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Synthesis of Cu-Ag core-shell nanoparticles and its electrochemical characterization

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***Abstract*—The Cu-Ag core-shell nanoparticles (Cu@Ag NPs) are prepared by chemical reduction method with polyvinyl pyrrolidone (PVP) as a capping agent, ascorbic acid ($C_6H_8O_6$) and sodium borohydride ($NaBH_4$) were used as reducing agent. Cu@Ag NPs were synthesized with three variations of (Cu:Ag) 1:3, 1:4, and 1:5. The uniformity of Cu@Ag NPs samples with three variations was verified by the particle size analyzer test. The sizes of Cu@Ag 1:3, 1:4, and 1:5 were obtained sequentially at the range of 270-280 nm, 300-304 nm, and 690-700 nm respectively. Indications of the successful synthesis of Cu@Ag nanoparticles can be seen from UV-Vis spectra of Cu@Ag 1:3, 1:4, and 1:5 respectively forming AgNP at wavelengths of 434 nm, 450 nm, and 428 nm. Furthermore, the stability of Cu@Ag NPs was carried out over a period of 0 day, 4 days, 7 days, 11 days, and 14 days. It can be observed that the variation of 1:5 tends to be more stable as the chart continues to experience significant improvements compared to the variation of 1:3 and 1:4. The electrochemical study was then performed by applying cyclic voltammetry from 0 V to 1.8 V. It is clearly shown that the peak of Cu oxidation is appeared at a potential of 1.2 V while the peak value of Ag oxidation is at a potential of 0.9 V.**

***Keywords*—nanoparticles, core-shell structure, copper, silver, chemical reduction**

I. INTRODUCTION

Silver nanoparticles (AgNPs) are widely used in various fields such as electronics industry [1], [2], sensors [3], [4], catalysis [5], and medical devices [6], [7]. AgNPs are also known to have good potential in electrochemical sensor application. AgNPs are known to be able to detect pollutants discharged into the environment such as ammonia, heavy metals, and pesticides. In addition, AgNPs can be used for early detection of cancer cell identification [8]. In addition, in recent years, AgNPs have been used for conductive inks due to their high electrical conductivity and excellent oxidation stability [9]. However, AgNPs have electromigration resistance and expensive [10].

Copper (Cu) is a transition metal with an affordable price. Cu has excellent mechanical strength and conductivity which makes it frequently used in the steel construction and electronics industries. Recently, copper nanoparticles (CuNPs) have received attention from researchers due to their potential as electrochemical sensor applications. CuNPs have many advantages such as high catalytic activity, excellent redox and electrical conductivity that is equivalent to noble metals and a lower price [11], [12]. These properties make CuNPs often used as an alternative to AgNPs. However, CuNPs can easily be oxidized to Cu_2O or CuO even under environmental conditions that leads to direct decrease in their electrical conductivity and limiting their applications [13], [14].

On the other hand, bimmetalic nanoparticles have been extensively investigated and utilized to improve the chemical, catalytic, optical, biological, and plasmonic properties of single metals [15]. Cu-Ag core-shell nanoparticles (Cu@Ag NPs) are an alternative that can overcome the weaknesses of AgNPs and CuNPs. By combining AgNPs and CuNPs in a core-shell structure, the oxidation resistance of CuNPs can be increased and the electromigration resistance of AgNPs can be reduced [16].

Currently, many methods have been proposed to fabricate Cu@Ag NPs such as electroplating methods [17], electroless plating [18], sputtering [19], evaporation [20], chemical reduction [21], and galvanic displacement [22]. Among these methods, the chemical reduction method has several advantages such as simple procedures, low cost, and energy saving [23]. In addition, this method can reduce galvanic transfer reactions in the form of deposition or oxidation which leads to preventing agglomeration of nanoparticles [24]. In this work, Cu was coated with Ag using chemical reduction method to form Cu-Ag core-shell nanoparticles (Cu@Ag NPs) to protect Cu from excessive oxidizing activity. Different composition were studied to find the optimum ratio of Cu and Ag. Some characterization including electrochemical study was carried out for the first time in this work. In Addition, the stability of the nanoparticles were evaluated.

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II. EXPERIMENTAL

A. Materials

Copper(II) sulfate pentahydrate ($CuSO_4.5H_2O$, 99-100.5%) and silver nitrate ($AgNO_3$, 99.8-100.5%) from Merck as a precursor, polyvinylpyrrolidone (PVP) was used as the capping and stabilizer agent, ascorbic acid ($C_6H_8O_6$, 99.0-00.5%) and sodium borohydride ($NaBH_4$, >96%) from Merck was used as the reducing agent. Ammonium hydroxide (NH_4OH, 28-30%) was purchased from Merck. All chemicals were sued without further purification.

B. Preparation of reductor solution

PVP (2 g) was dissolved in 50 mL of distilled water and then stirred at 50ºC with a speed of 500 rpm. Ascorbic acid (0.088 g) was dissolved in 50 mL of distilled water and then stirred until dissolved

C. Synthesis and characterization of Cu-Ag core-shell (Cu@Ag)

Cu@Ag NPs was synthesized using three Cu:Ag ratio of (1:3, 1:4, 1:5). $CuSO_4$ and $AgNO_3$ with a predetermined composition (Table 1) dissolved in 10 mL NH_4OH 0.1 M. $CuSO_4$ (2 mL) and the $AgNO_3$ solution is added to the reductor solution slowly while stirring at 50ºC with a speed of 500 rpm for 45 minutes. Cu@Ag NPs solution were characterized by UV-Vis spectrophotometer (Thermo scientific Genesys 50) particle size analyzer (PSA) (Beckman Coulter N4 PLUS).

Table 1. Composition of Cu@Ag solution

Variations	$CuSO_4$ (gr)	$AgNO_3$
1:3	0.025	0.051
1:4	0.025	0.068
1:5	0.025	0.085

D. Electrochemical behavior on Cu@Ag/BDD electrode

BDD electrode are pre-treated before being modified using an ultrasonicator to dissolve impurities on the electrode surface. The 20 µL of Cu@Ag with ration of 1:3 was dropped on a BDD electrode and then dried at room temperature. The as-prepared modified electrode was then immersed in 0.1 M phosphate buffer pH 7 and cyclic voltammetry was performed from potential 0V to 1.8 V using Emstat3+ blue from Palmsen. The Ag/AgCl and Pt wire as reference and counter electrode respectively.

III. RESULT AND DISCUSSION

A. Synthesis of Cu-Ag core-shell

A color change occurred in the Cu@Ag NPs solution after stirred for 45 min. The three samples show different results. In Cu@Ag 1:3 solution, the color changed from clear yellowish to light brown (Fig 1a and 1d), in Cu@Ag 1:4 solution, the color changed from clear yellowish to dark brown and there was a black colored sediment (Fig. 1b and 1e), and in Cu@Ag 1:5 solution, the color changed from light brown to dark brown after stirred for 45 minutes (Fig. 1c and 1f). The black colored sediment in Cu@Ag 1:4 solution is most likely due to agglomerating nanoparticles. Agglomeration might be occured because PVP was less soluble, which results in a decrease in its performance as a stabilizer agent. The color change that should be occured in the synthesis of Cu@Ag NPs was transparent yellow into deep green, green, and ended with yellowish green [25]. However, all Cu@Ag NPs samples have light brown or dark brown color which is the color of AgNPs [26]. This was due to the higher concentration of AgNPs than CuNPs. The darker the solution color indicates that the AgNPs concentration is also increasing [11].

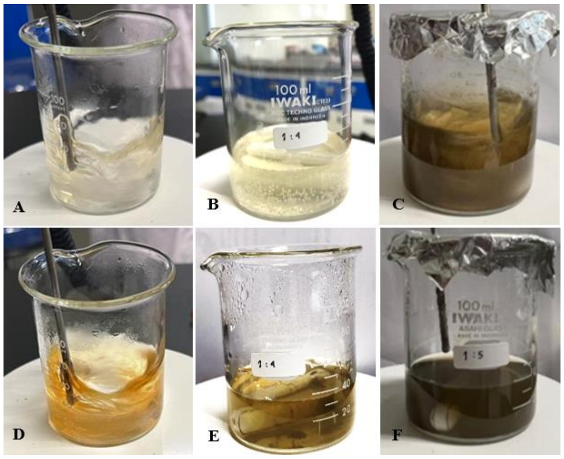

Figure 1. Cu@Ag NPs solution before a) 1:3, b) 1:4, c) 1:5 and b) after d) 1:3, e) 1:4, f) 1:5 stirred for 45 min.

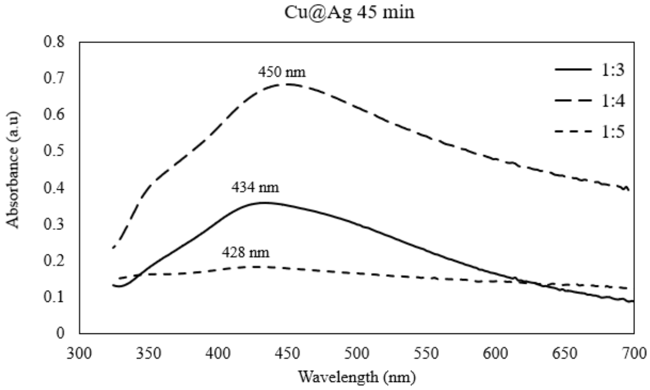

Figure 2. UV-Vis absorption spectra of Cu@Ag NPs.

The brown AgNPs solution has a maximum absorption peak in the wavelength range of 380-450 nm [27]. This is peak is due to the collective oscillation phenomenon of free conduction band electrons in a particle (SPR) [28]. There were maximum absorption peaks at 434 nm, 450 nm, and 428 nm respectively in Cu@Ag 1:3, 1:4, and 1: 5 samples. This is suitable with the color of Cu@Ag NPs solution. The maximum absorption peak of CuNPs is in the wavelength range of 525-580 nm [11]. The UV-Vis spectrum of the three samples did not show peak of CuNPs which might be due to the concentration of AgNPs that coats CuNPs is too high than concentration of CuNPs inside which causes CuNPs cannot be detected by UV-Vis spectrophotometer. The absence of CuNPs peak also indicates that there is no free CuNPs which means that CuNPs are completely coated by AgNPs that leading to the formation of Cu@Ag core-shell NPs [25].

B. *Particle size analysis*

Cu@Ag NPs sample has a large size, specifically between 240-320 nm for 1:3 ratio (Fig. 3a), 240-360 nm for 1:4 ratio (Fig. 3b), and 520-780 nm for 1:5 ratio (Fig. 3c). All samples had good polydispersity index (PI) values in the range of 0.25-0.30 which indicates that the nanoparticles are homogeneous [29].

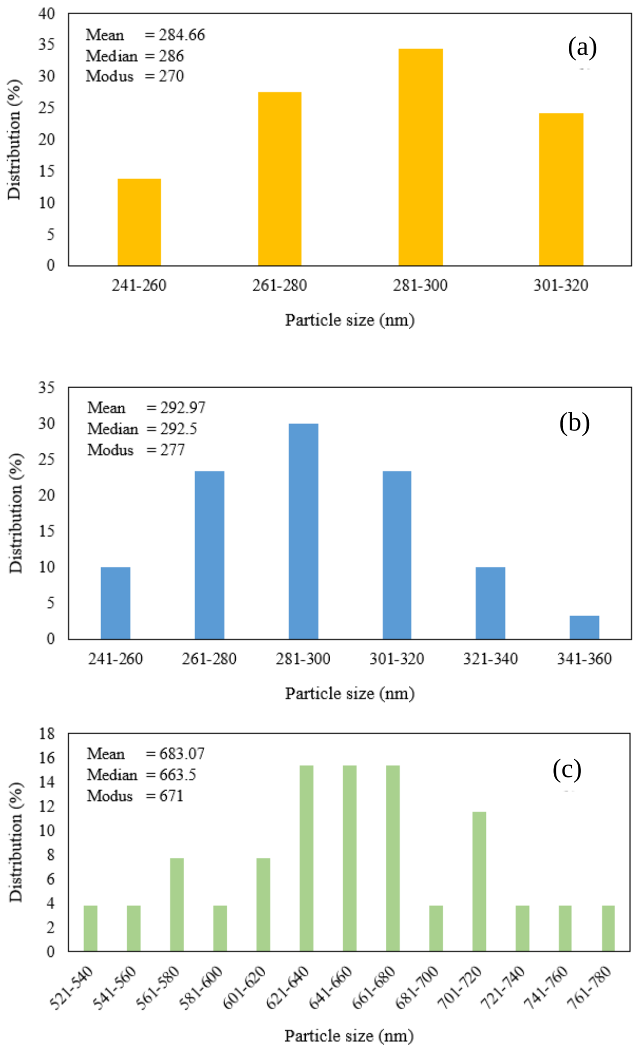

Figure 3. Particle size distribution of Cu@Ag NPs a) 1:3, b) 1:4, c) 1:5

C. *Stability test*

Stability test of Cu@Ag NPs was carried out with time ranges of 0, 4, 7, 11, and 14 days. Cu@Ag 1:3 sample was stable up to 7 days of storage as can be seen from an increase in absorbance intensity on day 4 and no decrease was observed in the absorbance intensity on day 7. The sample became unstable after being stored for more than 7 days as seen from the decrease in absorbance intensity on the day 11 and more on the day 14. Cu@Ag 1:4 sample was unstable as seen from the significant decrease in absorbance intensity on day 4 and more until day 11. The decrease in absorbance intensity in Cu@Ag 1:3 and 1:4 samples can be caused by the loss of AgNPs due to agglomeration. Cu@Ag 1:5 sample had good stability as seen from the constant increase in absorbance intensity until day 14. The increase in absorbance intensity indicates that the reduction reaction is still ongoing which result in an increase in the concentration of nanoparticles.

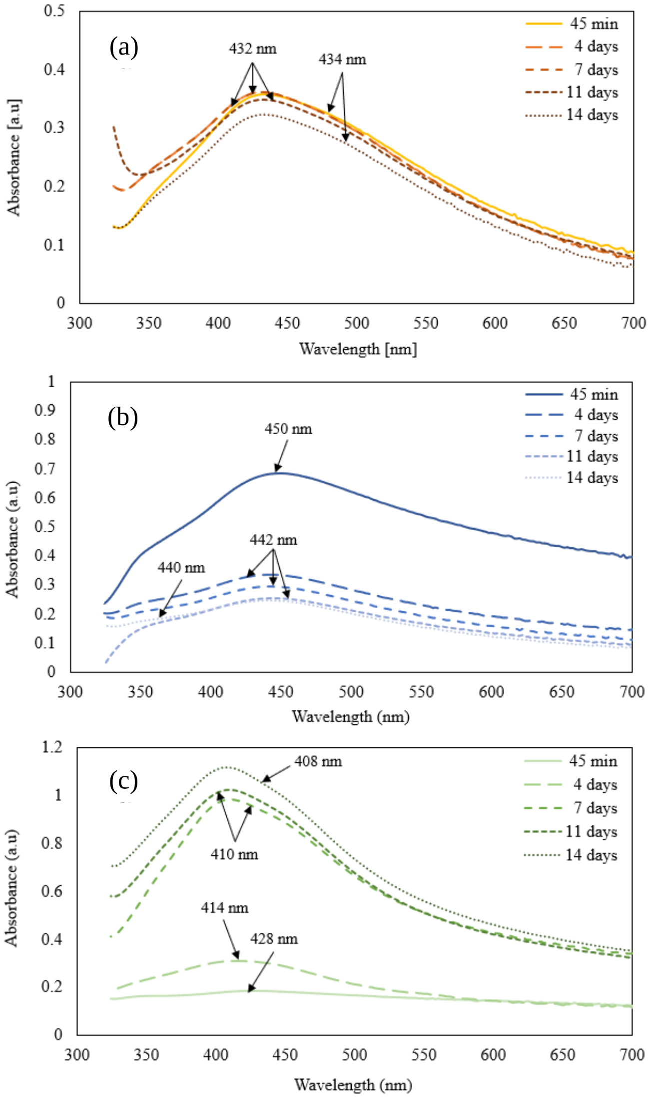

Figure 4. Stability test of Cu@Ag NPs a) 1:3, b) 1:4, c) 1:5

D. Cyclic voltammetry characterization

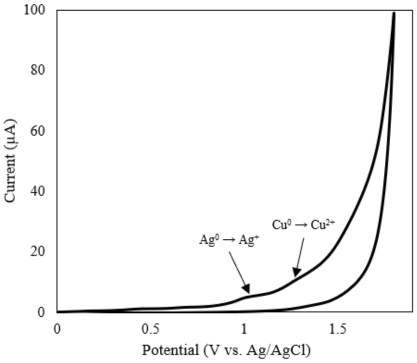

Figure 5. Cyclic voltammogram of Cu@Ag/BDD with Cu@Ag ratio of 1:3

Cyclic voltammetry (CV) was used to investigate the samples through oxidation and reduction reaction of each component used. The analysis was carried out at a potential of 0.0-1.8 V with a scan speed of 100 mV/s. The CV graph shows the presence of two oxidation peaks indicating $Ag^0 \rightarrow Ag^+$ and $Cu^0 \rightarrow Cu^{2+}$ at a potential of 0.9 V and 1.2 V respectively [30].

IV. CONCLUSION

Cu@Ag NPs were successfully synthesized using chemical reduction method. Cu@Ag NPs were prepared using three variations at the addition of $AgNO_3$ concentration (1:3, 1:4, 1:5). All sample solution had a brown color that indicating the presence of AgNPs. Each variation of Cu@Ag NPs shows a typical absorption peak of AgNPs at a wavelength range of 400-450 nm while the peak of CuNPs was not observed in all variations. This is caused by the concentration of AgNPs that coats CuNPs is much higher than the concentration of CuNPs inside. The diameter of Cu@Ag NPs increases as the concentration of $AgNO_3$ is increased. Each variation of Cu@Ag shows that the nanoparticles are homogeneous and evenly distributed. Stability test shows that the most stable sample was Cu@Ag 1:5. Cyclic voltammetry characterization show a sloping oxidation peak of AgNPs and CuNPs at a potential of 0.9 V and 1.2 V which validates the formation of Cu@Ag NPs.

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