

# Synthesis of Core-Shell Nanoparticles of Cu-Ag for Application in Electrohydrodynamic Printing Technique

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**Abstract:** Core-shell nanoparticles of Cu-Ag (Cu core and Ag shell) were synthesized using chemical method. Polyvinyl pyrrolidone (PVP) was used as a surfactant, and ascorbic acid ( $C_6H_8O_6$ ) and sodium borohydride ( $NaBH_4$ ) were used as reducing agents to reduce the metal complexes  $[Cu(NH_3)_4]^{2+}$  and  $[Ag(NH_3)_2]^+$ . The results of transmission electron microscope (TEM) analysis, ultraviolet-visible spectroscopic (UV-Vis) analysis, X-ray diffraction (XRD) analysis showed that the core-shell nanoparticles of Cu-Ag were successfully synthesized. The average particle size was 32 nm. The dispersion of the nanoparticles was still good after 80 days without the formation of the oxides of Cu and Ag. The properties of the nanoparticles suggested that they were suitable to be used as an electrically conductive material for conductive ink-jet printing inks.

**Key words:** Nanoparticles, nano bimetal, Ag nanoparticles.

## 1. Introduction

In the recent years, the ink-jet printing technique has become popular with many applications [1]. Ink-jet printing provides excellent resolution on paper and many other materials. The recent reports suggested that ink-jet printing could be used to fabricate the thin membranes [2]. One of the advantages of this technique is that it can be used to fabricate the membranes without the need of mask. Thus, it provides excellent application potential in fabrication of microelectronic boards on plastic substrates. The printing methods include: offset printing, printing with the aid of sun light, printing using soft mold, and ink-jet printing. All of these methods provide similar resolution, about 10-30  $\mu m$ . The advantage of ink-jet printing compared to other methods is no need of mask. A computer will control to print each dot based on a designed image, giving quick printing at low cost. The ink-jet printing techniques include: piezoelectric ink-jet printing,

bubble jet ink-jet printing, and aerosol ink-jet printing. They work by pressing ink through a small hole (micrometer size or smaller) to produce very small ink droplets on substrate. Ink-jet printing technique can be used to print on every material from paper, metal, semiconductor to plastics.

The inks for ink-jet printing are normally fabricated based on functional nanoparticles such as Au, Ag, or rare earth. In the ink-jet printing technology, research of fabrication of inks based on the functional nanoparticles is very important because it directly relates to properties and application purposes of products after printing.

Ag nanoparticles possess many advantages for fabrication of conductive inks, because the electrical conductivity of Ag is the best among metals and it is also difficult to be oxidized in normal conditions [3, 4]. However, because of the high cost of Ag, the conductive inks based on Ag nanoparticles will be very expensive, making them difficult to be used in the industrial applications. Because of this reason, we attempt to reduce the content of Ag in the inks without sacrificing their electrical conductivity by fabrication

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of conductive inks based on core-shell nanoparticles with Cu core and Ag shell instead of using Ag nanoparticles. We expect that the fabrication of conductive inks using the Cu-Ag core-shell nanoparticles will help to reduce a significant amount of Ag, because the cores of the nanoparticles are Cu having low cost. The Cu-Ag core-shell nanoparticles will be expected to have similar electrical conductivity compared to Ag nanoparticles, because the shells of the core-shell nanoparticles are Ag. In this paper, we present the method for synthesis of the Cu-Ag core-shell nanoparticles for fabrication of conductive inks for ink-jet printing.

## 2. Experimental Setup

### 2.1 Materials

Silver nitrate ( $\text{AgNO}_3$ ) (Merck), copper (II) sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) (Merck), ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ ) (Merck), sodium borohydride ( $\text{NaBH}_4$ ) (Merck), polyvinylpyrrolidone 40000 ( $\text{C}_6\text{H}_9\text{NO}$ )<sub>n</sub> (BASF) were used as received.

### 2.2 Synthesis Method and Measurement

#### 2.2.1 Synthesis Method

PVP and ascorbic acid were dissolved in deionization (DI) water to obtain PVP solution (0.0015 M) and ascorbic acid solution (0.1 M). After that, the two solutions were mixed using magnetic stirrer.  $\text{CuSO}_4$  solution (0.05 M) was then added dropwise to the above solution followed by adding  $\text{NaBH}_4$  solution. After 10 minutes,  $\text{AgNO}_3$  solution (0.05 M) was added dropwise to the above solution. Temperature of the solution was kept constantly at 50 °C in all steps.

#### 2.2.2 Measurement

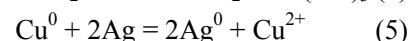
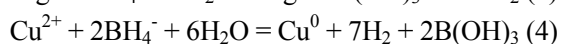
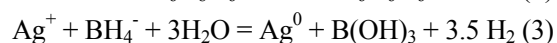
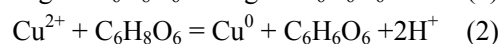
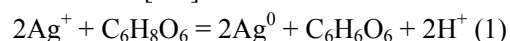
The obtained core-shell nanoparticles were

characterized using X-ray diffractometer (XRD), ultraviolet-visible spectrometer (UV-Vis) (Cary 100), transmission electron microscope (TEM) (JEM model 1400, 100 kV). Particle size distribution was obtained using ImageJ software.

## 3. Experimental Results

### 3.1 Effects of $\text{NaBH}_4$ Reducing Agent on the Formation of Cu-Ag Core-Shell Nanoparticles

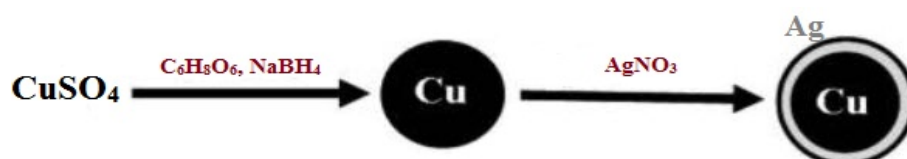
In this work, Cu-Ag core-shell nanoparticles having particle size of around 40 nanometer were synthesized using chemical reduction method. The reactions are presented as followed [5-7]:



In this synthesis method, the metal salts of  $\text{CuSO}_4$  and  $\text{AgNO}_3$  were treated with  $\text{NH}_4\text{OH}$  to obtain the metal complexes of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{Ag}(\text{NH}_3)_2]^+$  followed by reducing to metallic  $\text{Cu}^0$  and  $\text{Ag}^0$ . Fig. 1 shows the development steps of the Cu-Ag core-shell nanoparticles.

To investigate the effects of  $\text{NaBH}_4$  reducing agent on the formation of Cu-Ag core-shell nanoparticles, the samples a, b, c were prepared with variation of volume ratio of  $\text{NaBH}_4/\text{Cu}^{2+} = R$  ( $R = 0.5, 1, 2$ ). Concentration and ratio of other chemicals were kept constant as in Table 1.

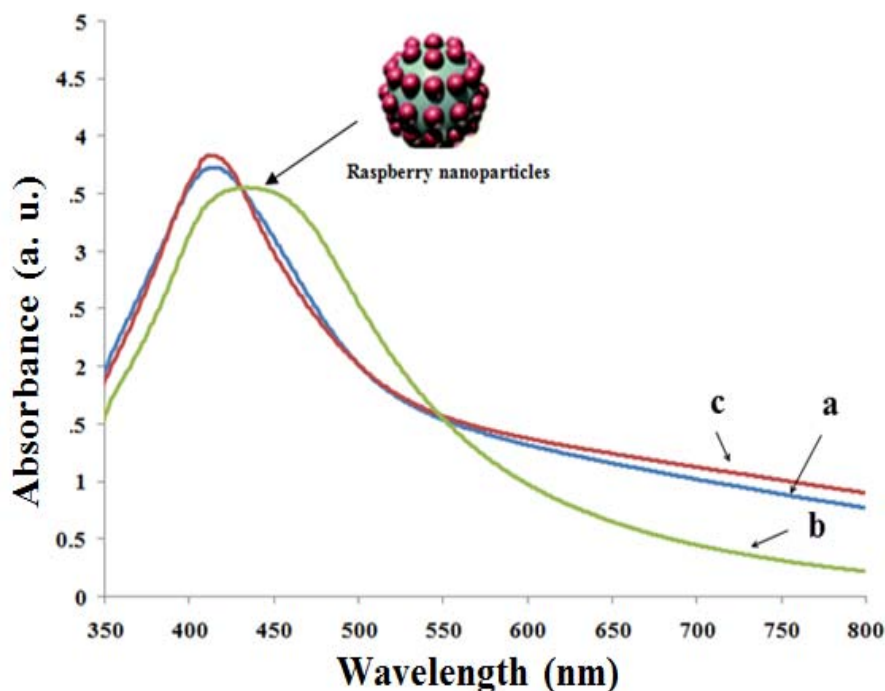
Fig. 2 shows that the UV-Vis spectra of samples a and c exhibit only one peak at 415 nm (surface plasmon resonance of spherical Ag nanoparticles), suggesting the presence of Ag nanoparticles in the solution but without the presence of Cu nanoparticles. The spectrum of sample b exhibits a broad band from



**Fig. 1** The development steps of Cu-Ag core-shell nanoparticles.

**Table 1** The samples with the ratio of the reactants in the Ag nanoparticles preparation reactions.

Samples	$Ag^+/Cu^{2+}$	$Cu^{2+}/C_6H_8O_6$	$Cu^{2+}/PVP$	$NaBH_4/Cu^{2+}$
a	0.2	0.2	0.02	0.5
b	0.2	0.2	0.02	1
c	0.2	0.2	0.02	2



**Fig. 2** UV-Vis spectra of the samples synthesized with different volume ratio of  $NaBH_4/Cu^{2+}$ .

415 nm to 460 nm. This kind of UV-Vis spectrum suggests the presence of bimetallic raspberry nanoparticles [8]. A bimetallic raspberry nanoparticle is a structure in which a metal nanoparticle served as a core is covered by nanoparticles of another metal, but not fully covered. The plasmon resonance peak of Cu nanoparticles appeared at a longer position (~530 nm) compared to that of Ag nanoparticles. This may be the reason for the broadening of the peak of the spectrum. The results suggest that, with sample a, the amount of  $NaBH_4$  was not enough to reduce  $Cu^{2+}$  to metallic Cu. With sample c, a great amount of reducing agents may cause a quick oxidation of the surface of the Cu nanoparticles. These resulted in the absence of the peak of Cu nanoparticles in the spectra of the two samples a and c.

### 3.2 Effects of $Ag^+/Cu^{2+}$ Ratio on the Formation of Cu-Ag Core-Shell Nanoparticles

To investigate the effects of ratio of  $Ag^+/Cu^{2+} = L$  on the formation of Cu-Ag core-shell nanoparticles, the samples were synthesized with  $L = 0.2, 0.4, 0.6, 0.8$ . The ratio of other chemicals was kept constant and  $R = 1$ .

Fig. 3 shows the UV-Vis spectra of the samples synthesized with different ratio of  $Ag^+/Cu^{2+}$ . Inset is the spectrum of Cu-Ag nanoparticles reported by Tsail et al. [9]. As seen in Fig. 3, the spectra of the samples with  $L = 0.2$  and  $0.4$  exhibit two peaks at ~400 nm (peak 1) and 525-535 nm (peak 2). These two peaks correspond to the absorption regions of Ag nanoparticles (peak 1) and Cu nanoparticles (peak 2).

### Synthesis of Core-Shell Nanoparticles of Cu-Ag for Application in Electrohydrodynamic Printing Technique

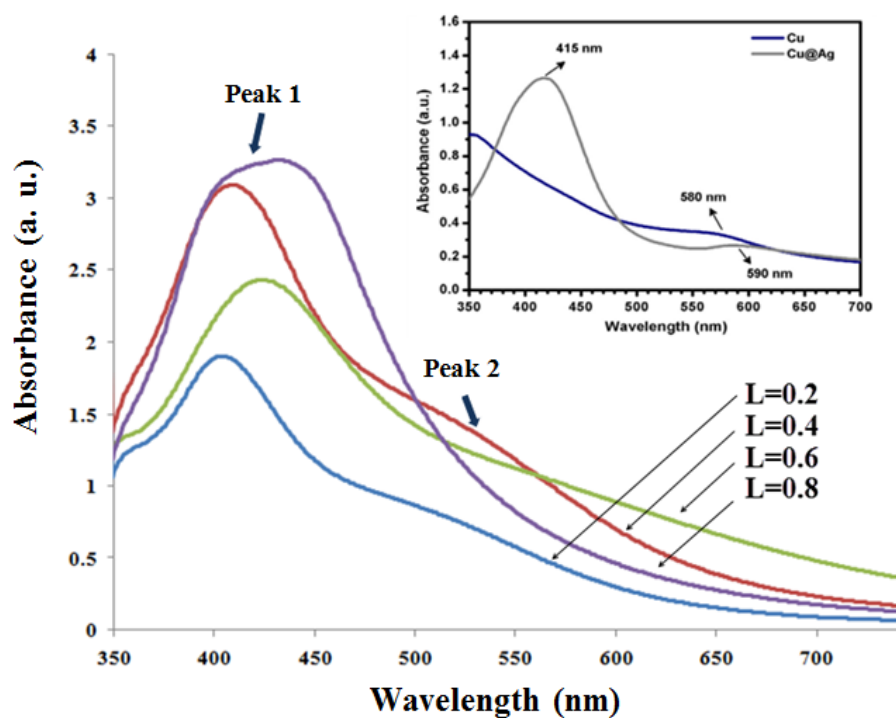


Fig. 3 UV-Vis spectra of the samples synthesized with different ratio of Ag<sup>+</sup>/Cu<sup>2+</sup>. Inset is the spectrum of Cu-Ag nanoparticles reported by Tsail et al. [9].

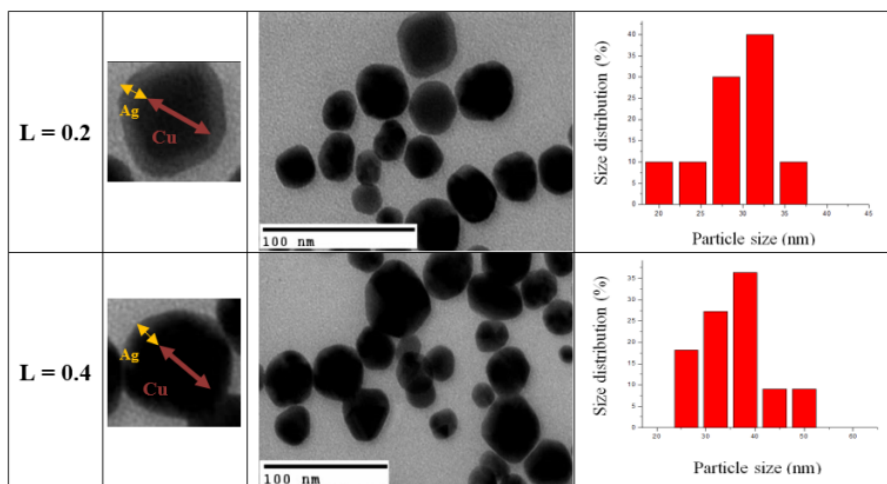


Fig. 4 TEM images and particle size distributions of the samples synthesized with different ratio of Ag<sup>+</sup>/Cu<sup>2+</sup>.

The spectra of the samples are similar to the spectrum of Cu-Ag nanoparticles reported by Tsail et al. [9]. The spectra of the samples with  $L = 0.6$  and  $0.8$  exhibit only one peak at the absorption region of Ag nanoparticles ( $\sim 420$ - $432$  nm), suggesting the absence of Cu nanoparticles in the samples. The absorption intensity at  $\sim 400$  nm of the sample with  $L = 0.4$  is higher than that of the sample with  $L = 0.2$ , indicating

a higher density of Ag nanoparticles.

Fig. 4 shows the TEM images and particle size distributions of the samples with  $L = 0.2$  and  $0.4$ , indicating the presence of core-shell nanoparticles in both samples. From the results of UV-Vis absorption (Fig. 3), it can be concluded that these core-shell nanoparticles are Cu-Ag core-shell nanoparticles. The sample with  $L = 0.2$  has average particle size of about

32 nm, while the sample with  $L = 0.4$  has average particle size of about 40 nm. This shows that when the volume of  $\text{Ag}^+$  solution increased, the particle size tends to increase. It may relate to reaction (5), because when the volume of  $\text{Ag}^+$  solution increased, the amount of  $\text{Cu}^{2+}$  also increased, and they were reduced by the reducing agents in the solution that caused the particle size increased [8].

### 3.3 Effects of pH on the Formation and Stability of Cu-Ag Core-Shell Nanoparticles

Metal nanoparticles dispersed in a solution always have a surface electric charge to avoid aggregation [10]. The mechanism for the formation of electric charge depends on the properties of the metal nanoparticles and the solvent. In this method, we used DI water as solvent, thus the surface electric charge of the metal nanoparticles will be affected by the pH of the solution (Nernst equation). Therefore, the pH of the solution will affect the dispersion or the aggregation of the metal nanoparticles. We synthesized the samples with  $L = 0.4$  and with pH = 2,

4, 6, 8, 10.

Fig. 5 shows that, with pH = 6, the UV-Vis spectrum is similar to the results reported for Cu-Ag nanoparticles. The spectrum exhibits two peaks corresponded to Ag nanoparticles at ~400 nm and Cu nanoparticles at ~530 nm. The spectra of other samples are not clear with broad peaks. The spectrum of sample with pH = 2 exhibits no peak. The color of the solutions of the samples was also varied and tended to darken when the pH increased. Observation of the samples after 10 days from synthesis showed that the sample with pH = 6 had no agglomeration. The samples with pH = 8, 10 slightly aggregated, and the color of the solutions was unchanged. The samples with pH = 2, 4 heavily aggregated, and the color of the solutions became lighter. Thus, with pH = 6, the Cu-Ag core-shell nanoparticles were formed and stably dispersed in the solution after 10 days from synthesis. However, the stability of the sample in a longer time needs to be further investigated, because it is very important for application of the Cu-Ag core-shell nanoparticles for fabrication of conductive inks.

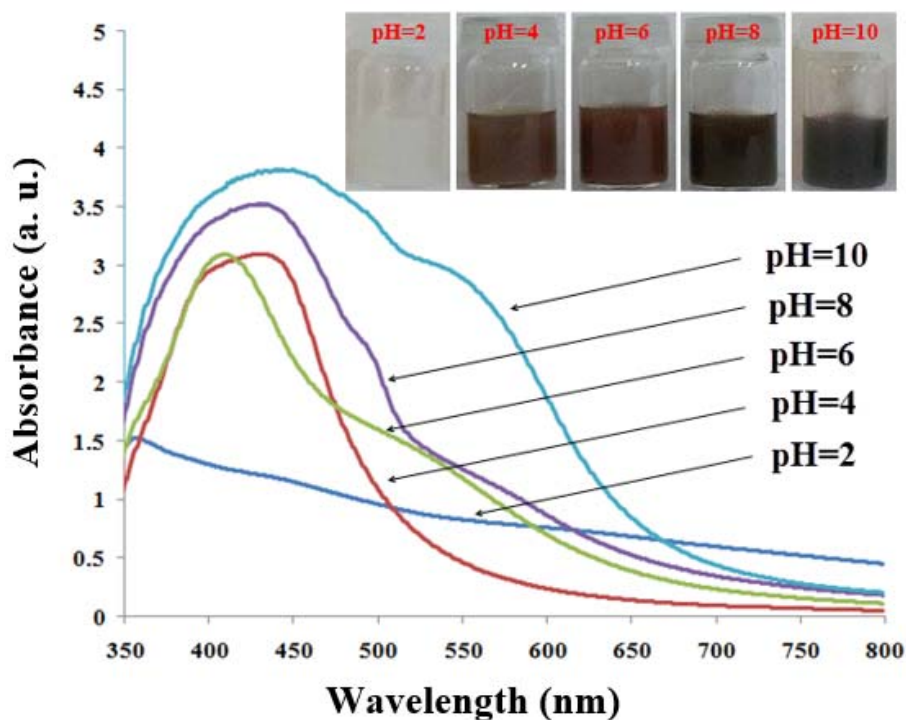


Fig. 5 UV-Vis spectra and photographs of the samples synthesized with pH = 2, 4, 6, 8, 10.

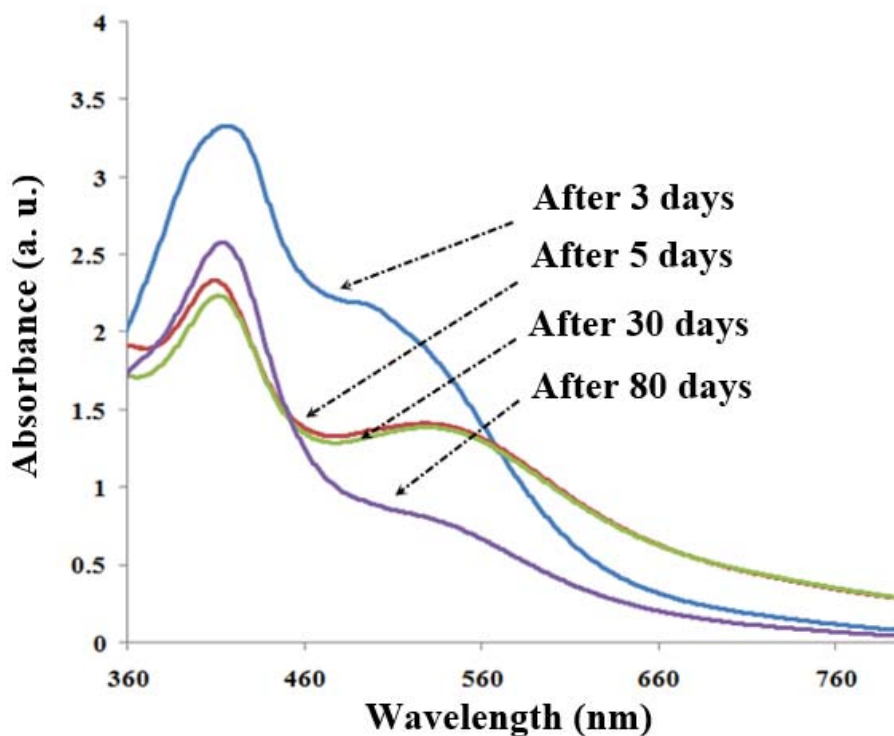


Fig. 6 UV-Vis spectra of the sample with pH = 6 measured after different time from synthesis.

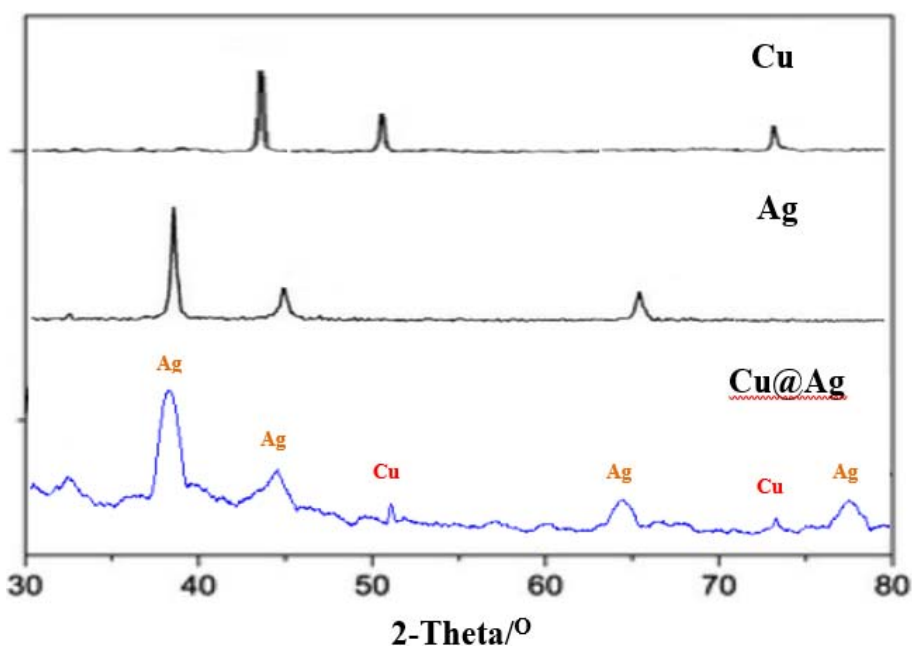


Fig. 7 XRD pattern of the Cu-Ag core-shell nanoparticles synthesized with pH = 6.

Fig. 6 shows that the sample was still stable after 80 days from synthesis. After 80 days from synthesis, the peak at the longer wavelength tends to decrease in intensity compared to that of other samples. In our previous studies, keeping Cu nanoparticles stable in a

long time from synthesis was very difficult, because they were easily oxidized in solution. The results indicate that the reduction of the metal complexes  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{Ag}(\text{NH}_3)_2]^+$  formed nanoparticles having better stability compared to the reduction of

Ag<sup>+</sup> and Cu<sup>2+</sup>.

To evaluate the crystallization of the Cu-Ag core-shell nanoparticles, we used the sample synthesized with pH = 6. The sample was centrifuged at 6,000 rpm for 15 minutes followed by drying to obtain powder for XRD measurement. Fig. 7 shows the peaks corresponded to Cu and Ag. The Cu nanoparticles are easily oxidized in solution under normal conditions. However, the XRD pattern of the sample shows no peaks of copper oxide Cu<sub>2</sub>O. This indicates that the obtained Cu-Ag core-shell nanoparticles had good structure and quality, because recent works of other research groups on the synthesis of Cu-Ag core-shell nanoparticles reported that the XRD patterns of their samples still exhibited peaks of Cu<sub>2</sub>O [7, 11-13]. The results show that the Cu-Ag core-shell nanoparticles synthesized with pH = 6 were stable under normal conditions without being oxidized. The obtained core-shell nanoparticles possessed suitable properties for using as conductive particles in fabrication of inks for ink-jet printing.

#### 4. Conclusions

We have successfully synthesized the Cu-Ag core-shell bimetallic nanoparticles using chemical reduction method. The results of XRD, TEM, and UV-Vis show that the obtained nanoparticles had a core-shell structure with average particle size of around 32 nm. The results indicate that ratio of Ag<sup>+</sup>/Cu<sup>2+</sup> = 0.4 and pH = 6 were the optimum conditions for the formation and stability of the nanoparticles. The nanoparticles dispersed stably after 80 days from synthesis under normal conditions without being oxidized. The properties of the obtained nanoparticles were suitable for use as conductive particles in fabrication of conductive inks for ink-jet printing.

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**Synthesis of Core-Shell Nanoparticles of Cu-Ag for Application in  
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