Theoretical Analysis Properties of Gold Nanoparticles Resulted by Bioreduction Process

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Abstract. Analysis of the properties of gold nanoparticles produced through the bioreduction process using Abelmoschus esculentus leaves was carried out. The gold bioreduction process was carried out using Abelmoschus esculentus leaf extract mixed with stirring. Gold nanoparticles formed can be known from the color change of the yellow solution to the color purple. The gold nanoparticles produced were analyzed using XRD to determine the properties of the nanoparticles produced. The results of the analysis using XRD obtained four diffractograms as a characteristic of gold nanoparticles at an angle of 2θ: 37.82, 44.06, 64.42, and 77.53. Based on the calculation, the average size of the nanoparticles and the average size of the lattice length were 31.90 nm and 73.79 nm, respectively. The strain and stress values of gold nanoparticles produced were 4.8 x 10⁻⁵ and 12.57 MPa. In addition, the resulting crystal tends to have a crystal array with the Miller index (311). The energy density of gold nanoparticles is 3.35 KJ/m³.

1. Introduction
Nanoparticles are one material that has many potentials that can be developed with various applications for human life. Due to nanoparticles have unique characteristics compared to their bulk material, it can use as raw materials for various applications [1–3]. One of these nanoparticles is gold nanoparticles. Gold nanoparticles have concerned by the researcher because they have different characteristics from gold materials in general, including high material stability, the resistance of material, oxide reactions, and excellent biocompatibility properties [4–7].

To date, the application of gold nanoparticles has reported as antibacterial, drug supporting material, gene transfer, nucleic acid markers, to detect pathogenic bacteria and cosmetics. The various functions possessed by gold nanoparticles cause various methods to synthesize these nanomaterials continuously developed. The sol-gel method, the hydrothermal method, the ion sputtering, are some of the conventional synthesis methods have used. These methods are conventional have the disadvantage of producing pollution to the environment, requiring expensive technology, involving toxic chemical compounds [8–10].

In recent years, the synthesis of gold nanoparticles has been directed at synthesis using the bioreduction process. Gold nanoparticles can be produced through a bioreduction process using
various bioreductors such as bacteria, fungi, and plant extracts. Plant extracts are widely used as bioreductors because the nanoparticles produced can be resized, the shape of the nanoparticles can arrange, and their properties can be adjusted [11–13]. Various plant extracts that can use as bioreductors, the main requirements for plant extracts to be used as bioreductors, must contain reducing agent compounds such as flavonoids, tannins, phenolic, and alkaloid. One plant with these contains compounds, and their derivatives are *Abelmoschus esculentus* leaf extract. *Abelmoschus esculentus* leaf extract contains quercetin-4”-O-methyl-3-O-β-D-glucopyranoside can be used as an excellent reducing agent [14].

Based on our knowledge to date, there are no researchers to synthesize gold nanoparticles and to analyze the characteristics of the nanoparticles produced using *Abelmoschus esculentus* leaf extract as bioreductor. Therefore in this study, the synthesis of gold nanoparticles was carried out by using *Abelmoschus esculentus* leaf extract and analyzing the structural properties of the nanoparticles product.

2. Experimental

2.1 Materials

The materials are distilled water, *Abelmoschus esculentus* leaves, bi-distilled water, HAUO₃, Whatman paper No.42

2.2 Biosynthesis of silver nanoparticles

Biosynthesis of gold nanoparticles was carried out by mixing a solution of Au³⁺ and boiled water of Okra leaves. As much as 10 mL of boiled water mixed with *Abelmoschus esculentus* leaves into a solution of 40 mL Au³⁺, then stirred for 2 hours. The formation of nanoparticles marked by changing the solution from yellow to purple. The formed nanoparticle gold solution was dried with a Spray Dryer (Buchi 190) to obtain samples powder. The powder tested using X-ray diffraction (X-RD) at an angle of 2θ: 20–80°. Then a structural analysis is carried out.

3. Results and Discussion

3.1 Production gold nanoparticles.

Synthesis of gold nanoparticles using *Abelmoschus esculentus* leaf extract has done by observing the change in the color of the incubation solution. The formation of gold nanoparticles is the process of the bioreduction of Au³⁺ into AuNPs. Color changes indicate that the process of bioreduction of Au³⁺ to AuNP occurs at a particular time, and there has been a change in Surface Plasmon Resonance. The color of the Au³⁺ solution was initially yellow, changing after adding the extract, accompanied by stirring into purple color. The color variation from yellow to purple is characteristic of the formation of gold nanoparticles [6,15].

3.2 Analysis of gold nanoparticles using X-Ray Diffraction

The gold nanoparticles produced have a diffraction pattern that describes the crystalline pattern and the crystallinity of the gold nanoparticles that have formed through the bioreduction process. The resulting gold nanoparticle diffractogram pattern is shown in Fig. 1. The characteristics of gold nanoparticles can be determined by comparing the diffractogram obtained to the JCPDS data file: 04-0784 [15]. There are four peaks that are characteristic of gold nanoparticles, namely at 2θ: 37.82; 44.06; 64.42; 77.53.
3.3 Strain analysis of crystal gold nanoparticles (ε)

The alignment of the resulting gold nanoparticle crystals can be demonstrated by using the strain value of the crystal. The crystalline value of gold nanoparticles determined by using the diffraction pattern related to the line broadening value that resulted in XRD [16]. The amount of strain value of the gold nanoparticles reduced is calculated using equation 1. $K_i$ is the full-width half-maximum (FWHM), $\theta$ is the resulting diffraction angle, $R = \frac{K_i x 0.1541}{D}$ and $\varepsilon$ is the nanoparticle strain of each peak produced.

$$K_i \cos \theta = \nabla + 4\varepsilon \sin \theta$$  

(Fig. 1) Figure 1. Diffractogram of gold nanoparticles

Equation 1 using the assumption that all crystals produced have uniformity in crystallographic form. In addition, the resulting crystal must have isotopic properties and have properties that do not depend on one another [17]. The plot results of equation 1 shown in Fig. 2. The result of calculating the strain

(Fig. 2) Figure 2. Plot $K_i \cos \theta$ versus $4\sin \theta$
value using the regression line from Figure 2 is $4.8 \times 10^{-4}$ MPa. The strain value of the very low gold nanoparticles is an indication that the crystals that formed have crystal cell unit spacing not overlapping. In addition, it is an indication the product produced is experiencing a small strain [18].

3.4 Analysis of the value of stress of crystal ($\sigma$)

Determination of the stress value of gold nanoparticle crystals can be obtained by modifying the Williamson-Hall equation into a model of uniform voltage deformation (USDM). This model assumes that the lattice deformation process that occurs in crystals is uniform in all directions of the crystal plane.

$$K_i \cos \theta = R + \frac{4\sigma \sin \theta}{Y}$$

The stress value of the gold nanoparticle crystal can be calculated using equation 2. $K_i$ is FWHM, $\sigma$ is the stress crystal, and $Y$ is the Young (or) modulus of elasticity. The young modulus for gold cubic nanoparticles is $167.6$ GPa.

$$\text{Figure 3. Plot } K_i \cos \theta \text{ versus } 4\sin(\theta/Y)$$

The results of the plot to determine the stress value of gold nanoparticles are shown in Fig. 3. Based on the results of the regression analysis obtained the value of the slope, which shows the value of the stress crystal produced $12.57$ MPa.

3.5 Estimation of the average particle size and the dislocation density

To calculate the average size of gold nanoparticles performed using the Debye-Scherer equation [17]. Based on the Debye-Scherer equation, the average size of gold nanoparticles is calculated using equation 3.

$$P_{z\text{ave}} = \frac{K \lambda}{\beta \cos \theta}$$

$P_{z\text{ave}}$ is the average size of gold nanoparticles, $K$ is Debye Scherer's constant (0.94), $\lambda$ is the wavelength of the CuK$_\alpha$ radiation (0.154 nm), $\beta$ is the FWHM of each gold nanoparticle peak, $\theta$ is the angle of each peak of gold nanoparticles.
Table 1. Diameter size and lattice parameter of the gold nanoparticles

| 2θ (°) | h k l | D (nm) | Parameter of the lattice (a) (nm) |
|--------|-------|--------|----------------------------------|
| 37.82  | (1 1 1)| 36.49  | 0.412                            |
| 44.06  | (2 0 0)| 40.87  | 0.411                            |
| 64.42  | (2 2 0)| 33.59  | 0.409                            |
| 77.53  | (3 1 1)| 16.64  | 0.408                            |
| Average|       | 31.90  | 0.410                            |

The results of the calculation of the average size and lattice parameters of gold nanoparticles are shown in Table 1. The average size of gold is 31.90 nm, with the lattice length 0.410. These results indicate that the reduction process can produce particles with nano-size (<100 nm) [3,11]. The dislocation density of gold nanoparticles is further determined using the average size obtained. The dislocation density value is a clue that can give an idea of the dislocation that occurs in each crystal volume unit. Indirectly provide clues about the level of crystallinity of the gold nanoparticles produced. The dislocation density is calculated using equation 4.

\[
\delta_{np} = \frac{1}{D^2} \]

The calculation results show that the value of energy density (\(\delta_{np}\)) of gold nanoparticles produced 0.00098 (nm)^2. Based on the results of these calculations indicate that the dislocation that occurs in gold nanoparticles is very small. This condition illustrates that the gold nanoparticles produced have a high level of crystallinity.

3.6 Size distribution of AuNPs

The size distribution of AuNPs particles is estimated using the approach that all nanoparticle crystals produced have a normal distribution in all fields. Based on this approach, the size distribution of AuNPs particles is formulated using equation 5.

\[
D(x) = \frac{1}{\sqrt{2\pi} \sigma y} \exp \left\{ -\frac{[ln(x/m)]^2}{2\sigma^2} \right\} 
\]

Where: the size of the crystal (x), the variance (\(\sigma\)), and the median (m). Based on the equation the AuNPs particle size distribution graph obtained from the bioreduction process using *Abelmoschus esculentus* leaf extract as shown in Fig. 4. Gold nanoparticles have a particle size distribution smaller than 16.64 nm. The calculation results also show that the obtained particle size has a median value and a variant value of 35.04 and 112.47. These results indicate that the amorphous phase in the crystal produced is not a large percentage. It also veiled by sharp peaks on the XRD diffractogram of gold nanoparticles produced as well as the sloping background peaks [17].
3.7 Analysis of the energy density of gold nanoparticles ($U_{ed}$)

The energy density value of gold nanoparticles can be analyzed by assuming that the crystals produced have homogeneous, isotropic conditions. Based on these assumptions, the energy density is determined using the uniform deformation energy density model (UDEDPM). The value of the energy density of gold nanoparticles can be obtained by using Hooke’s law equation in a flexible system. Based on these approaches, the energy density value of gold nanoparticles can be calculated using equation 6.

$$
\beta_{hkl} \cos \theta = R + \left(4 \sin \theta \left(\frac{2U_{ed}}{Y}\right)^{1/2}\right)
$$

**Figure 4.** The size distribution of gold nanoparticles

The results of the plots of $\beta_{hkl} \cos \theta$ versus $4 \sin (2Y)^{1/2}$ is shown in Fig 5. Based on the linear regression calculation of the graph, the gold nanoparticle energy density value is 3.35 KJ/m$^3$. 

**Figure 5.** Plot $\beta_{hkl} \cos \theta$ versus $4 \sin (2Y)^{1/2}$

$$
y = 0.8 \times 10^{-3}x + 0.003
$$
3.8 Coefficient of texture
Gold nanoparticles obtained from the crystal can be analyzed for orientation using the calculation of coefficient of texture. The coefficient of texture value for each peak as a characteristic of gold nanoparticles can be determined by applying the intensity value of each peak. The coefficient of texture value for each peak can be determined using equation 7.

\[
CT = \frac{I_{(hkl)} / I_{o(hkl)}}{\sum N_{(hkl)} / I_{o(hkl)}} \times 100% 
\]

The relative intensity of diffraction of gold nanoparticles \(I_{(hkl)}\), the intensity produced by standard measurement \(I_{o(hkl)}\) and \(N\) is the number of diffractograms produced. The calculation results of the coefficient of the texture of each peak shown in Table 2.

| No. | \(h\) \(k\) \(l\) | \(I_{(hkl)}\)measured | \(I_{o(hkl)}\)standard | \(CT_{(hkl)}\) |
|-----|-----------------|-----------------|-----------------|-------------|
| 1   | (111)           | 20              | 68              | 0.29        |
| 2   | (200)           | 100             | 100             | 1.00        |
| 3   | (220)           | 61              | 58              | 1.05        |
| 4   | (311)           | 100             | 79              | 1.27        |

The coefficient of texture calculation results in Table 2 shows the highest value obtained is 1.27 in the crystal lattice plane (311). This result indicates that the crystalline gold nanoparticles produced tend to have the shape of the crystal field (311).

4. Conclusions
Based on the results of the analysis carried out, it is known several parameters of the structure of gold nanoparticles. The results of the analysis using XRD obtained four diffractograms as a characteristic of gold nanoparticles at an angle of 2θ: 37.82, 44.06, 64.42, and 77.53. Based on the calculation the average size of the nanoparticles and the average size of the lattice length were 31.90 nm and 73.79 nm, respectively. The strain and stress values of gold nanoparticles produced were \(4.8 \times 10^{-5}\) and 12.57 MPa. In addition, the resulting crystal tends to have a crystal array with the Miller index (311). The energy density of gold nanoparticles is 3.35 KJ/m³.

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