## SYNTHESIS AND CHARACTERIZATION OF NANOSTRUCTUREDP-TYPE CUPROUS OXIDE USING BENEDICT’S SOLUTION

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## 1. Introduction

Metal oxide nanostructures with controllable size and shape are receiving increasing attention in material synthesis and device fabrication. Among the various transition metal oxides, copper oxides are attractive semiconducting materials due to non-toxicity, low cost and abundance of precursors (McShane & Choi, 2012). Cuprous oxide (Cu2O) is an intrinsic p-type semiconductor owing to the copper ion vacancies or deficiency (1.5% - 3%) in the crystal structure (Kooti & Matouri, 2010). Its direct band gap of 2.0 eV has drawn considerable attention of the condensed matter physicists and materials chemists mainly in relation to its rich excitonic structure and potential applications in solar energy conversion, catalysis, biosensors, magnetic storage and electrode materials in lithium-ion batteries, etc. (Sawant, Bhagwat, & Mahajan, 2016). The main objective of this study was to synthesis Cu2O nanoparticles by chemical reduction of Benedict’s solution with glucose at different environments and to characterize those particles using Mott-Schottky analysis and X-ray diffraction (XRD) for different applications.

2. Methodology

2.1. Synthesis of Cu2O nanoparticles

In this study the following procedure was used to prepare a Benedict’s solution in the laboratory as the precursor for synthesis of Cu2O nanoparticles. 50 g of anhydrous sodium carbonate and 86.5 g of citric acid was dissolved in 400 ml of deionized water in a beaker under vigorous stirring at 75 °C. 100 ml of 0.346 mol dm-3 copper (II) sulfate pentahydrate solution was added to this mixture and mixed thoroughly. 5 mol dm-3 sodium hydroxide was added to the above solution in the beaker under stirring until the pH value of the mixture reached ten.

To obtain Cu2O nanoparticles, 6 g of glucose dissolved in 20 ml of distilled water was slowly added to each 100 ml of Benedict’s solutions in three conical flasks placed on a hotplate set at 160 °C under vigorous stirring. The mixtures reached 50 °C in 10 minutes forming a yellow colour precipitate. At that instant one of the solutions was taken out from the hot plate and cooled down in an ice bath when the yellow colour precipitate dominated. Orange colour precipitate appeared when the temperature of the solutions reached 60 °C after 20 minutes. At that moment one heated solution was taken out from the hotplate and kept in an ice bath to obtain the orange colour Cu2O particles. The red Cu2O precipitate appeared in the third solution in the conical flask when temperature reached to 80 °C after 30 minutes. Precipitates as prepared were separated from each solution and washed three times with deionized water using centrifugation at 3600 ppm for 1 minute. The washed precipitates were collected into three Petri dishes and dried in an oven at 100 °C. The yellow, orange and red colour Cu2O were labeled as samples 1, 2 and 3 respectively. Three samples were stored in a desiccator until use for characterizations.

 2.2. Preparation of Cu2O films

Fluorine-doped Tin Oxides (FTO) glass plates were cut into size of 1 cm × 2 cm which were cleaned in an ultrasonic bath using 1 drop of conc. HNO3 in deionized water and again with deionized water for 5 minutes. Washed glass plates were boiled with acetone in a water bath at 80˚C for 15 minutes. 2 mg of copper oxide samples and 0.5 ml of deionized water were placed in a mortar. The mixture of each sample was ground in the mortar using pestle for 15 minutes separately until a tiny paste of samples were obtained. The two drops of the paste of the samples were spread on the conducting side of the FTO glass sheets and placed on a hotplate at 120 °C for 30 minutes for drying.

* 1. Characterization of Cu2O

The structural properties of the Cu2O particles were investigated using high energy X-Ray Diffraction (XRD) analysis. XRD pattern was obtained using a Rigaku Ultima IV. Cu Kβ radiation with a scanning angle (2θ) ranges from 20 ° to 80°. The films of Cu2O were characterized by the mott-Schottky (MS) measurements using a computer coupled with Metrohm Autolab PGSTAT204 to find the flat band potential. The MS performances of the prepared Cu2O thin films were evaluated using a three-electrode configuration with copper oxide thin film on FTO, Ag/AgCl electrode, and Pt Electrode as working electrodes, reference electrode, and counter electrode, respectively. The electrolyte used was 10 mM CH3COONa solution at pH 6.5.

3.Results and Discussion

The addition of glucose to the Benedict’s solution which has aldehyde groups causes the reduction of copper ions resulting formation of precipitates of Cu2O. The chemical reaction may be expressed in the following equation.



 3.1.XRD Analysis

Figure 1: XRD-patterns for three samples of Cu2O nanoparticles

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The XRD measurements were conducted to study the crystalline structure of Cu2O. X-ray diffraction pattern of Cu2O shown in figure 1 confirmed that the particles of Cu2O were highly crystalline consistent with Joint committee on Powder Diffraction Standards (JCPDS) card files No. 071-4310. No characteristics peaks of impurities such as those of copper or cupric oxide were detected, suggesting that the products obtained were highly pure. Diffraction peaks appeared corresponding to (110), (111), (200), (220), (311) and (222) planes of cuprite, indicated the formation of cubic copper (I) oxide nanocrystals (Khan, Rashid, Younas, & Chong, 2016). The crystallite size was calculated by using the Debye Scherrer equation.

D=0.9λ/βCosθ

Where λ is the X-ray wavelength, β is the line broadening at the half width of maximum intensity in radians, θ is the Bragg angle. From the calculations, the average crystallite sizes of yellow, orange and red colour of Cu2O nanoparticle are found to be around 18 nm, 40 nm and 76 nm respectively.

* 1. Mott-Schottky measurements

The MS measurement was carried out on three samples of Cu2O thin films deposited on FTO glass as shown in figure 2. The flat band potential of each sample of Cu2O particles was determined from the intercept of the graph plotted potential vs reciprocal square capacitance. The negative slope of the Mott-Schottky plot confirmed that the Cu2O is p-type. The values of the flat band potential of the yellow, orange and red colour Cu2O were shown in table 1. The Mott-Schottky relationship for a p-type semiconductor is described by the following equation (Zhangab & Wang, 2012).



Where C represents the capacitance of the space Charge region, ԑ0 is permittivity of vacuum, ԑ is the relative dielectric constant of the sample, e is the electron charge, E is the applied potential, k is Boltzmann constant, T is the absolute temperature and NA is the acceptor concentration. With a ԑ value of 7.6 for Cu2O (Zhangab & Wang, 2012), the acceptor concentrations of the samples were determined from the slope of Mott–Schottky plots as shown in Table 1.

Figure 2: Mott-Schottky plot for three samples of Cu2O

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Table 1: Flat band potentials and acceptor concentrations of the three samples of Cu2O

|  |  |  |  |
| --- | --- | --- | --- |
| The sample number of Cu2O | 1 | 2 | 3 |
| Flat band potential (V) | 0.87 | 0.85 | 0.75 |
| Acceptor concentration (cm-3) | 2.996 x 1018 | 1.29 x 1018 | 1.27 x 1018 |

 4.Conclusion

The study verified a favourable and easily applicable method to synthesize p-type cuprous oxide nanoparticles by reduction of Benedict’s solution with glucose. XRD results indicated that the yellow, orange and red coloured Cu2O nanoparticles are cubic shapes with average particle sizes of 14 nm, 40 nm and 76 nm respectively. The flat band potentials of the yellow, orange and red coloured Cu2O nanocrystalline particles were 0.87 V, 0.85 V, and 0.75 V respectively. It was also evidence that the acceptor concentration of yellow colour Cu2O nanoparticles has high acceptor concentration due to presence of Cu+ sites in the crystal lattice.

5.Acknowledgment

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6. References

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