Enhancement of the stability of silver nanoparticles synthesized using aqueous extract of *Diospyros discolor* Willd. leaves using polyvinyl alcohol

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Abstract. Biosynthesis of silver nanoparticles is recently attracting considerable attention because of it reduces the environmental impact and already used in numerous applications. However, the disadvantages such as easy aggregation and instability properties, prevent its' application. In this papers, biosynthesis of silver nanoparticles using aqueous extract of *Diospyros discolor* Willd. leaves have been prepared. The effect of biosynthesis variables, like ratio of reactants and reduction time on the particle size distribution, stability, and morphology of the silver nanoparticles were investigated. The resulted silver nanoparticles were characterized using UV spectroscopy, Transmission Electron Microscopy, and Particles Size Analyzer. Polyvinyl alcohol (PVA) was used to enhance the stability of the silver nanoparticles. Silver nanoparticles modification with 1% PVA concentration has produced a better characteristic of particle size distribution compared to the original silver nanoparticles, from highly polydisperse into moderately disperse. The results of the Zetta potential measurement also confirmed the increase stability of cluster distribution in the colloidal Ag/PVA compared to the original Ag.

1. Introduction
The nanoparticles research have given a lot of contribution in material engineering, which opening the opportunities for its’ usage and applications in various fields, such as medical [1], pharmaceutical [2, 3], environmental [4, 5], and sensors [6, 7]. From a wide range of the applied nanoparticle materials, gold and silver nanoparticles are the most renowned [8, 9].

Nanoparticles have physical and chemical properties which are different from its bulk material. This uniqueness in character grants nanoparticles a lot of remarkable properties that it is used for various applications. On the other hand, nanoparticles are usually unstable since it easily agglomerates, forming particles which are bigger in size. Additionally, creating nanoparticles with homogeneous particle size distribution is a challenging task [10].

In this research, silver nanoparticles (silver NPs) biosynthesis using aqueous extract of *Diospyros discolor* Willd. leaves have been performed. Biosynthesis method is chosen as it is environmentally friendly [11]. The stable character of silver nanoparticles is aimed to be fixed by modifying it with PVA. Moreover, PVA influence on the resulted nanoparticles polydisperse characteristic improvement is also observed.
2. Materials and methods
Leaf extract of *D. discolor* was prepared by using the raw leaf material, previously dried in the oven at the temperature of 40°C for 24 hours. The leaf was then ground into powder, weighed 2 gram, and subsequently boiled for 10 minutes with 100 mL of aquabidest. The extract was then filtered with Whatman filter paper no 1.

AgNO₃ solution with the concentration of 1 mM was then prepared from AgNO₃ powder, obtained from Dhucefa Biochemies. Next, in order to synthesize nanoparticles, 10 mL of *D. discolor* leaf extract was mixed with 100 mL AgNO₃ solution and stirred using magnetic stirrer for 2 hours at the temperature of 24°C.

The influence of Polyvinyl Alcohol (PVA) modifier on the resulted silver nanoparticles was studied by adding PVA solvent in different volume ratio to the mixture of leaf extract and AgNO₃ solution. PVA solution was prepared by dissolving PVA powder into aquabidest. PVA solution concentration was then varied to 1%, 2%, 3%, 4%, and 5%. This solution was then heated at the temperature of 80°C for 5 hours. In order to synthesize PVA-modified silver nanoparticles, the ratio of leaf extract volume, AgNO₃, and PVA solution of 1:10:3 was applied, respectively. The mixture was then stirred using magnetic stirrer for 2 hours at the temperature of 24°C.

Characterization of the resulted silver nanoparticles was performed using UV-Vis spectrometer Thermo UV-vis 10 S Genesys, transmission electron microscopy TEM FEI Tecnai G2 Supertwin, and particle size analyzer (PSA) Delso Nano Beckman Coulter. The reduction of Ag⁺ ion into silver was monitored by observing the color change and UV-visible spectrum of the solution orderly in the period of 2, 6, 24, 30, 36, 44 hours. Meanwhile, the PVA-modified silver nanoparticles formation was observed five times at 24, 30, 36, 42, 48 hours reaction time.

The granule size of the formed nanoparticles was then measured using PSA and TEM. This measurement was performed for original and PVA-modified silver nanoparticles samples. The achieved stability of the produced nanoparticles was observed by measuring Zeta potential, while silver nanoparticles molecular weight distribution was studied by calculating the Polydispersity Index.

3. Results and discussion
Figure 1 shows the photograph of the solutions’ color and absorption spectrum result achieved from UV-visible spectroscopy measurement of silver nanoparticles biosynthesis by using aqueous extract of *D. discolor* leaves. The color of leaf extract and AgNO₃ solution changed after being mixed. The color of the solvent mixture becomes yellow, and the yellow color becomes darker until it turns tawny over the mixing process period. These changes of colors are in line with the absorption spectrum change from the result of UV-visible measurement in figure 2. The spectrum of AgNO3 and leaf extract solution does not have a peak of absorption around the wavelength of 400 nm. After the two solutions are mixed, an absorption peak appears in the wavelength of approximately 418 nm. As known, silver nanoparticles has value of surface plasmon resonance (SPR) around the wavelength of 400 nm to 500 nm [12]. A similar absorption peak in these areas has also been achieved by Nagaranj et al. [13]. From figure 1, it can also be observed that silver nanoparticles nucleation is influenced by time of reaction. The longer reaction time, the more quantity of silver nanoparticles are formed, as seen in the parallel condition between the gradual increase of absorbance value in UV-visible spectrum and the amount of reaction time passed in figure 2.

The result of UV-visible spectrum and PVA modification of silver nanoparticles is given in figure 3. Such observation was done for the reaction time of 24 h. The wavelength of absorption peaks and PVA-modified silver nanoparticles was not shifted; however, the absorbance value at the peak was changed. The change in absorbance value from the observed absorption peak was increased along with more addition of PVA concentration. This result proves that after nanoparticles are modified with PVA, there is no change in value of the surface plasmon resonance.

TEM image from the original and PVA-modified silver nanoparticles are displayed in figure 4. Both types of nanoparticles have spherical basic form. The particle size of the original silver nanoparticles is around 5 nm, while the size of silver nanoparticles modified with 1% PVA is approximately 20 nm. The electron diffraction measurement shows that the achieved silver nanoparticles possess good crystallinity.
Figure 1. The difference of color between AgNO₃ and leaf extract solution. After reaction occurs, solution color changes over the time, from bright yellow to dark brown.

Figure 2. UV-visible recorded spectrum as the function of silver ion reduction time.

Figure 3. UV-visible Spectrum from silver nanoparticles modified with PVA which is recorded as the function of PVA volume ratio change. The observation was done for the reaction time of 24 h.

Figure 4. TEM imaging for silver nanoparticles (a) original and (b) PVA(1%)-modified.
The result of the particle size observation through TEM image is sufficiently consistent with the particle size measurement using PSA. Based on PVA measurement, the original silver nanoparticles is approximately 6 nm in size and the 1% PVA-modified silver nanoparticles average size is approximately 27 nm.

The measurement result of average particle size using PSA for original silver nanoparticles and the nanoparticles which are modified with PVA at the concentration of 1% to 5% is shown in figure 5. After silver nanoparticles were modified with PVA, the nanoparticles size was increased. The higher PVA concentration resulted in a bigger nanoparticle size. This increase in nanoparticle size is apparently linear with the increment of addition of PVA concentration.

Figure 6 shows the measurement result of Zeta potential (ZP) and Polydispersity Index (PDI) of original and PVA-modified silver nanoparticles as the function of PVA concentrations. The Zeta potential value shows nanoparticles colloid stability, which is formed in the solution [14]. The Zeta potential value that ranges from ±0-10 mV shows a highly unstable colloid, with ZP value of ±10 - 20 mV, ±20 - 30 mV and > ± 30 mV shows relatively, moderately, and highly stable colloid in the respective order. Figure 5 shows the original silver nanoparticles has -2.4 mV ZP, which means the formed colloid system is highly unstable, and this conclusion is also confirmed with UV-Visible measurement result in figure 1. The figure shows that the formed silver nanoparticles is still changing, proven with great value change of absorbance, even after 44 hours measurement of the solution mixture.

After the silver nanoparticles were modified with 1% PVA, a drastic change of ZP value was observed to be 90.8 mV. When the PVA concentration was raised to 2%, the ZP value decreased to 79.8 mV. Both ZP values are far beyond the stable colloid border value, which is > ± 30 mV. PVA addition to the concentration of 3%, 4%, and 5% gives ZP value in the respective order of 4.1 mV, -2.1 mV, and -3.0 mV. These three ZP values show that the resulted silver nanoparticles colloids are highly unstable. Consequently, the 1% PVA concentration value for modifying silver nanoparticles biosynthesis using aqueous extract of *D. discolor* leaves have given the highest ZP value, resulting in highly stable colloid.

Colloid stability is one of the properties of nanoparticles. Another important characteristic is the particle size distribution in non particle system. Nanoparticle size distribution can be articulated through polydispersity index (PDI) value. A nanoparticle system with PDI value < 0.1 is considered as highly monodisperse, while PDI value > 0.4 and value in range of 0.1 – 0.4 are indicated that the system has highly polydisperse and moderately disperse distribution in the respective order [15]. The PDI measurement of original and PVA-modified silver nanoparticles with different concentrations is shown in figure 6. Original silver nanoparticles have PDI value of 0.50 that shows as highly polydisperse. After
they were modified with 1% PVA, the PDI value sharply decreased to the value of 0.29 that shows a moderate dispersity. When PVA concentration was raised to 2%, 3%, 4% and 5%, PDI value once again increased, each of which has the value of 4.6, 5.2, 4.1, and 4.7 respectively. These PDI values give highly polydisperse characteristic. Thus, silver nanoparticles modification with 1% PVA concentration has produced a better characteristic of particle size distribution compared to the original silver nanoparticles.

4. Conclusions
Silver nanoparticles have been successfully prepared with biosynthesis method using aqueous extract of *D. discolor* leaves. The resulted silver nanoparticles are small in particle size, which is around 6 nm, and have highly polydisperse and highly unstable properties. After the modification with PVA was performed, the properties were improved. PVA concentration as high as 1% shows an improvement from highly polydisperse into moderately disperse with remarkable improvement in colloid stability, which becomes highly stable. Even so, this improvement in properties has a cost to the increase of nanoparticle size into 27 nm.

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