

Chitosan as Capping Agent for Silver Nanoparticles

Hanim Istatik Badi'ah*

Department of Medical Laboratory Technology, Institute of Health Science Banyuwangi,
Jl. Lieutenant Colonel Istiqlah No. 109, Banyuwangi, Indonesia

*Corresponding Author: hanimistatik8@gmail.com

Received: January 2021

Received in revised: February 2021

Accepted: May 2021

Available online: May 2021

Abstract

Silver nanoparticles have been developed in many applications because of their optical and reactivity properties. One of the disadvantages of silver nanoparticles is their low level of stability because their surface is easy to aggregate. It is necessary to have other materials such as chitosan as a capping agent on the surface of silver nanoparticles to prevent aggregation. This study aimed to determine the ability of chitosan as a capping agent for silver nanoparticles. The ability of chitosan was evaluated based on the stability test and characterization using a UV-Vis, PSA, and FTIR spectrophotometer. The silver nanoparticles formed producing a yellow color with a wavelength of 401 nm and a size of 13.48 nm. The volume of chitosan that gave optimal results in stabilizing silver nanoparticles was 2.0 mL.

Keywords: Silver nanoparticles, chitosan, capping agent, stability, FWHM

INTRODUCTION

Metal materials in nanomaterial size or also known as metal nanomaterials are currently widely used as objects of research because they have several advantages compared to their bulk size, such as unique optical properties, physical properties and chemical reactivity (Renteria & Garcia-Macedo, 2005). Some applications of metal nanomaterials include colorimetric sensors for various analytes (Badi'ah, Seede, Supriyanto, & Zaidan, 2019; D'souza, Pati, & Kailasa, 2015; Rostami, Mehdi, & Jabbari, 2017; Shiva Prasad, Shruthi, & Shivamallu, 2018), conductors (Matsuhisa et al., 2017), anti-microbial and anti-bacterial (Ahmed, Ahmad, Swami, & Ikram, 2016; Azmath, Baker, Rakshith, & Satish, 2016), energy conversion (Li, Gan, & Li, 2016). One of the metal nanomaterials that is widely used is silver nanoparticles.

Silver nanoparticles have an interesting morphology, size, and different maximum thermal conductivity compared to other types of metal (Gupta & Prakash, 2014). In addition, silver nanoparticles have good compound reactivity with relatively good abundance, essential physical properties and a lower price compared to other types of metals (Aragay, Pino, & Merkoçi, 2012). Therefore, silver nanoparticles are more widely used in various types of applications. Some methods have been developed to synthesize silver nanoparticles such as chemical reduction (Szczepanowicz, Stefańska, Socha, & Warszzyński,

2010), using Ketapang leaf extract (Rusnaenah, Zakir, & Budi, 2017), using Using Syzygium polyanthum Extract (Taba, Parmitha, & Kasim, 2019) and using Mangosteen bark extract (Irwan, Zakir, & Budi, 2020). Silver nanoparticles by chemical reduction can use a NaBH₄ as a reducing agent (Szczepanowicz et al., 2010). However, silver nanoparticles have a low stability and is able to easily aggregate form silver nanoparticles with larger size. Therefore, the other materials as a capping agent of silver nanoparticles are needed to prevent the aggregation between the surface of silver nanoparticles.

Stabilization of silver nanoparticles with a polymer can improve the stability, electro-optical properties and biological applications. Polymers can bind to the surface of metal nanoparticles with several interactions such as a chemical adsorption, electrostatic interactions and hydrophobic interactions (Sperling & Parak, 2010). Polymers that can be used as stabilizers for silver nanoparticles include poly-(propyleneimine) dendrimer (PPI) (Sun & Xia, 2002), poly-(vinylpyrrolidone) (PVP) (Wiley, Sun, & Xia, 2005) and hyperbranched polyethylenimine (PEI) (Liu et al., 2014). Chitosan was used in this study as a capping agent for silver nanoparticles. Chitosan (1-4-2-amino-2-deoxy-D-glucosamine) is a linear polysaccharide which consists of of N-acetylglucosamine and D-glucosamine. Chitosan has a -NH₂ group that can interact with the surface of silver nanoparticles. The use of modification of silver nanoparticles with chitosan as a colorimetric sensor was carried out by

utilizing the amine group found in chitosan. Chitosan has three reactive groups consisting of one amino and two hydroxyl groups, each at the C-2, C-3 and C-6 positions, which allows adhesion to occur with silver nanoparticles or an analyte.

METHODOLOGY

Materials and Instrumentals

The instruments that used in this study were analytical balance (Kern: ABS 220-4), UV-Vis spectrophotometer (Shimadzu-1800), Particle Size Analyzer (PSA) Zetasizer Ver. 7.01 (Malvern 1061025), Fourier Transform Infrared (FT-IR), and some beaker tools. The materials used in this study were AgNO₃ (>99%, CAS number 7761-88-8), NaBH₄ (99% Sigma Aldrich Co) and chitosan.

Methods

Synthesis of Silver Nanoparticles

Silver nanoparticles were synthesized using AgNO₃ as a source of Ag⁺ and NaBH₄ as a reducing agent. A total of 10 mL AgNO₃ 1mM solution were added dropwise into 30 mL of 2 mM NaBH₄ solution that had been cooled by ice bath while stirring. Stirring was carried out for 3 minutes until the AgNO₃ was completely added and the solution changed color from colorless to yellow. The solution was then centrifuged for 15 minutes at 12000 rpm and filtered. Before the silver nanoparticles were used, colloid obtained was left at a room temperature for 24 hours.

Silver Nanoparticles Stabilization with Chitosan

The stabilization of silver nanoparticles with chitosan was carried out by adding 5 mL of colloidal silver nanoparticles that had been formed with 3 mL of 1% chitosan. The mixture was then sonicated at a frequency of 20 KHz for 10 minutes.

Optimization of the Amount of Chitosan as Capping Agent for Silver Nanoparticles

Optimization of the amount of chitosan was carried out to determine the optimum amount of chitosan added to enable an optimum role as a capping agent for silver nanoparticles. Variations in the amount of chitosan were 1 mL, 2 mL and 3 mL.

Stability of Chitosan as Capping Agent for Silver Nanoparticles

The stability test of chitosan was carried out to determine the extent of the role of chitosan as a capping agent in maintaining the stability of silver

nanoparticles and preventing aggregation of silver nanoparticles.

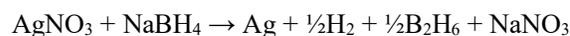
Characterization

Characterization was carried out using a UV-Vis spectrophotometer, Particle Size Analyzer (PSA) and Fourier Transform Infrared (FT-IR).

RESULTS AND DISCUSSION

Synthesis of Silver Nanoparticles

The synthesis of silver nanoparticles was carried out using chemical reduction methods. This synthesis uses the Brust (Creighton) method, which is a method of synthesize silver nanoparticles through the reduction of AgNO₃ using NaBH₄, while AgNO₃ compounds were used as a source of Ag⁺ and NaBH₄ as a reducing agent which reduces AgNO₃ to Ag⁺. The reactions that occur during the synthesis process of silver nanoparticles are as follows:



The formation of silver nanoparticles was indicated by a change in the color of the solution from colorless to yellow as shown in Figure 1. The color change in this solution occurs due to the excitation of plasmon vibrations on the surface of silver nanoparticles (D'souza et al., 2015).



Figure 1. Colloidal silver nanoparticles

The presence of plasmon vibrations on this surface enabled silver nanoparticles to have a wavelength in the area of about 400 - 450 nm. The optimum wavelength produced in this study was 401 nm as shown in Figure 2. The silver nanoparticles formed was characterized using a Particle Size Analyzer (PSA) and the size of the silver nanoparticles was 13.48 nm with a size distribution as shown in Figure 3.

Silver Nanoparticles Stabilization with Chitosan

Silver nanoparticles were stabilized to prevent its aggregation which can result in larger silver nanoparticles. Therefore, a stabilizing agent or capping agent is needed to prevent aggregation of silver nanoparticles. Chitosan was chosen as a capping agent

because chitosan is able to create steric stabilization on the surface of silver nanoparticles through the interaction of amine groups (-NH₂) on chitosan with the surface of silver nanoparticles.

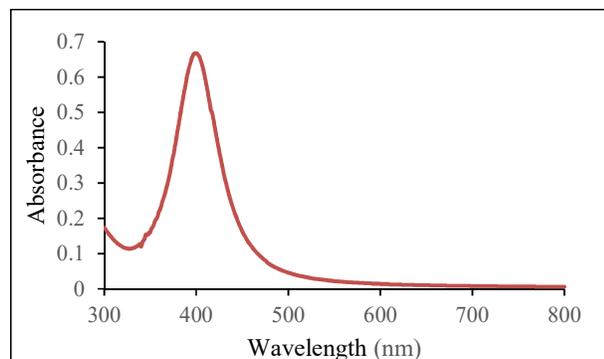


Figure 2. UV-Vis spectra of silver nanoparticles

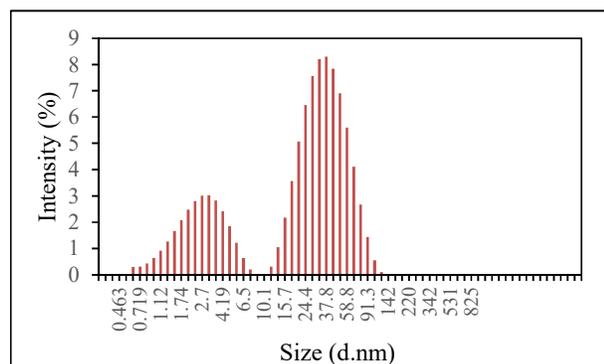


Figure 3. Size distribution of silver nanoparticles

The stabilization with chitosan caused higher and narrower UV-Vis spectra as seen in Figure 5. The higher and narrower absorbance peaks indicate, the use of chitosan led to the higher number and homogeneously distributed of silver nanoparticles formed and more.

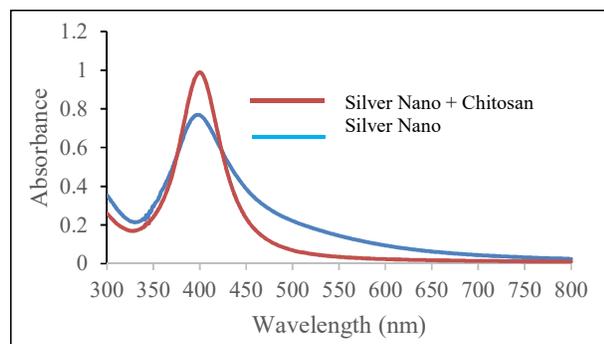


Figure 5. UV-Vis spectra of silver nanoparticles with and without the addition of chitosan

The success of stabilization of silver nanoparticles with chitosan was also shown from the FTIR results as shown in Figure 6. Both the FTIR results of chitosan and chitosan-stabilized silver nanoparticles had absorption bands of -OH groups in the 3427.62 cm⁻¹ and 3448.84 cm⁻¹ regions, respectively. Both the absorption bands of CH (-CH₂-) groups on chitosan and chitosan stabilized silver nanoparticles had absorption bands in the 2926.11 cm⁻¹ and 2854.74 cm⁻¹ regions. The CO group in chitosan had an absorption band in the area of 1072.46 cm⁻¹ and showed a slight shift (1053.17 cm⁻¹) in the absorption of chitosan stabilized silver nanoparticles. In addition, the NH group had an absorption band in the area of 1575.89 cm⁻¹ for chitosan and the NH group vibration lost absorption after stabilization of silver nanoparticles with chitosan.

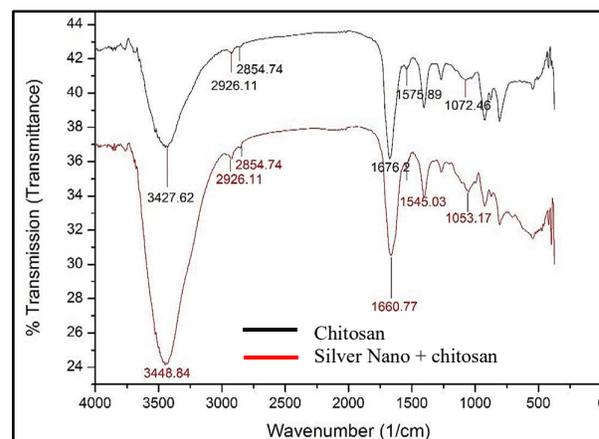


Figure 6. FTIR spectra of silver nanoparticles with and without the addition of chitosan

Optimization of the Amount of Chitosan as Capping Agent for Silver Nanoparticles

Optimization was carried out to determine the effect of the volume of chitosan added in the modification process. Chitosan was added in variation of 1 mL, 2 mL and 3 mL. The variation in the volume of chitosan added to the modification process had an effect on the absorbance and the resulting FWHM value as shown in Table 1. The absorbance value at 2 mL chitosan volume had a higher absorbance value than the other volumes. This suggested that 2 mL of chitosan volume was sufficient to cover silver nanoparticles and produce more silver nanoparticles. In addition to producing a high absorbance value, the addition of 2 mL chitosan volume also resulted in a smaller Full Width at Half Maximum (FWHM) value compared to other chitosan volumes. The FWHM value is a value that indicates the width of the half peak in the maximum absorption spectrum. This showed

that the addition 2 mL of chitosan resulted in a more homogeneous distribution of the size of the nanoparticles.

Table 1. Comparison of the absorbance value and FWHM with the volume variation of chitosan

Chitosan volume (mL)	Absorbance	FWHM
1	0.423	68.92
2	0.812	50.56
3	0.67	70.31

The Stability of Chitosan as Capping Agent for Silver Nanoparticles

The effect of chitosan as a capping agent on the stability of silver nanoparticles was analyzed based on the FWHM value between silver nanoparticles with and without chitosan. Stability was observed for 60 days as shown in Figure 7. Silver nanoparticles in the presence of a capping agent had a lower FWHM value than silver nanoparticles without a capping agent.

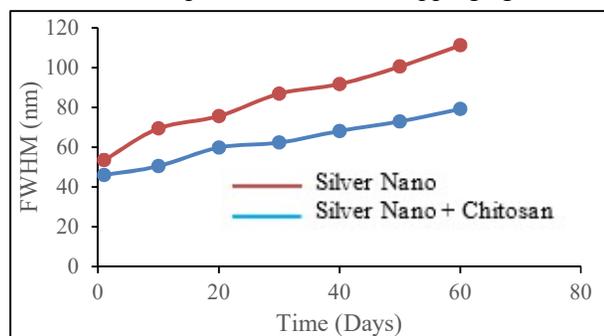


Figure 7. Relationship between FWHM and time of stability

Figure 7 showed that the silver nanoparticles in the presence of a capping agent using chitosan had a more homogeneous size distribution. Chitosan prevented aggregation to form a larger size of silver nanoparticles (Rentería & García-Macedo, 2005; Rostami et al., 2017).

CONCLUSION

Chitosan has been used successfully as a capping agent for silver nanoparticles. The presence of chitosan on the surface of silver nanoparticles was able to prevent the aggregation of silver nanoparticles for up to 60 days with stable size and size distribution.

REFERENCES

Ahmed, S., Ahmad, M., Swami, B. L., & Ikram, S. (2016). A Review on Plants Extract Mediated

Synthesis of Silver Nanoparticles For Antimicrobial Applications: A Green Expertise. *Journal of Advanced Research*, 7(1), 17–28. <https://doi.org/10.1016/j.jare.2015.02.007>

Aragay, G., Pino, F., & Merkoçi, A. (2012). Nanomaterials for Sensing and Destroying Pesticides. *Chemical Reviews*, 112(10), 5317–5338. <https://doi.org/10.1021/cr300020c>

Azmath, P., Baker, S., Rakshith, D., & Satish, S. (2016). Mycosynthesis of Silver Nanoparticles Bearing Antibacterial Activity. *Saudi Pharmaceutical Journal*, 24(2), 140–146. <https://doi.org/10.1016/j.jsps.2015.01.008>

Badi'ah, H. I., Seede, F., Supriyanto, G., & Zaidan, A. H. (2019). Synthesis of Silver Nanoparticles and the Development in Analysis Method. *IOP Conference Series: Earth and Environmental Science*, 217, 012005. <https://doi.org/10.1088/1755-1315/217/1/012005>

D'souza, S. L., Pati, R., & Kailasa, S. K. (2015). Ascorbic Acid-functionalized AgNPs as A Probe for Colorimetric Sensing of Glutathione. *Applied Nanoscience*, 5(6), 747–753. <https://doi.org/10.1007/s13204-014-0371-9>

Gupta, S., & Prakash, R. (2014). Photochemically Assisted Formation of Silver Nanoparticles By Dithizone, and Its Application In Amperometric Sensing of Cefotaxime. *Journal of Materials Chemistry C*, 2(33), 6859–6866. <https://doi.org/10.1039/C4TC01090F>

Li, Y., Gan, W., & Li, B. (2016). Silver Nanoparticles-Coated Glass Frits for Silicon Solar Cells. *Applied Physics A*, 122(4), 417. <https://doi.org/10.1007/s00339-016-9979-9>

Liu, Z., Wang, Y., Zu, Y., Fu, Y., Li, N., Guo, N., ... Zhang, Y. (2014). Synthesis of Polyethylenimine (PEI) Functionalized Silver Nanoparticles by A Hydrothermal Method and Their Antibacterial Activity Study. *Materials Science and Engineering: C*, 42, 31–37. <https://doi.org/10.1016/j.msec.2014.05.007>

Matsuhisa, N., Inoue, D., Zalar, P., Jin, H., Matsuba, Y., Itoh, A., ... Someya, T. (2017). Printable Elastic Conductors by In Situ Formation of Silver Nanoparticles From Silver Flakes. *Nature Materials*, 16(8), 834–840. <https://doi.org/10.1038/nmat4904>

R, I., Zakir, M., & Budi, P. (2020). Synthesis of Silver Nanoparticles and The Effect of p-Coumaric Acid for Detecting Melamine. *Indonesian Journal of Chemical Research*, 7(2), 141–150. <https://doi.org/10.30598/ijcr.2019.7-irw>

- Rentería, V. M., & García-Macedo, J. (2005). Modeling of Optical Absorption of Silver Prolate Nanoparticles Embedded In Sol–Gel Glasses. *Materials Chemistry and Physics*, *91*(1), 88–93. <https://doi.org/10.1016/j.matchemphys.2004.10.053>
- Rostami, S., Mehdinia, A., & Jabbari, A. (2017). Seed-Mediated Grown Silver Nanoparticles as A Colorimetric Sensor for Detection of Ascorbic Acid. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *180*, 204–210. <https://doi.org/10.1016/j.saa.2017.03.020>
- Rusnaenah, A., Zakir, M., & Budi, P. (2017). Biosynthesis of Silver Nanoparticles Using Ketapang Leaf Extract, Modification With p-Coumaric Acid for Detecting Melamine. *Indonesian Journal of Chemical Research*, *4*(2), 367–372. <https://doi.org/10.30598/ijcr.2017.4-and>
- Shiva Prasad, K., Shruthi, G., & Shivamallu, C. (2018). Functionalized Silver Nano-Sensor for Colorimetric Detection of Hg²⁺ Ions: Facile Synthesis and Docking Studies. *Sensors*, *18*(8), 2698. <https://doi.org/10.3390/s18082698>
- Sperling, R. A., & Parak, W. J. (2010). Surface Modification, Functionalization and Bioconjugation of Colloidal Inorganic Nanoparticles. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, *368*(1915), 1333–1383. <https://doi.org/10.1098/rsta.2009.0273>
- Sun, Y., & Xia, Y. (2002). Shape-Controlled Synthesis of Gold and Silver Nanoparticles. *Science*, *298*(5601), 2176–2179. <https://doi.org/10.1126/science.1077229>
- Szczepanowicz, K., Stefańska, J., Socha, R. P., & Warszyński, P. (2010). Preparation of Silver Nanoparticles Via Chemical Reduction and Their Antimicrobial Activity. *Physicochemical Problems of Mineral Processing*, *45*(1), 85–98.
- Taba, P., Parmitha, N. Y., & Kasim, S. (2019). Synthesis of Silver Nanoparticles Using Syzygium polyanthum Extract as Bioreductor and Applied as Antioxidant. *Indonesian Journal of Chemical Research*, *7*(1), 51–60. <https://doi.org/10.30598/ijcr.2019.7-ptb>
- Wiley, B., Sun, Y., & Xia, Y. (2005). Polyol Synthesis of Silver Nanostructures: Control of Product Morphology with Fe(II) or Fe(III) Species. *Langmuir*, *21*(18), 8077–8080. <https://doi.org/10.1021/la050887i>