Sensors and Actuators B 183 (2013) 144–149

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

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

Green synthesis of silver nanoparticles and their application for the development of optical fiber based hydrogen peroxide sensor

Chandrakant K. Tagad[a,b], Sreekantha Reddy Dugasani[c], Rohini Aiyer[b], Sungha Park[c], Atul Kulkarni[b,*], Sushma Sabharwal[a,b,**]

[a] Biochemistry Division, Department of Chemistry, University of Pune, Pune 411007, India
[b] Centre for Sensor Studies, Department of Electronic Science, University of Pune, Pune 411007, India
[c] Sungkyunkwan Advanced Institute of Nanotechnology (SAINT) and Department of Physics, Sungkyunkwan University, Suwon 440746, South Korea

ARTICLE INFO

Article history:
Received 27 December 2012
Received in revised form 21 March 2013
Accepted 25 March 2013
Available online 2 April 2013

Keywords:
Green synthesis
Silver nanoparticles
Locust bean gum
Hydrogen peroxide
Optical fiber sensor

ABSTRACT

Green synthesis of nanoparticles and their applications in sensing area is of great interest to the research community. Herein we report a green approach for the synthesis of silver nanoparticles (Ag NPs) by using locust bean gum (LBG) polysaccharide and its application to detect hydrogen peroxide (H_2O_2). Ag NPs were synthesized by mixing optimized weight percent of LBG with a known quantity of silver nitrate ($AgNO_3$) at 55–60 °C. Synthesized Ag NPs were characterized by UV–vis spectroscopy and atomic force microscopy (AFM). The size of synthesized Ag NPs was in the range of 18–51 nm depending upon the concentration of LBG and $AgNO_3$. Further, a low cost and portable optical fiber based sensor using LBG stabilized Ag NPs was developed for monitoring the H_2O_2 concentration as low as 0.01 mM.

1. Introduction

Nanoparticles (NPs) have received considerable attention in recent years due to their wide range of applications in the field of catalysis, optoelectronics, chemical sensing, bio-sensing and biotechnology [1,2]. In most of the cases, the chemical route is adopted for the synthesis of various NPs; however, this has potential hazards to health and environment. Hence in recent years the green synthesis approach has emerged as one of the active areas of research. Green synthesis of NPs has several advantages over chemical synthesis, such as simplicity, cost effectiveness as well as compatibility for biomedical and pharmaceutical applications [3]. Green synthesis of silver nanoparticles (Ag NPs) by using plant leaf extracts, seed extracts, plant latex, microorganisms and some biopolymers have been reported earlier [4]. Polymers such as polyethylene glycol [5], polyvinylpyrrolidone (PVP) [6], polyacrylonitrile (PAN) [7], poly(methyl methacrylate) [8], polyaniline [9] and poly (vinyl alcohol) [10]. have been widely used as reducing and stabilizing agent for synthesis of well-dispersed Ag NPs. Biopolymers like natural rubber [11], polysaccharides [12], cellulose [13], gum acacia polymer [14], and starch [15] have been used as matrices or stabilizers for the synthesis of NPs because of their biocompatibility and nontoxic nature. However, locust bean gum (LBG) has not been explored yet as a reducing and stabilizing agent for Ag NPs.

Hydrogen peroxide (H_2O_2) is widely used in water treatment plants, for disinfection, cleaning microcircuits and other industries [16]. The determination of H_2O_2 level is of great importance, as it is found to induce many kinds of cellular damages even at relatively low concentration. Also its concentration needs to be monitored especially in food and pharmaceutical industries and clinical laboratories [16–18]. Detection of H_2O_2 has been carried out using several analytical techniques like spectrophotometer [19] and chemiluminescence [20]. Several reports are available on application of Ag NPs for detection of H_2O_2 by amperometric [21] as well as electrochemical [22,23] methods. In addition H_2O_2 sensing based on decolorization of Ag NPs using spectrophotometer has also been reported [18,24]. However, these instruments are bulky, costly and not portable. Therefore there is a need to develop a portable and easy-to-use sensor for the detection of H_2O_2.

Currently fiber optic sensors have gained considerable attention in bio-chemical fields due to their unique characteristics such as small size, light weight and high flexibility [25]. Most of the fiber optic chemical sensor principles are based on the monitoring of

* Corresponding author. Tel.: +91 20 25601414; fax: +91 20 25699841.
** Corresponding author at: Centre for Sensor Studies, Department of Electronic Science, University of Pune, Pune 411007, India. Tel.: +91 20 25696061; fax: +91 20 25691728.
E-mail addresses: atul.css@unipune.ac.in (A. Kulkarni), ssab@chem.unipune.ac.in (S. Sabharwal).

0925-4005/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2013.03.106

absorbance, reflectance, luminescence, change in refractive index and light scattering [26–29].

In the present work, we describe the green synthesis of Ag NPs by using LBG. Further, we report the application of Ag NPs for the development of a portable optical fiber based sensor to monitor variations in the H_2O_2 concentration.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$, analytical-reagent-grade) was purchased from Sisco Research Laboratory, India. 30% (w/v) H_2O_2 solution was purchased from Qualigens Fine Chemicals, India. LBG extracted from the seeds of *Ceratonia siliqua* was purchased from Sigma Aldrich India and used without any pretreatment. All solutions used in the experiments were prepared using deionized water.

2.2. Synthesis of silver nanoparticles

For the synthesis of Ag NPs, 0.1 gm of LBG was dissolved in 100 ml deionized water by heating at 80 °C under constant stirring for dissolution of LBG to achieve 0.1% (w/v) solution. After dissolution, LBG solution was brought to room temperature. 25 ml of Ag NO_3 (1 mM) solution was then added to the LBG solution in Erlenmeyer flask at room temperature and the mixture was kept at 60 °C in an incubator to carry out the reaction of Ag NPs synthesis. Aliquots from the reaction bulk were withdrawn at 6, 24, 48, and 72 h of time interval and the synthesis of Ag NPs was monitored by UV–vis spectroscopy. The effect of $AgNO_3$ concentration on Ag NPs synthesis was evaluated by carrying out reaction at different concentrations of $AgNO_3$ (1 mM–5 mM) where the LBG concentration was kept constant at 0.1% (w/v). Similarly the effect of LBG concentration on the synthesis of Ag NPs was studied by carrying out reactions at various concentrations of LBG (0.1 to 0.4% (w/v)) where the $AgNO_3$ concentration was kept constant at 1 mM. The effect of pH on the synthesis of Ag NPs was studied by carrying out reactions at different pH (pH 4, 6, 8, 10 and 12) using 0.1% LBG and 1 mM Ag NO_3.

2.3. Characterization

UV–vis analysis was performed on Shimadzu 1800 UV spectrophotometer operated at a resolution of 1 nm as a function of reaction time during the synthesis of Ag NPs. A control was run in which only $AgNO_3$ solution was used without the reducing agent. AFM images were obtained by Digital Instruments Nanoscope III (Vecco, USA) with a multimode fluid cell head by liquid tapping using a NP-S oxide-sharpened silicon nitride tip (Vecco, USA).

2.4. Fabrication of optical fiber sensor

The polymer optical fiber (POF) was used to fabricate a U bent sensing probe for the detection of H_2O_2. The protecting jacket and clad of 2 cm was removed [26] and the un-cladded region was bent in U-shape keeping the bend diameter to 5 mm to form the U-bent fiber optic sensing probe. A similar U-bent sensing probe was reported earlier for humidity sensing [27,28] by our group. The RED light is launched in the fiber by using transmitter (660 nm, SFH 756 V, Siemens) and the light through the fiber is received by the photo detector (200–1100 nm, SFH350, Siemens) as depicted in Fig. 1. The sensing region of fiber optic probe was then dipped in a cell containing reaction mixtures (Ag NPs and different concentrations of H_2O_2 in 1:1 proportion) and the output voltage from the detector was recorded as a function of time using a multimeter (2000, Keithley, USA). The reaction was monitored for up to 1200 s. Different concentrations of H_2O_2 (0.01 mM, 0.1 mM, 1 mM and 10 mM) were used to measure the sensing response. The experiments were carried out at normal room temperature and pressure.

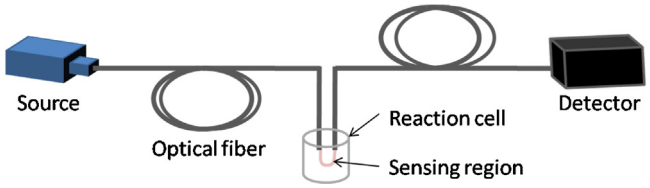

Fig. 1. Experimental set up for optical fiber based sensor for detection of hydrogen peroxide.

3. Results and discussion

3.1. Synthesis of silver nanoparticles

In this study low cost LBG has been used as a reducing and stabilizing agent for the synthesis of Ag NPs. Scheme 1 gives a brief illustration of the synthesis of Ag NPs embedded in LBG polymer matrix. The mixture of optimized concentrations of LBG and $AgNO_3$ was incubated for 6–72 h around 60 °C to achieve the synthesis of Ag NPs (orange color spheres). LBG is a polyhydroxylated biopolymer consisting of (1 → 4)-linked β-D-mannopyranose backbone with branch points from their 6-positions linked to α-D-galactose (that is, 1 → 6-linked α-D-galactopyranose) [30]. Polyhydroxylated macromolecules possess inter and intramolecular hydrogen bonding resulting in network formation within the polymer chain which acts as templates for nanoparticle growth [15]. The extensive number of hydroxyl groups and a hemiacetal reducing ends on LBG polysaccharide act as active reaction centers to facilitate the reduction of Ag^+ to Ag^0. Ag NPs thus formed, get embedded and stabilized within the polymer matrix.

UV–vis absorption spectra of Ag NPs synthesized using 1 mM $AgNO_3$ solution and 0.1% LBG at 60 °C, recorded as a function of reaction time is shown in Fig. 2. The appearance of a single, bell shaped, surface plasmon band at the wavelength of maximum absorbance at 424 nm, indicated the formation of Ag NPs [15].Absorbance was found to increase as a function of reaction time and was highest for 72 h of incubation. This increase in absorption intensity with time

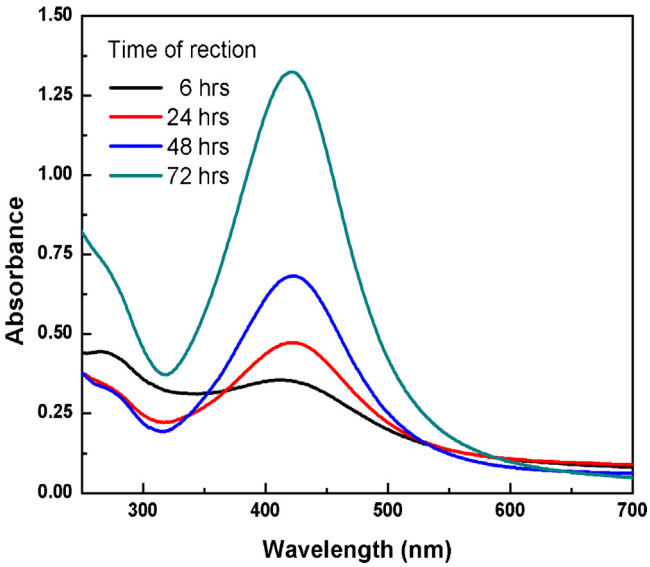

Fig. 2. UV–vis spectra recorded as a function of reaction time for Ag NPs synthesized using 1 mM $AgNO_3$ and 0.1% LBG solution at 60 °C.