

Reduction mechanisms of Ag(I) and Au(III) in the synthesis of silver and gold nanoparticles using leaf extract of *Terminalia catappa*

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Abstract. Synthesis of silver nanoparticles (AgNP) and gold nanoparticles (AuNP) was carried out by the reduction method with leaf extract of Ketapang (*Terminalia catappa*). The biomolecules present in the extract generated the reduction of Ag^+ and Au^{3+} ions from AgNO_3 and HAuCl_4 , respectively. The growth of nanoparticles was monitored by UV-Vis spectrophotometer. The maximum absorption of biosynthesis of AgNP and AuNP were observed in the respective range of 421-431 nm and 530-535 nm. Those peaks correspond to surface plasmon absorbance of AgNP and AuNP, respectively. Analysis on the functional groups change of the extract by Fourier Transform Infra Red (FTIR) Spectroscopy showed the formation of carbonyl- from hydroxyl-groups which suggested the oxidation and reduction processes involved in the formation of both nanoparticles. The average size distributions determined by PSA (Particle Size Analyzer) are 55-71 nm and 18-44 nm for AgNP and AuNP, respectively. Morphology of the silver nanoparticles was observed by Scanning Electron Microscope (SEM) and the structure of the compounds was characterized using X-ray Diffraction (XRD). The shape of AgNP varied from triangular, cubic and hexagonal polyshaped, while AuNP were spherical. XRD studies showed that the nanoparticles obtained were crystalline gold and silver.

Keywords: reduction mechanism, Ag(I), Au(III), AgNP, AuNP, *Terminalia catappa* leaf extract

INTRODUCTION

Nanoparticles exhibit unusual optical and catalytic properties and are considered as a new physico-chemical dimension between molecules and bulk materials. The surface to volume ratio of nanoparticles is extremely large. Electronic properties of nanoparticles such as light absorption, color, fluorescence, catalytic activity and electrochemistry depend on the size of nanoparticles. Due to these properties of nanoparticles, variable researches for nanoparticles synthesis are extended. A lot of nanoparticles preparation methods were reported. Nanoparticles can be prepared not only by chemical methods, but also by photochemical, electrochemical, radiolytic methods, sonolytic methods, and bioreduction using natural products [1, 2]. The last method is usually classified as a new branch of nanotechnology, the so called

nanobiotechnology. Nanobiotechnology combines biological principles with physical and chemical procedures to generate nano-sized particles with specific functions. These methods of synthesis can be divided into intra- and extra-cellular. Biosynthetic methods can employ either microorganism cells or plant extract for nanoparticles production [3, 4, 5]. Formation of metal nanoparticles, such as silver and gold nanoparticles, is an example that will be discussed here.

Gold and silver nanoparticles are presently under intensive study for applications in optoelectronic devices, ultrasensitive chemical and biological sensors and as catalysts. The nanoparticles have been used for their potential applicability in bioremediation of radioactive wastes [1], sensor technology, optronics, recording media and optics, and their bioactivity effects [4, 6, 7]. Their ecotoxicity to the environment is another reason to study the metal nanoparticles [8].

Utilization of plant extract for the synthesis of nanoparticles could be advantageous over other environmentally benign biological processes by eliminating the elaborate process of

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maintaining cell cultures. The above synthetic protocol by plant extract or biomass exemplifies the promising application of the green synthesis of metal nanoparticles. Very recently, green metal nanoparticles have been synthesized using various natural products such as opuntia (*Opuntia ficus-indica*) [9], aqueous extract of *Codonopsis pilosula* roots [10], cinnamon (*Cinnamomum zeylanicum*) bark extract and powder [11], leaf extract of *Dalbergia sissoo* [12].

Ketapang (Makassarese: *talise*) is found as a specific plant in South Sulawesi region and has been used for traditional medicine since the ancient time. The plant is a medium sized tree with leaves clustered towards the ends of the branches. The various extracts of leaves and bark of the plant have been reported to be anticancer antioxidant [13], hepatoprotective [14], hepatitis [15], and aphrodisiac [16]. Fruit of Ketapang contains cyanidin-3-glucoside, corilagin (Topoisomerase I and II) inhibitor [17], xanthin oxidase inhibitor [18], ellagic-acid as anti-HIV [19] and flavonoids [20]. Ketapang is rich in tannins that are reported to be antidiabetic properties [21, 22]. Those compounds might be responsible in the bioreduction reaction of silver and gold ions to produce silver nanoparticles (AgNP) and gold nanoparticles (AuNP), respectively.

In this paper we demonstrate method for the synthesis of silver and gold nanoparticles by the reduction of respective aqueous silver (Ag(I)) and chloroaurate (Au(III)) ions using leaf extract of Ketapang (Makassarese: *talise*). The scenario of oxidation and reduction mechanism is proposed in this paper. To the best of our knowledge, it is rarely discussed in the previous papers related to biosynthesized gold and silver nanoparticles [12, 23].

METHODOLOGY

Materials

The silver nitrate (AgNO_3 , 99.8%) and gold (III) chloride hydrate, ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.999%) were purchased from the Merck Agent (Makassar, Indonesia) and have been used for the synthesis of AgNP and AuNP, respectively. The fresh leaves were taken from the tree of Ketapang (*Makassarese: talise*) located in Hasanuddin University Campus, Makassar, South Sulawesi, Indonesia.

Methods

Preparation of leaf extract

Synthesis of silver and gold nanoparticles was carried out through the following procedure: 10 g fresh leaves of Ketapang (*Terminalia catappa*; Makassarese: *talise*) were taken and

washed thoroughly to remove dust and other impurities. These washed leaves were cut into 2 cm x 2 cm pieces and immersed into the 50 mL Millipore water and then boiled for 5 min. The extract was filtered and the residual material was thrown away.

Synthesis of silver and gold nanoparticles

For the bioreduction of Au(III) into the Au(0), a freshly prepared leaf extract (3 mL) was added drop wise using a syringe to 50 mL of 0.5 mM HAuCl_4 solution. Similarly for the bioreduction of Ag(I) into the Ag(0), 1 mL of leaf extract was added to 40 mL of 1 mM AgNO_3 solution. After the addition of leaf extracts both the solutions were kept in the incubator at 37 °C until used.

UV-Visible spectroscopic analysis

The reduction of both Ag^+ and AuCl_4^- in the aqueous solution was monitored with the regular sampling of the 0.3 mL aliquots. The sample was diluted with 3 mL of the Millipore water and measuring the UV-visible spectra of the diluted sample. Shimadzu UV-2600 spectrophotometer at a resolution of 1 nm was used for the analysis electronic transition in the sample.

Particle size analysis

Solution of AgNP and AuNP as much as 50 μL is pipetted and then put into the sample holder of Particle Size Analyzer (PSA) Vasco DLS. The Vasco DLS uses the thermal motions of particles in suspension (Brownian Motion) to determine their size. Here the sample suspension is irradiated by a laser and the light scattered in a certain direction detected with high time resolution. From the fluctuation of the intensity of the scattered light, the mobility of the particles can be calculated and then again via the Stokes-Einstein formula, their size can be calculated.

X-ray diffraction analysis

Solution of Ag(0) and Au(0), which was obtained from complete reduction of AgNO_3 and HAuCl_4 solution, respectively, was maintained at -80 °C for 5 hours and then lyophilized for 24 hours. This lyophilized powder was further used for the XRD analysis. The XRD analysis was done using an XRD Rigaku MiniFlex diffractometer operating at 40 mA current and 45 kV voltages with $\text{CuK}\alpha$ radiation to confirm the crystalline form of silver and gold nanoparticles.

Fourier Transform Infrared (FTIR) spectroscopic analysis

Sample preparation for FTIR analysis is as follows: 15 mL solution of silver and gold nanoparticles were taken separately and

centrifuged at 4000 rpm for 10 min. The resulting suspension was redispersed into 20 mL of sterile water and centrifuged again. The process of centrifugation and redispersion was repeated three times to make the solution free from any biomass which is not present as the capping agent in the solution. The sample is then put into FTIR instrument (Shimadzu IRPrestige-21).

Scanning Electron Microscopy (SEM) measurements

Samples for SEM measurement were taken after the complete bioreduction of Ag(I) and Au(III) into Ag(0) and Au(0), respectively. SEM samples of aqueous silver and gold nanoparticles were prepared by taking a small drop and putting it on the carbon-coated copper grid and dried at room temperature. The SEM observations were performed on the instrument Tescan Vega3SB Analytical SEM, operating at accelerating voltage of 100 kV.

RESULTS AND DISCUSSION

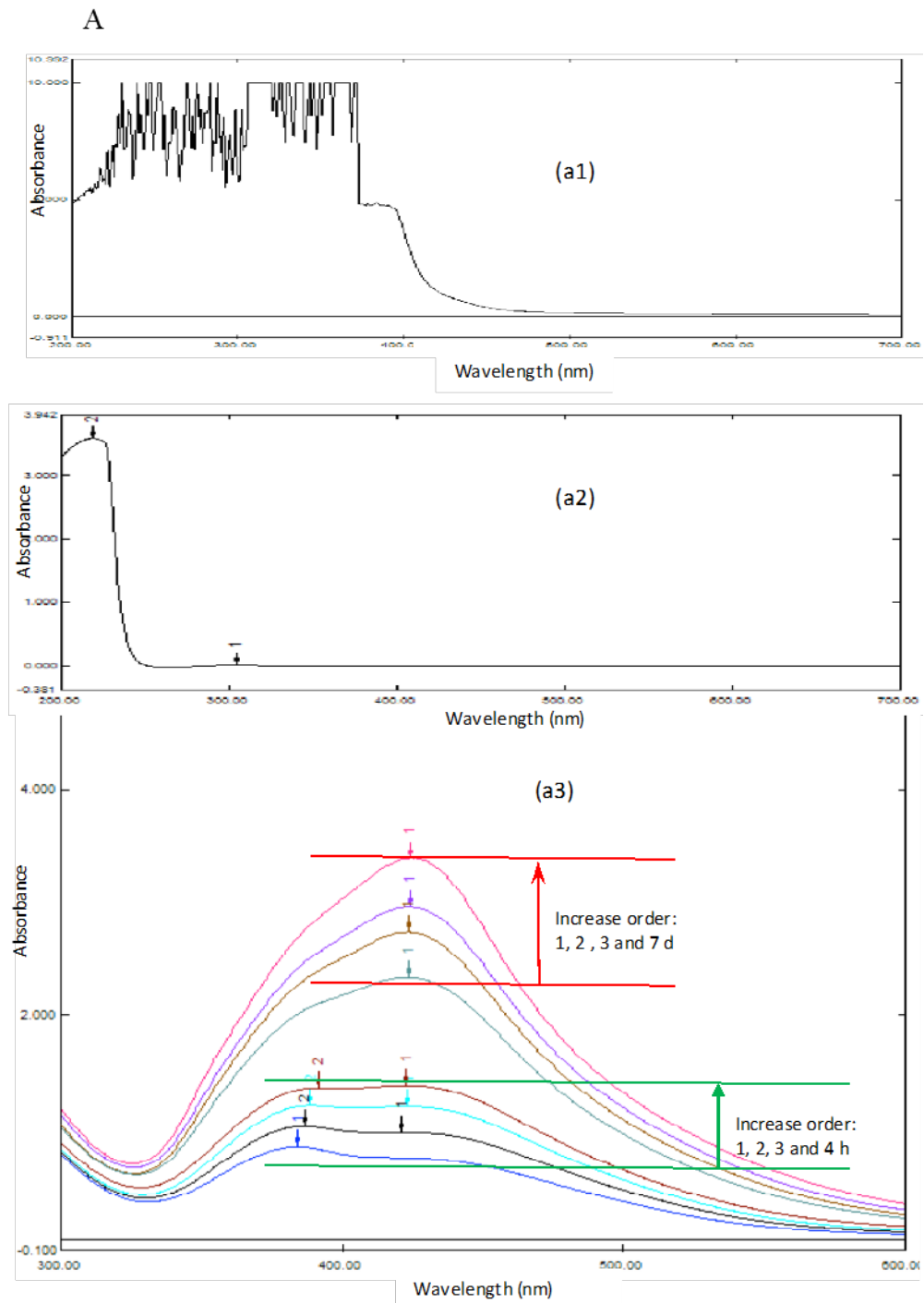
The reduction of aqueous solution of Ag^+ and AuCl_4^- can be easily monitored by UV-Vis spectroscopy. Qualitative analysis for the formation of AgNP and AuNP can also be determined due to the specific characteristic of surface plasmon resonance ("absorption") of both nanoparticles. The excitation of surface plasmon vibrations of silver and gold nanoparticles exhibits yellowish-brown and red wine color, respectively (Fig. 1 and 2). This makes possible to follow the formation of AgNP and AuNP in the aqueous solution [12, 23].

The color of gold solution in AuNP formation was initially colorless and after the addition of boiled leaf extract of Ketapang (*Terminalia catappa* Linn) the color transformed into red wine color within 5 minutes. The reduction continued for 4 hours (Fig. 2(a)). In the case of AgNP formation, the solution was also initially colorless and after the addition of boiled leaf extract of Ketapang (*Terminalia catappa* Linn), the color was changing into light yellow in at least 4 hours. The color proceeded further into yellow and yellowish-brown, but the complete reduction took more time, i.e 24 hours as compared to that for the complete reduction of Au(III) (Fig. 1(b)). The most possible reason could be difference in their redox potential

(Ag^+/Ag , $E_{o,\text{red}} = 0.8$ volt; Au^{3+}/Au , $E_{o,\text{red}} = 1.4$ volt). Figure 1b(iv) presents black crystal after centrifugation of colloidal AgNP. The black crystal is the aggregates of AgNP. This is an evidence that Ag(I) has been reduced to Ag(0). The same precipitate/crystal was also found by Chudasama *et al.* [24].

The maximum absorption for AuNP was observed in the range 530-535 nm (Fig. 2(b2)). In the case of AgNP, the maximum absorption was observed in the range 420-430 nm (Fig. 1(a3)). Both of them are characteristic surface plasmon absorption of both nanoparticles [12, 23]. These absorption peaks were not observed in the spectrum of starting material solutions of AgNO_3 1 mM and HAuCl_4 0.5 mM, and leaf extract of *Terminalia catappa* as well. Furthermore, this can be a proof that reduction reactions of $\text{Au(III)} \rightarrow \text{Au(0)}$ and $\text{Ag(I)} \rightarrow \text{Ag(0)}$ have been occurred [10, 25, 26]. Nevertheless, the existence of elemental Au and Ag should be demonstrated by advanced spectroscopic techniques such as XPS (X-Ray Photoelectron Spectroscopy) or EDXS (Energy Dispersive X-Ray Spectrometry), as suggested by those authors [10, 25, 26].

The SEM images of AgNPs show that their morphology were cubic, hexagonal and triangular in nature (Fig. 3(a)). The SEM images of AuNPs clearly show regularity in shape, which was spherical in nature (Fig. 3(b)). The EDS spectrum of AuNP is shown in Fig. 3(c), while AgNP spectrum is not available. It is clearly seen that the elemental composition presents in AuNP precipitate. In the EDS spectrum for AuNP, the strong peaks appeared at Au: 0.25 keV, 2.2 keV, and 9.75 keV indicate the existence of Au element (Au(0)). The strongest peak was observed at 2.2 keV. The same peak for Au element was also confirmed by Doan *et al.* [10]. Based on the elemental content, AuNP precipitate consists of Au (79.75%) and O (9.01%), and the remainings are Si, Na and Al (1.44-5.56%). This suggests that bioreduction reaction converted $\text{Au(III)} \rightarrow \text{Au(0)}$ and produced gold nanoparticles (AuNP).



B

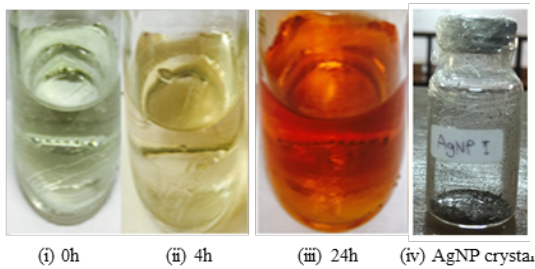


Figure 1. UV-Visible absorption spectra of (a1) leaf extract of *Terminalia catappa*, (a2) AgNO_3 1 mM, (a3) colloidal AgNP, and (B) color change of colloidal AgNP and the existence of AgNP crystal after centrifugation.

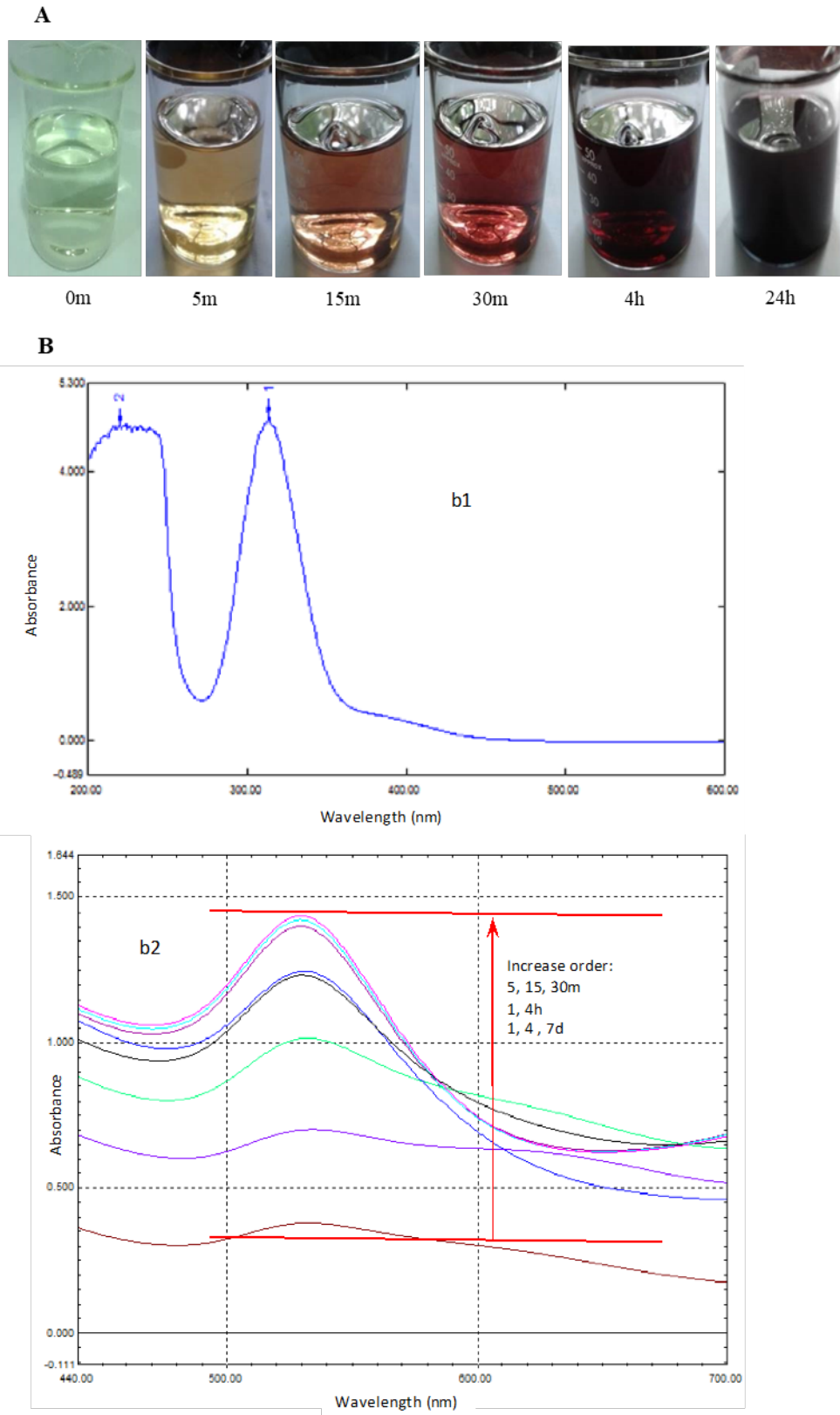
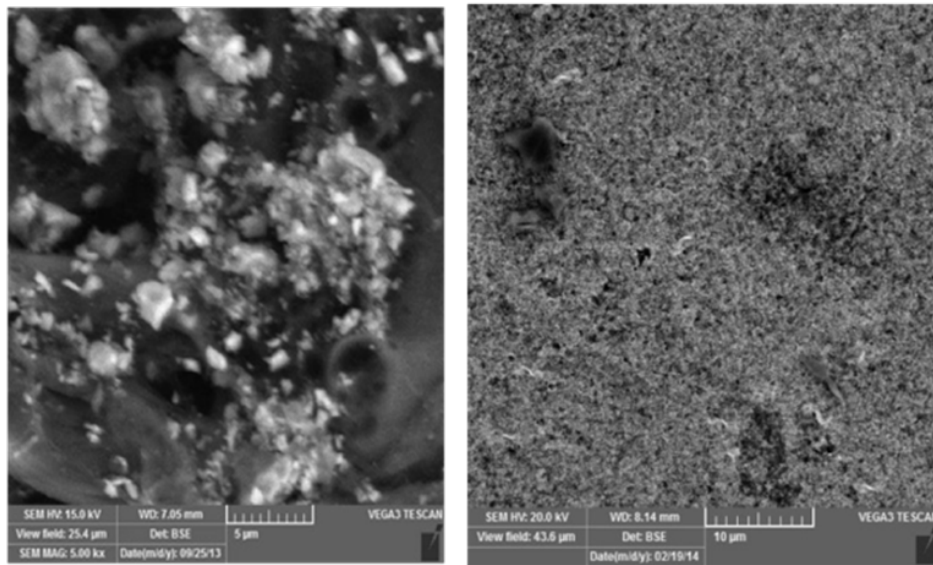
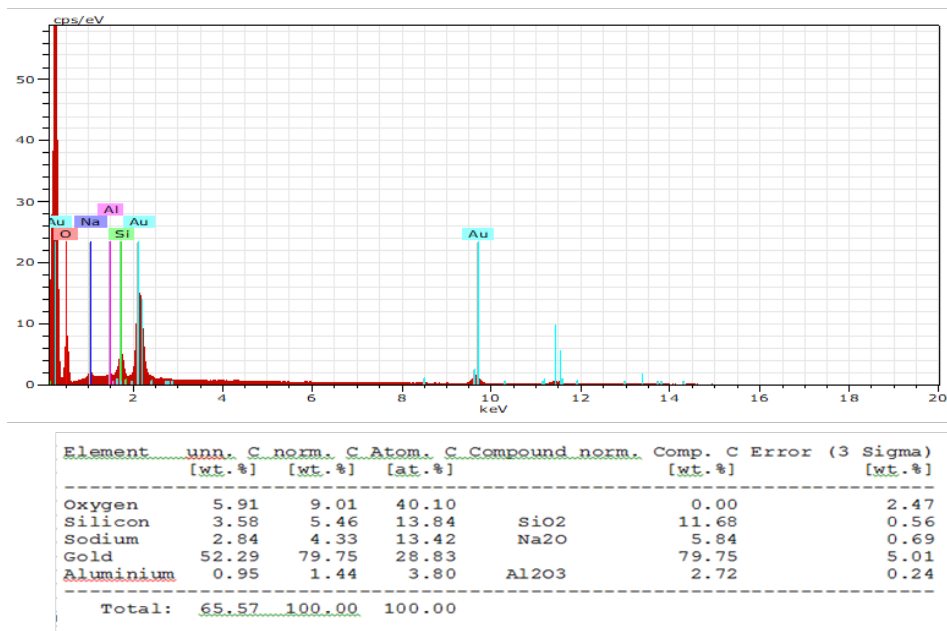


Figure 2. Color change of colloidal AuNP (a) and UV-Visible absorption spectrum of HAuCl₄ 0.5 mM (b1) and colloidal AuNP.



(a) AgNP

(b) AuNP



(c) EDS spectrum and average content elemental gold

Figure 3. SEM images of (a) AgNP and (b) AuNP, and (c) EDS spectrum of AuNP. Peak at 0.25 keV; 2.2 keV and 9.75 keV indicated the existence of Au element

FTIR measurements were carried out to identify the possible biomolecules in the leaf extract of Ketapang which is responsible for the reduction of Ag^+ and AuCl_4^- ions in the formation AgNP and AuNP, respectively. Phytochemical test carried out on the leaf extract of Ketapang showed that phenolic compounds are the dominant compound found in the extract. The phenolic compounds might be tannins as it is known that Ketapang is rich in tannins [21, 22]. Tannin from Ketapang is a potential inhibitor for DNA-topoisomerase II [17] and xanthine oxidase [18]. Therefore, it is supposed in this

paper that tannins also play an important role in the reduction process of Ag^+ and Au^{3+} ions. Table 1 shows the analysis results on the FTIR spectra recorded in the synthesis of AgNP and AuNP. The increase in the intensity of -C=O at around $1720\text{-}1740\text{ cm}^{-1}$ and the decrease in the intensity of -OH at around 3400 cm^{-1} indicate the formation of -C=O groups from -OH groups which is also an indication of oxidation of -OH groups into -C=O groups. The respective Ag^+ or AuCl_4^- ions will be reduced concurrently into their metal nanoparticles AgNP or AuNP. The change in the amplitude

of peaks and a small shift was observed in both cases which also may be attributed to the formation of carbonyl groups from hydroxyl groups.

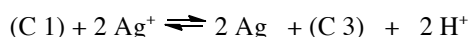
Based on that information, we propose the scenario of oxidation and reduction mechanisms in the formation of AgNP and AuNP as follows:

- (i) Formation of bonding between Ag^+ with -OH group from tannins, and
- (ii) Reduction of Ag^+ to Ag or Au^{3+} to Au is occurred concurrently with the oxidation of hydroxyl groups (-OH) into carbonyl groups (-C=O). This scenario is described in the scheme of reduction and oxidation mechanism in Fig. 4(c).

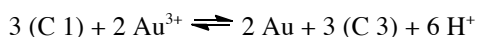
Table 1. Changes in wave number of functional groups of biosynthesized silver and gold nanoparticles observed in FTIR analysis

Wave number (cm^{-1})			Functional groups
Leaf extract of Ketapang	AgNP	AuNP	
3414	3444	3446	O-H
1051	1049	1045	C-O
1707	1739	1720	C=O

The reaction stoichiometry for AgNP formation can be summarized as follows:



It is clearly shown that for the reduction of 2 moles of Ag^+ ions as one ion system (Ag(I)), one molecule of tannins (C1) is required and 2 protons (H^+) will be released. Interestingly, if we apply this mechanism to the formation of AuNP, the reaction stoichiometry will be as follows:



So, for the reduction of 2 moles of Au^{3+} ions as three ions system (Au(III)), three molecules of tannins are required and 6 protons (H^+) will be released. This mechanism is consistent with our experimental results where the final pH is 5 and 3 for the AgNP and AuNP synthesis, respectively. Therefore, the more protons (H^+) are released the lower will be the pH. Clarification at the molecular level to this reaction will be carried out in the future. Very recently, Mittal *et al.* [26] also clarified the formation of -C=O groups from -OH groups in the bioreducing agents of flavonoid families. However, the occurrence of reaction of $\text{NADP}^+ \rightarrow \text{NADPH}$ should be further clarified [3], since plant extract is not a living organism [9], including leaf extract of Ketapang.

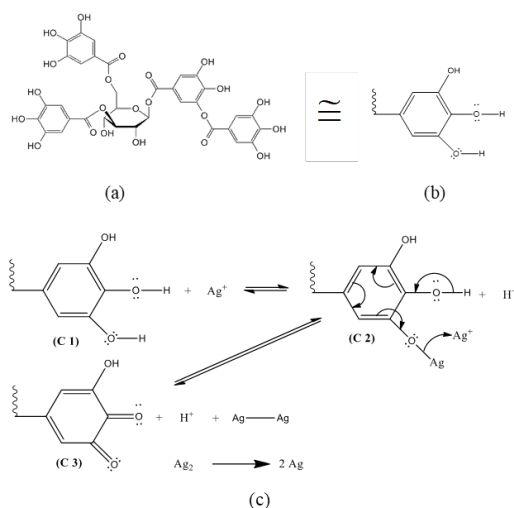


Figure 4. Molecular structure of (a) tannin, (b) simplified structure of tannin, (c) Possible reaction mechanism of AgNP formation.

The XRD analysis was conducted to determine the crystalline nature of biologically synthesized silver and gold nanoparticles on the formation of AgNP and AuNP. Various Bragg's reflections are clearly visible in both silver and gold XRD pattern. In Fig. 5(a) the diffraction pattern is clearly shown with Miller indices (111), (021), (120), (031), (101), (11-2), and (21-1). Diffraction pattern with Miller indices (111) correspond cubic crystal system of AgNP. Crystal system for AgNO_3 is orthorhombic occurred with Miller indices (021), (120), (031), and (101). The occurrence of AgNO_3 patterns appears from silver ions which were not reduced in the biosynthesis reaction. Bragg's reflection are also seen for XRD pattern of AuNP (Fig. 5(b)), which are corresponding to the (111) and (200) set of lattice planes. This pattern suggests that synthesized gold nanoparticles are face centered cubic and essentially crystalline in nature. (200) set of lattice plane is observed to be very weak. The average diameter of silver nanoparticles (AgNP) observed with PSA was in the range 18-44 nm while AuNP was in the range 55-71 nm (Figure 6).

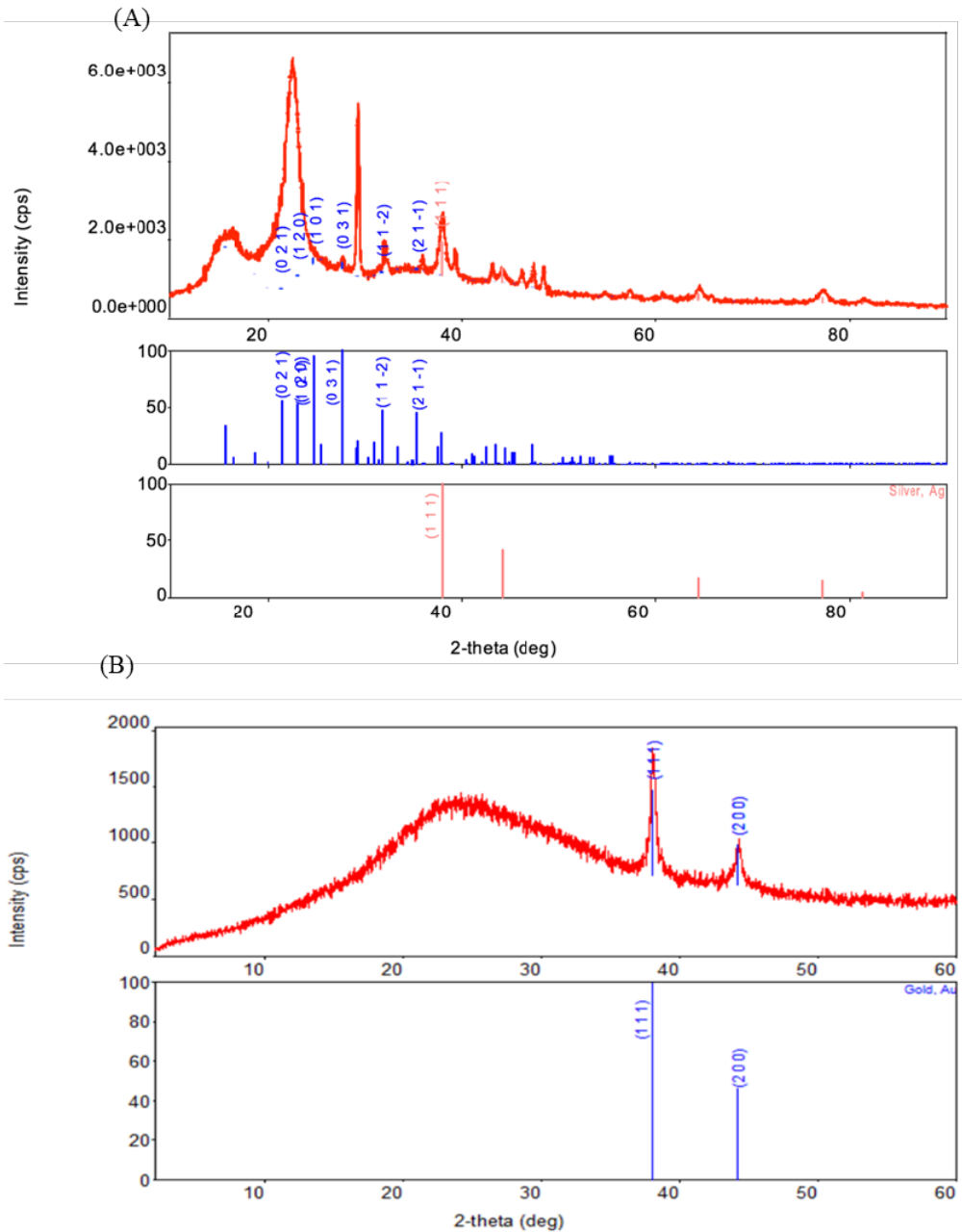


Figure 5. XRD pattern of biosynthesized (A) AgNP and (B) AuNP

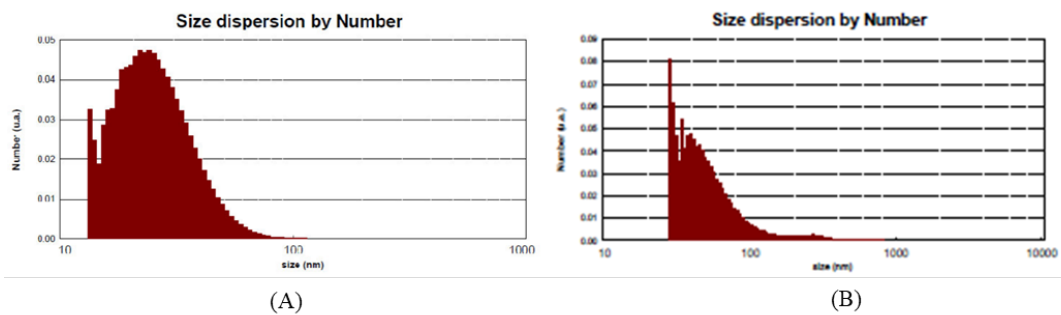


Figure 6. Particle size analysis of biosynthesized (A) AgNP and (B) AuNP.

CONCLUSION

Green and rapid synthesis of AgNP and AuNP using the leaf extract of Ketapang (*Terminalia catappa* Linn) has been performed with possible role of phenolic compounds (tannins) as reducing agent. It is proposed that reduction reaction takes place concurrently with the oxidation of reducing agents, i.e tannins, which was clarified by analysis on the functional groups change of the extract by Fourier Transform Infra Red (FTIR). The current research has shown a new possibility for synthesis of AgNP and AuNP using leaf extract of Ketapang (Makassarese: *talise*) as a traditional plant in South Sulawesi region. The existence of both AgNP and AuNP is verified by (i) surface plasmon absorption of AgNP and AuNP, (ii) average size distribution measured by PSA, and (iii) determination of their structure and morphology by XRD and SEM, respectively.

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