SYNTHESIS OF COPPER NANOPARTICLES FOR APPLICATION OF CONDUCTIVE INK

Mi Mu Mu Khaing [1], Nan Thidar Chit Swe [2], Lwin Ko Oo[3], Myo Aung[4], Ye Chan[5]

Abstract

This paper focused on the preparation of copper (Cu) nanoparticles from copper (II) Nitrate as metal precursor. Sodium borohydride was used as a reducing agent and polyethylene glycol and ascorbic acid were used as stabilizer. The copper particles formed were identified by UV-Vis, XRD and SEM. Small spherical copper nanoparticles and the good dispersion of nanoparticles are observed from the samples. From XRD pattern, the average crystallize size of Cu nanoparticles is 38 nm as each particle observed from SEM is not a single crystallite of Cu but the agglomerates of many single crystallites. The aggregation of nanoparticles caused the inhomogeneous size distribution. Well-dispersed stable copper based conductive ink was prepared in which the copper nanoparticles possess a excellent dispersive, monodispersed size distribution and strong anti-oxidation. From UV analysis, the absorption band in visible light region (350 nm-700 nm, plasmon peak at 588 nm).

Keywords: Copper nanoparticles, spherical shaped nanoparticles, inhomogeneous size distribution

Introduction

During these years, conductive inks have attracted considerable attention due to their growing application in electrodes of silicon-crystal solar cells and the printed electronics industry such as smart labels, flexible displays, and radio frequency identification (RFID). Currently, silver inks have been commonly developed to enable outstanding conductivity and excellent printability. However, the high price and scarcity of such material limit wide industrial applications. In view of these, copper is a good alternative material for silver because of its high electrical conductivity and low price.

1. Lecturer, Department of Physics, Hpa-an University
2. Lecturer, Universities' Research Center (Physics), University of Yangon
3. Assistant Lecturer, Universities' Research Center (Physics), University of Yangon
4. Professor and Head of Department, Universities' Research Center, University of Yangon

Therefore, the synthesis of Cu nanoparticles has become of great interest from a scientific as well as an industrial point of view, due to its huge potential for replacing the expensive nano silver ink (Bell *et al*, 2001) (Hutter et al, 2001). Owing to extremely small size, copper nanoparticles exhibit enhanced properties when compared with the bulk material including large surface area relative to their volume, ability to easily interact with other particles and increased antibacterial efficiency (Carrol et al, 2011). Many research groups have been made to synthesize nano copper by wet chemistry, as well as by gas or solid phase methods. Such as the sonochemical method, microemulsion techniques, polyol processes, radiation methods, thermal reduction, reducing flame synthesis, metal vapor synthesis, vacuum vapor deposition and chemical reduction in solution (Ozin, 1992).

The synthesis method represented in this paper is a chemical reduction method which are based on the reduction of metal ions by reducing agents in liquid media. It is well suited for the preparation of nano-sized metal or oxide particles of various shapes. This method is simple, but the great attention must be needed to make stable and reproducible colloid. Many parameters such as solution temperature, concentrations of the metal salt and reducing agent, reaction time influence the particle size.

Experimental

2.1 Materials

Analytical grade (BDH, England) Copper (II) Nitrate ($Cu(NO_3)_2$), Sodium Hydroxide (NaOH) , Polyethylene glycol (PEG), Ascorbic Acid and Sodium borohydride ($NaBH_4$) were used as starting precursors. All chemicals were used as purchased without further purification.

2.2 Synthesis of copper nanoparticles

The copper nanoparticles were prepared by reduction of copper nitrate [$Cu(NO_3)_2$] with polyethylene glycol (PEG) and ascorbic acid. Copper nitrate was used as a starting material, polyethylene glycol is used as a capping agent and ascorbic acid were used as a reducing agent. Sodium Hydroxide is used for faster the chemical reaction. Cu $(NO_3)_2$ (0.01 M) was dissolved in 10 ml distilled water. 10 ml of polyethylene glycol and 10 ml of ascorbic acid were added to Cu $(NO_3)_2$ solution. NaOH (0.1 M) with 10 ml distilled water was

added in that mixture. The solution colour was changed to yellow colour. And then sodium borohydride ($NaBH_4$) (0.1 M) with 10 ml of distilled water were mixed that mixture, the colour was changed to dark red. Then mixture of that solution was heated on a hot plate stirrer at temperature of 70 °C for 1 hr. The red coloured solution was removed from the heating magnetic stirrer and cooled down. Then, the colloidal solution was separately centrifuged for 15 min at 6000 rpm, the wet precipitates were dried at 70 °C overnight to obtain the Cu nanoparticles.

2.3 Characterization

Centrifuge machine (Kokusan H-200 series) was used to separate the colloid from the solutions. The influence of solvent on formation of Cu nanoparticles was confirmed

UV-Vis spectrophotometer (Lamda 35), X-ray powder diffractometer (Type: RIGAKU–RINT 2000), and SEM (Type: JEOL 15 kV).

Results and Discussions

Figure1 (b) shows the UV-Vis spectra of the copper colloid in the range 300 nm – 700 nm. The absorption band in visible light region (350 nm – 700 nm, plasmon peak at 588nm) is typical for copper nanoparticles (Hutter *et al,* 2001). The plasmon peak and the full-width of half-maximum (FWHM) depends on the extent of colloid aggregation (Yamamoto *et al*, 2004). As it can be noted, the spectrum is broad, asymmetric and it has been suggested that this optical feature is due to the non-uniform size of the copper nanoparticles.

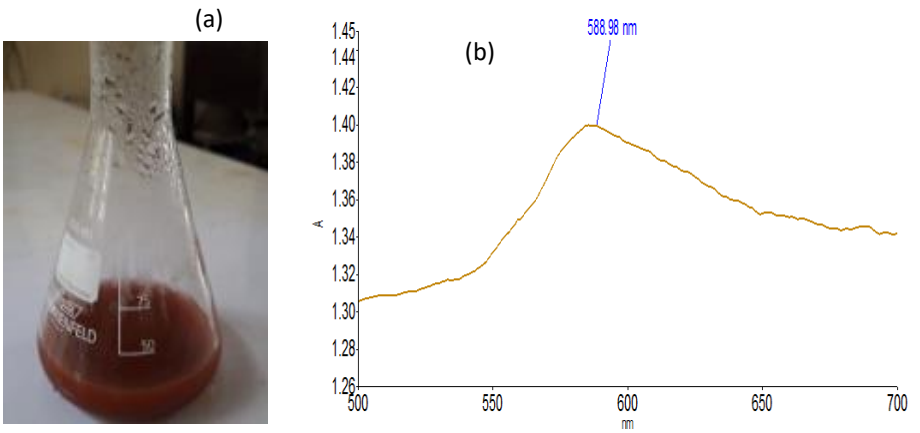

Figure 1: (a) The photograph of copper nanoparticle solution (b)The UV-Vis spectra of Copper colloid, synthesis temperature at 70 °C

After UV analysis, SEM measurements were performed on dried Cu nanoparticles to investigate the size and surface morphology of figure 3(a)–(b) show the top-view SEM images of the prepared Cu samples after centrifugation and drying. According to SEM images, the size of copper nanoparticles are ranging in diameter from 100 to 200 nm, as each particle observed from SEM is not a single crystallite of Cu but the agglomerates of many single crystallites. The aggregation of nanoparticles caused the inhomogeneous size distribution.

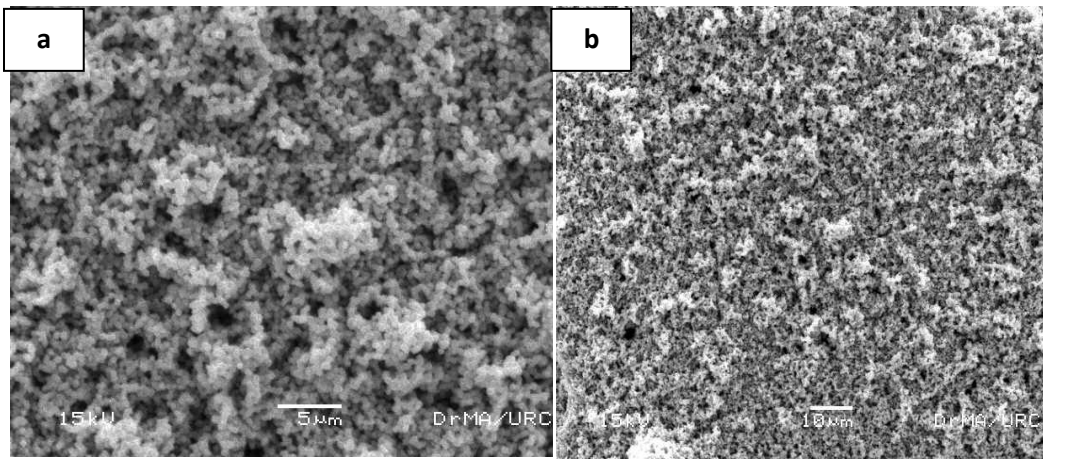

Figure 2:(a) high and (b) low magnification of SEM images: The spherical nanoparticles are observed in high magnification SEM image in which the diameters are around 100 nm.

To confirm the crystalline structure, the prepared copper, (Cu) nanoparticles were analyzed on X-ray diffractometer (Model RIGAKU–RINT 2000). The polycrystalline properties for drop coated glass thin film of Cu powder were analyzed by using Cu / K-α_1 radiation (40 kV, 40 mA) in 2θ range from 10° to 70° on a Rigaku powder X-ray diffractometer equipped with a diffracted-beam graphite monochromator. The crystallite domain diameters D were obtained from XRD peaks according to the Scherrer equation: $D = \frac{0.89\lambda}{\Delta W \cos\theta}$, where λ is the wavelength of the incident X-ray beam (1.5405 Å for Cu / K-α1), θ is the Bragg's reflection angle, ΔW is the width of X- ray pattern line at peak half peak height in radians. The Miller indices in XRD pattern of Cu nanoparticles (upper spectrum) and standard Cu

particles (lower) were shown in Figure 5. This pattern showed that two XRD peaks appeared at 43.5°and 50.16°, due to strong Bragg reflections from (111) and (200) planes of fcc (face centred cubic) copper respectively. All reflections are agreed with standard library file (ICDD-PDF#04-0836) of pure copper metal with fcc symmetry. Based on Scherrer equation, the average crystallite size of Cu nanoparticles was found to be 38nm.

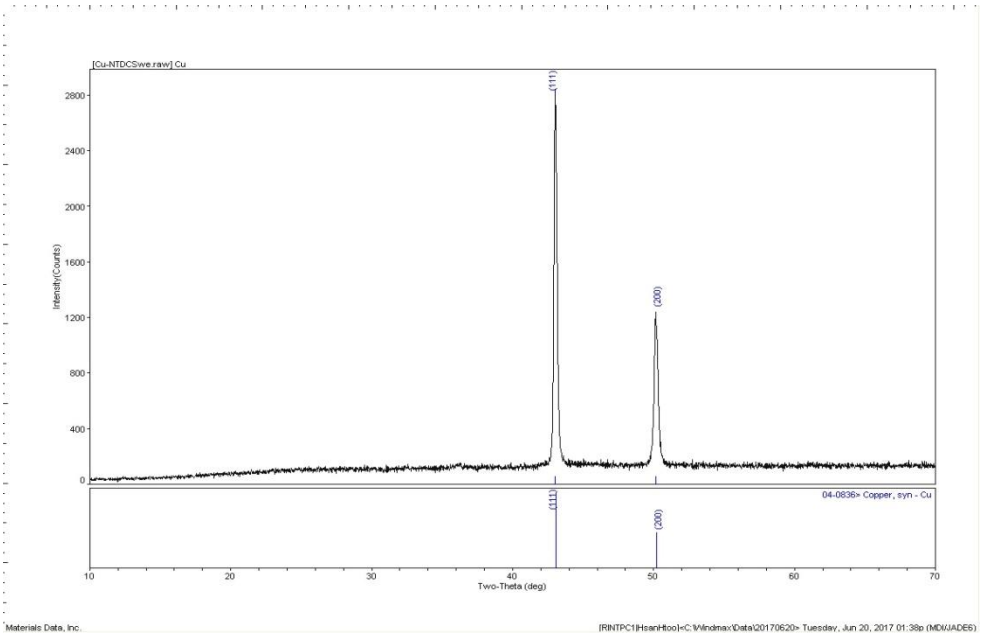

Figure3: XRD plots obtained from copper nanoparticles sample to investigate the structures and crystallinity. Reference bulk reflections of pure Cu phases are shown at the bottom (ICDD-PDF#04-0836).

Copper Nanoparticles Ink Deposition on Glass Substrates

Before copper nanoparticles ink deposition, the glass substrate was washed with deionized water, followed by acetone, methanol and isopropanol and dried with air blow. First, 0.5 wt % poly vinyl pyrrolidone (PVP)-based ink was prepared by dissolving 0.5 g of PVP-30 K in 100 ml of isopropyl alcohol (IPA ,99%) . The stored Cu nanoparticles were transferred to a 1.5 ml tube and washed once more with the 0.5 wt % PVP-based ink solution by centrifuging at 2000 rpm for 5 min. Lastly, depending on the desired concentration, the required amount of PVP-based ink was pipetted into the

tube containing the copper nanoparticles to make the copper nanoparticle ink. The synthesized ink was ultrasonicated to break up the large agglomerates formed in the well dispersed copper nanoparticle ink. After sonication, the ink was deposited on glass substrates, which were preheated to 160°C. The copper films deposited on the glass substrate were dipped in an acitic acid for 3 minutes to remove the oxide layer. Interestingly, the dried silver pastes exhibited low sheet resistance of 56 Ω (Figure 4).

Figure 4: copper paste on glass substrate show the sheet resistance 56 Ω

Conclusion

A simple, fast and economical chemical reduction method to synthesize copper nanoparticles is presented. There is no need to use high pressure, energy, temperature, toxic chemicals, downstream processing etc. Handling of the nanoparticles is also much easier than other methods. The synthesized copper nanoparticles are in spherical shape with particle size of around 100 nm. Their characterizations have been successfully done using XRD, SEM and UV-Vis spectroscopic techniques. Investigation on the conductive behavior of nanosized copper ink reveals high efficiency of copper nanoparticles as conductive ink. This synthesized copper nanoparticles can be useful as conductive ink in electronics.

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