Green Synthesis of Ag, Cu and AgCu Nanoparticles using Palm Leaves Extract as the Reducing and Stabilizing Agents

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Abstract. This paper reports the green synthesis of Ag, Cu and AgCu nanoparticles at room temperature using palm leaves extract. The purpose of this study is to eliminate the use of chemicals in the synthesis of nanoparticles and evaluate the efficiency of the palm leaves extract as the reducing and stabilizing agents. The palm leaves extract was added to metal salt solution and continuously stirred until reaction completed. The produced nanoparticles were analyzed using atomic absorption spectroscopy (AAS), Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The analyses revealed that palm leaves extract has efficiently reduced the silver ions, but not the copper ions. During synthesis of AgCu nanoparticles, simultaneous reduction was occurred leading to formation of alloyed nanoparticles. Biomolecules from the palm leaves extract adsorbed on the surface of nanoparticles forming a capping layer thus stabilized the nanoparticles. The produced Ag and Cu nanoparticles were predominantly spherical with the particle size of Cu nanoparticles were larger than Ag nanoparticles. The AgCu nanoparticles closely resembled the Ag nanoparticles due to high Ag content with average size of 13nm. Therefore, palm leaves extract has a potential to be a good reducing and stabilizing agents.

1. Introduction
Ag and Cu nanoparticles were proven to have an efficient antibacterial activity [1,2]. Both of them also have good electrical conductivity, but Cu nanoparticles are easily oxidized, while Ag nanoparticles are expensive. Combination of Ag and Cu nanoparticles is one of the alternatives to overcome those limitations. Shin et al. [3] observed that AgCu nanoparticles exhibit enhanced structural stability compared to Ag or Cu nanoparticles. Valodkar et al. [4] found that AgCu nanoparticles have effective antibacterial activity against Enterichia coli and Staphylococcus aureus, while Li et al. [5] reported that AgCu nanoparticles successfully improved the electrical migration of ink in printing conductive lines.

Green synthesis is a favourable method to produce nanoparticles at room temperature and pressure without use of hazardous chemicals. Through green synthesis, plant extract act as reducing agent thus reduce the metal ions into nanoparticles. Various plant parts have been previously used in the synthesis of Ag and Cu nanoparticles such as mango peel [6], pineapple leaf [7], latex [8] and Magnolia kobus leaf [2]. Although synthesis of AgCu nanoparticles has been extensively explored, but to the best of our knowledge none of the approached involved used of plant extract. Research team from Universiti Putra Malaysia [9] found that palm leaves extract contained high polyphenols content. The high polyphenols content in plant extract can act as both reducing and stabilizing agents for nanoparticles [10]. Work by Valodkar et al. [4] confirmed the role of hydroxyl groups from phenolic compounds as reducer and stabilizer in synthesis of AgCu nanoparticles. Herein, we demonstrate formation of AgCu
nanoparticles through simultaneous reduction of Ag and Cu ions using palm leaves extract as the reducing and stabilizing agents.

2. Materials and methods

2.1. Materials
AgNO₃ and Cu(NO₃)₂ were of analytical grade purchased from Merck Malaysia. Ag and Cu standards for AAS were purchased from Sigma-Aldrich Malaysia. Palm leaves from Elaeis guineensis species were collected from oil palm plantation located at Pasir Panjang, Sekinchan, Selangor, Malaysia. The extract was prepared following the previous work by Arham et al. [11].

2.2. Synthesis of Ag, Cu and AgCu nanoparticles
Palm leaves extract (10mL) was added to 1mM of metal salt solution (90mL); AgNO₃ was used for synthesis of Ag nanoparticles and Cu(NO₃)₂ was used for synthesis of Cu nanoparticles. For synthesis of AgCu nanoparticles, palm leaves extract (10mL) was added to equally mixed 1mM AgNO₃ and 1mM Cu(NO₃)₂ (90mL). The reaction took place at room temperature under constant stirring.

2.3. Characterizations
Atomic absorption spectroscopy (AAS) model Hitachi Z-2000 was used to monitor the conversion of metal ions into nanoparticles. The solutions were centrifuge at 14000rpm for 20mins and the supernatant was analyzed for unreacted ions. After the reaction reached its saturation, the nanoparticles solutions were centrifuged at 10000rpm for 15mins and redispersed in distilled water. This centrifugation step was repeated thrice and the collected particles were dried overnight at 60°C. Palm leaves extract and the dried nanoparticles were subjected to Fourier transform infrared (FTIR) spectroscopy using model Perkin Elmer Spectrum One FTIR spectrometer. Surface images of the nanoparticles were captured using scanning electron microscope (SEM) model Quanta 450 FEG ESEM. Compositional study was carried out using energy-dispersive X-ray spectroscopy (EDX) attached to the SEM. High resolution images of the nanoparticles were captured using transmission electron microscope (TEM) model Tecnai G² 20. EDX attached to TEM was used to obtained line profile of a single particle.

3. Results and discussions
The formations of Ag and Cu nanoparticles were monitored every 30mins using AAS. Figure 1 shows the conversion of Ag and Cu ions with respect to time. There is significant increase in the conversion of Ag ions upon 30mins addition of palm leaves extract.

![Figure 1. Conversion versus reaction time for synthesis of Ag and Cu nanoparticles.](image-url)
Ag ions begins to achieve constant from 90-120 mins suggesting saturation in the reaction. However, the palm leaves extract poorly reduced the Cu ions. This might be due to difference in the reduction potential of Ag and Cu ions. The reduction potential of Ag is larger than Cu (Ag: 0.8V, Cu: 0.34V) [13], signifying that Ag has greater tendency to be reduced. After 2hrs, about 54.8% of Ag ions and 2.7% of Cu ions have been reduced by the same amount of palm leaves extract. Figure 2 shows the conversion of Ag and Cu ions with respect to time for the synthesis of AgCu nanoparticles. Detailed analysis within the first 30 mins of reaction suggests a rapid conversion in which significant increase in the conversion of ions occurred upon 5 mins addition of the palm leaves extract.

![Conversion versus reaction time for synthesis of AgCu nanoparticles.](image)

This result indicates that reduction of Ag and Cu ions by the palm leaves extract occurred simultaneously. However, due to difference in reduction potential, the conversion of Ag ions was higher compared to Cu ions. The simultaneous reduction has accelerated the reduction process. The conversion of both ions during synthesis of AgCu nanoparticles reached saturation after 60 mins compared to 90 mins during synthesis of Ag and Cu nanoparticles. Previous work by Tamuly et al. [14] also discovered that synthesis of AuAg nanoparticles completed faster than synthesis of Au and Ag nanoparticles. In addition, the final conversion has increased compared to the recorded conversion during synthesis of Ag and Cu nanoparticles. After 90 mins, about 86.6% of Ag ions and 10.7% of Cu ions were reduced. However, detail study is required to understand the kinetics behind the reaction. Finally, based on the total reduction of Ag and Cu ions, the produced AgCu nanoparticles were estimated to contain 89.2% of Ag and 10.8% of Cu. This composition is almost similar to standard composition of coin silver which contained 90% of Ag and the remaining 10% is Cu [15].

From figure 3, the spectrum for palm leaves extract indicates presence of hydroxyl (3307 cm⁻¹), carbonyl (1738 cm⁻¹), amide I (1635 cm⁻¹), aromatic amine (1366 cm⁻¹) and aliphatic amine (1229 and 1217 cm⁻¹). Ag nanoparticles show peaks at 3274 cm⁻¹, 1739 cm⁻¹, 1510 cm⁻¹, 1366 cm⁻¹, 1236 cm⁻¹, 1217 cm⁻¹, 2878 cm⁻¹ and 1014 cm⁻¹, while Cu nanoparticles show peaks at 3242 cm⁻¹, 1606 cm⁻¹, 1352 cm⁻¹, 1209 cm⁻¹, 1152 cm⁻¹, 2956 cm⁻¹ and 1048 cm⁻¹. AgCu nanoparticles show peaks at 3261 cm⁻¹, 1606 cm⁻¹, 1366 cm⁻¹, 1217 cm⁻¹, 2917 cm⁻¹ and 1047 cm⁻¹. Based on the spectra of all three types of nanoparticles, the significant reduction in the intensity of hydroxyl and carbonyl groups suggested that these functional groups might involve in the reduction of the metal ions. Presence of other functional groups suggested that the nanoparticles were capped with biomolecules from the palm leaves extract, hence stabilized nanoparticles were produced.

EDX spectra in figure 4 confirms presence of Ag and Cu elements in the produced Ag, Cu and AgCu nanoparticles. Presence of C and Si might be originated from the palm leaves extract that adsorbed on the surface of nanoparticles. Previous work on green synthesis of Au nanoparticles also discovered the presence of C and Si elements [16]. The finding from EDX is in accordance with FTIR analysis in which the biomolecules from the palm leaves extract was responsible as the stabilizing agent. It was also observed that the signal for Ag was stronger than Cu indicating greater amount of Ag compared to Cu, thus verifying the findings obtained through AAS analysis. Line profile of a single AgCu nanoparticle depicted in figure 5 suggests that the produced nanoparticle composed of
two alloyed metal elements. The intensity of Ag was greater than Cu, thus further supported the finding from AAS that the produced nanoparticles contained high amount of Ag.

![Figure 3](image-url)

**Figure 3.** Comparison between FTIR spectra of palm leaves extract and the nanoparticles.

![Figure 4](image-url)

**Figure 4.** EDX spectra of (a) Ag, (b) Cu and (c) AgCu nanoparticles.

![Figure 5](image-url)

**Figure 5.** Line profile of AgCu nanoparticles.
Figure 6 shows the SEM images of Ag, Cu and AgCu nanoparticles captured at 100000x magnification. The Ag nanoparticles were mostly spherical but some agglomeration was observed for Cu nanoparticles. The size of Cu nanoparticles was larger compared to Ag nanoparticles. Similar finding was reported through chemical synthesis of Ag and Cu nanoparticles [17]. The AgCu nanoparticles on the other hand closely resemble to the Ag nanoparticles. This might be due to the large Ag content in the produced AgCu nanoparticles.

![SEM images](image)

**Figure 6.** SEM images for (a) Ag, (b) Cu and (c) AgCu nanoparticles.

TEM image of AgCu nanoparticles in figure 7 revealed that the nanoparticles were predominantly spherical and monodispersed. This finding was comparable to AgCu nanoparticles synthesized through chemical method [18].

![TEM images](image)

**Figure 7.** TEM images for AgCu nanoparticles captured at low and high magnifications.

A faint thin layer was observed on the surface of nanoparticles confirming the adsorption of stabilizer from the palm leaves extract. The presence of capping layer was also reported by Tamuly et al. [14]. The uniform contrast for each nanoparticle suggests a homogenous electron density within the particle, thus resemble to alloy structure. Previous study on green synthesis of AuAg nanoparticles through simultaneous reduction also resulted in formation of alloy structure [19,20]. The inset selected area electron diffraction (SAED) image showed a ring-like diffraction pattern indicating that the produced AgCu nanoparticles were crystalline [21]. The measured interplanar distance is 0.21nm which could be indexed to (111) plane of AgCu alloy. The average size of at least 100 particles is 13nm. Based on the inset histogram, the AgCu nanoparticles lie in the range of 5-30nm, almost similar to the range of polymer-stabilized AgCu nanoparticles which is 10-30 nm [18]. This finding indicates that palm leaves extract is not only an efficient reducing agent, but also has a potential to be a good stabilizing agent.

4. Conclusion
Ag, Cu and AgCu nanoparticles were successfully produced through reduction with palm leaves extract. The rapid reduction process and the resulting monodispersed nanoparticles proved the efficiency of the palm leaves extract as reducing and stabilizing agents. It is the novelty of this study to
discover formation of silver rich alloy through simultaneous reduction method. The average size obtained was 13nm, comparable to the polymer-stabilized AgCu nanoparticles.

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