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Spectrophotometric determination of L-cysteine by using polyvinylpyrrolidone-stabilized silver nanoparticles in the presence of barium ions

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ABSTRACT

In this article a simple and selective colorimetric probe for cysteine determination using silver nano particles ($AgNP_S$) is described. The determination process was based upon the surface plasmon resonance properties of polyvinylpyrrolidone-stabilized $AgNP_S$. Interaction of $AgNP_S$ with cysteine molecules in the presence of barium ions induced a red shift in the surface plasmon resonance (SPR) maximum of AgNPs, as a result of nanoparticle aggregation. Consequently, yellow color of AgNP solution was changed to pink. The linear range for the determination of cysteine was 3.2–8.2 μM ($R = 0.9965$) with a limit of detection equal to 2.8 μM (3σ). The proposed method was successfully applied to the determination of cysteine in human plasma samples. Acceptable recovery results of the spiked samples confirmed the validity of the proposed method.

1. Introduction

Cysteine (2-amino-3-mercaptopropanoic acid, $HSCH_2CH(NH_2)COOH$) is a sulfur-containing α-amino acid. It is a biologically important amino acid which is a dominant constituent of the most of peptide and protein molecules, in fact it has been proposed that all known organisms contain cysteine in their proteins [1]. It also exhibits autooxidative properties in the presence of metal ions [2]. Contribution of cysteine in some pathological diseases such as development of skeletal muscle wasting and immunodeficiencies in several diseases of unrelated etiology [3] makes it important to find out a simple and sensitive strategy to quantify the plasma concentration of this amino acid. Most of reports about the determination of cysteine in biological samples and drugs involve separation techniques or require a derivatization step such as gas chromatography with mass spectrometry (GC–MS) [4,5], high performance liquid chromatography (HPLC) [6,7], spectrofluorimetry [8,9] and chemiluminescence [10,11]. Unfortunately most of these methods are rather expensive, complicated and time-consuming.

Considering the attractive features of nanotechnology, development of new nanoparticle based sensors has been one of the most important issues in various fields of science and technology in recent years. Emergence of various colorimetric sensors has revolutionized the efforts for developing, sensitive and accurate nanoparticle based sensors for detection of biomolecules in physiological samples. Gold nanoparticles (AuNPs) have been intensively developed as probes or sensors for the determination of aminothiols [12–16], but recently silver nanoparticles ($AgNP_S$) have been used as an inexpensive alternative for colorimetric detection of these molecules [17,18]. Compared to AuNPs the methods using AgNPs are more affordable. Silver nanoparticles have gained popularity owing to their unique chemical and physical properties such as high extinction coefficient and narrow plasmon resonance band in the visible region [19–23]. Hence a colorimetric method based on the shift in the maximum of plasmon resonance band of AgNPs is proposed as an alternative approach for the determination of cysteine levels in human plasma samples. The strategy used in this work was based on three main steps, a) preparation of stabilized AgNp solution using the well known polyvinylpyrrolidone (PVP) as stabilizer, b) addition of analyte (cysteine) solution to the AgNp solution and c) applying Ba^{2+} cations as a binding agent between cysteine-capped AgNps. Aggregation of nanoparticles would be the final result, which could be used as a colorimetric sensor for selective determination of cysteine molecules. Few reports using similar strategy could be found in literature, which suffer from using toxic cations [14,24] and limited applicability in simple matrix aqueous media [25]. In addition PVP, that used in this study, is an excellent stabilizing agent and dispersant amongst the other organic counterparts [26,27] which permits

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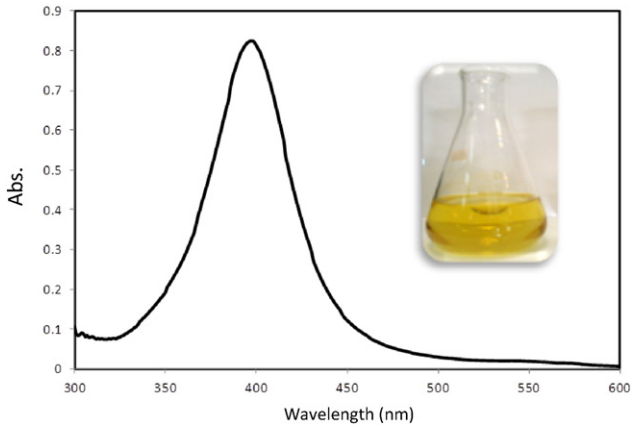

Fig. 1. UV–vis spectrum of PVP-stabilized AgNP solution. Inset shows a photo of AgNP solution prepared in this work.

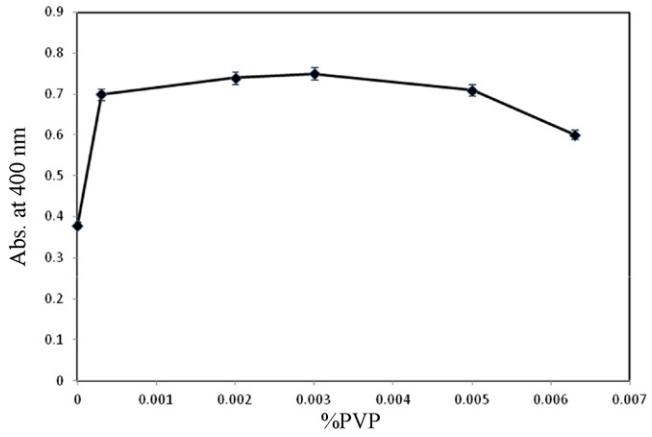

Fig. 2. Effect of the amount of PVP on the absorption peak of AgNPs.

formation of a highly stabilized nanoparticle sol. This feature, allows accurate determination of the analyte in samples with high electrolyte content and complex matrix.

In this study, considering the green chemistry aspects, an alkaline earth cation was considered as aggregation inducer, Ba^{2+} was selected amongst the other alkaline earth cations as the best choice for this purpose. In the presence of Ba^{2+}, color of the AgNp solution was changed from yellow to pink on addition of certain amounts of cysteine. The proposed method allowed the naked eye assessment of cysteine and colorimetric determination of it in human plasma samples. The whole

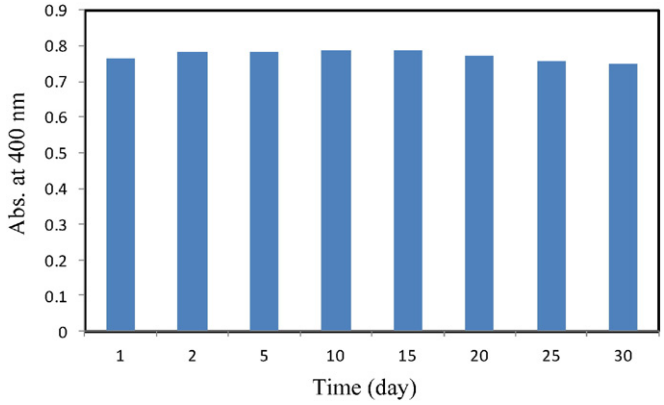

Fig. 3. Bar graph showing the AgNP absorbance (400 nm) at various time intervals.

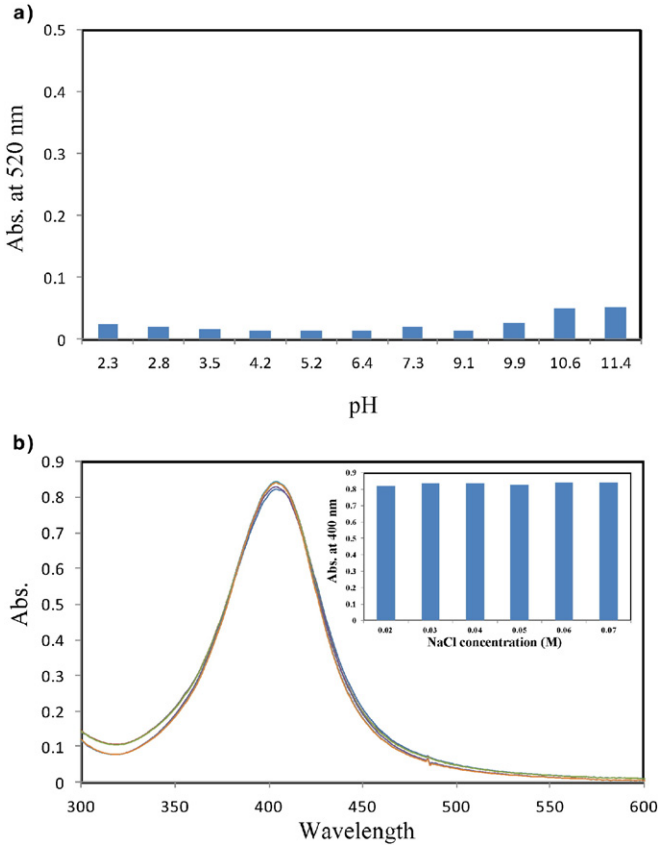

Fig. 4. (a) Variations in the absorbance of AgNPs at 520 nm versus pH. (b) Absorption spectra of AgNP solutions in the presence of various amounts of NaCl (inset shows the absorbance at 400 nm versus NaCl concentration).

process takes only 15 min at room temperature and as mentioned above is free of using toxic cations.

2. Experimental

2.1. Reagents

Deionized doubly distilled water was used throughout all experiments. Silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), barium chloride and chloride salt of the other cations were purchased

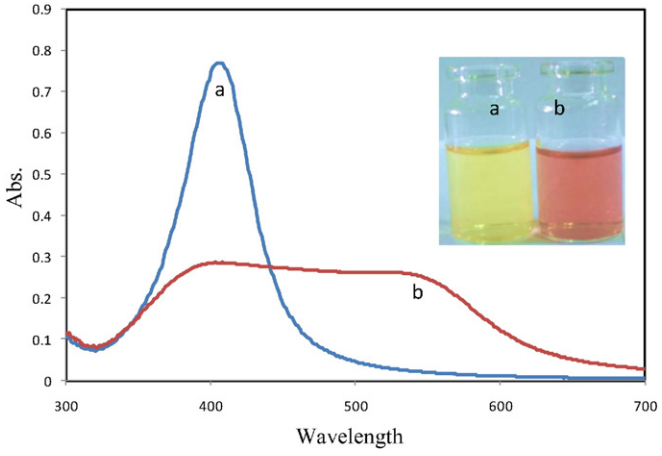

Fig. 5. Absorption spectra of PVP-stabilized AgNP solution in the absence (a) and presence (b) of 7 μM cysteine. Measurements were made at the presence of 3.0×10^{-4} M Ba^{2+}. Inset shows the photos of the corresponding solutions.