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Effect of size and shape dependent of synthesized copper nanoparticle using natural honey

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Abstract
A study on the effect of size and shape of copper nanoparticles (Cu-NPs) by varying the amount of honey has been done using a facile green synthesis method with the presence of ultrasonic assistance. Several amount of different % w/v of honey (0%, 1%, 5%, 10%, 15% and 20% w/v) that contain carbohydrate which are mainly glucose and fructose, and other polyhydroxyl groups act as stabilizing agent and a weak reducing agent supported by ascorbic acid were used to produce the Cu-NPs. The synthesized Cu-NPs were characterized using UV-visible, XRD and HRTEM to prove the size and shape of the nanoparticles. The best amount of honey used to produce Cu-NPs with uniform particle size and shape is at 15 % w/v. The size is 3.81 ± 1.135 nm and it shows a consistence spherical shape using HRTEM analysis image. UV-visible supported the results from the HRTEM. And XRD shows good diffraction pattern for pure Cu-NPs. It proves that honey has the ability to act as stabilizing agent in controlling the size and shape of nanoparticles.

1. Introduction
Nanomaterial has becoming a new promising materials nowadays that exhibits many specialties for a various number of applications such as water treatment, energy storage and biological applications as compared to corresponding bulk materials [1-4]. Due to the small size and high surface area-to-volume ratio, nanoparticles have unique physical properties that attract attentions among the researchers worldwide [5]. Metal nanoparticles such as gold, silver and copper are applicable to use in several industries where each of nanoparticles has different properties depending on the size, shape and other physicochemical properties [6]. Most of the nanoparticles could be used in food packaging [7], wound dressing [8], drug delivery [9] and catalytic application [10].

Copper nanoparticles (Cu-NPs) are known in the field of electronic, sensors and biomedical application aside from silver nanoparticles and gold nanoparticles due to easy availability, low cost, easy of mixing with polymers and their similar properties to those noble metals [11-13]. In synthesizing Cu-NPs, conventional methods is rather costly, slow reaction time and the uses of toxic chemical such as sodium borohydride and hydrazine as reducing agent are involved [12, 14, 15]. However, by using ultrasound irradiation assistance, it can reduce the reaction time, more uniform size distribution and improve phase purity for the nanoparticles [10]. Ascorbic acid, vitamin C which is a non-toxic chemical

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and reducing agent, also has been used as supported reducing agent in this work to replace the toxic chemicals [16].

A major limitation in preparing Cu-NPs is, it really sensitive to air and easily to oxidize to copper oxides phases which is much more stable state. However, the formation of an oxide layer could decrease the efficiency of Cu-NPs especially for the antibacterial activity properties [5, 17]. Thus, stabilizing agent or capping agent is needed to prevent the agglomeration of nanoparticles to occur as reported in previous literatures [18-20].

Honey is a natural food and a sweet viscous liquid consisting of carbohydrate, enzymes, vitamins, minerals and antioxidant [21, 22]. The monosaccharides, proteins, amino acid and vitamin C in honey which contain polyhydroxyl group could help in reducing and stabilizing the nanoparticles. The use of honey as reducing and stabilizing agent is convenient as it does not require drying, extraction of plant materials and cell culture maintenance [23, 24]. This study is a continuation study based on previous work [24] whereby it is focusing on the effect of size and shape for Cu-NPs by using different amount of honey (% w/v). The synthesized Cu-NPs were then characterized using UV-visible spectroscopy, XRD and HRTEM.

2. Experimental

2.1. Materials
Capilano honey (Australia), double distilled water, copper nitrate trihydrate ($(CuNO_2)_3.3H_2O$), sodium hydroxide (NaOH), and ascorbic acid. All chemical are purchased from R&M chemical, Germany, and used as received without any purification.

2.2. Synthesis of Copper Nanoparticles
Different amount of natural honey from Australia (0, 1, 5, 10, 15 and 20% w/v) was dissolved in appropriate amount of copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$). The pH of the mixture was adjusted to neutral pH (~ pH 7) with sodium hydroxide and undergo ultrasonic irradiation for 10 minutes with addition of a proper amount of ascorbic acid. The synthesized copper nanoparticle was washed with distilled water and separated by centrifugation at 4000 rpm for 15 minutes. Then, samples are dried in vacuum oven at 60 °C.

2.3. Characterizations of Copper Nanoparticles
All samples were characterized using Ultraviolet-visible (UV-vis) spectroscopy (UV-2600, SHIMADZU). The clean quartz solution cells were used. The sample solution with desired concentration and a blank sample (water) were used for this experiment. The samples were homogenized in the quartz soluti on cells and placed into the UV-vis chamber. The UV-vis spectra were recorded over the range of 220 nm to 800 nm. The structure of Cu-NPs were evaluated using X-ray diffraction (XRD, Philips, X'pert, Cu Ka) in the small-angle range of 20° to 80° (2θ). High Resolution Transmission Electron Microscopy (HRTEM) (model JEM-2100F) was used to examine the size and shape of Cu-NPs.

3. Results and Discussion

3.1. Characterization of Copper Nanoparticles
UV-visible is used to check the formation of Cu-NPs. Figure 1 shows the UV-visible of Cu-NPs for different amount of honey (% w/v). It shows the surface plasmon resonance peaks for all the synthesized Cu-NPs which appeared around 550 to 600 nm. As can be observed from figure 1, only slight difference in peak shifted from red to blue shift which indicate small changes in term of size and shape occur by using different amount of honey. Besides, different shape of nanoparticles also could contribute to the peak of UV-visible where wide peak might be due to different shape of nanoparticles and the peak intensity indicates that same shape of nanoparticles were produced [25]. An increasing of absorbance in

the UV-visible shows that an increase for concentration of Cu-NPs and higher concentration of metal nanoparticles were produced during the synthesis process.

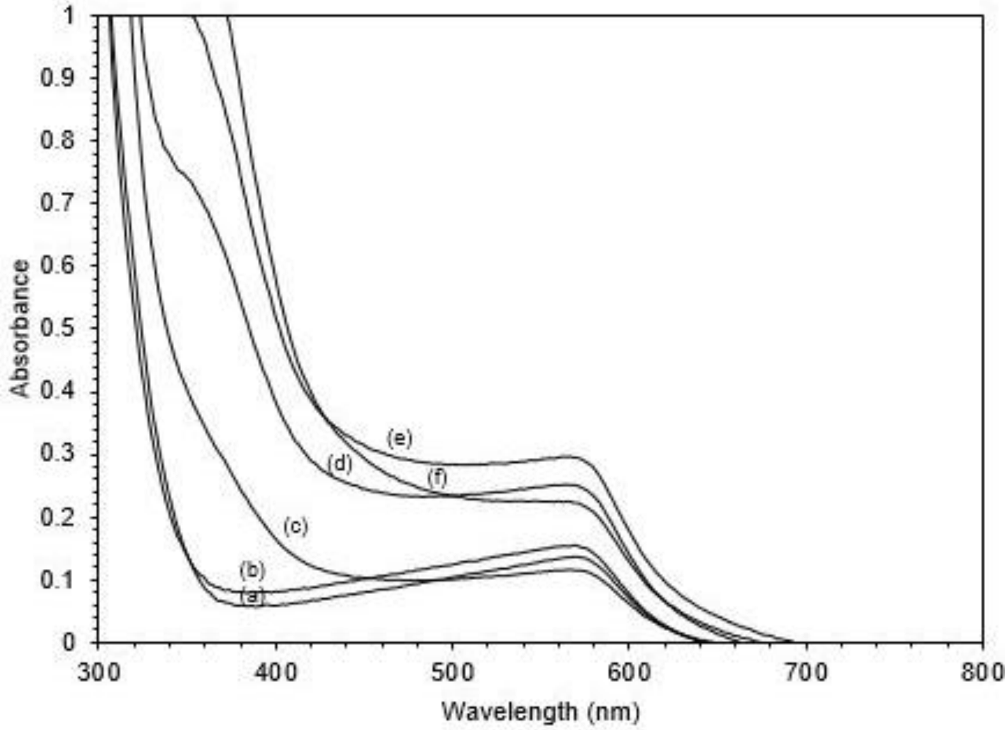

Figure 1. UV-visible of Cu-NPs for different amount of honey 0, 1, 5, 10, 15 and 20% (a-f) respectively.

Meanwhile, the formation of Cu-NPs synthesized by using honey are proved by the XRD analysis where the diffraction pattern matches with the XRD database reference (reference: JCPDS 04-0836) of pure copper nanoparticles as in figure 2. The diffraction peaks for all Cu-NPs honey based synthesized show pure copper without the presence of oxide which are at 2θ = 43.3°, 50.5° and 74.4° which could be assigned to (111), (200) and (220). However, small peak of Cu_2O (111) appeared for Cu-NPs at 0 % that might be because of the oxidation of nanoparticles which start to occur to form the Cu_2O. Scherer equation was used to determine the average crystallite size as in equation (1) where the average size for all the synthesized Cu-NPs were between 20-80 nm. These results are correspond with the previous reported study [1].

$$D = \frac{K\lambda}{FWHM \cos\theta} \quad (1)$$

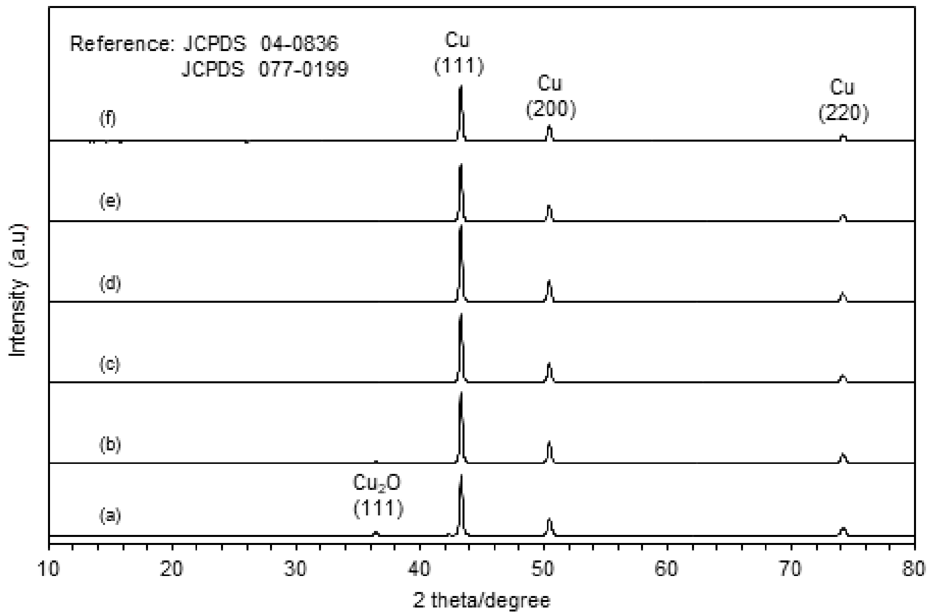

Figure 2. XRD diffraction pattern for Cu-NPs using difference amount of honey 0, 1, 5, 10, 15 and 20% (a-f) respectively.

High resolution transmission electron microscopy was used to monitor the size and morphology of the Cu-NPs. Figure 3 illustrates that the difference of size and shape of each Cu-NPs using different amount of honey. It can be seen that the size of nanoparticles are between 3-100 nm. As can be seen in Figure 3, the size of nanoparticles are decreasing as the amount of honey increase. This is because the presence of the polyhydroxyl groups in honey help in preventing the aggregation of nanoparticles. However, for the Cu-NPs with 5 % and 20 % w/v of honey, the agglomeration of nanoparticles seems to happen and the shape of nanoparticles also inconsistence. These phenomena might be due to the high surface energy of nanoparticles which have high chances for the nanoparticles to attract to each other [26]. This data is correspond to the UV-visible peaks results. The best condition for amount of honey at 0.025 M copper nitrate precursor using honey is at 15 % w/v where the particles have a consistent shape with high amount of Cu-NPs production correspond to the UV-visible results. All results are tally with the UV-visible results obtained.

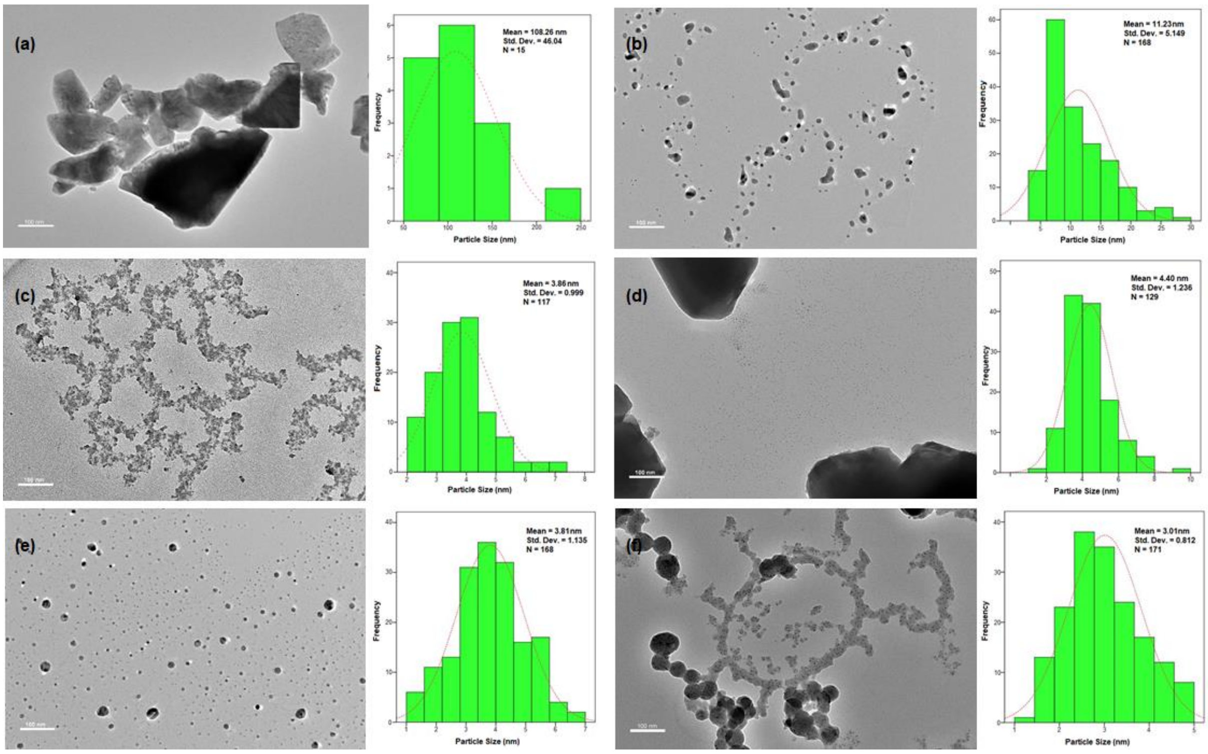

Figure 3. HRTEM of Cu-NPs with different amount of honey 0, 1, 5, 10, 15 and 20% (a-f) respectively.

4. Conclusions

As a conclusion, carbohydrate and polyhydroxyl groups in honey has contributing to control the effect of size and shape of copper nanoparticles. The copper nanoparticles with the range size of 3 to 100 nm are produce depending on the amount of honey used. However, the best amount of honey % w/v for this study is at 15 % w/v with the mean size of 3.81 nm where the shape of nanoparticles are more consistence at this value.

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