

# Structural and optical properties of copper nanoparticles synthesized by organic precursor

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In this paper, we report the facile method of synthesized the copper nanoparticles by using bulk copper powder and organic solvent by different time dependant (24 °C, 52 °C, 70 °C, 95 °C and 130 °C). In this work, we used Monoethanolamine (MEA) as a solvent and Sodium hydroxide (NaOH) as a main reducing agent. From temperature versus reaction time it shown that copper nanoparticle was completely synthesized at temperature 130 °C. Then, for Photoluminescence (PL), X-Ray diffraction (XRD), UV-Visible spectroscopy (UV-VIS) and Field Emission Scanning Electron Microscopy (FESEM) contributed to the analysis of size and optical properties of the nanoparticles, respectively at temperature 130 °C.

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*Keywords:* Copper nanoparticles, MEA, NaOH and temperature dependent

## 1. Introduction

Nanoparticles, acting as nanoscale building blocks, can self-assemble into different ordered superstructures with a range of practical applications [1-2]. Therefore, the development of uniform nanoparticle has been intensively pursued [3-7]. There are many types of technique or process to prepared the nano-materials including hydrothermal or solvothermal [8-10], microwave-solvothermal synthesis [11,12], microwave synthesis [13,14], magnetic-field-assisted hydrothermal [15], sol-gel process [16-17], electrochemically induced sol-gel [18], microemulsion [19] and reverse micelle/microemulsion [20-21], homogeneous precipitation method [22], cluster growth method [23], chemical vapour deposition [24], vapour-liquid-solid process [25-26], soft chemical method [27], electrophoretic deposition [28], electrochemical fabrication [29], chemical reduction method [30,31], electrolysis of metal salt [32], rapid expansion of super critical solvents [33-34], photoreduction of metal ions [35-36], microwave plasma synthesis [37], sonochemical method [38,39] and mechanochemical process [40]. Recently, it is observed an enhanced interest in copper nanoparticle with the useful properties such as good thermal and electrical conductivity and also low cost preparation. This leads to potential application in cooling fluids for electronic system [41] and conductive inks [42]. In this context, copper is good candidate material because it is highly conductive but significantly cheaper than Au and Ag.

Among all the methods above, chemical reduction is the most preferred, because this method is simple and economical. This method can realize better size and better size distribution control by optimizing the experimental parameter such as the ratio of solvent and reducing agent.

A chemical reduction method usually involves the reduction of metal in some type of solvent and a separate reducing agent.

We were worked on simple and low cost preparation of copper nanoparticle. Where, MEA was used as building block, pH-neutralisation and dilution agent for the copper powder. For NaOH, it used as reducing agent in this work, where the function was to adjust the pH and accelerate the reduction reaction in MEA.

## 2. Experimental

All the chemical were analytical grade and used as purchased without further purification. Copper powder, 99 % for organic synthesis (sigma Aldrich). Monoethanolamine (RAM Chemical) was used as a solvent. Sodium Hydroxide pallet (QREC) was used as the main reducing agent.

First, dissolve 10 mg of copper powder in 100 ml of monoethanolamine (yellow solution) to obtain a dark green solution. This solution was stir on magnetic stirrer for 24 hours at room temperature. Second, add sodium hydroxide (1.5 ml) into the dark green solution until it becomes red solution. Then, this mixture was stirred for 5 minute with different temperature (24 °C, 52 °C, 70 °C, 95 °C and 130 °C). An instant color change occurred in the aqueous phase from dark green to red. The appearance of this dark red color indicated that the reduction reaction has started. After that, solution of dark red color was used for drop casting on silicon substrate and baked for 60 min at temperature 100 °C for XRD, PL, and FESEM characterization.

Synthesized sample was studied by use of UV-VIS absorption spectroscopy from a double beam

spectrophotometer (Shimadzu UV spectrophotometer) in the wavelength range 190 to 1100 nm. XRD (PANalytical X'Pert PRO MRD PW3040) was used to study the particle size of nanoparticles. PL (Jobin Yvon HR800 UV) is a process in which a substance absorbs photons (electromagnetic radiation) and then re-radiates photons. Then, structure and composition of copper nanoparticle was characterized using FESEM and EDX (NOVANANOSEM 450).

### 3. Results and discussion

Temperature versus reaction time for 5 samples were taken from the synthesis solution (dark green) and heated with different temperature. Table 1 showed reaction time of dark green to red solution with different temperature dependent.

Table 1. Reaction time of dark green to red solution with different temperature.

Sample	Temperature(°C)	Reaction time of dark green to red solution (min)	Color change
1	24 (Reference)	Not change	Dark green
2	52	Not change	Green-light red
3	70	2:00	Light red
4	95	1:58	Red
5	130	1:11	Dark red

From Table 1 when the temperature is increase the reaction time of the dark green solution to turn red is decrease. After pour 1.5 ml of NaOH (reducing agent) solution and temperature is more than 70 °C the solution becomes red, which suggest the appearance of small clusters or nanoparticles. So, function of these hydroxyl ions is to improve the reduction kinetics. Effect of temperature and time play important rule because the absorbance increase with increasing of temperature. This may be due to the increase of the particle size and decrease of the inter distance between copper nanoparticle in the solvent causing increased absorbance with increasing temperature [43].

UV-Vis characterization was done from wavelength range 190 to 1100 nm. From Fig. 1a, it shows that before the addition of NaOH in dark green solution (24 °C or room temperature), the peak of absorbance appears at 340 nm. When the temperature increase to 52 °C, and adding with 1.5 ml NaOH as reducing agent, the peak of absorbance shift to 344 nm, but appearance of nanoparticle still not been seeing. After increase the temperature to 70 °C, 95 °C and 130 °C and also adding with 1.5 ml NaOH the peak of absorbance also shift to 356 nm, 400 nm and 480 nm. Besides that, with increasing the temperature also the changing of color from dark green to dark red solution can be observed from Fig. 1b. So from here it concludes

that, when temperature is increase the peak of absorbance also increases indicating the reduction of the copper ions. Intensity of color in this work increases gradually, suggesting a slow growth in size of the copper nanoparticle. It shows that the solution started to form copper nanoparticle when the temperature is increase more than 70 °C. Samples consist of small particle when the reaction temperature is high and below the boiling point of solvent [44]. Thus, at low temperature, the reduction potential of MEA is not enough to get metal copper although copper oxide is obtained. At temperature 130 °C the copper nanoparticle (sample 5) was completely formed and chooses this temperature for other characterization.

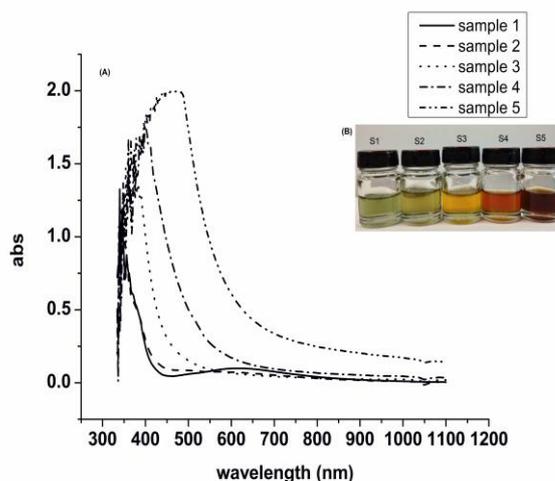


Fig. 1. UV-Vis spectra of copper nanoparticle (a) uv-vis spectra (b) picture of copper nanoparticle with different time.

Fig. 2 show the XRD pattern of copper nanoparticle for sample 5. The XRD spectrum shows that the nanoparticle have two peaks at  $2\theta$  values of  $43.40^\circ$  and  $50.55^\circ$ , which correspond to diffraction from the (111) and (200) plans of copper metal (JCPDS NO.04-0836), respectively, having cubical symmetry [45]. Crystalline size for sample 5 is 33.7 nm.

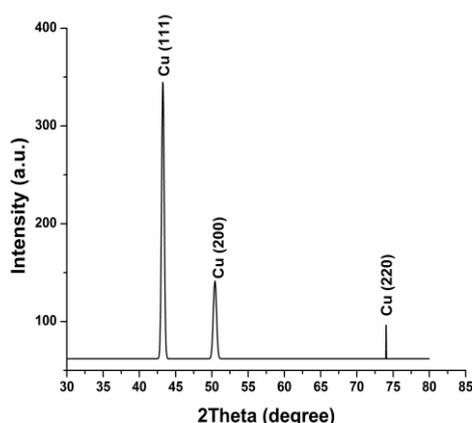


Fig. 2. XRD of copper nanoparticle coated on silicon wafer for temperature 130°C.

The photoluminescence (PL) spectra of copper nanoparticle have been studied at a temperature 130 °C. Surface Plasmon resonance is not available at the nanoscale, for dissipation of incident energy, so transition takes place from discrete valence states to excited valence state in the case of nanoparticle [46]. 3d valance and 4sp conduction electrons responsible for fluorescence pertaining to copper nanoparticle. From Figure 3 it shows two peaks of PL emission, where the first peak at 408 nm (3.08 eV) and the second peak at 512 nm (2.45 eV). Mooradian [47] reported for the bulk copper the maximum of PL band at 2.11 eV that is somehow lower than the copper band that observed in the PL spectra of our sample 512 nm (2.45 eV). The proximity of this value gives assumption that copper band has to be attributed to the emission from copper nanoparticle.

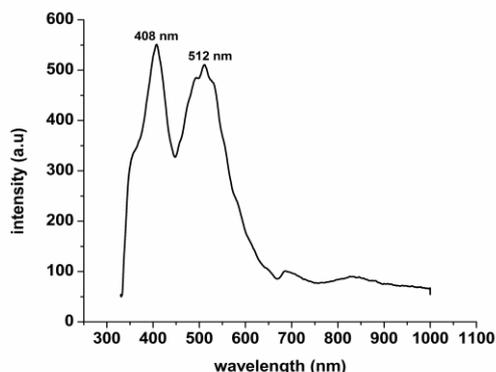


Fig. 3. PL of copper nanoparticle coated on silicon wafer for temperature 130°C.

The shape and composition of the copper nanoparticle were determined using FESEM and EDX. Fig. 4 shows FESEM image of copper nanoparticle as prepared by reported process (sample 5), revealing spherically shaped particle with some agglomeration and aggregation.

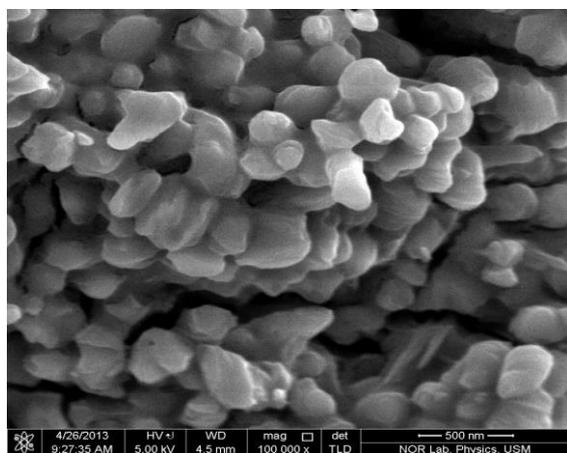


Fig. 4. Show Fesem of Copper nanoparticle at temperature 130°C with magnification of 100k.

#### 4. Conclusion

In summary, copper nanoparticle with crystalline size 33.7 nm, have been successfully synthesized at temperature 130 °C. The copper absorbance peak also can be seen at wavelength 480 nm using UV-Vis. From PL result it also shown that copper band can be observed at 512 nm (2.45 eV). Finally, FESEM had shown that reduction of this whole process cause the copper nanoparticle to be agglomeration and aggregation condition.

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