



Simple silver nanoparticle colorimetric sensing for copper by paper-based devices

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ARTICLE INFO

Article history:

Received 20 April 2012

Received in revised form

14 June 2012

Accepted 15 June 2012

Available online 20 June 2012

Keywords:

Silver nanoparticle
Colorimetric sensing
Paper-based devices
Copper

ABSTRACT

The first investigation of silver nanoparticle (AgNP) colorimetric sensing of Cu^{2+} by paper-based analytical devices (PADs) is reported here. AgNP colorimetric sensing for the detection of Cu^{2+} was first characterized by UV–visible spectroscopy. The –SH groups on homocysteine (Hcy) and dithiothreitol (DTT) were used to modify the AgNP surface whereas the –COOH and – NH_2 functional groups have strong affinity to Cu^{2+} relative to other ions in solution. The plasmon resonance absorption peak intensity at 404 nm decreased and a new red-shifted band at 502 nm occurred in the presence of Cu^{2+} . Paper devices coated with the modified AgNP solution changed from yellow to orange and green-brown color after the addition of Cu^{2+} due to nanoparticle aggregation. The color intensity change as a function of Cu^{2+} concentration gave a linear response in the range of 7.8–62.8 μM ($R^2=0.992$). The limit of naked-eye detection is 7.8 nM or 0.5 $\mu\text{g L}^{-1}$. A color change observed by the naked eye with the addition of Cu^{2+} can be clearly differentiated from the other metals (As^{3+} , Cd^{2+} , Co^{2+} , Hg^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} , Mg^{2+} , Mn^{2+} , Ca^{2+} , Fe^{3+} , Na^+ , and K^+) at 15.7 μM . The use of different flow directions in the PADs and μPADs for Cu^{2+} detection was also demonstrated. Levels of Cu^{2+} in real water samples were measured using the paper devices to be $2.9 \pm 0.24 \mu\text{M}$ (tap water) and $3.2 \pm 0.30 \mu\text{M}$ (pond water), respectively, and were within error of the values measured using an atomic absorption spectrometer ($2.8 \pm 0.08 \mu\text{M}$ in tap water, and $3.4 \pm 0.04 \mu\text{M}$ in pond water). Thus, this work shows the successful integration of paper devices and AgNP colorimetric sensing as a simple, rapid, easy-to-use, inexpensive and portable alternative point-of-measurement monitoring.

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1. Introduction

The development of simple, rapid, and inexpensive detection method for diagnostics and environmental monitoring is still needed in developing and undeveloped countries for sustainable development in public health [1]. Currently, paper devices including paper strip tests, paper-based assays, and paper-based microfluidics are attractive for portable point-of-measurement (POM) monitoring and on-site detection due to advantages which include low cost, portability, ease of use, high speed, and low reagent and sample consumption [2–4]. Furthermore, paper provides a high surface area/high optical contrast substrate for colorimetric detection. Paper devices are also suited for use by nontechnical personnel. Finally, paper devices are made from naturally abundant, biodegradable and inexpensive materials (i.e.,

cellulose) [5,6]. Most commercial paper devices use colorimetric detection and have been applied for qualitative and/or semi-quantitative analyte detection [1,7–11]. For colorimetric sensing, analyte flow is directed along the paper matrix by capillary action, and analyte then reacts with a label or organic dye in the test zone. The assay results are quantified by comparing the color hues and/or intensities generated by unknown analytes to known analyte concentrations. Nontechnical personnel can interpret the result by the naked eye in many cases. Paper devices therefore do not require external instrumentation for interpretation or mechanical forces to drive flow.

Gold nanoparticle (AuNP) colorimetric probes have been widely used for colorimetric assays because their extinction coefficients are high relative to common organic dyes [12–17]. AuNP colorimetric sensing has been used with two approaches. First, the result can be determined by the accumulation of an intense red color that is associated with the color of AuNPs with a diameter of 10–50 nm. The most common example of this detection mode is the commercial immunochromatographic test strip [18,19]. Alternatively, the color change of AuNPs due to aggregation or

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dispersion with the addition of analyte can be used [20,21]. For example, Lu and coworker first reported the AuNP aggregation in a dipstick assay [22]. Their devices detect analyte by immersing a lateral flow device immobilized with aggregated AuNPs into a testing solution. The blue aggregated AuNPs turned red when dispersed by the analyte in a concentration dependent manner. Inspired by Lu's work, Zhao and coworkers demonstrated the feasibility of using a AuNP-based colorimetric sensing platform on paper devices [23].

Recently, silver nanoparticles (AgNPs) have been used as an alternative colorimetric sensing system due to lower cost and higher extinction coefficients than AuNPs [24]. The high molar extinction coefficient of AgNPs leads to improved visibility based on the difference in optical brightness and increased sensitivity of UV–visible spectroscopic detection [25]. Although colorimetric applications of AgNP aggregation provide high sensitivity and selectivity for the determination of analytes such as histidine [26], homocysteine [25], cysteine [27], mercury ions [28,29], and nickel ions [30] using UV–visible spectroscopy, AgNP colorimetric sensing for copper ion by PADs has not been reported [31]. The only analytical application of AgNPs on cellulose paper that has been reported is for the determination of Rhodamine 6 G dye using Raman Spectroscopy [32]. Therefore, the aim of this study was to investigate AgNP colorimetric sensing for PADs. The utility of AgNP aggregation on paper devices was demonstrated for the detection of copper (II) ions. Copper ions play an important role in living organisms and industry but excess intake of copper ions can be toxic [33]. High copper levels in blood and liver are implicated in Alzheimer's disease and inflammatory disorders. Moreover, excessive copper in children is associated with hyperactive behavior, learning disorders such as dyslexia, and ear infections. The World Health Organization (WHO) prescribes the maximum allowable levels of copper (II) ions in drinking water at 1.3 mg L^{-1} or $20.5 \mu\text{M}$ [34]. In this work, homocysteine and dithiothreitol bind to AgNPs ($\sim 10 \text{ nm}$ in diameter presenting yellow color) through Ag–S bonds, and then binding between Cu^{2+} and the surface-modified AgNPs results in their aggregation (Fig. 1A). The aggregation of AgNPs in the presence of copper (II) ions leads to a decrease in the surface plasmon resonance absorption peak and the formation of a new red-shifted peak. Both paper-based assay devices and paper-based microfluidic devices for Cu^{2+} detection using AgNP colorimetric sensor were studied. After the addition of Cu^{2+} solution into paper devices, the yellow color of AgNPs changed to orange or green–brown depending on the Cu^{2+} concentration. Finally, our devices were successfully applied to the detection of Cu^{2+} in real water samples.

2. Experimental

2.1. Chemicals and Materials

All chemicals used in experiment were analytical reagent (AR) grade and solutions were prepared using high pure water with a resistance of $18 \text{ M}\Omega \text{ cm}^{-1}$. Homocysteine (Hcy), dithiothreitol (DTT), cysteine (Cys), glutathione (Glu) and metal ions (As^{3+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , K^+ , Mg^{2+} , Mn^{2+} , Na^+ , Ni^{2+} , Pb^{2+} and Zn^{2+}) were bought from Sigma–Aldrich (St. Louis, Missouri). AgNP solution was obtained from Sensor Research Unit at Department of Chemistry, Chulalongkorn University, Thailand. Whatman No.1 filter paper was bought from Cole-Parmer (Vernon Hills, IL). All glassware was thoroughly cleaned with freshly prepared 1:1 HCl/ HNO_3 and rinsed with Mill-Q $18 \text{ M}\Omega \text{ cm}^{-1}$ water prior to use. All metal ion stock solutions were prepared in 0.1 M HNO_3 . Working standard solutions of metal ions were

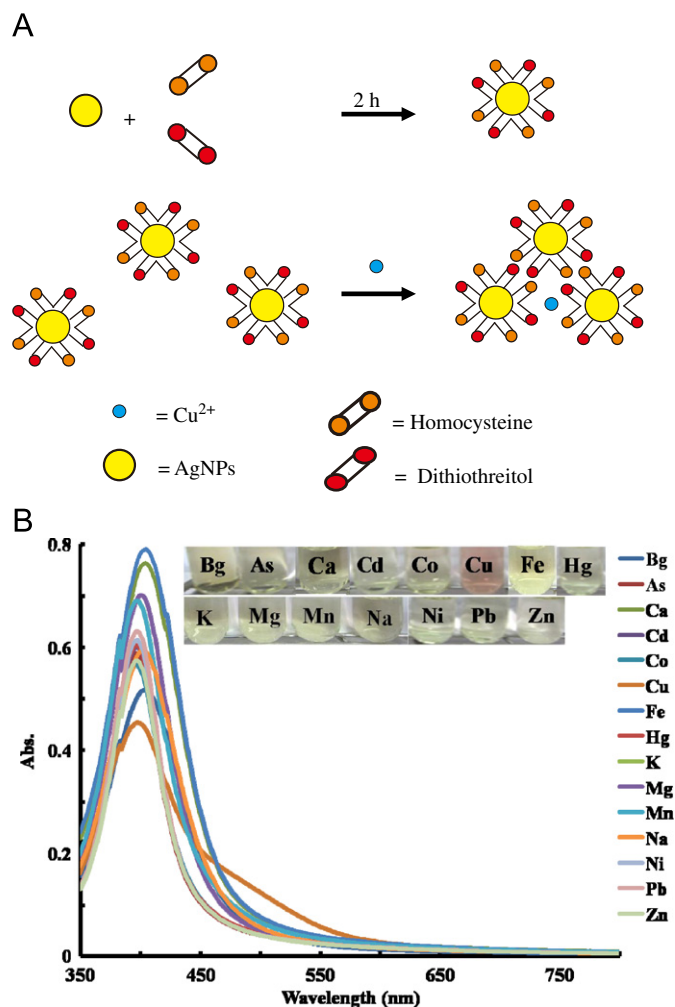


Fig. 1. (A) Schematic of aggregating process of AgNPs induced by adding Cu^{2+} and (B) UV–visible spectra and photos of Hcy-DTT-AgNPs with metal ions (7.8 nM of Cu^{2+} and $1.6 \mu\text{M}$ of other metals).

prepared daily by appropriate dilution of $157 \mu\text{M}$ stock solutions with 0.1 M phosphate buffer pH 8.0.

2.2. Instrumentation

UV–visible absorption spectra were recorded by a UV–visible spectrometer (Lambda 35, Perkin Elmer Instruments, USA) using quartz cuvettes (1-cm pathlength). Photographic results were recorded using a digital camera (PowerShot S95, 10.1 Megapixels, Canon). An atomic absorption spectrometer (AAS) with a hollow cathode lamp and standard air/acetylene flame (Analyst 300, Perkin Elmer Instruments, USA) was used for atomic absorbance measurements. A hollow cathode lamp was used under the following operations conditions: wavelength: 324.8 nm ; slit-width: 0.70 nm ; lamp current: 25 mA .

2.3. Synthesis of the modified AgNPs

AgNPs were synthesized using our previously reported methods using the chemical reduction process [25]. Sodium borohydride and methyl cellulose solution were used as the reducing agent and stabilizer, respectively. The shapes and particle size distributions of the AgNPs with nominal mean diameters of 10 nm were measured using TEM.

The Hcy-DTT-AgNP solution was prepared using self-assembly of the aminothiols on the AgNP surface. A yellow 0.1 mM AgNP

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