**pH-dependent synthesis of copper oxide phases by polyol method**

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**Abstract.** Copper oxide nanostructures (Cu$_2$O and CuO) were successfully synthesized via pH adjustments in a glycolic medium. XRD analysis confirmed the formation of cubic Cu$_2$O at acidic condition and monoclinic CuO at basic condition. SEM images showed the production of copper oxide nanoparticles with sizes 90-96 nm and flower-like structures using the complex solution. Using UV-Vis spectroscopy, the measured band gap energies are 2.6 and 3.5 eV for Cu$_2$O and CuO, respectively.

1. **Introduction**

Metal oxide nanoparticles have shown great interest in the field of materials science due to their unique and excellent properties. Among all the metal oxides, copper oxide caught the attention of researchers due to its excellent optical, electrical, magnetic and physical properties [1]. Copper oxide has two phases namely, cuprous oxide (Cu$_2$O) and cupric oxide (CuO) [2]. Cuprous oxide and cupric oxide are p-type semiconducting materials having a band gap of 2.0 and 1.08–2.08 eV, respectively [3]. The favourable band gap of both materials permits them to operate at higher voltages, temperatures and frequencies, so that they are useful in numerous applications such as gas sensors [4], lithium-ion batteries [5] and optoelectronics [6].

Different methods have been employed in the fabrication of copper oxide nanostructures. Common approach includes microwave irradiation [7], chemical reduction [1] and sonochemical method [8]. Shahmiri et al studied the use of polyvinylpyrrolidone (PVP) to form stabilized CuO nanosheets [9]. PVP was effective in promoting nucleation, as well as a growth directing agent for the formation of rod-like and sheet-like CuO. Isah et al also studied the effect of oxidation temperature on the properties of copper oxide from evaporated copper films. Their results showed a mixture of Cu$_2$O and CuO at lower temperatures and pure phase CuO at higher temperatures [10]. However, these methods require the use of additional reagents, high reaction temperature, and longer reaction time. Moreover, studies regarding the effect of other synthesis parameters such as pH to produce pure phases of Cu$_2$O and CuO have not been fully explored.

In this study, copper oxide nanostructures were synthesized via simple polyol method using ethylene glycol as the medium. The effect of pH on the copper oxide phase formed, as well as on its morphology and optical property, was investigated.
2. Experimental Methods

Cu$_2$O and CuO nanoparticles were synthesized via polyol method. In a typical experiment, 1.98 g of copper (II) acetate monohydrate (Cu(CH$_3$COO)$_2$-H$_2$O, TPC India) is dissolved into 100 ml of ethylene glycol and stirred for 1 h. From a pH 6 solution, either 1 M hydrochloric acid (37% w/w HCl, RTC Laboratory Services) or 5 M sodium hydroxide (NaOH, MACRON Fine Chemicals AR) was added dropwise to the solution until the desired pH (3, 7, and 12) was obtained. Resulting solution was heated at 60°C under constant stirring for 2 h. The solution was then allowed to cool to room temperature. The resulting precipitates were collected by centrifugation at 2500 rpm for 10 minutes. This was followed by washing with distilled water and ethanol.

Phase composition and crystal structure of the as-synthesized products were analyzed using X-ray diffraction (XRD, Shimadzu XRD-7000). Surface morphologies were examined using a field-emission scanning electron microscopy (FE-SEM, JSM-7800f Prime Japan). Optical properties were investigated using UV-visible (UV-Vis) spectroscopy. Finally, the energy band gap of the copper oxides was determined by constructing the Tauc’s plot from the UV-vis spectra.

3. Results and Discussion

Figure 1 shows the XRD patterns of the as-synthesized products with increasing pH. Characteristic peaks of cubic Cu$_2$O (JCPDS No. 00-005-0667), copper complex (Cu$_2$C$_3$H$_7$O$_5$-H$_2$O) [2], and monoclinic CuO (JCPDS No. 00-005-0661) were observed. At acidic conditions (pH~3), characteristic peaks at 29.6°, 36.4°, 42.3°, 61.3°, and 73.5° corresponding to the (110), (111), (200), (220), and (311), respectively, were observed, which shows Cu$_2$O is the favourable phase. At neutral conditions (pH~7), copper complex is formed from the reaction of the copper precursor salt and ethylene glycol. Finally, at basic conditions (pH~12), characteristic peaks at 35.6° and 38.7° corresponding to the (-111) and (111), respectively, which shows that cupric oxide is the abundant phase produced. Only the two highest peaks were observed due to the amorphous state of the CuO material.

![Figure 1](image.jpg)

**Figure 1.** X-ray diffraction patterns using Cu kα radiation of the as-synthesized products at pH (a) 3, (b) 7, and (c) 12.
During the reaction process, initially blue colored solution turned into orange at acidic state and black at basic condition. At first, Cu-EG complex was formed upon the dissolution of copper acetate in ethylene glycol based from equation 1. Complex is then transformed into Cu(OH)$_2$ upon the addition of sodium hydroxide. Equation 2 shows the displacement of OH$^-$ and EG molecules. Lower amount of hydroxide ions makes it favourable to form Cu$_2$O due to the dehydration of ethylene glycol [3]. Dehydration of ethylene glycol to acetaldehyde is induced due to heating during the reaction which is shown in equation 3. On the other hand, higher concentrations of OH$^-$ would result in a faster dehydration promoting a rapid transformation to a more stable CuO phase [11]. The chemical equations are as follows:

\[
\text{OH} - \text{CH}_2 - \text{CH}_2 - \text{OH} + \text{Cu}^{2+} \rightarrow [\text{Cu(C}_2\text{H}_4\text{O})]^2+ \tag{1}
\]

\[
[\text{Cu(C}_2\text{H}_6\text{O})]^2+ + 2\text{OH}^- \rightarrow \text{Cu(OH)}_2 + \text{HOCH}_2\text{CH}_2\text{OH} \tag{2}
\]

\[
\text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{COH} + \text{H}_2\text{O} \tag{3}
\]

\[
2(\text{Cu(OH)}_2 + 2\text{CH}_3\text{COH} \rightarrow \text{Cu}_2\text{O} + \text{CH}_3 - \text{CO} - \text{CO} - \text{CH}_3 + 3\text{H}_2\text{O} \tag{4}
\]

\[
\text{Cu(OH)}_2 \rightarrow \text{CuO} + \text{H}_2\text{O} \tag{5}
\]

Figure 2 shows the structure of the products with increasing pH. At basic conditions (pH~12), cupric oxide nanoparticles with an average particle size of 90 ± 0.033 nm were produced. At neutral conditions (pH~7), the copper complex formed were shaped like flakes and nanoparticles tend to agglomerate into flower-like structures. Finally, at acidic conditions (pH~3), cuprous oxide nanoparticles with an average particle size of 96 ± 0.024 nm were formed. Measured particle sizes for basic and acidic conditions were higher compared to the crystallite sizes computed for both solutions implying polycrystalline materials. Crystallite sizes were calculated using the Scherrer’s equation based from the (111) and (−111) peak of Cu$_2$O and CuO, respectively. Cu$_2$O has a crystallite size of 10.93 nm while CuO has a crystallite size of 4.83 nm. Smaller crystallite size especially for CuO is evident from the broadening in the XRD pattern of the material.

Figure 3 shows the UV-Vis spectra of the samples synthesized at varying pH. Maximum absorption can be found at 836, 744, and 636 nm for Cu$_2$O, Cu-complex, and CuO respectively. The energy band gap of each sample was estimated using the Tauc’s plot derived from the UV-vis spectra. The estimated band gap values are 2.62, 3.22, and 3.52 eV for Cu$_2$O, Cu-complex, and CuO, respectively. The values obtained for Cu$_2$O and CuO are relatively higher compared to the theoretical energy band gaps of the bulk Cu$_2$O (2.0 eV) and CuO (1.2 eV). Larger band gaps of the synthesized products might be due to the smaller sizes in contrast of the bulk materials [3]. The observed change in the band gap values is due to the quantum confinement in the nanoparticles. Since the material is in nano-scale, there will be a decrease in the number of orbitals causing an increase in the energy gap between the valence and conduction band [12]. Bulk materials induce a delocalization of the conduction band edge creating traps in electronic energy, which is in contrast of having smaller size particles. As the particle size gets finer, it will be composed of finite number of atoms causing the decrease in overlapping orbitals [13]. Thus, the obtained products are good materials for applications that require wider band gaps.
4. Conclusions

Pure Cu$_2$O and CuO phases were successfully synthesized from facile polyol method. Different copper oxide phases were formed depending on the pH of the precursor solution. Consequently, different morphologies were also observed. The energy band gap of the copper oxides were obtained from the Tauc’s plot are 2.6 and 3.5 eV for Cu$_2$O and CuO, respectively. These values were higher compared to theoretical values of bulk Cu$_2$O and CuO which makes the synthesized copper oxides a good candidate for wide band gap applications.

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