Synthesis of colloidal copper nanoparticles using pulse laser ablation method

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Abstract. Synthesis of copper nanoparticles has been conducted by using a pulse laser ablation method utilizing a pulse Nd:YAG laser. Experimentally, a pulse Nd: YAG laser (1064 nm, 50 mJ) was focused on a pure copper metal placed in aquades. Colloidal copper nanoparticles have been successfully synthesized. The effect of laser pulse repetition rate was also examined using 10, 15, and 20 Hz. The colloidal nanoparticles were then characterized by using UV-Vis spectrometry and scanning electron microscopy. The result shows that the copper nanoparticles was sucessfully produced with the sphere shape and averaged diameter of 12 nm.

1. Introduction
In recent years, metal nanoparticles received a lot of attention because of their applications in technology advances such as optoelectronics, nanodevices, nanoelectronics, nanosensors, information storage and analysis [1-4]. Among the various metal nanoparticles, copper nanoparticles have attracted more attention because of its application in catalytic, optical, electrical and antibacterial [5-11]. The research that has been carried out in the application of nanotechnology to produce antimicrobial products is through the engineering of metal particles and metal oxides such as silver (Ag), copper (Cu), TiO2, ZnO, and MgO sized in nanometer scale, and then applied to the process of various other products which are antimicrobial such as textiles, pulp, ceramics and so on. [6,12-19].

Copper is a metallic element that is very useful in human life. Copper has a cheap price and abundant in nature [6]. Copper nanoparticles are more reactive in killing bacteria compared to other metal nanoparticles such as gold and silver [28]. Copper particles on the nanoscale proved to be antibacterial because of adhesion to bacterial cell membranes, giving effect to the proteins structure of cell membrane, denaturation of intracellular proteins and interfere DNA replication [30,31]. Furthermore, copper is recently registered as a first metal applied for anti-microba by American Environmental Protection Agency (EPA) [32].

The production of nanoparticles by physical technique using laser ablation is very different from making nanoparticles using chemical technique or combination technique [20,21]. The advantage of laser ablation plasma technique (PLA) is that this technique has a very simple mechanism and exposure time can be controlled properly [22,23]. Also, the nanoparticle colloids are purely produced from the target and not contaminated with any impurities [24,25], while the nanoparticle colloids produced by chemical processes are usually contaminated by reducing compounds [26,27].
In this study, colloidal copper nanoparticles (CuNPs) was synthesized using a PLA method utilizing a Nd:YAG laser 1064 nm. Low laser energy of 30 mJ was used to ablate the metal and produce a plasma on the metal target.

2. Experimental

2.1. Sample preparation

The samples or material target used in this research were copper metal plate with a high purity of 99.9% (thickness 1 mm, size 20 x 10 mm²). For synthesis process, the sample was cleaned using ultrasonic cleaner and alcohol to make sure that the sample is clean from the dust or impurity deposited on the material surface. The sample was then rinsed using distilled water.

2.2. Synthesis of colloidal copper nanoparticles

Colloid al copper nanoparticles were made from the pure copper plates placed at the base of a petri dish containing 10 ml of aquades as illustrated in Fig. 1(a). The copper target was irradiated by Nd: YAG laser with 50 mJ laser energy, 1064 nm wavelength, and 7 ns pulse duration. The laser beam was bombarded for 80 minutes by varying the repetition rate of 10, 15, and 20 Hz. The mirror serves to deflect the laser beam. The laser beam was focused on the target surface with a convex lens (focal length of 3 cm).

2.3. Characterization of produced colloidal nanoparticles

The colloidal copper nanoparticles produced in this study was characterized using UV–vis spectrophotometer. Morphology of the copper nanoparticles were determined by using scanning electron microscopy (SEM). For the characterization using SEM, a little amount of CuNPs colloid was dripped on a Silicone plate with a size of 5 x 5 mm² and waited until it dried. The averaged diameters and size distribution of CuNPs was measured by using Imagej software from the SEM photograph.

3. Results and Discussion

Colloidal CuNPs were successfully synthesized in aquades, with a variation of repetition rate of 10, 15, and 20 Hz producing colloidal CuNPs with different color concentrations. Figure 2 shows photographs of CuNPs colloids.
The mechanism of laser ablation takes place in a liquid environment, called laser ablation in liquid (LAL). First, the plasma is produced when the laser beam hits a target located at the bottom of the liquid. Plasma is formed from multifoton absorption, ionization and inverse Bremsstrahlung. Thus plasma contains a lot of neutral atoms, ions and electrons from the target. Unlike in a vacuum or gas environment, plasma expansion resulting from LAL is very limited by liquid. When the target absorbs laser energy it causes continuous evaporation so that the plasma continues to expand adiabatically and forms shockwave waves, which causes an increase in temperature and pressure on the plasma. During the plasma expansion process, the plasma gives energy to the surrounding liquid, thus forming a thin vapor layer. This thin vapor layer is the initial stage of the cavitation bubble. The final stage of plasma evolution in liquids is cooling and shrinkage accompanied by a decrease in pressure and temperature. Finally the plasma extinguishes and releases the nanoparticles into the liquid. This mechanism takes place very quickly, when the vapor layer is formed, the vapor layer will expand and then press the plasma back to the target. When the cavitation bubble reaches its maximum size and eventually breaks down, there is a state of thermodynamic equilibrium. With bubbles damaged, the mass including the nanoparticles is released into the liquid [29].

The absorption spectrum of CuNPs measurements using ultraviolet visible (UV-Vis) spectroscopy, the results shows a single absorption for each repetition rate, for 10 Hz and 15 Hz at the center wavelength of 292nm wavelength and for 20 Hz at 295 nm wavelength as shown in Fig. 3. The UV-Vis spectrum at 292-295 nm indicates the existence of CuNPs, this is also evidenced by the EDX test results.
repetition rate was varied from 10, 15 to 20 Hz. It is shown in Fig. 3, low repetition rate of 10 Hz has a low intensity of 1180 and for a high repetition rate of 20 Hz has a high intensity of 1580 and at a repetition rate of 15 Hz the intensity is 1335. The intensity (absorbance) shows the number of constituents including the nanoparticles contained in the liquid. At high repetition rates, the laser beam shoots at the target more frequently causing more ablation of target material and produces more constituents, which are diffused in the liquid. Conversely, at a low repetition rate, the frequency of laser shoots at the target is lower, the ablated material is reduced causing only a few constituents in liquid. This is also evidenced by the color density of the colloids (Fig. 2). It can be seen that colloid CuNPs produced at high repetition rates shows dark gray color indicating the number of constituents (CuNPs) and in low repetition, the color is light gray indicating less CuNPs in the liquid.

The second factor that affects plasma laser is a sample hardness, where the copper sample is a hard sample, so it takes a longer ablation time, which is 80 minutes in our study. On the other hand, for a longer time, some of the CuNPs were agglomerated because CuNPs are very unstable in the water environment so further research is needed using stabilizers such as Polyvinylpyrrolidone (PVP) and polyetilena Glikol (PEG) [28]. The third factor is the environmental pressure. In this present study, the research was carried out at the pressure of 1 atm.

Next, we observed Cu particles by using Scanning Electron Microscope (SEM). Figure 4(a) shows morphological photograph of Cu particles fabricated in aquades, and Fig. 4(b) is the size distribution of copper nanoparticles calculated by using ImageJ software. It can be clearly seen that the particle shape is spherical shape with an average diameter of 12 nm and a standard deviation of 4 nm.

**Figure 4.** (a) morphological photograph of CuNPs using SEM, (b) particles size distribution of CuNPs

Aggregation of CuNPs was observed in a sample that was prepared at first 60 minutes of ablation time of CuNPs synthesis. However, this state of aggregation appears on SEM morphological photographs. It has been explained above to overcome the aggregation state and its tendency to be oxidized in aqueous environment is by using stabilizing compounds such as PEG and PVP.

### 4. Conclusion

Colloid Copper nanoparticles with high purity were successfully synthesized in aquades. The UV-Vis spectrum at 292-295 nm indicates the existence of CuNPs. The results show that the copper nanoparticles have a spherical shape with an average diameter of 12 nm and standard deviation of 4 nm. The produced colloidal copper nanoparticles are very potential to be applied as an anti-bacteria.

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