



Room Temperature Synthesis and Stabilization of Silver and Gold Nanoparticles Using Polyamic Acid

Maxwell Obumba¹, Naumih Noah^{2*} and Mildred Nawiri¹

¹Chemistry Department, Kenyatta University, P.O Box 43844-00100, Nairobi

² School of Pharmacy and Health Sciences, United States International University-Africa, P.O Box 14634-00800, Nairobi

Abstract

Metal nanoparticles have been studied for their unique physical and chemical properties which make them efficient in various models and applications. Specifically, Silver nanoparticles (AgNPs) and Gold nanoparticles (AuNPs) have recognizable importance in chemistry, physics and biology because of their unique electrical, photothermal and optical properties. The size, surface chemistry, dispersion media and shape of AgNPs and AuNPs have a profound impact on their properties. The need to synthesize AgNPs and AuNPs with a predetermined size, shape and fair stability has been growing over the past and present decades. Several methods have been developed in the recent past, they include; chemical reduction, photochemical reduction, radio-lytic methods and electrochemical techniques. Most of these methods have shown success in the synthesis of AgNPs and AuNPs but their potential to provide smaller particle sizes and prevent agglomeration is still a major drawback. The use of polymeric materials as reducing agents and stabilizers is a promising method for obtaining monodispersed AgNPs and AuNPs with desirable stability. The current study demonstrates the feasibility of synthesizing small-sized AgNPs and AuNPs with better stability using nanostructured polyamic acid (PAA) as both reducing and stabilizing agent under the condition of room temperature. Polyamic acids are a class of polymer formed through polycondensation reactions between a dianhydride and a diamine. The amine and anhydride groups react to form carboxylic acid groups which release electrons in the reaction thereby reducing silver and gold ions. The carboxylic acid groups then encapsulate the newly formed AgNPs and AuNPs stopping their further growth and hence preventing them from agglomeration. Studies using UV-Vis spectrometry showed absorption spectra that correspond to the peaks of silver and gold nanoparticles. The bands in the region of 425nm to 433nm confirmed peaks for AgNPs while 533nm to 541nm confirmed peaks for AuNPs. The Mie's equation depicted estimated particle sizes ranging between 26nm to 32nm and 24nm to 30nm for AgNPs and AuNPs respectively. The Surface Plasmon Resonance (SPR) bands remained unchanged over a period of beyond three months depicting better stability of the silver and gold nanoparticles. Therefore, it can be correctly concluded that PAA is a prominent reducing and stabilizing agent in the synthesis of stable AgNPs and AuNPs.

Keywords: Agglomeration, silver and gold nanoparticles, Polyamic acid, stability

1. Introduction

In the recent past, noble metal nanoparticles have attracted significant attention due to their characteristic quantum size effects and large surface area to volume ratio. These have made Noble metal nanoparticles to be important in a wide range of applications in several fields including medicine and biology (Di Guglielmo *et al.*, 2010; Khan *et al.*, 2014). Research done over the last decade has clearly shown that the properties of nanoparticles, in particular, gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs) are strongly influenced by size, shape, distribution and so on (Rónavári *et al.*, 2021). Such properties are dictated by the method of

synthesis adopted (Sajid and Plotka-Wasyilka, 2020). One of the major challenges in the synthesis of AgNPs and AuNPs is not only to control particle size but also to stabilize the nanoparticles as well (Kulkarni and Muddapuram, 2014). AgNPs and AuNPs provide a more interesting research area due to their valence bands and close-lying conduction in which electrons freely move. The freely moving electron(s)

*Corresponding author e-mail: mnoah@usiu.ac.ke

Received: 24 November 2022

Revised: 19 April 2023

Accepted: 24 April 2023

gives rise to an absorption band which depends on both the particle size and chemical environment. Thus the colour varies depending on the method of synthesis and the state of stability of the nanoparticles (Christy *et al.*, 2015). The fundamental challenge in the application of AgNPs and AuNPs is associated with the stability of their dispersion in solvents allowing prevention of the agglomeration process. Agglomerations has been reported to cause loss of plasmonic functionalities (Singh *et al.*, 2012; Dai *et al.*, 2014). Many methods have been proposed for the synthesis of AgNPs and AuNPs. These include photochemical reduction, electrochemical techniques, radio lytic methods, and chemical reduction among others (Shah *et al.*, 2015). These methods have been successful in producing nanoparticles but their inherent properties to agglomeration are a major drawback. Agglomeration of nanoparticles arises from van der Waals interactions between particles. It is believed that the use of nonionic, anionic and cationic polymer materials as a stabilizer is a promising method of obtaining dispersed nanoparticles with fair stability (Ibrayeva *et al.*, 2013). The mechanism of stabilizing Novel metal nanoparticles by polymers is obtained via two kinds of protection mechanisms. These mechanisms include electrostatic stabilization which is based on the double layer repulsion between the particles and steric stabilization of the particles achieved by physical adsorption of the polymer chains on the surface of particles (Baygazieva *et al.*, 2014). Stabilizing agents must be present during nanoparticle synthesis, nucleation and growth, without which, neither AgNPs nor AuNPs can maintain their structures and will aggregate resulting in loss of plasmonic functionality (Grillet *et al.*, 2013; Dai *et al.*, 2014; Ustarroz *et al.*, 2017). A highly reactive intermediate of polyimides, polyamic acid (PAA) can be used as both a reducing agent and stabilizer for the synthesis of AuNPs and AgNPs due to its high charge density. PAA also has the advantage of having very good mechanical stability and undergoes structural change only at extreme conditions for example high temperature. (Kariuki *et al.*, 2015). Various PAAs have been studied for the synthesis of AuNPs and AgNPs (Kimotheo *et al.*, 2020). However, to the best of our knowledge, the stabilization of AuNPs and AgNPs by PAA prepared from 4, 4'-Oxidianiline (ODA) and 4, 4-oxydiphthalic anhydride (ODPA) as monomers in Dimethylformaldehyde (DMF) at room temperature (25 °C) has never been reported. Our work aimed to investigate the potential of PAA synthesized at room temperature to synthesize and stabilize AgNPs and AuNPs for 90 days at room temperature. The effect of variation in the PAA concentration used on the stability of the nanoparticles was also investigated.

2. Methodology

2.1. Chemicals and Materials

4,4-Oxidianiline (ODA), 4, 4-oxydiphthalic anhydride (ODPA), Commercial Gold nanoparticles and Commercial silver nanoparticles were purchased from Sigma Aldrich, USA. N,N dimethylformamide (DMF), AuCl₃ and AgNO₃ were all analytical grades and were used with no further purification. Glassware were treated with regia solution (1V HNO₃: 3V HCl), rinsed with distilled water and dried.

2.2. Synthesis of Polyamic acid

The synthesis of PAA was based on the method described by Cao *et al.*, (2020) but with some modifications. Briefly, 210.25 mg of ODA was dissolved in 10 ml DMF and stirred under nitrogen at room temperature for 10 minutes. This was followed by the addition of 293.30 mg of ODPA that was added slowly for 1 hour while stirring until the mixture became homogeneous. The mixture was stirred at 500 rpm under nitrogen for 24 hours. The mixture turned yellow with an increased viscosity indicating the formation of PAA.

2.3. Synthesis and stabilization of AgNPs

The synthesis and stabilization of silver nanoparticles was a modification of the work previously reported by Velgosova *et al.*, (2017) and Kimotheo *et al.*, (2020). In this procedure, 5 mg of AgNO₃ was dissolved into 10 ml DMF, and then different amounts (20 µL, 50 µL and 100 µL) of PAA added. The mixture was then stirred at 500 rpm for 24 hours at room temperature. The reduction of silver ions to silver nanoparticles was confirmed by the gradual change of colour from clear to dark brown. To determine the stabilization of the AgNPs, the mixture obtained was stored at room temperature (25 °C) on the bench for 98 days with regular characterization using UV-Vis spectrometer.

2.4. Synthesis and stabilization of AuNPs

The synthesis and stabilization of gold nanoparticles was modified from the method previously reported by Nguyen *et al.*, (2021) and Kimotheo *et al.*, (2020). 2.88 mg of AuCl₃ was dissolved in 10 ml DMF then different amounts (20 µL, 50 µL and 100 µL) of PAA were added. The mixture was then stirred at 500 rpm for 24 hours at room temperature. The reduction of gold ions to gold nanoparticles was remotely confirmed by the gradual change of colour from clear to dark purple. To determine the stabilization of the AgNPs, the mixture obtained was stored at room temperature (25 °C) on the bench for 98 days with regular characterization using UV-Vis spectrometer.

2.5. Sample characterization

UV-Vis absorption measurements were performed using a UV-Vis spectrometer (Hewlett Packard 8453) in dual beam mode from 350nm to 600nm and 500nm to 650 for AgNPs and AuNPs respectively. DMF was used as blank. The nanoparticle size was determined from the data obtained from the UV-vis using the Mie's equation below (Mie, 1908).

$$E_{nanoparticle} - E_{bulk} = \frac{h^2\pi^2}{2\mu R^2} + \frac{1.8e^2}{\epsilon R}$$

Where $E_{nanoparticle}$ and E_{bulk} are the band gaps (eV) of the sample and the bulk semiconductors respectively, h is the Planck's constant ($6.62607 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$), μ is the electron-hole reduced effective mass, R is the radius of the nanoparticle confinement region while ϵ is the dielectric constant and e is the elementary electric charge ($1.6022 \times 10^{-19} \text{ C}$).

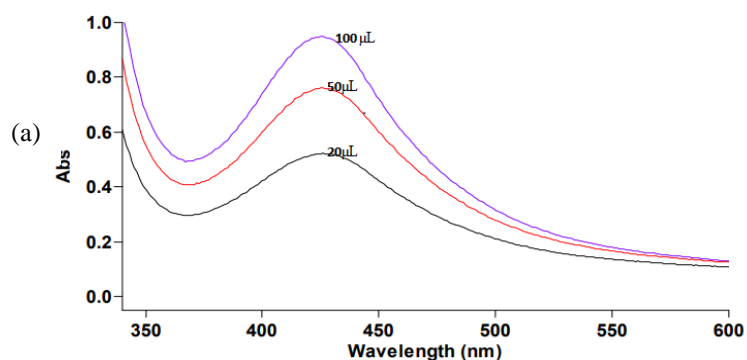
3. Results and Discussion

A preliminary confirmation test was used to predict the ability of the PAA to synthesize AuNPs and AgNPs by observing the appearance of the characteristic colours of the individual nanoparticles dispersed in DMF as the liquid medium. The colour change to dark brown predicted the formation of AgNPs while the colour change to dark purple predicted the formation of AuNPs. This was in agreement with the findings of Rezazadeh *et al.*, (2020) and Malarkodi *et al.*, (2013). The reduction of Ag^+ to Ag^0 and Au^{3+} to Au^0 by PAA was possible due to the presence of carboxyl and hydroxyl groups within the structure of PAA. These groups reduce metallic ions by donating electrons and hydrogen atoms that get stabilized by the anionic functional groups in the polymer structure (Prabu and Johnson, 2015).

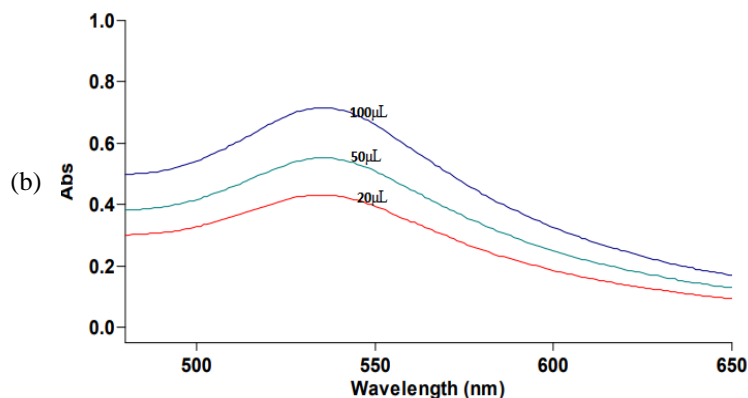
3.1 Spectroscopic measurements

UV-Vis spectroscopy was employed to provide valuable information on the identity, size and distribution of nanoparticles based on Surface Plasmon Resonance (SPR). The SPR bands are usually as a result of the interactions between the electron cloud on the nanoparticle surface and the incident electromagnetic radiation (Labulo *et al.*, 2016). The bands in the region of 425nm to 433nm confirmed peaks for AgNPs. These findings agreed with what was reported by Wan *et al.*, (2020). According to Sowmya and Lakshmi, (2018), the estimated size of AgNPs around these SPR bands ranges from 10 to 30nm. As postulated by Mie's equation, the silver nanoparticle size obtained in the present study ranged between 26nm to 32nm. On the other hand, SPR bands centred

between 533nm-541nm of UV-Vis absorption spectra confirmed peaks for AuNPs. These findings were in agreement with those reported by Fanoro *et al.*, (2021). As postulated by Mie's equation, the gold nanoparticle size obtained in the present study ranged between 24nm to 30nm. The AgNPs and AuNPs were subjected to test on the first day of synthesis and the results were as shown in Figure 1a-b.



Amount of PAA (μL)	max	Abs (nm)
100	425.3±0.58	0.948±0.002
50	425.7±0	0.761±0.002
20	425.7±0.58	0.522±0.001



Amount of PAA(μL)	max	Abs (nm)
100	533±1.0	0.718±0.002
50	433±0.58	0.550±0.002
20	432±1.53	0.530±0.002

Figure 1: UV-Vis absorption peaks for (a) AgNPs and (b) AuNPs. Values are expressed as mean ± standard deviation (n=3).

Figure 1 (a) shows UV-Vis spectra for AgNPs produced by varying amounts of PAA ranging from 20 μ L to 100 μ L and **(b)** shows UV-Vis spectra for AuNPs produced by varying amounts of PAA ranging from 20 μ L to 100 μ L (The insets show the absorbance depending on the amount of PAA used). It can be deduced that there was no significant difference in the SPR bands shown by each of the nanoparticles formed with respect to the amount of PAA used as a reducing agent this shows that similar particles of silver were synthesized regardless of the change in the amount of reducing agent used. But there was a gradual decrease in the intensities of absorbance of both AuNPs and AgNPs with respect to the amount of PAA used in the reduction process from 20 μ L to 100 μ L. This could be due to an increase in the number of AgNPs and AuNPs formed due to an increase in the amount of the reducing agent.

There was a shift of surface plasmon bands at around 425 to 429nm for AgNPs between day one and day 42 when 100 μ L was used as shown in Figure 2.

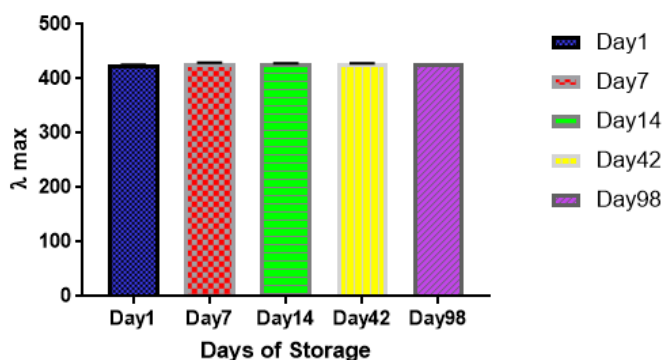


Figure 2: Surface plasmon bands for the different days.

The results indicated a significant difference between day 1, day 7, day 14 and day 42 (one way ANOVA at a confidence level of 95% and the Tukeys multiple comparisons test, $\alpha=0.05$, $n=3$).

According to Kurmar *et al.*, (2018), a shift to the longer wavelengths of UV-Vis indicated the formation of bigger-sized nanoparticles. But after day fourteen there was no significant change in the wavelengths of both AgNPs and AuNPs up to day 98. This indicated no further growth of the nanoparticles hence particles were protected from agglomeration. These results were superior to the work published by Velgosova *et al.*, (2017) where the AgNPs synthesized using algae *Parachlorella kesslerias* stabilizers showed a loss of stability after 20 days of storage under room temperature. This confirms that PAA has better stabilizing ability.

4. Conclusion

A simple protocol for synthesis and stabilization of monodispersed AgNPs and AuNPs of small size regime has been developed. The stability of the nanoparticles was achieved by using PAA which successfully minimized agglomeration of the nanoparticles for a storage period of above 90 days at room temperature.

Acknowledgement

We thank the Organization for women in science for the developing world (OWSD) for financing this project, USIU-Africa for the laboratory space and instrumentation, Kenyatta University, the Teachers Service Commission and Kenya Chemical Society.

References

- Baygazieva, E. K., Yesmurzayeva, N. N., Tatykhanova, G. S., Mun, G. A., Khutoryanskiy, V. V., and Kudaibergenov, S. E. (2014). Polymer protected gold nanoparticles: synthesis, characterization and application in catalysis. *International Journal of Biology and Chemistry*, 7(1), 14-23.)
- Christy, A. J., Kevin, A., Nehru, L. C., and Umadevi, M. (2015). Optical, structural and morphological properties of silver nanoparticles and their antimicrobial activity. *International Journal of ChemTech Research*, 7, 1191-1197.
- Dai, D.; Xu, D.; Cheng, X.; He, Y. Direct Imaging of Single Gold Nanoparticle Etching: Sensitive Detection of Lead Ions. *Anal. Methods* 2014, 6, 4507–4511.
- Di Guglielmo, C., López, D. R., De Lapuente, J., Mallafre, J. M. L., and Suárez, M. B. (2010). Embryotoxicity of cobalt ferrite and gold nanoparticles: a first in vitro approach. *Reproductive Toxicology*, 30(2), 271-276.
- Fanoro, O. T., Parani, S., Maluleke, R., Lebepe, T. C., Varghese, J. R., Mavumengwana, V., and Oluwafemi, O. S. (2021). Facile Green, Room-Temperature Synthesis of Gold Nanoparticles Using Combretum erythrophyllum Leaf Extract: Antibacterial and Cell Viability Studies against Normal and Cancerous Cells. *Antibiotics*, 10(8), 893.
- Grillet, N., Manchon, D., Cottancin, E., Bertorelle, F., Bonnet, C., Broyer, M., ... and Pellarin, M. (2013). Photo-oxidation of individual silver nanoparticles: a real-time tracking of optical and morphological changes. *The Journal of Physical Chemistry C*, 117(5), 2274-2282.

- Ibrayeva, Z. E., Kudaibergenov, S. E., and Bekturov, E. A. (2013). Stabilization of metal nanoparticles by hydrophilic polymers. *LAP Lambert Academic Publishing, Saarbrücken, Germany*, 376pp.
- Khan, A. K., Rashid, R., Murtaza, G., and Zahra, A. J. T. R. (2014). Gold nanoparticles: synthesis and applications in drug delivery. *Tropical journal of pharmaceutical research*, 13(7), 1169-1177.
- Kulkarni, N., and Muddapur, U. (2014). Biosynthesis of metal nanoparticles: a review. *Journal of Nanotechnology*, 2014.
- Malarkodi, C., Rajeshkumar, S., Vanaja, M., Paulkumar, K., Gnanajobitha, G., and Annadurai, G. (2013). Eco-friendly synthesis and characterization of gold nanoparticles using *Klebsiella pneumoniae*. *Journal of Nanostructure in Chemistry*, 3(1), 1-7.
- Mie, G. (1908). Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen. *Annalen der physik*, 330(3), 377-445.
- Nguyen, Q. K., Hoang, T. H., Bui, X. T., Nguyen, T. A. H., Pham, T. D., and Pham, T. N. M. (2021). Synthesis and application of polycation-stabilized gold nanoparticles as a highly sensitive sensor for molecular cysteine determination. *Microchemical Journal*, 168, 106481.
- Prabu, H. J., and Johnson, I. (2015). Plant-mediated biosynthesis and characterization of silver nanoparticles by leaf extracts of *Tragia involucrata*, *Cymbopogon citronella*, *Solanum verbascifolium* and *Tylophora ovata*. *Karbala International Journal of Modern Science*, 1(4), 237-246.
- Rezazadeh, N. H., Buazar, F., and Matroodi, S. (2020). Synergistic effects of combinatorial chitosan and polyphenol biomolecules on enhanced antibacterial activity of biofunctionalized silver nanoparticles. *Scientific reports*, 10(1), 1-13.
- Rónavári, A., Igaz, N., Adamecz, D. I., Szerencsés, B., Molnar, C., Kónya, Z., ... and Kiricsi, M. (2021). Green silver and gold nanoparticles: Biological synthesis approaches and potentials for biomedical applications. *Molecules*, 26 (4), 844.
- Shah, M., Fawcett, D., Sharma, S., Tripathy, S. K., and Poinern, G. E. J. (2015). Green synthesis of metallic nanoparticles via biological entities. *Materials*, 8(11), 7278-7308.
- Ustarroz, J., Kang, M., Bullions, E., and Unwin, P. R. (2017). Impact and oxidation of single silver nanoparticles at electrode surfaces: one shot versus multiple events. *Chemical science*, 8(3), 1841-1853.
- Velgosova, O., Čížmárová, E., Málek, J., and Kavuličova, J. (2017). Effect of storage conditions on long-term stability of Ag nanoparticles formed via green synthesis. *International Journal of Minerals, Metallurgy, and Materials*, 24(10), 1177-1182.
- Wan Mat Khalir, W. K. A., Shameli, K., Jazayeri, S. D., Othman, N. A., Che Jusoh, N. W., and Hassan, N. M. (2020). Biosynthesized silver nanoparticles by aqueous stem extract of *Entada spiralis* and screening of their biomedical activity. *Frontiers in chemistry*, 8, 620.