



Contents lists available at ScienceDirect

# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: [www.elsevier.com/locate/saa](http://www.elsevier.com/locate/saa)

## Colorimetric detection of manganese(II) ions using gold/dopa nanoparticles



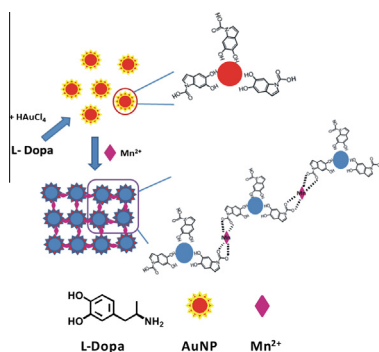
Kannan Badri Narayanan, Hyun Ho Park\*

Department of Biochemistry, School of Biotechnology, Yeungnam University, Gyeongsan 712 749, South Korea

### HIGHLIGHTS

- Facile colorimetric detection of Mn(II) ions by dopa-capped gold nanoparticles.
- Synthesis of AuNPs is cost-effective and eco-friendly without toxic chemicals.
- Ratio of absorbance ( $A_{700}/A_{550}$ ) was linear against the concentration of  $[Mn^{2+}]$  ions.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 11 January 2014  
 Received in revised form 5 April 2014  
 Accepted 17 April 2014  
 Available online 26 April 2014

#### Keywords:

Gold nanoparticles  
 Metal ions  
 Dopa  
 Manganese(II)  
 Sensor  
 Eco-friendly

### ABSTRACT

We report here a one-pot, greener, eco-friendly strategy for the synthesis of gold nanoparticles using L-dopa. The as-prepared dopa-functionalized gold nanoparticles (AuNPs/dopa) can detect low concentrations of manganese(II) metal ions in aqueous solution. The binding forces between dopa and  $Mn^{2+}$  ions cause dopa-functionalized gold nanoparticles to come closer together, decreasing the interparticle distance and aggregating it with a change in color of colloidal solution from red to purplish-blue. Dynamic light scattering (DLS) analysis showed a decreased surface charge on the surface of gold nanoparticles when exposed to  $Mn^{2+}$  ions, which caused cross-linking aggregation. Transmission electron microscopic (TEM) images also revealed the aggregation of gold nanoparticles with the addition of  $Mn^{2+}$  ions. The extinction ratio of absorbance at 700–550 nm ( $A_{700}/A_{550}$ ) was linear against the concentration of  $[Mn^{2+}]$  ions. Thus, the optical absorption spectra of gold colloidal solution before and after the addition of  $Mn^{2+}$  ions reveal the concentration of  $Mn^{2+}$  ions in solution.

© 2014 Elsevier B.V. All rights reserved.

### Introduction

Nanomaterials are nanodimensioned materials with a size of <100 nm that exhibit unique optical, electronic, magnetic, and catalytic properties that differ from those of their bulk materials, making them potential candidates for utilization in detection of organic and inorganic analytes including metal ions and organic

analytes such as DNA [1–3], antibodies, aminothiols, proteins [4], cancer cells and neurons [5]. Among several sensing nanomaterials that have been reported to date, gold nanoparticles (AuNPs) are commonly used owing to their biocompatibility and low cytotoxicity, as well as their unique shape- and size-dependent optical properties. Though, the past decade follows several analytical approaches such as atomic absorption spectroscopy (AAS) and inductively coupled plasma-optical emission spectroscopy (ICP-OES) for detection of metal ions. Some analytical strategies have utilized the properties of metal nanoparticles such as fluorescence,

\* Corresponding author. Tel.: +82 53 810 3015; fax: +82 53 810 4619.  
 E-mail address: [hyunho@ynu.ac.kr](mailto:hyunho@ynu.ac.kr) (H.H. Park).

color, SPR, and electrochemistry. However, metal nanoparticles based colorimetric assays are widely applied for detection of metal ions owing to their simplicity, portability and real-time detection.

Bulk gold normally appears yellow in color due to its reflection of visible light. However, as its size decreases, the color becomes pinkish-red owing to its absorption of visible light at around 550 nm, which corresponds to the collective oscillation frequency of plasmon resonance frequency within the gold metal. The intrinsic properties of gold nanoparticles (AuNPs) are attributed to their size, shape, and crystal structure. Unlike in bulk gold, there is a gap between the valence band and conduction band in nanodimensioned gold particles. In 1857, Faraday prepared colloidal gold solution with deep red solution via reduction of  $\text{HAuCl}_4$  with white phosphorus in a two-phase carbon disulfide ( $\text{CS}_2$ )-water mixture [6]. The growth of gold nanoparticles using citrate as reductant was later reported using Turkevich's method [7]. During the last few decades, several methodologies for the synthesis of gold colloids that are applicable in diagnostics, therapeutics, sensors, and catalysis have been explored. Among several applications, the optical properties of AuNPs are of primary importance for the development of colorimetric sensors. The strong color of the metal nanoparticles is caused by surface plasmon absorption. In 1908, Gustav Mie revealed the reason for the hues of colloidal solution by solving Maxwell's equation for the absorption and scattering of electromagnetic radiation by spherical particles [8]. The light absorption by metallic nanoparticles is the coherent oscillation of the surface conduction band electrons excited by interaction with the electromagnetic field, which is known as surface plasmon resonance (SPR) and does not occur in individual atoms or bulk material [9].

The aggregation of AuNPs (>3.5 nm diameter) induces interparticle surface plasmon coupling, resulting in a visible color change from red to blue at nanomolar concentrations. This color change aids in the utilization of plausible absorption-based colorimetric sensing of any target analyte that induces AuNPs aggregation [10,11]. Thus, strategies based on nanoparticle aggregation have attracted a great deal of attention. Since the surface of AuNPs can be easily functionalized with various ligands, it is possible to modulate the interaction of external ions with stabilizing functional groups for development of diverse metal sensors. Gold nanoparticles exhibit higher extinction coefficients, as well as size or distance-dependent optical properties. The aggregation/dispersion states of AuNPs show changes in color when observed by the naked eye, enabling easy detection of DNA [12,13], protein [14,15], and metal ions [16,17]. Upon aggregation, spherical AuNPs undergo red-shifts of the SPR band due to increased size, which are used to sense analytes based on colorimetric assays. Several cross linking and non-cross-linking aggregations of AuNPs have been reported to have sensing ability.

Several biocompatible molecules such as proteins, amino acids, and sugars are used as reducing and capping agents in the synthesis of metal nanoparticles [18,19]. The use of L-dopa in protein engineering has recently been increasing in protein engineering due to its structural similarity with the natural amino acid tyrosine. Dopa has multifunctional groups including amino, carboxylic and hydroxyl groups, which have the ability to reduce metal ions such as  $\text{Au}^{3+}$  and  $\text{Ag}^+$  to metal nanoparticles. Manganese (Mn) is an essential trace element for both plants and animals that is most stable in the 2+ valence state.  $\text{Mn}^{2+}$  activates many enzymatic reactions in carbohydrate metabolism and in the metabolism of organic acids, nitrogen and phosphorous. Although it is required for humans, Mn deficiency is associated with lipid and carbohydrate metabolism, growth retardation and reproductive failure in adults and ataxia and skeletal abnormalities in neonates [20]. Additionally, higher concentrations can cause adverse neurological effects, and high levels of manganese (>14 mg/l) in drinking water

can cause manganism, which is characterized by a Parkinson-like syndrome [21]. Mn is also a Toxic Release Inventory (TRI) chemical, and some of its compounds are also listed as air contaminants by the Occupational Safety and Health Administration (OSHA). In 1973, the Food and Nutrition Board of the National Research Council (NRC) determined the safe and adequate daily dietary intake of Mn to be 2–5 mg/day for adults [22]. Herein, we describe the synthesis of gold nanoparticles using L-dopa (L-3,4-dihydroxyphenylalanine) and the subsequent utilization of gold/dopa nanoparticles (AuNPs/dopa) to detect and quantify manganese ( $\text{Mn}^{2+}$ ) ions.

## Experimental

### Chemicals and reagents

L-3,4-dihydroxyphenylalanine (L-dopa) and manganese(II) chloride ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) were purchased from Sigma-Aldrich (USA). Chloroauric acid ( $\text{HAuCl}_4$ ) was purchased from Alfa Aesar Chemicals (South Korea). All experiments were carried out in deionized Milli-Q (18.2  $\Omega$ ) water.

### Preparation of dopa-capped gold nanoparticles

A total of 50 ml aqueous L-dopa solution (100  $\mu\text{M}$ ) at pH 6.5 was stirred at 80 °C for 30 min with the addition of 1.5 ml of  $\text{HAuCl}_4$  (6 mM) and then cooled to room temperature to prepare dopa-functionalized gold nanoparticles (AuNPs/dopa). The as-synthesized gold colloidal solution was further characterized and also directly exposed to various concentrations of metal ions for colorimetric assays.

### Characterization of L-dopa-capped gold nanoparticles

The reduction of gold ions to gold nanoparticles was monitored using UV-Vis spectroscopy (Beckman Coulter DU-730) and visual observation. Additionally, the morphology and size of as-synthesized AuNPs/dopa were characterized by TEM analysis of samples that had been placed on carbon-coated copper grids and dried prior to observation using a Hitachi (Model: H-7600) microscope at an accelerating voltage of 120 kV. Furthermore, the dynamic light scattering (DLS) method was employed to measure the size and surface charge of nanoparticles and the interparticle interactions. The hydrodynamic diameter and zeta potential of AuNPs/dopa were characterized using a Zetasizer Nano series (Malvern Instruments) equipped with a He-Ne laser ( $\lambda = 633 \text{ nm}$ ) and operated at a scattering angle of 173°. Powder X-ray diffraction (XRD) was conducted to determine the crystallinity of gold nanoparticles. The powdered nanoparticles were measured in transmission mode on a PANalytical X'pert PRO X-ray diffractometer (Netherlands) at a voltage of 40 kV and a current of 30 mA with  $\text{Cu K}\alpha 1$  radiation (1.541 Å). Samples were scanned in the region of  $2\theta$  from 30° to 85°. The nanocrystallite size was calculated using Scherrer equation [23]. Fourier transform infrared spectroscopy (FTIR) measurements were performed to identify the functional groups involved in the formation and stabilization of dopa-functionalized AuNPs. The AuNPs/dopa in the solution were separated using high-speed centrifugation (25,000g) for 20 min and then washed twice using sterile deionized water. Finally, the dried pellets were ground with KBr and analyzed on a Jasco FTIR 5300 spectrophotometer in transmittance mode over 4000–400  $\text{cm}^{-1}$ .

### Colorimetric detection of manganese(II) ions using AuNPs/dopa sensor

To demonstrate the detection of metal ions using AuNPs/dopa, a stock solution of 10 mM manganese(II) chloride was prepared.

Download English Version:

<https://daneshyari.com/en/article/7672061>

Download Persian Version:

<https://daneshyari.com/article/7672061>

[Daneshyari.com](https://daneshyari.com)