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A surface plasmon resonance sensing method for determining captopril based on in situ formation of silver nanoparticles using ascorbic acid

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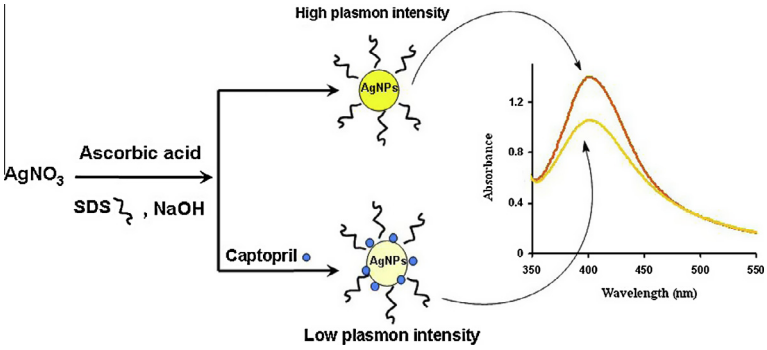
HIGHLIGHTS

- A new spectrophotometric method for sensitive determination of captopril by AgNPs plasmon.
- Stable and dispersed AgNPs with intensified plasmon peak were synthesized in situ.
- First time ascorbic acid was used as reducer for in situ formation of AgNPs in sensing method.
- Detection limit is better than other methods based on spectrophotometric captopril detection.

GRAPHICAL ABSTRACT



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ABSTRACT

A new method has been proposed to sensitive detection of captopril based on surface plasmon resonance band of silver nanoparticles (AgNPs). The stable and well-dispersed AgNPs with strong plasmon resonance signal were synthesized in situ using a simple and rapid procedure by applying ascorbic acid as reducer and sodium dodecyl sulfate as stabilizer, at room temperature. It was found that, the decreasing of AgNPs plasmon absorbance is proportional to the concentration of captopril which allows the spectrophotometric sensing of this compound. The presented method is capable of determining captopril over a range of 0.20–2.75 μmol L^{-1} with a limit of detection 0.07 μmol L^{-1}. The relative standard deviation for eight replicate measurements of 1.00 and 2.50 μmol L^{-1} of captopril was 2.37% and 1.02%, respectively. The method was applied to the determination of captopril in pharmaceutical formulations with satisfactory results, which were in agreement with those of the official method.

Introduction

Captopril, (2S)-1-(3-mercapto-2-methylpropionyl)-L-proline (Fig. 1), is a synthetic dipeptide can be served as an angiotensin-converting enzyme inhibitor, which reduces peripheral resistance and lowers blood pressure [1–3]. In addition, this compound is used in the management of heart failure, following myocardial infraction and to preserve the kidney function in diabetic nephropathy [4,5]. Other uses for captopril have also been reported including decreasing high blood pressure caused by blood vessels in the kidneys, decreasing symptoms of cystinuria and reducing rheumatoid arthritis symptoms [6]. The influence of this medicine has been reported in cancer treatment [5]. Despite its therapeutical usefulness, some adverse effects were reported for captopril, which included dry and persistent cough, angiodema, abdominal pain, constipation, dizziness, fatigue, headache, loss of appetite, nausea and vomiting, difficulty breathing, fainting, sore or swollen throat, teratogenecity and acute renal failure. In rare instances, liver dysfunction, skin yellowing (jaundice) and significant loss of zinc in urine due to the intake of captopril have been also reported [1,5,6]. Toxicity from captopril is uncommon, but when occurs, it may include bone marrow suppression and proteinuria. Serious

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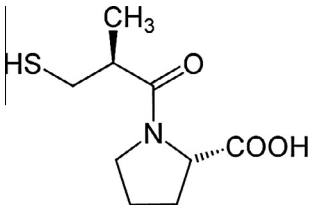

Fig. 1. Chemical structure of captopril.

toxicity has occurred primarily when captopril was given in high doses to patients with collagen vascular disease or renal insufficiency [4]. Since, captopril is applied in a broad range of pharmaceutical products the development of a simple and accurate assay method for the drug quality control is desired.

In order to determine captopril many methods based on different principles have been reported, including chromatography [7–10], spectrophotometry [3,11–13], fluorimetry [14], FT-Raman spectroscopy [15], atomic absorption spectrometry [16], electrochemistry [17–22], volumetry [23], chemiluminescence [5] and capillary electrophoresis [24].

However, captopril usually quantified in pharmaceuticals by volumetry or high performance liquid chromatography (HPLC) methods, as described in the United States Pharmacopeia [25]. Although these methods show good precision but volumetric procedure is time-consuming and HPLC requires expensive and complex equipment as well as consuming significant amounts of solvents. Therefore, a simple and reliable method is required for the low cost and rapid determination of captopril in the pharmaceutical formulations.

Nanotechnology and nanoparticles (NPs) are increasingly recognized for their potential applications in different branches of science including materials scientists interested in synthesizing samples with novel structures and optical properties, analytical chemists who develop new molecular sensing schemes, biomedical researchers seeking to target and kill cancer cells, and engineers interested in creating high speed circuits [26,27].

Among these, metal NPs such as Au and Ag have attracted much attention because of their unique optical properties, which derive from the localized surface plasmon resonance, a collective oscillation of the conduction electrons of metal NPs when their frequency matches that of the incident electromagnetic radiation. This characteristic of some metal NPs make strong absorption band that typically observed in the visible to near-UV region of the spectrum or increased scattering intensity of the radiation which occurred at certain wavelengths [28]. This phenomenon leads to new competencies for chemical sensing that are both useful and extraordinarily sensitive for detection of various species [29].

AgNPs are probably the most important metal NPs which offer excellent surface plasmon resonance properties exhibiting strong and well-defined colors and easy visualization of color change between individual and wellspaced NPs compared to aggregate ones; yellow to brown [30]. The colorimetric assays based on plasmon resonance of AgNPs have received considerable attention because of their excellent analytical performance that exhibited in terms of selectivity and sensitivity as well as of their extreme simplicity and low cost since this kind of method does not require any expensive or sophisticated instruments.

AgNPs with distinctive sizes and shape could be synthesized using different manners, such as the chemical reduction of silver ions with or without stabilizing agents, thermal decomposition in organic solvents and photoreduction in reverse micelles [31]. Since chemical reduction of silver ions has attracted more attention, the seeking for an appropriate reducing agent for developing an efficient and safe AgNPs based method is considerable.

In this study, the stable and monodispersive AgNPs with intensified plasmon resonance were synthesized in situ using a simple, rapid and eco-friendly procedure by applying ascorbic acid as reducer and sodium dodecyl sulfate (SDS) as stabilizer. The presence of captopril has a strong effect on plasmon absorbance of AgNPs which could be used for quantitative analysis of captopril in pharmaceutical formulations.

Experimental

Apparatus

All absorption measurements and absorption spectra were performed using PG instrument UV–vis spectrophotometer model T80 (UK) equipped with 1 cm matched quartz cells. Transmission electron microscopy (TEM) image of prepared AgNPs was recorded from a Zeiss Em10C instrument (Germany) and was operated at 80 kV. The particle size distribution was measured by dynamic light scattering (DLS) with a Malvern instrument (U. K.) model Nano ZS (red badge) ZEN 3600.

Reagents and materials

All chemicals were of analytical reagent grade and deionized water was used throughout. A 5.0×10^{-5} mol L^{-1} of captopril stock solution was prepared by dissolving 0.0108 g of captopril (Sigma) in water and diluting to 1 L in a volumetric flask. Working solutions were prepared by adequate dilution of the stock solution. A 0.025 mol L^{-1} of ascorbic acid solution was prepared daily by dissolving 0.4403 g of ascorbic acid (Merck) in water and diluting to 100 mL in a volumetric flask. The NaOH solution, 0.1 mol L^{-1}, was prepared by dissolving 2.0 g of NaOH (Merck) in water and diluting the solution to 500 mL. A 0.05 mol L^{-1} of SDS solution was prepared by dissolving 7.209 g of SDS (Merck) in water and diluting to 500 mL with water in a volumetric flask. A solution of $AgNO_3$, 1.0×10^{-3} mol L^{-1}, was prepared by dissolving 0.0425 g of $AgNO_3$ (Merck) in water and diluting to 250 mL in a volumetric flask. This solution was stored in amber glass bottles and protect from direct light.

Recommended analytical procedure

The appropriate amounts of NaOH, captopril, ascorbic acid, SDS and $AgNO_3$ solutions were placed respectively in a 10 mL volumetric flask. Then the solution was diluted to the mark immediately and mixed. An aliquot of the solution was transferred within 7 min into a 1 cm spectrophotometric cell and the plasmon resonance absorbance of AgNPs was measured at 400 nm. A blank solution was also run under the same procedure without adding captopril.

Preparation of pharmaceutical samples

Commercial tablets purchased from the local drugstores with nominal contents of 25 and 50 mg of captopril were analyzed. For the determination of captopril in each sample, twenty tablets were weighted and finely grounded. An accurately weighed amount of powder was dissolved in deionized water, mixed well for 20 min using a magnetic stirrer to aid dissolution and then filtered. The filtrate was diluted with water to obtain the appropriate concentration of captopril within the working range for determination using analytical procedure.