



Green controlled synthesis of monodispersed, stable and smaller sized starch-capped silver nanoparticles



Oluwatobi S. Oluwafemi^{a,*}, Ncapayi Vuyelwa^a, Manfred Scriba^b, Sandile P. Songca^c

^a Department of Chemistry and Chemical Technology, Walter Sisulu University, Mthatha Campus, Private bag XI, Mthatha 5117, Eastern Cape, South Africa

^b Council for Scientific and Industrial Research (CSIR), National Centre for Nano-structured Materials, Pretoria, South Africa

^c Faculty of Science, Engineering, and Technology, Walter Sisulu University, PO Box 19712, Tecoma, East -London, South Africa

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ABSTRACT

A completely green and large scale controlled synthesis of stable, smaller sized (< 5 nm) and monodispersed quasi spherical starch-capped silver nanoparticles (Ag NPs) using maltose as the reducing agent without any complexant or accelerator is presented. High concentration of the reducing saccharides produced via hydrolysis of maltose and partial hydrolysis of starch as the reaction time increases controls the particle diameter within the smaller size range.

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1. Introduction

Noble metal nanoparticles (NPs) have generated a lot of research interest in recent years. This is due to their unique electronic, optical, mechanical, magnetic and chemical properties which are significantly different from those of bulk materials [1]. These properties are being influenced by several parameters, most importantly their size and shape. Among these materials, interest in Ag NPs is very high due to their outstanding plasmonic activity, bacterial inhibitory and bactericidal effects as well as broad spectrum antibacterial activities compared with the other metal nanoparticles [2,3]. Thus Ag NPs have been used for wide range of applications ranging from medical, catalysis, sensors, to water treatment and so on [4–9]. Many synthetic methods have been established for the synthesis of Ag NPs. However, the chemical hazards to health and the environment associated with the toxic solvents, reducing agents and surfactants used, as well as some chemical processes followed during the syntheses have raised concerns. Hence, an environmentally friendly and sustainable green approach for the synthesis of Ag NPs is indispensable. Raveendral et al., [10] in their report outlined three main steps to be considered in the green synthesis of metal NPs which are (i) the choice of solvent medium used for the synthesis, (ii) use of environmentally benign reducing agent, and (iii) the choice of non-toxic material as stabilising agent. In addition, Markhalaf et al. [11] also emphasised the need

for synthetic approaches that are less dependent on the chemisorption of conventional stabilising ligands containing S, N or P. Based on these requirements, there have been few reports on the completely green synthesis of Ag NPs via a simple laboratory techniques/apparatus without the use of toxic materials as reducing agents, NH_3 as complexing agent or NaOH as an accelerator [10,12–15]. A common drawback of these few completely green methods is the difficulty in ensuring a high degree of monodispersity with respect to size and shape as well as cost effectiveness of the method for large scale production. In a very recent development Steinigeweg and Schlucker, based on extension of the classical Lee and Meisel synthesis, reported a simple method for controlling monodispersed Ag NPs using a glycerol–water mixture at 95 °C in the presence of sodium citrate as the reducing agent [16]. The particle sizes were in the range of 20–100 nm. Contrary to the bactericidal effects of ionic silver, the antimicrobial activity of colloidal silver particles are influenced by the dimensions of the particles; the smaller the particles, the greater the antimicrobial effect [17]. In addition smaller sized (≤ 5 nm) nanoparticles can offer enhanced antibacterial activity, catalysis, facilitation of renal clearance and DNA conjugation [18]. The most effective method for synthesising silver nanoparticles with smaller particle sizes is the chemical reduction of a silver salt solution using reducing agents such as NaBH_4 , citrate, tetrabutylammonium borohydride, and dimethylformamide [18–19]. However such reducing agents may be associated with environmental toxicity or biological hazards. Thus, developing a synthetic strategy for smaller sized Ag NPs with high degree of monodispersity in terms of size and shape via a completely green and cost effective method is of great

* Corresponding author. Tel.: +27 765 11 032 2.

E-mail address: oluwafemi.oluwatobi@gmail.com (O.S. Oluwafemi).

significance. We have recently reported the synthesis of gelatin-capped Ag-NPs via a completely green method [20]. By varying the precursor concentration and reaction time, the temporal evolution of the optical and structural properties of the Ag nanoparticles was monitored. As part of an effort to further reduce the particle diameter and increase the monodispersity, we herein report a large scale, simple completely green method for the controlled synthesis of stable and smaller sized (with mean diameter < 5 nm) starch-capped Ag NPs with a high degree of monodispersity. Maltose a non toxic disaccharide was used as the reducing agent without any complexant or accelerator. Contrary to other related reports on the completely green synthesis of Ag-NPs [10,13–15], smaller particles (< 5 nm) were obtained at the beginning of the reaction. The increase in the concentration of reducing saccharides in the reaction system via hydrolysis of maltose and the partial hydrolysis of starch played a major role in the synthesis of the as-synthesised smaller sized Ag NPs.

2. Experimental

The preparation is very easy, cost effective and straightforward. Briefly, 1.0 wt% of starch was added to 95 mL of distilled water under continuous stirring. A 1 M silver nitrate solution (5 mL) was added to the starch solution to obtain a Ag^+ /starch solution. This was followed by the addition of 10 mL of maltose solution (2 M) under continuous stirring. The solution was maintained at 75°C and allowed to react for several hours. Aliquots were taken at different time intervals to monitor the growth of the particles. The colour of the solution changed from colourless to light yellow indicating the formation of Ag NPs. A Perkin Elmer Lambda 20 UV–vis spectrophotometer was used to carry-out absorption spectra in the 200–1100 nm wavelength range, while a JEOL 2100 TEM operating at 200 KV was used for TEM and HRTEM measurements.

3. Results and discussion

Fig. 1A shows the UV–vis absorption spectra of the Ag NPs at different reaction times with characteristic silver surface plasmon resonance (SPR). The sharp SPR peak typically located around 400 nm for moderately large (10–40 nm) Ag NPs is absent in Fig. 1A. This UV–vis curve is consistent with that reported by Zheng et al. for the synthesis of smaller sized Ag NPs when NaBH_4 was used as the reducing agent [18]. The flat nature of the curve at 1 h is due to the low SPR intensity at this time in comparison to those at higher reaction times. The transmission electron microscopy (TEM) micrograph of the Ag NPs at 1 h reaction time (Fig. 1B) shows the presence of smaller particles in a neck-lace arrangement. The inset of Fig. 1C and the high resolution image (Fig. 1D), indicate that the particles are crystalline and are well distributed in this neck-lace arrangement. The particles are quasi-spherical with an average particle diameter of 3.70 ± 0.99 nm. The result shows the pronounced effect of using maltose as the reducing agent and the resultant partial hydrolysis of starch on the size of the obtained Ag NPs compared with report by Raveendran et al., [10] and other related methods which used glucose, [13–15] in which bigger average particle size were usually obtained at the beginning of the reaction. The solutions remained stable and well dispersed in water under air condition for some months with no sign of aggregation as evident by the lack of notable variation in the absorption spectra taken after long period of aging.

The possible chemical reaction involved in the formation of starch capped-maltose reduced silver nanoparticles is summarised in Scheme 1. In this reaction, hydrolysis of maltose gives two molecules of glucose, an aldehyde, which then reduces Ag^+ ions to

Ag^0 , and in the process the glucose is oxidised to gluconic acid. The half reactions and the standard reduction potentials for the reduction of Ag^+ with glucose are given in Scheme 2. The potential for the overall reaction is 0.750 V thus thermodynamically, the reaction is spontaneous. In order to increase the rate of this reaction and control the particle size, ammonia (NH_3) is usually added to the solution [21]. This produces the $\text{Ag}(\text{NH}_3)_2^+$ complex ion, a weaker oxidising agent with considerable smaller reduction potential than Ag^+ ion and also increases the reducing strength of glucose (Scheme 3). Thus reduction of silver ions to silver is more favourable in aqueous NH_3 solution. However, NH_3 is a very corrosive and hazardous chemical, thus its potential environmental and biological risks are a source of concern. In addition, the smallest particles obtained under these conditions are usually greater than 10 nm in size with some aggregation [20].

In our work, the hydrolysis of maltose increased the concentration of the reducing saccharides in the reaction system (Scheme 1). Thus, the number of H^+ ions released into the reaction system per hydrolysis increased (Scheme 4). This resulted in an increase in the rate of the reaction and partial hydrolysis of starch hence large number of smaller sized Ag NPs were produced at the beginning of the reaction as shown in Fig. 1. Therefore, the use of ammonia to lower the reduction potential of the Ag^+ ions was avoided. The TEM micrograph at 24 h reaction time (Fig. 2A) showed bigger monodispersed spherical particles with an average particle diameter of 5.52 ± 1.87 nm. High resolution TEM image revealed the crystallinity of the Ag NP and clear lattice fringe of face centred cubic (fcc) silver (111) with an inter-planar spacing of 0.23 nm (inset of Fig. 2A). We believed that as the reaction time increased, the rate of reduction increased as more H^+ ions are being released into the reaction system. This resulted in the production of smaller particles which are not effectively passivated due to the partial hydrolysis of starch thus, leading to the formation of larger particles. Fig. 2B presents the TEM micrograph and particle size distribution of the Ag NPs at 30 h reaction time. More than 50% of the particles are in the size range ≤ 4.5 nm. The particles are spherical and crystalline with average particle diameter of 3.99 ± 1.60 nm. The decrease in the particles size after 24 h indicates digestive ripening of the bigger particles. The high percentage of the smaller particles in the TEM micrograph compared to those at 24 h supports this. As the reaction time increased further (48 h), monodispersed, stable and smaller particles with narrow size distribution (2.47 ± 0.53 nm) were produced (Fig. 2C). This has been attributed to the increased in the acidity of the solution because more H^+ ions are being released in to the reaction system as the reaction time increased. At this high acidic medium starch hydrolysis is not significant anymore, thus the starch layer adequately passivate the surface of the nanoparticles. This prevents aggregation of the smaller particles. Stability of Ag-NPs at high acidic medium has also been reported by Singh et al., [22] and recently by Zhang et al. [23] The high resolution TEM image and electron diffraction of the particles at 48 h (Inset Fig. 2C) showed that they are single crystals with fcc structure. The non aggregation of the particles confirms that, the smaller starch capped Ag NPs obtained are quite stable. The TEM micrograph of the Ag NPs synthesised using glucose under the same condition at 48 h (Fig. 2D) as reported by Reveendran et al., [10] showed bigger particles with an average diameter of 6.89 ± 2.45 nm as compared to when maltose was used as the reducing agent. In addition, the particle sizes obtained under our synthetic method are smaller than those previously reported under completely green synthesis [10,13–15,20]. This shows that the hydrolysis of maltose which also led to the partial hydrolysis of starch played a major role in controlling the particle size within the smaller sized range. Since the synthetic procedure are entirely non-toxic, environmentally benign and produced smaller sized

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