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A Facile and Green Synthesis Route for the Production of Silver Nanoparticles in Large Scale

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Abstract

In the present work, a fast, green and simple synthesis method for the production of silver nanoparticles (AgNPs) is introduced. Silver nanoparticles are currently among the most widely used man-made nano materials, present in a wide range of consumer products. Green chemistry is characterized by careful planning of chemical synthesis of silver nanoparticles to reduce adverse outcomes. Synthesis of AgNPs was carried out at 100 ˚C temperature using glucose as reducing agent and starch as capping agent. Prepared AgNPs were characterized using transmission electron microscopy, UV-Vis spectrophotometry, Dynamic Light Scattering (DLS) and X-ray Diffraction (XRD) patterns. It was found that the synthesized AgNPs have an average diameter size of 50 nm. Further experiments showed that silver nanoparticles have good antibacterial properties and their production process is capable to scaling up. Due to the using of natural and low-cost materials, the production process is also environmental and eco-friendly.

Keywords: *Glucose, Green Chemistry, Silver Nanoparticle, Starch.*

1. INTRODUCTION

Colloidal silver because of its characteristic properties, such as good conductivity, chemical stability, catalytic and antibacterial activity has attracted much attention [1]. Silver is well known as a catalyst for the oxidation of methanol to formaldehyde, ethylene to ethylene oxide and it is widely used in real-time optical sensors for online detection of materials [2, 3]. Silver colloids are useful substrates for surface enhanced spectroscopy, since it requires an electrically conducting surface [4, 5]. One of the most effective applications of silver colloids and nano-particles is their potential antimicrobial property, so that they are toxic to various fungi, bacteria and viruses. In fact, it is well known that Ag ions and Ag-based compounds are highly toxic to micro-organisms, showing strong antibacterial effect on more than 12 species of bacteria. Silver has long been used as a disinfectant; for instance, the metallic silver has been used in treating of wounds and burns because of its toxicity to wide range of bacteria as well as limited toxicity to humans [6-10]. The properties of metal nanostructures strongly depend on their size and shape [4]. The synthesis of metal nanostructures with definite size and shape is very important especially for the research on their properties. The ability to control the size, shape and also distribution of the metal nanostructures, provides great opportunities to investigate of their properties such as catalytic and electro-optical attributes [11]. Various shapes of Ag nanostructures have been already synthesized. Also a variety of methods for the synthesis of silver nanostructures have been developed in aqueous and non-hydrolytic media. Generally, metal nanoparticles can be synthesized and stabilized by physical and chemical methods. The chemical routes, such as chemical reduction, electrochemical

techniques and green approach have been widely used [1, 12-20].

Green chemistry is an area of chemistry focused on the design of products and processes that minimize or eliminate the use and generation of hazardous and harmful materials[21, 22]. The idea of green chemistry was initially developed in 1990 A.D. [23]. The most important aspect of green chemistry is design of reaction. Design is a statement of human purpose and one cannot do design by accident. It includes novelty, planning and systematic conception. The 12 principles of green chemistry called "design rules" help chemists achieve the green products. Green chemistry is characterized by careful planning of chemical synthesis to reduce adverse outcomes[23, 24]. Preparation of green nanoparticles using b-D-glucose as the reducing agent was reported by Raveendran et al for the first time [25]. Here is a report on a simple, high speed, cost effective and ecofriendly preparation method for aqueous silver nanoparticles with the use of the natural and low-cost materials and available tools. The effect of concentrations of various reagents containing silver nitrate, glucose, and starch was also investigated.

2. MATERIALS AND METHODS

2.1. Reagents and Materials

Silver nitrate ($AgNO_3$, 99.8%) and D-glucose mono hydrous ($C_6H_{12}O_6.H_2O$, 99.9%) were purchased from Merck Chemicals. Water soluble starch was purchased from Sani Co., Iran. Fig. 1a and b show the structures of starch and glucose respectively [26, 27].

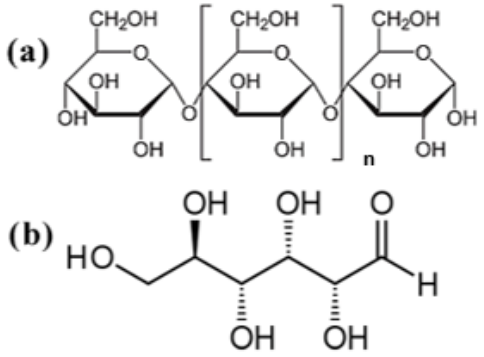


Figure 1. *Structures of starch (a), and glucose (b).*

2.2. Preparation of Silver Nanoparticles

AgNPs were prepared by chemical reaction process. Starch and b-D-glucose were used as capping agent and reducing agent respectively. 25 ml of 0.2 wt% starch solution in water was prepared and added to 10 ml of different concentrations of aqueous solution of silver nitrate according to table 1. The solution was stirred at 30 ℃ for about 2 min. 10 ml of 0.1 $mol.L^{-1}$ glucose solution in water was added to the solution of silver nitrate and the mixture was heated until boiling under continuous stirring. The solution presented as a pale yellow color at 80 ℃, indicating the initial formation of AgNPs. The time required to complete the reaction is less than 10 minutes.

In order to evaluate the effect of variables on the properties of synthesized AgNPs, further experiments were carried out. The concentration of silver nitrate solution, starch solution and glucose as reducing agent were optimized. Table 1, 2 and 3 show the synthesis conditions used for the optimization of silver nitrate, starch and glucose concentration respectively.

Table 1. *Synthetic conditions for the optimization of silver nitrate concentration.*

Sample	Silver nitrate		Starch		Glucose		λmax
	Volume (mL)	Concentration ($mol.L^{-1}$)	Volume (mL)	Concentration (wt%)	Volume (mL)	Concentration ($mol.L^{-1}$)	
S1	10	0.1	25	0.2	10	0.1	413
S2	10	0.001	25	0.2	10	0.1	414
S3	10	0.0001	25	0.2	10	0.1	417
S4	10	0.00001	25	0.2	10	0.1	417

Table 2. *Synthetic conditions for the optimization of starch concentration.*

Sample	Silver nitrate		Starch		Glucose		λmax
	Volume (mL)	Concentration ($mol.L^{-1}$)	Volume (mL)	Concentration (wt%)	Volume (mL)	Concentration ($mol.L^{-1}$)	
S1	10	0.1	25	4	10	0.1	419
S2	10	0.1	25	2	10	0.1	418
S3	10	0.1	25	1	10	0.1	418
S4	10	0.1	25	0.5	10	0.1	416
S5	10	0.1	25	0.1	10	0.1	412
S6	10	0.1	25	0.02	10	0.1	415

Table 3. *Synthetic conditions for the optimization of glucose concentration.*

Sample	Silver nitrate		Starch		Glucose		λmax
	Volume (mL)	Concentration ($mol.L^{-1}$)	Volume (mL)	Concentration (wt%)	Volume (mL)	Concentration ($mol.L^{-1}$)	
S1	10	0.1	25	0.2	10	0.4	407
S2	10	0.1	25	0.2	10	0.2	408
S3	10	0.1	25	0.2	10	0.1	410
S4	10	0.1	25	0.2	10	0.05	413

2.3. Bacterial Strains

Prepared colloidal AgNPs with various concentrations was individually tested against two gram negative and gram positive bacteria including *E. coli* ATCC 43894 and *S. aureus* ATCC 6538 respectively. Table 4 shows the concentrations of prepared colloidal AgNPs used for antibacterial tests.

Table 4. *Concentrations of colloidal AgNPs used for antibacterial tests.*

Sample	Concentration of AgNPs ($mol.L^{-1}$)
1	0.1
2	0.05
3	0.025
4	0.0125
5	0.00625
6	0.00312

2.4. Antibacterial Testing

The sterile blank disks were coated with various concentrations of synthesized colloidal AgNPs. Fresh cultures of bacteria was inoculated on nutrient broth and incubated for 24 hour at 37ºC. Adequate amount of nutrient agar was poured into the sterile plate until to be solid. The disks were impregnated in the inoculated agar. The inoculated plates were incubated at 37ºC for 24 h. Antibacterial activity was evaluated by measuring the inhibition zones in reference to the test organisms.

2.5. Characterizations

The UV–visible absorbance of silver colloidal solutions were recorded using a Shimadzu spectrophotometer, Japan. DLS analysis was performed on a Nanotrac Wave- Microtrac spectrophotometer. X-ray diffraction patterns were used to investigate the structure of silver nanoparticles. X-ray diffraction patterns were obtained using a Siemens D500 diffractometer, Germany. The morphology of AgNPs were studied using a Leo 906 Zeiss Transmission Electron Microscope.

3. RESULTS AND DISCUSSION

3.1. UV-Vis Spectroscopic Analysis

The formation of metal nanoparticles by reduction of the aqueous metal ions during exposure to the green reducing agents may be easily studied by UV-Vis spectroscopy. Also optical absorption spectrum of the silver nanoparticles can be used to estimate their size by considering the maximum absorption wavelength value (λ_{max}). On the other hand, shape and size

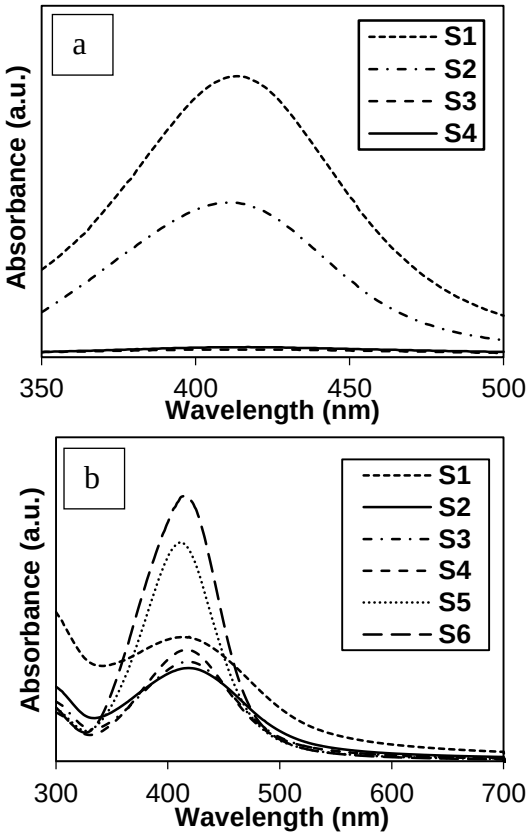
of AgNPs play an important role in the shift of the Surface Plasmon Resonance (SPR) band [28].

The UV-Vis spectra of prepared silver colloidal solution were recorded and analyzed for the investigation of the effect of silver nitrate, starch and glucose concentration on the maximum absorption wavelength value (λ_{max}) of silver colloidal solution. Fig. 2 shows the UV-Vis spectra of silver colloidal solutions prepared in different conditions. Fig. 2a shows the effect of silver nitrate concentration on the UV-Vis absorption spectrum of silver colloidal solution. The results indicate that decrease of silver nitrate concentration from 0.1 to 0.00001 mol.L^{-1} lead to increasing of the maximum absorption wavelength from 413 to 417 nm and which indicates the increasing of the size of synthesized AgNPs (Table 1). Therefore the best concentration of Ag ions is 0.1 mol.L^{-1}. It seems that, by decreasing silver nitrate concentration, the ratio of starch to silver nitrate is increased and the greater amount of starch surrounding silver ions could avoid glucose molecules to reach silver ions and reduce them. So the fast reduction of Ag^{+} nuclei is restricted and AgNPs with bigger sizes are achieved.

Figure 2b shows the effect of starch concentration on the λ_{max} of AgNPs colloidal solution. According to the results, with decreasing the concentration of starch from 4 to 0.1 wt%, the maximum absorption wavelength value is decreased from 419 to 412 nm which represents the decreasing of the size of nanoparticles and further decreasing of the starch concentration increases the λ_{max} value (Table 2). The smallest AgNPs (λmax= 412 nm) were formed in the presence of 0.1 wt% starch solution (Table 2). It should be noted that starch plays an important role in the formation of the AgNPs. By decreasing starch concentration, the ratio of starch to silver nitrate was decreased and the Ag ions could be exposed to glucose molecules effectively and reduce by them rapidly. But decreasing starch concentration more than definite amount (0.1 wt%) cause to starch to couldn't play its rule as a capping agent.

Due to the hydrolyzation of starch at 100°C, presenting hydroxyl primary groups can be oxidized by AgNPs and transform to aldehyde groups, which can be oxidized to carboxylic acids. The carboxylic acid groups stabilize the AgNPs by the formation of a negatively charged coating on their surface, that preventing their aggregation and increasing of their size.

The effect of glucose concentration, used as reducing agent, on the UV-Vis spectrum of silver colloidal solution was exhibited in Fig. 2c. As the concentration of glucose increased from 0.05 to 0.4 mol.L^{-1}, the SPR band was decreased from 413 to 407 (Table 3). The optimal concentration of glucose for the preparation of smallest AgNPs was obtained 0.4 mol.L^{-1}. Glucose is a poor reducing agent and increasing the amount of that leads to improvement of reduction reaction and decreasing the size of AgNPs.



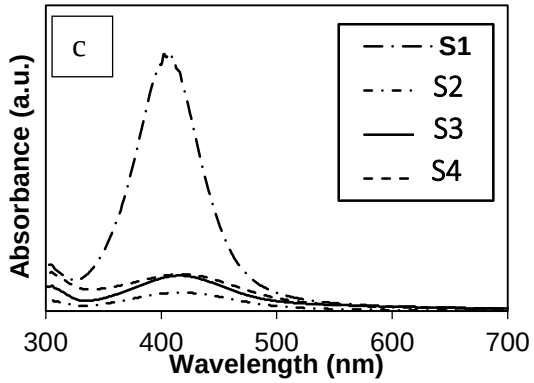


Figure 2. *UV-Vis absorption spectra of colloidal AgNPs prepared by different concentrations of silver nitrate (a), starch (b) and glucose (c).*

Equations 1 and 2 show the reactions of AgNPs synthesis. Fig. 3 shows a schematic of capped silver nanoparticles by starch chains.

$$Ag^{+}_{(aq)} + \text{starch}_{(aq)} \rightarrow [Ag(\text{starch})]^{+}_{(aq)} \quad \text{Eq. 1}$$

$$[Ag(\text{starch})]^{+}_{(aq)} + 2C_5H_{11}O_5 - CHO_{(aq)} \rightarrow \text{starch capped } Ag - NP_{(s)} + 2C_5H_{11}O_5 - COOH_{(aq)} \quad \text{Eq. 2}$$

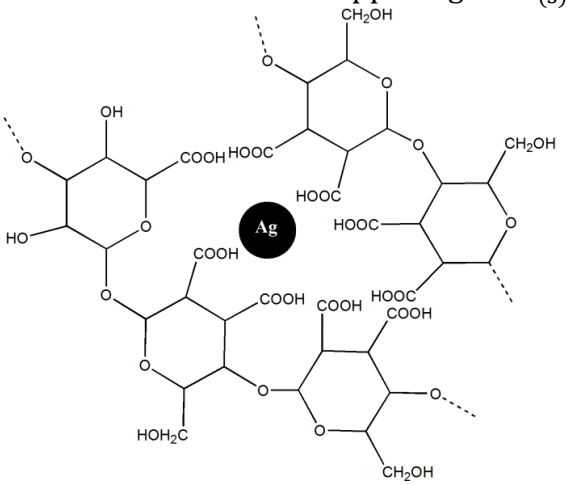


Figure 3. *Schematic of capped silver nanoparticle by starch chain.*

3.2. Dynamic Light Scattering

Dynamic Light Scattering also known as photon correlation spectroscopy or quasi-elastic light scattering is one of the most popular techniques which is used for determination of the size distribution of small particles in suspension or polymers in solution [7, 29]. Dynamic light scattering spectroscopy was recorded for AgNPs. According to the results the average particle size of synthesized AgNPs is 50 nm (Fig. 4).

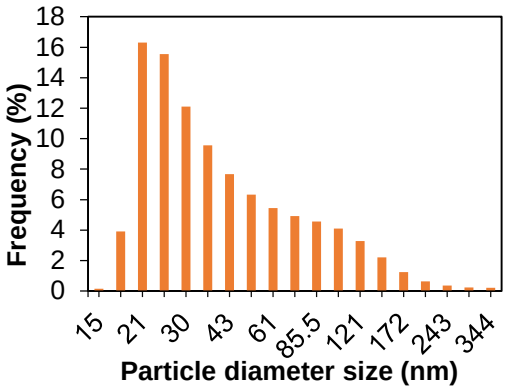


Figure 4. *DLS Diagram of silver nanoparticles (sample 2 of Table 3).*

3.3. X-ray Diffraction Analysis

In order to investigate the structure of prepared silver nanoparticles, the analysis of X-ray diffraction patterns was employed. The XRD patterns of AgNPs were shown in Fig. 5. According to the results, characteristic reflections of silver nanoparticles are recognizable in the XRD patterns (JCPDS, File No. 04–0783) and the structure of prepared silver nanoparticles were found to be face-centered cubic (FCC) crystal. The broad reflection at $2\theta = 20^{\circ}$ is attributed to the low crystalline soluble starch, and two other diffraction peaks appeared at $2\theta = 38^{\circ}$ and $2\theta = 44$, marked as (111) and (200) planes respectively, show the crystalline structure of AgNPs.

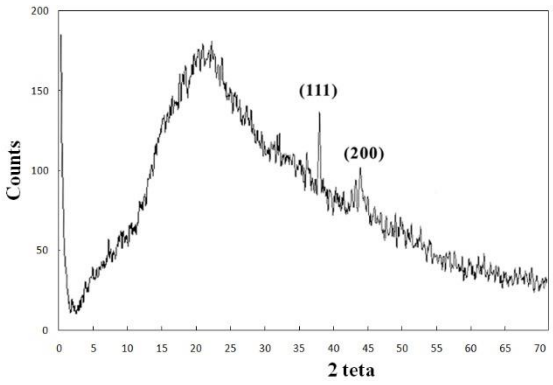


Figure 5. *XRD patterns of silver nanoparticles (sample 2 of Table 3).*

3.4. Morphological Studies

Transmission Electron Microscopy (TEM) was used to investigate the morphology of synthesized silver nano-particles. According to the TEM image of silver nanoparticles is shown in Fig. 6, any agglomeration among the silver nanoparticles are not seen and the shape of nanoparticles is spherical.

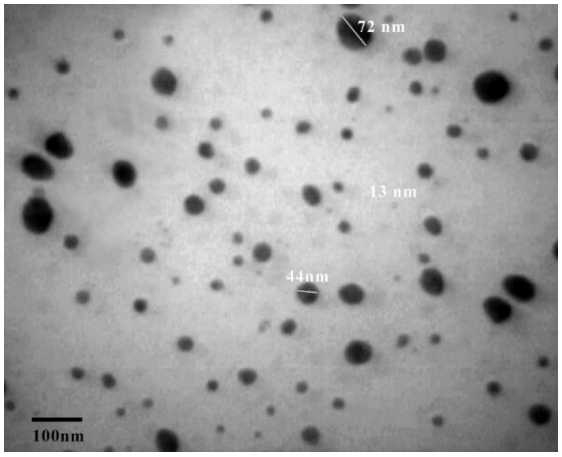


Figure 6. *TEM image of silver nanoparticles (sample 2 of Table 3).*

3.5. Antibacterial Tests

S. aureus as gram positive and *E. coli* as gram negative species were subjected to the prepared AgNPs to determine the antibacterial effect of the synthesized nanostructures. Colloidal AgNPs with various concentrations were casted on the sterile discs. Table 4 shows the concentration of AgNPs in each sample. As shown in Fig. 7a, gram positive *S. aureus* was showed to have no growth zone around the discs containing AgNPs. Diameter of no-growth zones around the discs decreased with decreasing the concentration of AgNPs. When the gram negative *E. coli* species according to Fig. 7b subjected to the AgNPs containing discs, no-growth zones were seen smaller than that of gram positive species, so that for discs with decreased concentrations such as samples number 5 and 6 no-growth zones were not seen. As silver ions leached from the Ag containing discs into the solution, they could migrate to the agar surface next to the discs [30]. This could prevent any growth of bacteria species in the immediate vicinity of the disc. Therefore synthesized AgNPs could prevent any growth of both *S. aureus* and *E. coli* bacteria species but the anti-bacterial effect for gram negative *E. coli* is less than that of *S. aureus* gram positive bacteria.

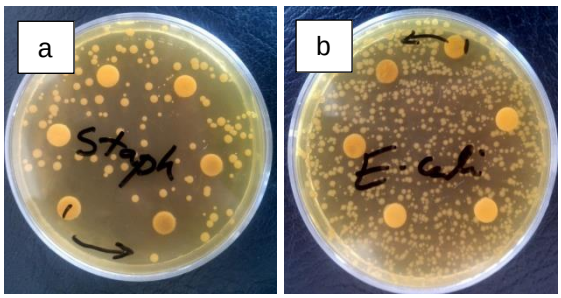


Figure 7. *Results of the antibacterial activity of silver nanoparticles in S. aureus (a), and E.coli (b) agar plates.*

4. CONCLUSION

Colloidal silver nanoparticles with a simple, fast, ecofriendly and cost effective method was prepared and investigated. Silver nitrate, glucose and starch were used as precursor, reducing and capping agents respectively. The best concentration of materials was 0.1 $mol.L^{-1}$ aqueous $AgNO_3$, 0.4 $mol.L^{-1}$ aqueous glucose and 0.1 wt% aqueous starch. Silver nanoparticles in the aqueous medium with average particle size of 50 nm were achieved. Antibacterial test showed that the synthesized AgNPs have antibacterial property so that prevent the growth of *S. aureus* and *E. coli* bacteria on disks containing AgNPs.

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CONFLICT OF INTEREST

We have no conflicts of interest.

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