Sensors and Actuators A 253 (2017) 41–48

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

Surface plasmon resonance based fiber optic sensor for the detection of cysteine using diosmin capped silver nanoparticles

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ARTICLE INFO

Article history:
Received 3 June 2016
Received in revised form 7 October 2016
Accepted 16 November 2016
Available online 18 November 2016

Keywords:
Silver nanoparticles
Diosmin
Green synthesis
Cysteine sensor
Fiber optic sensor
Surface plasmon resonance

ABSTRACT

A simple green method to synthesize silver nanoparticles (AgNPs) is described where diosmin acts as reducing and capping agent. Formation of diosmin capped silver nanoparticles (Dios-AgNPs) was characterized using UV–vis spectroscopy, X-ray diffraction, TEM, Raman imaging and FTIR analysis. Investigations on the biosensing of Dios-AgNPs among various amino acids showed excellent response towards cysteine. Further an SPR based fiber optic sensor for cysteine was fabricated and its sensitivity, selectivity and limit of detection were investigated and reported. The fiber optic sensor was developed by coating a thin film of silver over the unclad core of the fiber and then coated with Dios-AgNPs. The sensor has advantages of low cost of production, fast response, high selectivity and sensitivity. The sensor can be used for online monitoring and remote sensing applications.

1. Introduction

Green synthesis of metal nanoparticles is of great importance because of the eco-friendly approach [1]. Wide applications of nanomaterials cause increased toxicity issues, raising concern to human health and environment. Green synthesis is an efficient way to overcome these issues by the choice of nontoxic capping agents for the stabilization of the nanoparticles. Green synthesized nanoparticles were reported for its various applications [2,3]. Silver and gold nanoparticles were extensively synthesized using different green strategies and studied their properties because of potential applications in biomedical field [4–7]. Silver nanoparticles show unique Surface Plasmon Resonance (SPR) band which was utilized in biosensing applications [8,9]. SPR of silver nanoparticles can be tuned by using different functionalizing agents [10–12]. Stabilizing agents play critical roles in determining biocompatibility and sensing properties of the nanoparticles [13].

Diosmin is a glycosylated polyphenolic compound, commonly found in fruits and vegetables, and is used in the pharmacological formulation of some drugs [14]. Diosmin is clinically used as a vascular protector for the treatment of hemorrhoids and venous leg ulcers [15], anti-inflammatory and inhibitor of prostaglandin synthesis [16] and a potential drug for cancer treatment [17]. It is reported to have antihyperglycaemic activity by stimulating insulin production from the existing β-cells of the pancreas [18] Diosmin shows very good tolerability and is considered as a safe, non-toxic drug [19]. Functionalizing silver nanoparticles with diosmin through green synthesis may be potentially useful for biomedical applications.

Detection of cysteine is important as it plays a crucial role in a variety of cellular functions, such as protein folding, metabolism, detoxification etc. [20–23]. Cysteine deficiency causes many syndromes, such as hair depigmentation, edema, liver damage, skin lesions and lethargy. Recent researches have revealed that raised levels of cysteine in vivo are involved in neurotoxicity [24]. Various methods for cysteine determination have been reported, such as fluorometry [25], chemiluminescenc [26], electrochemical voltammetry [27] and fluorescence-coupled HPLC techniques [28]. However, these methods usually suffer from high cost, low sensitivity and specificity, and involve complicated sample pretreatment [29]. Therefore, developing a new method is of great interest for the quick and specific detection of cysteine. Silver and gold nanoparticles are widely used for detection of cysteine using colorimetric technique as well as spectroscopic methods [29,30]. Recently, a colorimetric sensor was developed for detection of cysteine using triangular silver nanoprisms based on the ability of cysteine in providing a blue shift of the dipole plasmon resonance absorption [31].

Over the last few years, fiber optic based LSPR sensors have received considerable attention in biochemical sensing because of their simplicity, low cost and high sensitivity [32]. Silver nanopar-

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http://dx.doi.org/10.1016/j.sna.2016.11.019
0924-4247/

ticles (AgNPs) sensors are a specific class of sensors that have received much interest due to the ease of functionalization with organic ligands, more over they have improved photostability and tunable optical properties [21,33].

SPR based fiber optic sensors are being widely used for biosensing applications [34–39]. Recently, there are several reports on different methods to improve sensitivity of fiber optic sensor using different morphologies of optical fiber. LSPR of the metal nanoparticles can be tuned by surrounding materials. Optical fiber SPR sensor clubbed with LSPR of noble metals (Ag, Au) is getting considerable interest in the recent years [40–42]. Optical fiber sensors have many advantages over conventional sensors, which include immunity to electromagnetic interference, small and compact size, sensitivity, remote sensing, and ability to be multiplexed into various textile structures [43].

In this paper, we demonstrate a novel green synthesis of Dios-AgNPs and investigated its sensing properties towards cysteine and also developed a SPR based fiber optic sensor for cysteine sensing.

2. Materials and methods

2.1. Materials

Silver nitrate ($AgNO_3$, analytical-reagent-grade) and NaOH were purchased from Merck, India. Diosmin was purchased from Sigma Aldrich, India and all the experiments were conducted using Milli-Q water.

2.2. Synthesis of silver nanoparticles

Diosmin, a flavonoid glycoside was used as the capping agent due to its biomedical importance as a drug. In the present work diosmin in aqueous NaOH solution was used as the reducing agent for $AgNO_3$, considering that $AgNO_3$ has strong oxidation capacity under alkaline conditions [44]. Diosmin is a poorly water soluble flavonoid but shows good solubility in alkaline pH [45]. Silver nanoparticles were synthesized using a one pot facile synthesis method. 1 mM Diosmin solution was prepared in 0.01 M aqueous NaOH solution and 2 ml of this solution was added drop wise to an aqueous solution of 1 mM $AgNO_3$ mixed under vigorous magnetic string for 15 min at room temperature. A colour change was observed indicating the formation of silver nanoparticle and the solution was incubated overnight and used for characterization. Synthesis procedure was carried out at different pH conditions.

2.3. Optical fiber preparation

Sensor region was prepared by removing plastic clad over a length of 3 cm from the middle of the fiber using acetone. The remaining plastic clad was burn out in the region and washed with distilled water. After cleaning, the unclad portion of the fiber was coated with silver layer to 40 nm thickness using thermal evaporation technique in a vacuum coating unit kept at 5×10^{-6} mbar pressure (Fig. 1). The sensing surface was then coated with green synthesized silver nanoparticles by dip coating method and then dried at 60 °C in hot air oven. A small glass cell was used as the sensing chamber (Fig. 1) in which the fiber optic sensor region was inserted. Different concentrations of cysteine solutions (0–100 μM) were prepared and passed into the sensing chamber.

2.4. Characterizations

UV–vis absorption measurements were done using Jasco V-650 spectrophotometer. FT-IR spectra were recorded with Shimadzu model: IR prestige 21, with ZnSe ATR crystal (Pike technologies) spectrometer. JEOL- 2010 electron micro scope operating at 200 kV was used for HRTEM measurements. XRD measurement was done using Model PANalytical X-ray diffractometer. The cys sensing setup for SPR wavelength shift measurements consisted of a white light source (Model HL2000, Ocean Optics., USA) with spectral emission between 360 and 1700 nm and a miniature fiber optic spectrometer (USB 2000+, Ocean Optics, USA) with spectral response from 300 to 1000 nm. The signal from the spectrometer was interfaced with a computer and the spectral graphs were recorded separately. Multimode plastic cladded silica fiber step index optical fiber of length 25 cm, diameter 600 μm (thor lab USA) and with a numerical aperture 0.39 was used with cleaved ends. The refractive index of the core was 1.449.

3. Result and discussion

3.1. Charecterisations of Dios-AgNPs

Formation, stability and pH dependence of AgNPs were monitored using UV–vis spectral analysis. Fig. 2 shows the UV–vis spectra of diosmin and Dios-AgNPs. Diosmin shows an absorption peak at 364 nm [14] while AgNPs synthesized utilizing diosmin shows broad absorption peak at 410 nm which pertaining to the localized surface plasmon resonance (LSPR) of AgNPs [9]. AgNPs synthesized using this method show good stability over time. LSPR peak of the nanoparticles did not change even after one month of synthesis (Fig. 2b). Broadness of the peak results from the combina-

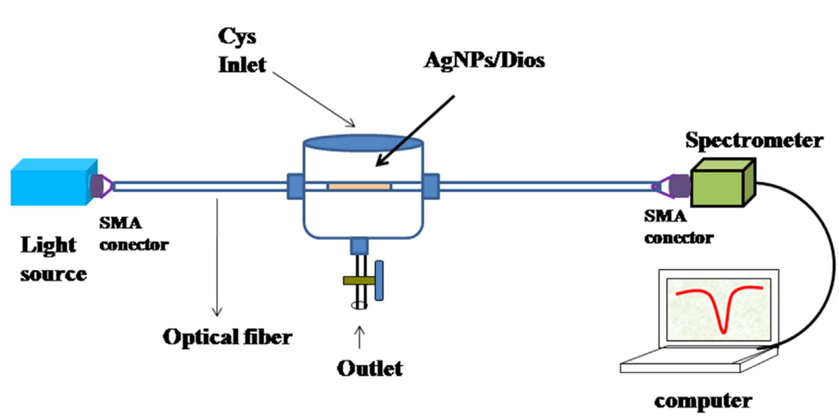

Fig. 1. Schematic representation of SPR based fiber optic cysteine (Cys) sensor. Plastic cladded silica fiber (diameter of 600 μM) is connected to the light source and spectrometer using SMA connector. Clad removed sensing region of the fiber plated with silver and coated using Dios-AgNPs was inserted inside the flow cell.