increased, the color of AgNPs solutions was gradually changed from yellow to orange and light purple as well as the SPR shifted from 400 nm to 556 nm upon an aggregation of AgNPs due to electrostatic interaction. The proposed colorimetric sensor was exhibited a linear response in the range of 0.1–100 nM ( $R^2 = 0.9992$ ), with low detection limit (LOD) of  $0.16 \pm 0.01$  nM. The sensor showed better precision with relative standard deviation

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(RSD) of 2.10% and 1.13% for ten repetitive measurements of 25 nM and 75 nM GSH solution, respectively. The sensitivity of AgNPs for GSH detection can be clearly differentiated towards other coexisting substances ( $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , glucose, sucrose, cysteine, ascorbic acid and citric acid). The AgNPs colorimetric sensor could discriminatively detect GSH in dietary supplement samples with the recoveries values in the range of 98.5%–103.0%.

## 1. Introduction

Glutathione (GSH) is a linear tripeptide composed of L-cysteine, L-glutamine and glycine. Just the sulfhydryl or thiol (SH) group on the L-cysteine portion is a necessary account for healthy cells and tissue in the human body [1]. The major functions of GSH in the human body have involved the regulation of cell growth and division, DNA synthesis and repair, amino acid transportation and enhancement of systemic immune function [2–4]. In medicine, GSH has been used to treat various diseases including peripheral neuropathies, treating cataracts and glaucoma, hepatitis and carcinoma of stomach and prostate [5–8]. The treatment is usually done by injecting GSH into the vein or into the muscle. One surprising side effect is that patients treated with GSH injections have a whiter skin tone because GSH can inhibit tyrosinase enzyme and helps prevent the enzymatic pathways from producing melanin. As a result, the pigmentations of the skin were changed from blackish brown to pinkish white [9].

Nowadays, the popularity of pinkish white skin is a beauty trend common in Bangkok of Thailand. The pinkish white side effects of GSH injection have been used as the advantages of producing white skin supplements. Therefore, there are GSH supplements sold widely in the drugstore. Most of the GSH products found in the market are in tablets and liquid formulations with varying amounts of GSH. The average recommended daily dosage of GSH is 60–250 mg [10]. If the dosage is greater than the prescribed dose may cause allergic reactions, unconsciousness and death [11]. Therefore, the improvement of a simple, rapid, sensitive and selective method for the determination of GSH in dietary supplements is highly crucial. Up to now, various instrumental techniques such as capillary zone electrophoresis, electrochemical analysis, fluorimetry, high performance liquid chromatography (HPLC), gas chromatography with mass spectrometry and surface enhanced raman scattering have been described for the detection of GSH [12–18]. However, some inherent issue of these analytical techniques still could not be avoided such as high in operation cost, expensive instrumentation, time-consuming and tedious sample pretreatments.

Recently, the colorimetric sensor based on noble metal nanoparticles are gaining increased attention due to its easily monitored, which has real-time analysis and without needing any complicated instruments [19–21]. Among metal nanoparticles, AgNPs have been extensively used as colorimetric probes for various analyses detection [22–24]. To our knowledge, the differentiation of various detection analyses are based on the association of size, morphologies, distance between nanoparticles and dielectric constant of the media surrounding medium of the nanoparticles [23,25]. In general, the key to develop AgNPs as colorimetric detecting probes is surface modification of AgNPs. For example, recently, our research team has used polyaniline blend poly(styrene sulfonic acid co maleic acid) modified AgNPs as a colorimetric probe for ammonia detection [25]. Lu et al. [26] developed a colorimetric assay for cysteine based upon the surface modification of AgNPs using Zonyl FSN (nonionic fluorosurfactants). H. Zhao has designed the sensor employing 4-mercaptobenzoic acid stabilized AgNPs for colorimetric detection of  $\text{Cu}^{2+}$  [27]. The challenge to produce colorimetric sensor for various detection is to find a suitable chemical to modify the surface of AgNPs. Although many AgNPs have been functionalized for the efficient colorimetric detection, no study has been published for GSH detection using PTA modified the surface of AgNPs.

In this research, a novel colorimetric assay for GSH detection using

PTA modified AgNPs was proposed. The present work was focused on the preparation, characterization and applied AgNPs probe in the visual detection of GSH. Moreover, this colorimetric system was applied to the detection of GSH in dietary supplements successfully with high accuracy and precision. The performance of the developed sensing probe was showed rapid, sensitive and selective colorimetric sensing platform to GSH. Under the optimal conditions, the detection system reached the limit of detection down to  $0.16 \pm 0.01$  nM. In the present of GSH, GSH can induced the color change of AgNPs from yellow to orange and light purple, which lead to a method for detection of GSH by naked eye.

## 2. Experimental

### 2.1. Chemicals

Silver nitrate ( $\text{AgNO}_3$ ), phthalic acid ( $\text{C}_6\text{H}_4(\text{COOH})_2$ ), sodium borohydride ( $\text{NaBH}_4$ ), reduced glutathione ( $\text{C}_{10}\text{H}_{17}\text{N}_3\text{O}_6\text{S}$ ) were acquired from Sigma–Aldrich, Co., Ltd USA. Calcium chloride ( $\text{CaCl}_2$ ), ammonium chloride ( $\text{NH}_4\text{Cl}$ ), magnesium chloride ( $\text{MgCl}_2$ ), potassium chloride ( $\text{KCl}$ ), monosodium phosphate ( $\text{NaH}_2\text{PO}_4$ ), methanol ( $\text{CH}_3\text{OH}$ ) and *ortho*-phthalaldehyde ( $\text{C}_6\text{H}_4(\text{CHO})_2$ ) were purchased from Carlo Erba Co., Ltd USA. All chemicals are of analytical reagent grade (AR grade) and used directly without further purification. Ultrapure water (Milli-Q, Millipore system) with a resistivity of 18.2 M $\Omega$  cm at 25 °C was used for preparing all aqueous solution.

### 2.2. Synthesis of colloidal AgNPs

Phthalic acid modified AgNPs was prepared by the  $\text{NaBH}_4$  chemical reduction method. Briefly, 10 mL of 100 mmol/L  $\text{AgNO}_3$  solution was mixed with 1 mL of 0.1 mmol/L PTA and 79 mL of ultrapure water. The mixture solution was stirred continuously for 5 min. Subsequently, an aliquot of  $\text{NaBH}_4$  (10 mL, 100 mmol/L) was then rapidly added to a homogeneous mixture solution. Yellow color marks the end of the reaction, confirming the formation of PTA stabilized AgNPs and the colloidal AgNPs was stored in the refrigerator at 4 °C for further use. The as-synthesized AgNPs was diluted five times by ultrapure water and the resulting concentration was found to be  $0.12 \pm 0.01$  nM as detected by UV–vis spectra according to Beer's law ( $A = \epsilon bc$ ); where:  $A$  = absorbance (a.u.),  $\epsilon$  = extinction coefficient ( $\text{M}^{-1} \text{cm}^{-1}$ ),  $b$  = path length through solution (cm) and  $c$  = AgNPs concentration (nM). The extinction coefficient ( $\epsilon = 7.19 \times 10^9 \text{M}^{-1} \text{cm}^{-1}$ ) was calculated using the equation  $\ln \epsilon = 1.4418 \ln D + 18.955$ , where  $D$  is the mean diameter of AgNPs in nm ( $13.4 \pm 1.2$  nm) [28].

### 2.3. Characterizations

Ultraviolet–visible (UV–vis) absorption spectra of AgNPs were measured using double beam UV1800 (Shimadzu, China) spectrophotometer with a 1 cm path length quartz cuvette. All the measurements were repeated at least three times. Morphology images, particle size and their distribution of AgNPs were photographed by a transmission electron microscope (TEM, JEM-2001 model, JEOL Co., Ltd Japan) at an accelerating voltage of 200 kV. TEM grids were prepared by dropping 5  $\mu\text{L}$  diluted AgNPs solution on carbon coated copper grid. Zeta potential and dynamic light scattering were carried out by a NanoZS-Malvern instrument, England with a 633 nm Helium–Neon laser. Before zeta potential and dynamic light scattering measurement,

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