

Article

Effect of Accelerator in Green Synthesis of Silver Nanoparticles

Majid Darroudi ¹, Mansor Bin Ahmad ^{2,*}, Abdul Halim Abdullah ^{1,2}, Nor Azowa Ibrahim ² and Kamyar Shamel ²

¹ Advanced Materials and Nanotechnology Laboratory, Institute of Advanced Technology (ITMA), Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia;

E-Mail: majiddarroudi@gmail.com

² Department of Chemistry, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia;

E-Mails: halim@science.upm.edu.my (A.H.A.); norazowa@science.upm.edu.my (N.A.I.);

kamyarshamel@gmail.com (K.S.)

* Author to whom correspondence should be addressed;

E-Mail: mansorahmad@science.upm.edu.my; Tel.: +603-8946-6793; Fax: +603-8943-5380.

Received: 19 August 2010; in revised form: 9 September 2010 / Accepted: 21 September 2010 /

Published: 12 October 2010

Abstract: Silver nanoparticles (Ag-NPs) were successfully synthesized in the natural polymeric matrix. Silver nitrate, gelatin, glucose, and sodium hydroxide have been used as silver precursor, stabilizer, reducing agent, and accelerator reagent, respectively. This study investigated the role of NaOH as the accelerator. The resultant products have been confirmed to be Ag-NPs using powder X-ray diffraction (PXRD), UV-vis spectroscopy, and transmission electron microscopy (TEM). The colloidal sols of Ag-NPs obtained at different volumes of NaOH show strong and different surface plasmon resonance (SPR) peaks, which can be explained from the TEM images of Ag-NPs and their particle size distribution. Compared with other synthetic methods, this work is green, rapid, and simple to use. The newly prepared Ag-NPs may have many potential applications in chemical and biological industries.

Keywords: silver nanoparticles; green synthesis; stabilizer; gelatin; glucose; accelerator

1. Introduction

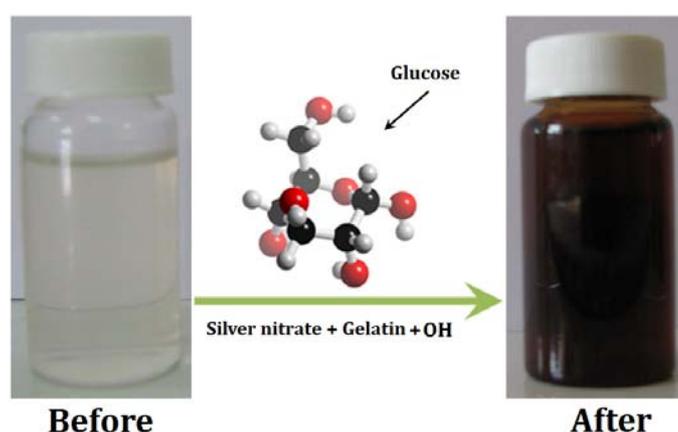
Nowadays, nanomaterials have been improved as a result of truly important recent advances by applying “green” chemistry rules to nanotechnology and materials science. Silver nanoparticles (Ag-NPs) have been widely used during the past few years in various applications, such as biomedicine [1,2], biosensor [3], and catalysis [4]. Many methods can be used to synthesize Ag-NPs, including microemulsion [5], γ -Ray [6], UV-irradiation [7], microwave irradiation [8], and spray pyrolysis [9]. Polymers have also been used as matrices in nanocomposites or as stabilizers to provide stability for the metal nanoparticles against oxidation, agglomeration, and precipitation [10,11]. Preparations of Ag-NPs in various polymers have been published to give well-dispersed Ag-NPs, such as polyvinylpyrrolidone (PVP) [12], polyethylene glycol [13], poly(methyl methacrylate) [14], poly(vinyl alcohol) [15], polyaniline [16], and polyacrylonitrile (PAN) [17]. Natural polymers have also been used because they are non-toxic and biocompatible. For example, natural rubber [18], polysaccharides [19], cellulose [20], chitosan [21], and starch [22] have been used as matrices or stabilizers for preparation of metallic nanoparticles. The present work is on the use of polymers as the stabilizing agent and use of OH as an accelerator in the synthesis of metallic nanoparticles e.g., Ag [23,24] and Cu [25]. Gelatin is a natural biopolymer extracted from the partial hydrolysis of collagen and has good biocompatibility and biodegradability; in recent years, it has been widely used in wound dressings, drug carriers, and tissue scaffolds [26].

The current work describes a green, rapid, and easy method for preparing well-dispersed Ag-NPs in natural polymeric media like gelatin. The morphologies of Ag-NPs and the mechanism of their formation by oxidation of glucose using an accelerator reagent are discussed.

2. Results and Discussion

Glucose as an aldehyde can reduce silver ions to metallic silver and through this process oxidizes itself to gluconic acid. The obtained colloidal Ag-NPs were characterized by spectroscopic results. The formation of Ag-NPs was studied using UV-vis spectroscopy, which has proven to be a very useful technique for the analysis of nanoparticle formation over time. The color of the obtained samples at different volumes of NaOH rapidly changed from colorless to dark brown, indicating the formation of Ag-NPs (Figure 1).

Figure 1. Schematic of the preparation process of Ag-NPs.



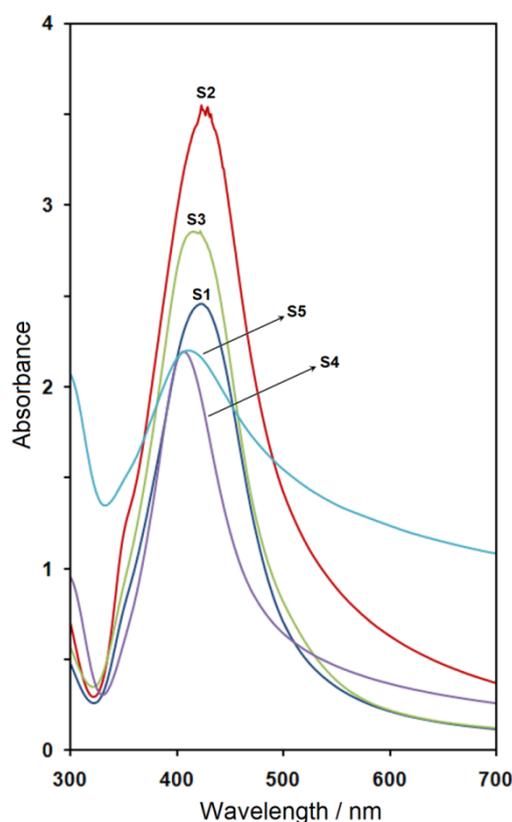
The UV-vis absorption spectra of prepared samples are shown in Figure 2. The obtained Ag-NPs displayed absorption peaks, the characteristic surface plasmon resonance (SPR) band for silver, centered from 407 to 424 nm. The location (λ_{\max}) of the SPR peaks and volumes of NaOH with corresponding pH are also summarized in Table 1.

Table 1. The characteristics of Ag-NPs prepared at different volumes of NaOH.

Sample	Volume of NaOH (mL)	pH	λ_{\max}
S1	0.5	3.5	424
S2	1	3.3	423
S3	1.5	3.2	422
S4	5	3.7	407
S5	10	4.3	412

As indicated, the first addition of NaOH led to the broadening of the SPR peak relative to the sample S1. Greater volumes of NaOH (S2) increased the absorbance due to increases in silver concentration [27]. In sample S3, this resulted in a stronger blue-shift in λ_{\max} to 422 nm. In sample S4, the increased volume of accelerator led to the SPR peak being considerably blue-shifted to a lower wavelength (407 nm). This blue-shift is related to a decrease in the particle size of Ag-NPs [28] because the SPR band in metal nanoparticles displays the blue-shift based on the decreased size of particles. For S5, the λ_{\max} was red-shifted to 412 nm due to the increased size of Ag-NPs [27,29]. These results demonstrated good agreement with the results obtained in the transmission electron microscopy (TEM) images of Ag-NPs and their particle size distribution.

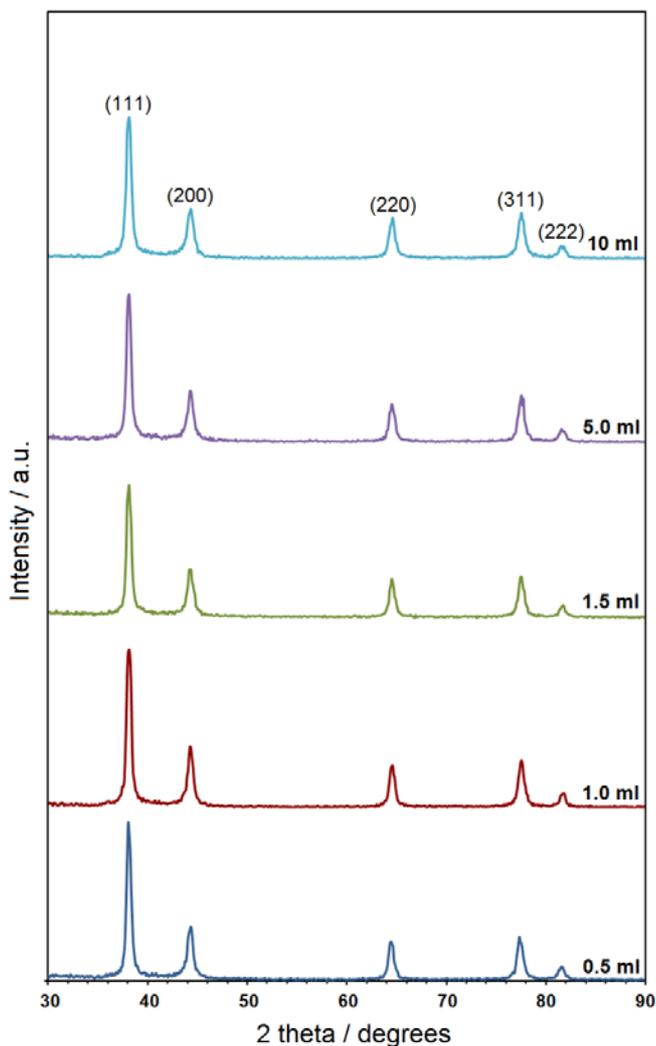
Figure 2. The UV-visible spectra of Ag-NPs prepared at different volumes of NaOH.



The powder X-ray diffraction (PXRD) patterns of the prepared samples at different volumes of NaOH indicate the formation of the Ag-NPs. As shown in Figure 3, all samples have similar diffraction profiles. The PXRD peaks at 2θ of 35.9° , 42.1° , 62.8° , 75.7° and 82.7° can be attributed to the (111), (200), (220), (311) and (222) crystallographic planes of face-centered cubic (fcc) silver crystals, respectively (Ref. # 01-087-0597). For the all samples, the main crystalline phase was silver; no obvious impurities (e.g., Ag_2O [22]) were evident in the PXRD patterns. Moreover, no other peaks related to an impurity, indicating that the silver metal was relatively pure. Gelatin was used as the stabilizer and matrix during this synthesis. The possible chemical equation for preparing the Ag-NPs is:



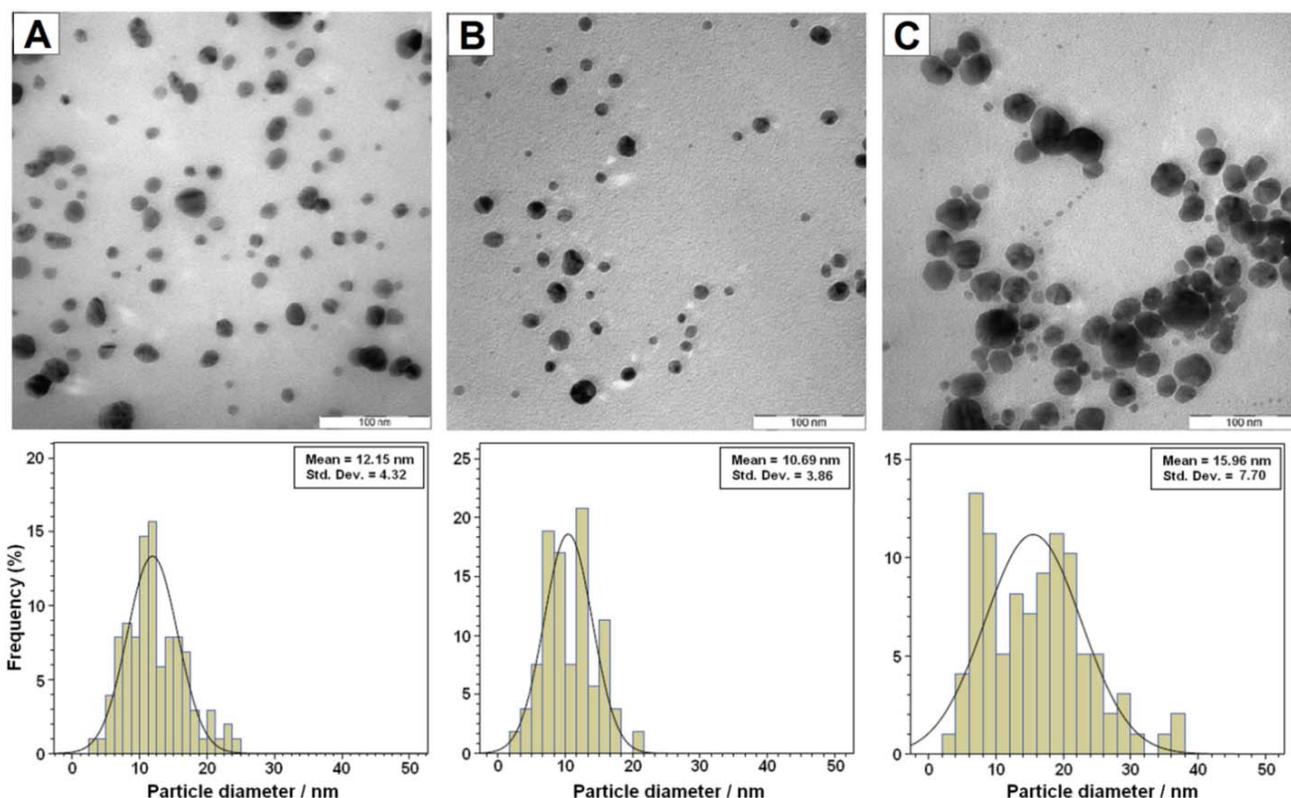
Figure 3. The PXRD patterns of Ag-NPs prepared at different volumes of NaOH.



After dispersion of silver ions in the gelatin matrix (Equation 1), gelatin reacted with the Ag^+ to form a stable gelatinous complex $[\text{Ag}(\text{gel})]^+$, which reacted with OH^- to form silver metal due to the reduction of silver ions through the oxidation of glucose to gluconic acid (Equation 2).

The TEM images demonstrate the formation of Ag-NPs at different volumes of NaOH. Figure 4 shows typical TEM images and the corresponding particle size distribution of the prepared Ag-NPs. The TEM results indicated that the obtained samples retained a narrow particle size distribution and the average size of all prepared Ag-NPs was less than 20 nm, and a smaller size (~10.7 nm) was obtained for S4.

Figure 4. TEM images of Ag-NPs and their particle size distribution at different volumes of NaOH; 1.5 (A), 5 (B), and 10 mL (C).



3. Experimental Section

3.1. Materials

All chemicals and reagents in this work were of analytical grade and used without any purification. Materials used for the synthesis of Ag-NPs included silver nitrate (Alfa-Aesar, 99.98%), gelatin (Sigma, Type A), D-glucose (BDH-Limited Poole, Analar), and sodium hydroxide (R & M Chemicals, 99.0%). Doubly distilled water was used throughout the experiments.

3.2. Synthesis of Silver Nanoparticles

In the present study, 1% wt. gelatin was added to an aqueous solution of AgNO_3 (10 mL, 1 M) in a flask. Different volumes of aqueous solution of NaOH (1 M) were added to prepare various samples (0.5 (S1), 1.0 (S2), 1.5 (S3), 5 (S4) and 10 mL (S5)). These solutions were heated at 60 °C and then 10 mL of aqueous solution of glucose (2 M) was added. The suspension immediately turned brown in

all samples, indicating the formation of silver nanoparticles. The reaction was continued for 15 minutes. The obtained suspensions were centrifuged at 15,000 rpm.

3.3. Characterization Methods and Instruments

The prepared Ag-NPs were characterized using ultraviolet–visible (UV-vis) spectroscopy, transmission electron microscopy (TEM) and powder X-ray diffraction (PXRD). The UV-vis spectra were recorded over the range of 300–700 nm with a Lambda 35-Perkin Elmer UV-vis spectrophotometer. TEM observations were conducted using a Hitachi H-7100 electron microscope while the particle size distribution were determined using the UTHSCSA Image Tool version 3.00 program. The structure of produced Ag-NPs has been studied using powder X-ray diffraction (PXRD, Philips, X’pert, Cu K α). PXRD patterns were recorded at a scan speed of 2°/min. After reactions, the samples were centrifuged using a high-speed centrifuge machine (Avanti J25, Beckman).

4. Conclusions

We have demonstrated a green synthesis of high purity Ag-NPs with glucose reduction of aqueous AgNO₃ at different volumes of NaOH as a reaction accelerator. Nanoparticle agglomeration was controlled with the addition of gelatin as a stabilizing agent. PXRD and TEM measurements displayed that the resultant nanoparticles were faced centered cubic (fcc) structures smaller than 20 nm in diameter. Thus, this work provides important advantages namely, simplicity, speed, and eco-friendliness.

Acknowledgements

The authors would like acknowledge technical supports from the staff of the Faculty of Science and the Institute of Bioscience at UPM in this work.

References

1. Schultz, D.A. Plasmon resonant particles for biological detection. *Curr. Opin. Biotech.* **2003**, *14*, 13–22.
2. Parak, W.J.; Gerion, D.; Pellegrino, T.; Zanchet, D.; Micheel, C.; Williams, S.C.; Boudreau, R.; Le Gros, M.A.; Larabell, C.A.; Alivisatos, A.P. Biological applications of colloidal nanocrystals. *Nanotechnology* **2003**, *14*, 15–27.
3. Nam, J.M.; Thaxton, C.S.; Mirkin, C.A. Nanoparticle-based bio-bar codes for the ultrasensitive detection of proteins. *Science* **2003**, *301*, 1884–1886.
4. Haneda, M.; Kintaichi, Y.; Inaba, M.; Hamada, H. Infrared study of catalytic reduction of nitrogen monoxide by propene over Ag/TiO₂-ZrO₂. *Catal. Today* **1998**, *42*, 127–135.
5. Husein, M.M.; Rodil, E.; Vera, J.H. A novel method for the preparation of silver chloride nanoparticles starting from their solid powder using microemulsions. *J. Colloid Interf. Sci.* **2005**, *288*, 457–467.

6. Huang, N.M.; Radiman, S.; Lim, H.N.; Khiew, P.S.; Chiu, W.S.; Lee, K.H.; Syahida, A.; Hashim, R.; Chia, C.H. γ -Ray assisted synthesis of silver nanoparticles in chitosan solution and the antibacterial properties. *Chem. Eng. J.* **2009**, *155*, 499–507.
7. Darroudi, M.; Ahmad, M.B.; Shameli, K.; Abdullah, A.H.; Ibrahim, N.A. Synthesis and characterization of UV-irradiated silver/montmorillonite nanocomposites. *Solid State Sci.* **2009**, *11*, 1621–1624.
8. Yin, H.; Yamamoto, T.; Wada, Y.; Yanagida, S. Large-scale and size-controlled synthesis of silver nanoparticles under microwave irradiation. *Mater. Chem. Phys.* **2004**, *83*, 66–70.
9. Kim H.-S.; Lee, K.-H.; Kim, S.-G. Growth of monodisperse silver nanoparticles in polymer matrix by spray pyrolysis. *Aerosol. Sci. Tech.* **2006**, *40*, 536–544.
10. Lin, C.-A.; Tsai, H.-C.; Tung, C.-C. Preparation of silver nanoparticles/pseudo-thermoplastic polyvinyl alcohol (PT-PVA) films by the synchronous chemical reduction method. *Polym.-Plast. Technol.* **2009**, *48*, 1171–1175.
11. Faraha, A.A.; Alvarez-Puebla, R.A.; Fenniri, H. Chemically stable silver nanoparticle-crosslinked polymer microspheres. *J. Colloid Interf. Sci.* **2008**, *319*, 572–576.
12. Zheng, M.; Gu, M.; Jin, Y.; Jin, G. Optical properties of silver-dispersed PVP thin film. *Mater. Res. Bull.* **2001**, *36*, 853–859.
13. Luo, C.; Zhang, Y.; Zeng, X.; Zeng, Y.; Wang, Y. The role of poly(ethylene glycol) in the formation of silver nanoparticles. *J. Colloid Interf. Sci.* **2005**, *288*, 444–448.
14. Singh, N.; Khanna, P.K. *In situ* synthesis of silver nano-particles in polymethylmethacrylate. *Mater. Chem. Phys.* **2007**, *104*, 367–372.
15. Zhou, Y.; Yu, S.H.; Wang, C.Y.; Li, X.G.; Zhu, Y.R.; Chen, Z.Y. A novel ultraviolet irradiation photo-reduction technique for preparation of single crystal Ag nanorods and Ag dendrites. *Adv. Mater.* **1999**, *11*, 850–852.
16. Khanna, P.K.; Singh, N.; Charan, S.; Viswanath, A.K. Synthesis of Ag/polyaniline nanocomposite via an *in situ* photo-redox mechanism. *Mater. Chem. Phys.* **2005**, *92*, 214–219.
17. Zhang, Z.; Zhang, L.; Wang, S.; Chen, W.; Lei, Y. A convenient route to polyacrylonitrile/silver nanoparticle composite by simultaneous polymerization–reduction approach. *Polymer* **2001**, *42*, 8315–8318.
18. Abu Bakar, N.H.H.; Ismail, J.; Abu Bakar, M. Synthesis and characterization of silver nanoparticles in natural rubber. *Mater. Chem. Phys.* **2007**, *104*, 276–283.
19. Huang, N.M.; Lim, H.N.; Radiman, S.; Khiew, P.S.; Chiu, W.S.; Hashim, R.; Chia, C.H. Sucrose ester micellar-mediated synthesis of Ag nanoparticles and the antibacterial properties. *Colloid Surface A* **2010**, *35*, 69–76.
20. Cai, J.; Kimura, S.; Wada, M.; Kuga, S. Nanoporous cellulose as metal nanoparticles support. *Biomacromolecules* **2009**, *10*, 87–94.
21. Huang, H.; Yuan, Q.; Yang, X. Preparation and characterization of metal-chitosan nanocomposites. *Colloid Surface B* **2004**, *39*, 31–37.
22. Raveendran, P.; Fu, J.; Wallen, S.L. Completely "green" synthesis and stabilization of metal nanoparticles. *J. Am. Chem. Soc.* **2003**, *125*, 13940–13941.
23. Singh, M.; Sinha, I.; Mandal, R.K. Role of pH in the green synthesis of silver nanoparticles. *Mater. Lett.* **2009**, *63*, 425–427.

24. Singh, M.; Sinha, I.; Singh, A.K.; Mandal, R.K. Formation of fractal aggregates during green synthesis of silver nanoparticles. *J. Nanopart. Res.* **2010**, doi:10.1007/s11051-010-0001-8.
25. Singh, M.; Sinha, I.; Premkumar, M.; Singh, A.K.; Mandal, R.K. Structural and surface plasmon behavior of Cu nanoparticles using different stabilizers. *Colloid Surface A* **2010**, *359*, 88–94.
26. Xu, X.; Zhou, M. Antimicrobial gelatin nanofibers containing silver nanoparticles. *Fiber. Polym.* **2008**, *9*, 685–690.
27. Bohren, C.F.; Huffman, D.R. *Absorption and Scattering of Light by Small Particles*; John Wiley & Sons Inc.: New York, NY, USA, 1998.
28. Heath, J.R. Size dependent surface plasmon resonances in bare silver particles. *Phys. Rev. B* **1989**, *40*, 9982–9985.
29. Aragon, S.R.; Elwenspoek, M. Mie scattering from thin spherical bubbles. *J. Chem. Phys.* **1982**, *77*, 3406–3413.

© 2010 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).