Carbohydrate Polymers 106 (2014) 154–159

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Facile and rapid thermo-regulated biomineralization of gold by pullulan and study of its thermodynamic parameters

Anirban Roy Choudhury[a,*], Ankit Malhotra[a], Paramita Bhattacharjee[b], G.S. Prasad[a]

[a] CSIR – Institute of Microbial Technology (IMTECH), Council of Scientific and Industrial Research, Sector 39A, Chandigarh 160 036, India
[b] Food Technology and Biochemical Engineering Department, Jadavpur University, Kolkata 700032, India

ARTICLE INFO

Article history:
Received 25 November 2013
Received in revised form 2 January 2014
Accepted 20 January 2014
Available online 7 February 2014

Keywords:
Pullulan
Biomineralization
Gold nanoparticles
Thermodynamics
Kinetics

ABSTRACT

A novel method for the production of gold nanoparticles (AuNPs) using pullulan as reducing and stabilizing agent has been developed. Quasi-spherical shaped AuNPs in the range of 50–100 nm were produced at three different temperature regimes 80 °C, 90 °C and 100 °C as characterized using UV–vis spectrophotometer, TEM and DLS. Study of reaction kinetics and thermodynamic parameters indicated that the reaction between pullulan and chloroauric acid for AuNPs formation followed first order reaction kinetics and higher temperature was favorable for the synthesis of smaller sized AuNPs. FT-IR data analyses, provided an insight towards the mechanism of gold nanoparticle formation which suggested that, the free —CH_2OH groups of pullulan molecule were oxidized to carboxylate ions resulted in formation of AuNPs whereas the basic skeletal structure of pullulan remained unaltered. This study may open up new avenues for synthesis of tailor made biogenic AuNPs with possible application in biomedical field.

1. Introduction

Nanobiotechnology is growing at fast pace and considered as an emerging field for the development of metal nanoparticles. These metallic nanoparticles have drawn significant attention due to their unique physicochemical properties and potential for high end applications including medicine, electronics, imaging technology, optics and diagnostics (Sau, Rogach, Jackel, Klar, & Feldmann, 2010). Therefore, synthesis of nanoparticles with controlled shape and size with desired level of purity and yield is of utmost importance in the area of nano-science and technology. Predominantly, chemical and physical methods have been utilized for rapid synthesis of different metallic nanostructures including gold nanoparticles, silver nanocubes, zinc nanowires, copper nanotubes *etc.* (Chen, Chi, Zhang, Chen, & Chen, 2007; Sun & Xia, 2002; Yang et al., 2007). However, recent reports suggested that toxic effects of several harsh chemicals and solvents used in these type of methods have promoted utilization of biological agents for the synthesis of functional metal nanoparticles.

Mostly, soil and marine microflora and plant extracts were exploited to provide green route for the biosynthesis of different metal nanoparticles (Sharma et al., 2012). However, synthesis of nanoparticles using microbial and plant system is a slow process with low yield and often resulted in the production of polydisperse nanoparticles. Moreover, considering the cumbersome methodology and tedious process of down-streaming required to obtain nanoparticles using microbial and plant system, there is a need to develop a facile, green and rapid process for the synthesis of metal nanoparticles by utilizing materials that are non-hazardous and does not cause cellular toxicity. Polysaccharides may act as an ideal alternative to earlier reported biological agents (Park, Hong, Weyers, Kim, & Linhardt, 2011).

Offlate, polysaccharides, such as guar gum, starch, dextran, cellulose, and chitosan have been used as biological agents for production of gold nanoparticles (Engelbrekt et al., 2009; Huang & Yang, 2004; Pandey, Goswami, & Nanda, 2013; Uryupina, Ya Vysotskii, Matveev, Gusel'nikova, & Roldughin, 2011; Wang, Zhan, & Huang, 2010). However, all these polysaccharides have inherent problems of low solubility (Uryupina et al., 2011), high viscosity and also require derivitization and hence, cannot be employed in large scale production of gold nanoparticles (Ma, Yang, Li, & Yang, 2005; Park, Hong, Weyers, Kim & Linhardt, 2011). Moreover, requirement of additional stabilizing agents often make these processes more complex (Engelbrekt et al., 2009).

To address these challenges, a facile, rapid and green method for the synthesis of stable gold nanoparticles using pullulan as reducing and stabilizing agent was developed. The gold nanoparticles produced were characterized by measuring time dependent change in surface plasmon resonance (SPR) using UV–vis spectrophotometer, transmission electron microscopy (TEM) and dynamic light scattering (DLS). Further, a mechanism of gold nanoparticle formation

* Corresponding author. Tel.: +91 172 6665312; fax: +91 1722695215.
E-mail addresses: anirban@imtech.res.in, wb.anirban@gmail.com (A.R. Choudhury).

0144-8617/$ – see front matter
http://dx.doi.org/10.1016/j.carbpol.2014.01.072

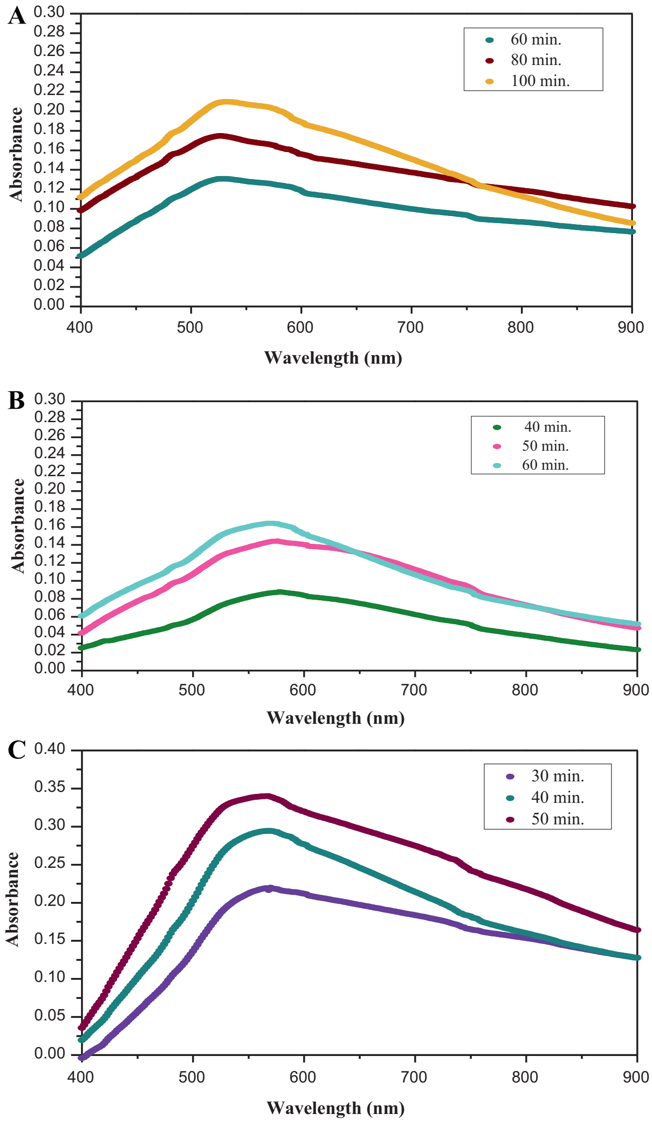

Fig. 1. Surface plasmon resonance data of gold nanoparticle formation after different time interval at (A) 80 °C (B) 90 °C (C) 100 °C.

and stabilization by pullulan has also been hypothesized based on comparative analysis of FT-IR data. The kinetics of formation of the gold nanoparticles has been investigated and the thermodynamic parameters such as Gibb's free energy, enthalpy and entropy have also been studied at different temperature regimes. To the best of our knowledge, this is the first report of gold nanoparticle synthesis using pullulan and also first attempt to understand the kinetic and thermodynamic parameters of metal nanoparticle formation using a biological agent.

2. Experimental

2.1. Synthesis of gold nanoparticles

To begin with the process of synthesizing gold nanoparticles, initially $HAuCl_4$ solution was made by adding weighed quantity of chloroauric acid (Loba Chemie Pvt. Ltd., India) in Milli-Q water. Further, pH of $HAuCl_4$ solution was adjusted to 5.3 by using 1 M NaOH (HiMedia Laboratories Pvt. Ltd., India) solution. Then, pullulan (Hayashibara Co. Ltd., Japan) was weighed accurately (0.5% w/v) and added directly to $HAuCl_4$ solution (250 mg/L, pH 5.3). The reaction mixture was incubated at three different temperatures

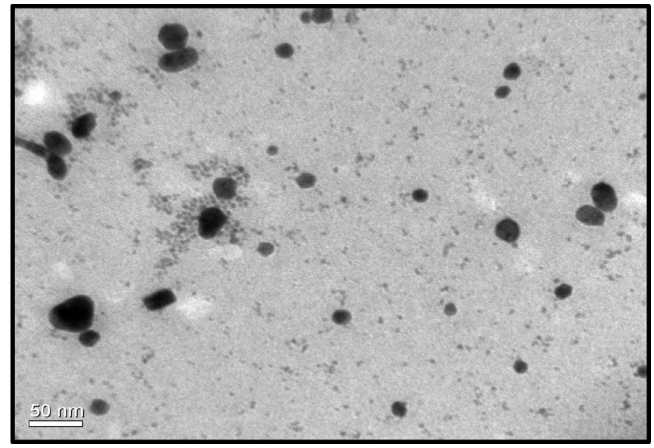

Fig. 2. Transmission electron micrograph of gold nanoparticles obtained at 100 °C illustrated quasi-spherical shaped nanoparticles.

(80 °C, 90 °C and 100 °C). Temperature regimes below 80 °C showed insignificant reaction rates and therefore higher temperature zones were investigated.

2.2. Characterization of gold nanoparticles

Spectral analysis of gold nanoparticles was carried out in a quartz cuvette of 1 mm path length by using HITACHI U2900 spectrophotometer. Scans were performed and SPR data were generated for samples obtained at different temperatures (80 °C, 90 °C and 100 °C) after regular time interval at a wavelength ranging 200–900 nm. Morphological analysis and particle size distribution of the nanoparticles produced under different conditions were studied using TEM and DLS as described by Malhotra et al. (2013). In addition, FT-IR spectra of both pure pullulan and pullulan stabilized gold nanoparticle were carried out in accordance to Kanmani and Lim (2013).

3. Results and discussion

3.1. Synthesis and characterization of gold nanoparticles

Synthesized gold nanoparticles were qualitatively analyzed by visual checking of color formation, appearance of purple color considered as the formation of gold nanoparticles. To further confirm the formation of gold nanoparticles in support of visual indication, quantitative analysis was performed by measuring time dependent variation in SPR using UV–visible spectrophotometer. Initially the reaction was carried out at room temperature and the rate of formation of gold nanoparticles was observed to be slow. Increase of temperature to 50 °C did not cause significant enhancement in the rate of reaction. Hence, time dependent SPR data were generated at elevated temperatures of 80 °C, 90 °C and 100 °C. Increase in absorption maxima was recorded during time course study in all the cases at different temperatures indicating increase in number of nanoparticles formation with time. Formation of gold nanoparticles starts after 60 min of incubation at 80 °C as indicated by the absorption maxima at 530 nm and plateau formation appeared after 90 min of incubation (Fig. 1A). At 90 °C, SPR showed formation of gold nanoparticles after 40 min of incubation with absorption maxima at 570 nm (Fig. 1B). Also, the fastest rate kinetics was observed at 100 °C where gold nanoparticles formation commenced after 30 min of incubation time and plateau appeared after 50 min of incubation with absorption maxima recorded at 570 nm (Fig. 1C). The overall data indicate that the AuNPs formed by pullulan showed maximum absorption at a wavelength