Asian Journal of Chemistry; Vol. 30, No. 11 (2018), 2399-2403

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2018.21386

Rapid Synthesis of Gold Nanoparticles without Heating Process

SHOHIFAH ANNUR[1,2,*], SRI JUARI SANTOSA[1,*], NURUL HIDAYAT APRILITA[1], NGUYEN THANH PHUONG[3] and NGUYEN VAN PHUOC[3]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, PO Box BLS 21, Yogyakarta 55281, Indonesia
[2]Department of Chemical Engineering, Faculty of Engineering, Universitas Serang Raya, Jl. Raya Serang-Cilegon Km. 5, Taman Drangong, Serang 42116, Indonesia
[3]Institute for Environmental and Resources, Vietnam National University-Ho Chi Minh City, Vietnam

*Corresponding author: E-mail: sjuari@ugm.ac.id; shohifah.annur@mail.ugm.ac.id

Received: 13 April 2018; *Accepted*: 2 August 2018; *Published online*: 27 September 2018; AJC-19083

Several methods have been developed to synthesize gold nanoparticles (AuNPs), but it is not effective since a high temperature and long time reaction are required. This research developed a rapid and simple synthesis of gold nanoparticles at room temperature using a green reducing agent, L-ascorbic acid. The AuNPs could be synthesized using this method only in 2 s without assisted ultrasonic bath or another reactor. The effects of the concentration of $HAuCl_4$ and L-ascorbic acid, pH and time reaction were investigated in this work. The AuNPs were characterized with the UV-visible spectroscopy, transmission electron microscopy and X-ray diffraction. The UV-visible spectroscopy confirmed surface plasmon resonance (SPR) of AuNPs at 524-535 nm, depends on the synthesis parameters. The TEM result showed that the AuNPs synthesized was monodisperese and have a spherical shape. The XRD measurement performed that AuNPs has a crystallite phase with correspond to the fcc structure of gold nanocrystal. The information obtained in this experiment can be used to design AuNPs synthesis without heating step. Moreover, the method is green, effective and efficient.

Keywords: Gold nanoparticles, Synthesis, L-ascorbic acid.

INTRODUCTION

Gold nanoparticles are widely applied as sensors because of their unique physical and chemical properties. They have a large surface area and a high volume ratio, good conductivity, great mechanical strength and high electrocatalytic activities [1]. Their properties are unique due to the existence of the surface plasmon resonance (SPR) caused by electron oscillations in the conduction band when interacting with the light. The SPR of the AuNPs depends on the size, shape and composition of the particle as well as the distance between particles and its associated with the specific colour [2].

The AuNPs have a prominent advantage compare to the bulk metal. They change their SPR when binding with other materials. The AuNPs provide a range of colours from red, brown, to purple as the core size increases from 1 nm to 100 nm. In general, AuNPs gives a strong SPR peak in the range 500-550 nm. This phenomenon could not found in their bulk metal [3].

Generally, the synthesis of AuNPs was determined by two methods, the bottom-up method and the top-down method. The first one is conducted by reducing metal ions using reducing agents to form nano sized particles. The other one was distinguished by converting bulk metal into nano sized particles [4]. Numerous researchers apply the bottom-up method by developing various reducing agents. Reducing agents donate electrons to metal ions, then convert them into uncharged particles to form a nano sized cluster [5].

There are many of studies in synthesis AuNPs by reducing of gold ions. The AuNPs can be synthesized using reducing agents trisodium citrate [6], *p*-aminobenze sulfonic acid and $NaBH_4$ [7], as well as bovine serum albumin [8]. Some AuNPs were functionalized with capping agent or stabilizer to increase their stability. Several researchers used reducing and capping agent directly at the same time. Lin and co-workers [9] used $NaBH_4$ as both the reducing agent and the capping agent to make AuNPs adsorb the *p*-nitrophenol compound. Lu *et al.* [10]

used trisodium citrate as reducing agent and stabilizer for the synthesis of AuNPs. Unfortunately, those studies still required high temperatures to reduce Au^{3+} to Au^0. Innovations in the synthesis of AuNPs at room temperature, without heating process remain limited.

Ascorbic acid is the major component of vitamin C that reduce various metal ions in solution [11]. Some researchers have succeed to reduce gold into AuNPs using ascorbic acid and other compounds. Blocho *et al.* [12] have successfully synthesized AuNPs by ascorbic acid and $NaBH_4$ as reducing agents through a continuous flow process. Khan and co-workers [13] used ascorbic acid to reduce Au^{3+} in the cetyltrimethylammonium bromide (CTAB) media. The latest research, was developed by Hurtado *et al.* [14] which successfully synthesized AuNPs at room temperature using ascorbic acid and sucrose. In this experiment, we have successfully synthesized AuNPs using L-ascorbic acid in the aqueous media without the assistance of other reducing agents, no need heating process and in a very short time. Optimizing the molar ratio between the precursor, the reducing agent and certain pH in the synthesis allow this synthesis could be conducted at room temperature.

EXPERIMENTAL

Gold(III) chloride ($HAuCl_4$) solution was prepared from 1 g certified gold metal 99.99 % (PT. Aneka Tambang, Indonesia) which was diluted in aqua regia 40 mL, then distilled water was added to the solution until 100 mL volume was achieved. L-Ascorbic acid (Merck, Germany), HCl (Merck, Germany) and NaOH (Merck, Germany) were used in this work. All chemicals were of analytical grade and used without further purification.

Synthesis of AuNPs: Gold nanoparticles (AuNPs) were produced by reduction of gold(III) chloride with L-ascorbic acid. Gold(III) chloride concentration varied from 0.1 to 0.5 $\times 10^{-3}$ M whereas the concentration of L-ascorbic acid varied from 0.5 to 15 $\times 10^{-3}$ M. The pH of L-ascorbic acid was adjusted from 1.0 to 13.0 by the addition of HCl and NaOH solution. The preparation of AuNPs was conducted by adding the $HAuCl_4$ solution with L-ascorbic acid solution in a test tube.

Characterization of AuNPs: The formation of AuNPs was monitored by UV-visible spectrophotometer (Shimadzu UV-1700 PharmaSpec) directly after synthesis using 1 cm optical path length quartz cuvette and 200-800 nm wavelength range. The morphology of AuNPs obtained was conducted by transmission electron microscopy/TEM (JEOL JEM-1400). AuNPs for TEM analysis was prepared by immersing the copper grid into AuNPs colloid then drying at room temperature. The accelerating voltage of 120 kV was used in the capturing the image. The crystallinity of AuNPs achieved was investigated by XRD (Rigaku Miniflex 600). The electricity of 40 kW, 15 mA was applied in this analysis.

RESULTS AND DISCUSSION

The formation of AuNPs in this experiment was conducted by mixing of gold(III) chloride solution with L-ascorbic acid. Since L-ascorbic acid reduced the gold ions, the colour of the solution changed rapidly in 2 s to red indicated the formation of gold nanoparticles. This colour is due to the surface plasmon resonance absorption [15]. This AuNPs synthesis involved a reduction-oxidation process. In the oxidation process, the electrons would be donated while in the reduction process, the electrons would be captured [16].

Ascorbic acid has an E^0 0.008 V, while gold has the highest E^0 compared to other metals, which is 1.69 V. It can be estimated that gold would be reduced while ascorbic acid would be oxidized. In the other hand, ascorbic acid has an OH functional group that can donate an electron to reduce the Au^{3+} in the gold (III) chloride solution to Au^0. Ascorbic acid was oxidized to dehydroxyascorbic acid (DHA) which is shown in this reaction [17].

$$2HAuCl_4 + 3C_6H_8O_6 \longrightarrow 2Au^0 + 3C_6H_6O_6 + 8HCl$$

The reaction product was AuNPs capped by dehydroxyascorbic acid as the oxidation product from ascorbic acid. The schematic diagram of this synthesis is shown in Fig. 1.

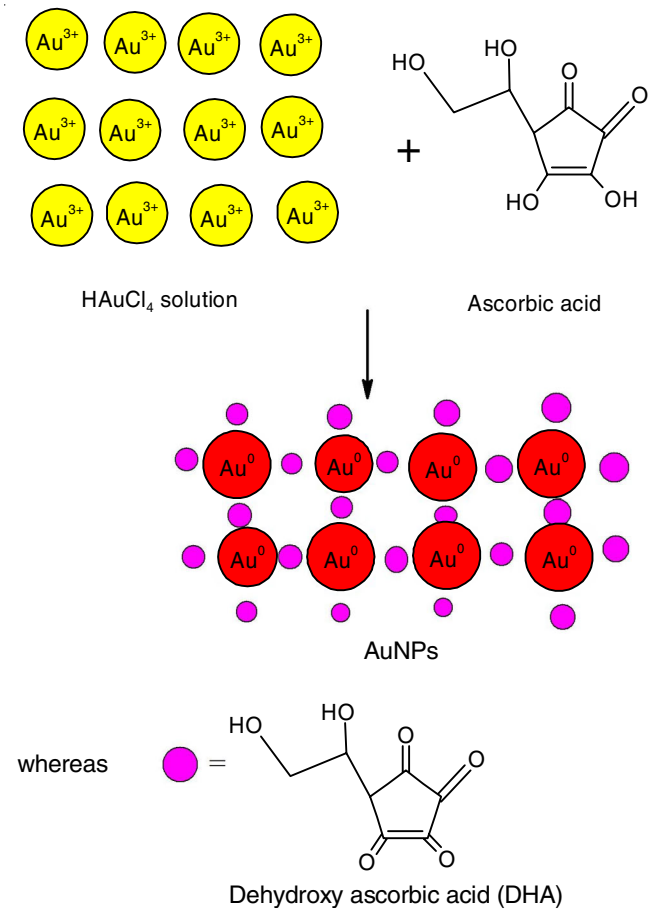

Fig. 1. Schematic diagram of AuNPs synthesis at room temperature

Sun *et al.* [17] succeed in the reducing gold ion using ascorbic acid but in the reverse micelles media. Khan *et al.* [13] reported the synthesis AuNPs using ascorbic acid in the cationic surfactant media, namely cetyltrimethylammonium bromide. They used nonaqueous media in the synthesis process. Nonaqueous media was applied due to unstabilized of AuNPs when using ascorbic acid as a reducing agent in the aqueous media. In present work, the AuNPs obtained are stable even synthesis was conducted in aqueous media, without heating process at room temperature.

Effect of $HAuCl_4$ concentration: The concentration of $HAuCl_4$ plays an important role in the synthesis of AuNPs due to the existence of gold precursor. If the concentration of $HAuCl_4$ is too low, it would not be sufficient to provide Au^{3+} that would be reduced by ascorbic acid [11]. Consequently, AuNPs produced were not optimum. To investigate the effect of $HAuCl_4$ concentration, a series of the $HAuCl_4$ solution with different concentrations (0.1×10^{-3} M to 0.5×10^{-3} M) were reduced by L-ascorbic acid with certain concentration (1×10^{-2} M). AuNPs were formed for all samples and showed SPR peak at 530-535 nm with different intensity as shown in Fig. 2. We could see from Fig. 2 that sample 2 which has a concentration of $HAuCl_4$ 0.2×10^{-3} M showed the highest intensity of SPR peak. Sample 3, 4 and 5 performed the decreased intensity of SPR peak due to the aggregation of AuNPs in the high concentration of $HAuCl_4$.

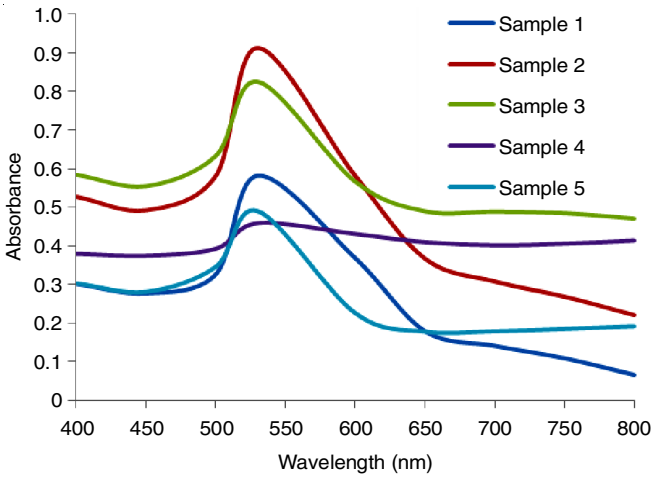

Fig. 2. UV-visible spectra of AuNPs at different concentrations of $HAuCl_4$, sample (1) 0.1×10^{-3} M (2) 0.2×10^{-3} M (3) 0.3×10^{-3} M (4) 0.4×10^{-3} M (5) 0.5×10^{-3} M

Effect of reducing agent concentration: This experiment showed that L-ascorbic acid acts as reducing agent. To obtain the effective molar ratio between $HAuCl_4$ and L-ascorbic acid, the synthesis of AuNPs was conducted at an optimum concentration of $HAuCl_4$ (0.2×10^{-3}M) while the concentration of L-ascorbic acid was varied from 0.5×10^{-3} M to 1.5×10^{-2} M. Fig. 3 showed the correlation between the intensity of SPR spectra with the concentration of L-ascorbic acid.

As shown in Fig. 3, sample 1 which has 0.5×10^{-3} M L-ascorbic acid, could not reduce Au^{3+} to Au^0 due to the low molar ratio of $HAuCl_4$ and L-ascorbic acid (4:5) cause AuNPs could not form at this condition. Fig. 3 stated that there was no SPR peak at 500-550 nm in sample 1, which indicates that AuNPs was not formed.

Sample 2 (1.0×10^{-3} M of L-ascorbic acid) which has a molar ratio of $HAuCl_4$ and ascorbic acid (4: 10) is sufficient to reduce Au^{3+} but not optimum. Sample 3, 4 and 5 showed the SPR peak at 530-535 nm wavelengths, which are characteristic the SPR peak for AuNPs. Raising the molar ratio leads to increase the intensity of the SPR peak. The SPR peak achieved the highest performance in sample 4, which has the molar ratio 1:25, which is the optimum molar ratio. After obtained an optimum condition, increasing concentration of L-ascorbic acid showed a decreasing of SPR peak due to the aggregation of AuNPs.

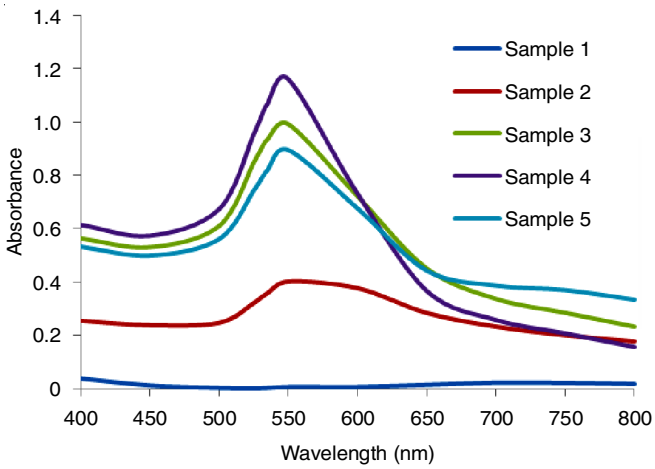

Fig. 3. UV-visible spectra of AuNPs at different concentrations of L-ascorbic acid, sample (1) 0.5×10^{-3} M, (2) 1.0×10^{-3} M, (3) 5×10^{-3} M, (4) 1×10^{-2} M, (5) 1.5×10^{-2} M

Effect of pH of reducing agent: Our initial work showed that the formation of AuNPs could be achieved if the pH of L-ascorbic acid was 3.0-12.0. UV-visible spectrophotometer measurements showed that all samples have SPR peak at 524-535 nm, depends on the pH which was applied (Fig. 4a). Fig. 4a showed that very low pH of L-ascorbic acid (pH 1.0), there was no SPR peak at 500-550 nm and the solution was colourless, confirmed that AuNPs were not formed at this condition. It is because protonation of L-ascorbic acid at low pH and consequently decreasing its reducing power [18].

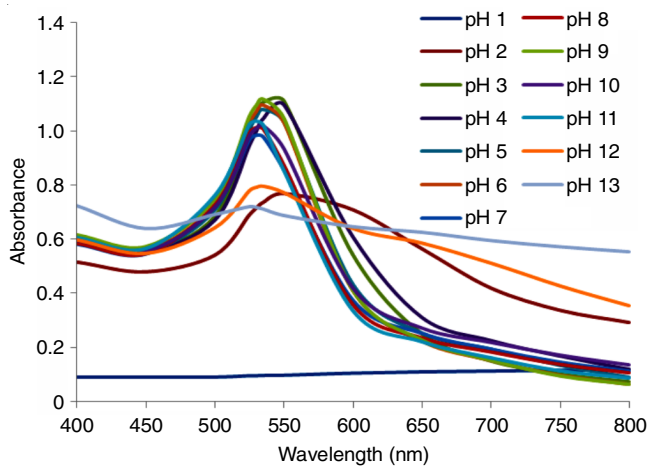

Fig. 4. UV-visible spectra of AuNPs using different pH of reducing agent

In pH 2.0, the colour of the solution was purple and SPR peak appeared in 533 nm during measurement with UV-visible spectrophotometer, which leads to a formation of AuNPs. Expanding pH of L-ascorbic acid from 3.0 to 11.0 caused an increasing of SPR peak intensity, which means the higher amounts of AuNPs were formed.

The pKa of ascorbic acid are 4.10 and 11.79 (Fig. 5). Regarding this pKa, at pH ≥ 3.0, hydroxyl group, which has pKa 4.10 were deprotonated. The anion of ascorbic acid formed a coordination with $[AuCl_3]^{2-}$. Another hydroxyl group, which has pKa 11.79 reduced Au^+ to Au^0. Complexation of Au^+ and

ascorbic acid become the center of oxidation and reduction process, contributed to the formation of AuNPs at pH ≥ 3.0. Ascorbic acid was oxidized to dehydroxyascorbic acid [11]. The optimum pH was achieved at alkaline condition, at pH 10.0. The AuNPs performed the most stable at this pH. This research is in agreement with the previous research, which reported that at higher pH value, the redox reaction was accelerated approximately six times. The increasing amount of deprotonated fraction of ascorbic acid at higher pH causes the smaller energetic barrier during the inner sphere electron transfer and results in acceleration of the redox reaction [19].

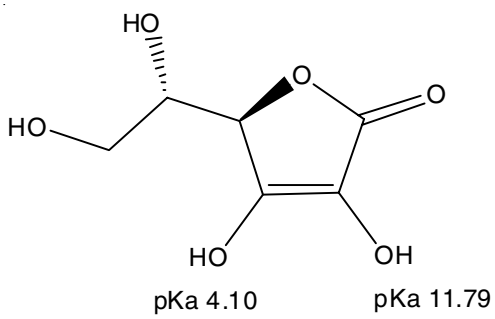

Fig. 5. Structure and pKa value of L-ascorbic acid

At pH 12.0 and 13.0, the SPR peak of AuNPs decreased due to the aggregation of these AuNPs at high pH. In the high alkaline condition, OH^- is the dominant species that could occupy the surface of AuNPs, which cause aggregation and precipitation. This aggregation was appeared in the blue colour of AuNPs and the broadening of the SPR peak at these pH. The colours of AuNPs synthesized in different pH were shown in Fig. 4b.

Gold nanoparticles synthesized using L-ascorbic acid at room temperature showed different SPR peak depends on the pH. Increasing the pH lead to lower wavelength (blue shift) and sharper of SPR peak due to the more stable of AuNPs formed. Lee *et al.* [20] reported that expanding the λ_{max} value to a higher wavelength (red shift) conduct to a bigger size of AuNPs obtained. The λ_{max} of SPR peak of AuNPs could be seen in Table-1.

TABLE-1
UV-VISIBLE MEASUREMENT OF SPR PEAK OF AuNPs in DIFFERENT pH OF L-ASCORBIC

pH of L-ascorbic acid	λ_{max} (nm)	pH of L-ascorbic acid	λ_{max} (nm)
1	–	8	524
2	533	9	524
3	533	10	524
4	530	11	524
5	526	12	535
6	525	13	535
7	525	–	–

Study of reaction time: In this work, the reaction was occurred directly after contact with reducing agent. Expanding reaction time to 30 min did not change the λ_{max} and the sharpness of SPR band when measure in UV-vis spectrophotometry (Fig. 6). It means that all of Au^{3+} has been reduced by L-ascorbic acid shortly after reaction and the reaction has been

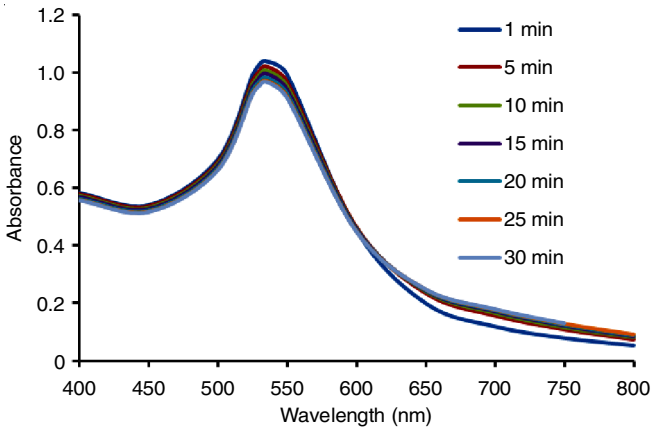

Fig. 6. UV-visible spectra of AuNPs synthesized at different time reaction

finished at the first minute. The antioxidant properties cause the process AuNPs formation become fast and effective. Ascorbic acid also contributes to the metallic surfaces coating and nanostructures stability [14].

Characterization of AuNPs: The TEM analysis was performed to AuNPs at optimum condition (the molar ratio between $HAuCl_4$:L-ascorbic acid 1:25, at pH of reducing agent 10.0). The result showed that AuNPs was monodisperse and has a spherical shape (Fig. 7). The morphology of the AuNPs are in line with the former research which found that AuNPs synthesized at room temperature using ascorbic acid and sucrose as reducing agent also have a spherical structure [14].

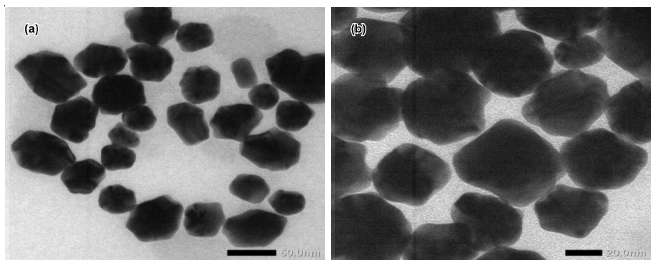

Fig. 7. TEM images of AuNPs reduced by L-ascorbic acid with different magnitude (a) scale bar 50 nm (b) scale bar 20 nm

The XRD measurement was conducted to determine the phase composition and crystal structure of AuNPs. Fig. 8 appeared the typical XRD pattern of AuNPs, which showed a broad peak which indicates the arrangement of AuNPs. There was four certain peaks at 2θ which conform to approximately 37.89°, 44.08°, 64.32° and 77.25°. These peak were correspond to diffraction from (111), (200), (220) and (311) faces of the fcc structure of Au nanocrytals. This experiment was in line with the database of Joint Committee on Powder Diffraction Standard (JCPDS file No. 00-004-0784). The peak that allocate to (111) was more intense than the other Bragg reflections (200), (220) and (311). It means that this AuNPs tend to locate at (111) plane. The XRD pattern confirm that AuNPs synthesized using L-ascorbic acid was crystalline nature. This results was in agreement with the previous research [21,22].

The average crystallite size of AuNPs was determined using XRD by calculated from the full width at half maximum (FWHM) of a diffraction peak using the Scherrer's equation:

$$d = K\lambda/B \cos\theta$$

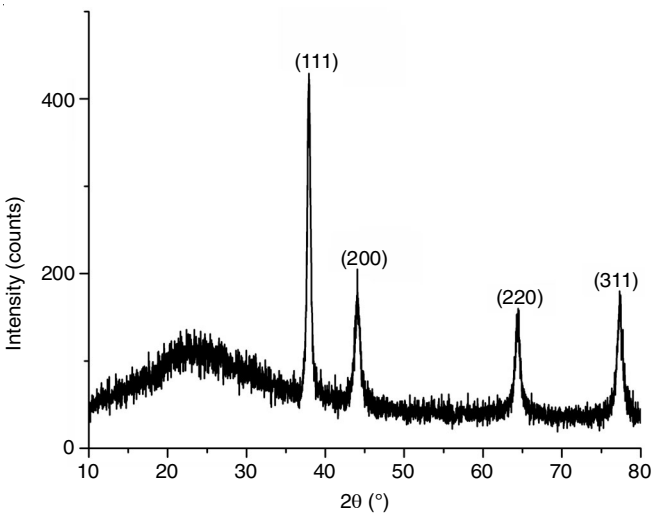

Fig. 8. XRD pattern of AuNPs prepared by L-ascorbic acid at pH 10

where d is the crystallite size, B is the corrected FWHM (in radian), θ is the diffraction angle (Bragg angle), λ is the X-ray diffraction wavelength (1.54056 Å) and K is Scherrer's constant (K = 0.94) [22]. Based on this formula, the AuNPs synthesized have a crystallite size approximately 15 nm.

Conclusion

An instant method is performed to synthesize AuNPs without heating process, at room temperature by using a green reducing agent, ascorbic acid. AuNPs synthesized using this method is easy to functionalize with the other compounds to increase the stability. It found that adjustment pH of L-ascorbic acid to alkaline would increase the stability of AuNPs and cause the SPR peak shifted to blue shift. The UV-visible spectrophotometer measurement performed the SPR peak at 524 nm when pH of L-ascorbic acid was 10. AuNPs formed at this condition was the most stable than the others. On the other hand, the future research in control size and stability of AuNPs should be conducted since many applications of AuNPs, which are needed in a chemical and biological sensor.

ACKNOWLEDGEMENTS

This research was supported by Doctoral Dissertation Grant 2017 by Directorate General of Higher Education, Ministry of Research, Technology and Higher Education, Republic of Indonesia. We also thank to Exceed-Swindon, Germany for the supporting the collaborative research between Chemistry Department of Universitas Gadjah Mada and Institute of Environment and Resources, Vietnam.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. T. Yin and W. Qin, *Trends Analyt. Chem.*, **51**, 79 (2013); https://doi.org/10.1016/j.trac.2013.06.009.
2. K. Shrivas, R. Shankar and K. Dewangan, *Sens. Actuators B Chem.*, **220**, 1376 (2015); https://doi.org/10.1016/j.snb.2015.07.058.;
3. A. Rohiman and B. Buchari, *Res. Dev. Nanotechnol. Indo.*, **1**, 74 (2014).
4. H.-W. Cheng, Z.R. Skeete, E.R. Crew, S. Shan, J. Luo and C. Zhong, *Compreh. Anal. Chem.*, **66**, 37 (2014). http://dx.doi.org/10.1016/B978-0-444-63285-2.00002-X.
5. E.N. Fatimah and N. Hidajati, The Synthesis and Characterization of Gold Nanoparticles as a Support Material of Sunscreen Activity of Cinnamic Derivatives; In: Proceeding of National Conference of Chemistry in UNESA: ISBN: 978-979-028-550-7, pp. 978-979 (2012).
6. K.M. Giannoulis, D.L. Giokas, G.Z. Tsogas and A.G. Vlessidis, *Talanta*, **119**, 276 (2014); https://doi.org/10.1016/j.talanta.2013.10.063.
7. Z. Sun, Z. Cui and H. Li, *Sens. Actuators B Chem.*, **183**, 297 (2013); https://doi.org/10.1016/j.snb.2013.04.032.
8. C.L. Gopu, A. Shanti Krishna and K. Sreenivasan, *Sens. Actuators B Chem.*, **209**, 798 (2015); https://doi.org/10.1016/j.snb.2014.12.004.
9. C. Lin, K. Tao, D. Hua, Z. Ma and S. Zhou, *Molecules*, **18**, 12609 (2013); https://doi.org/10.3390/molecules181012609.
10. L. Lu, J. Zhang and X. Yang, *Sens. Actuators B Chem.*, **184**, 189 (2013); https://doi.org/10.1016/j.snb.2013.04.073.
11. B. Zümreoglu-Karan, *J. Nanopart. Res.*, **11**, 1099 (2009); https://doi.org/10.1007/s11051-008-9498-5.
12. M. Luty-Blocho, K. Fitzner, V. Hessel, P. Lob, M. Maskos, D. Metzke, K. Paclawski and M. Wojnicki, *Chem. Eng. J.*, **171**, 279 (2011); https://doi.org/10.1016/j.cej.2011.03.104.
13. Z. Khan, T. Singh, J.I. Hussain and A.A. Hashmi, *Colloids Surf. B Biointerfaces*, **104**, 11 (2013); https://doi.org/10.1016/j.colsurfb.2012.11.017.
14. R. Britto Hurtado, M. Cortez-Valadez, L.P. Ramírez-Rodríguez, E. Larios-Rodriguez, R.A.B. Alvarez, O. Rocha-Rocha, Y. Delgado-Beleño, C.E. Martinez-Nuñez, H. Arizpe-Chávez, A.R. Hernández-Martínez and M. Flores-Acosta, *Phys. Lett. A*, **380**, 2658 (2016); https://doi.org/10.1016/j.physleta.2016.05.052.
15. S.B.D. Borah, T. Bora, S. Baruah and J. Dutta, *Groundw. Sustain. Dev.*, **1**, 1 (2015); https://doi.org/10.1016/j.gsd.2015.12.004.
16. K.A. Savin, Writing Reaction Mechanisms in Organic Chemistry, Academic Press, edn 3, pp. 1-502 (2014).
17. K. Sun, J. Qiu, J. Liu and Y. Miao, *J. Mater. Sci.*, **44**, 754 (2009); https://doi.org/10.1007/s10853-008-3162-4.
18. S. Rastegarzadeh and S. Abdali, *Talanta*, **104**, 22 (2013); https://doi.org/10.1016/j.talanta.2012.11.023.
19. M. Luty-Blocho, K. Paclawski, M. Wojnicki and K. Fitzner, *Inorg. Chim. Acta*, **395**, 189 (2013); https://doi.org/10.1016/j.ica.2012.10.031.
20. C.R. Lee, S. Kim, C.J. Yoon, M.S. Gong, B.K. Choi, K. Kim and S.W. Joo, *J. Colloid Interface Sci.*, **271**, 41 (2004); https://doi.org/10.1016/j.jcis.2003.10.020.
21. W.Y. Qiu, K. Wang, Y.Y. Wang, Z.C. Ding, L.X. Wu, W.D. Cai and J.K. Yan, *Int. J. Biol. Macromol.*, **106**, 498 (2018); https://doi.org/10.1016/j.ijbiomac.2017.08.029.
22. R. Shaikh, N. Memon, A.R. Solangi, H.I. Shaikh, M.H. Agheem, S.A. Ali, M.R. Shah and A. Kandhro, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **173**, 241 (2017); https://doi.org/10.1016/j.saa.2016.09.016.