HYDROTHERMAL SYNTHESIS OF CuO NANOPARTICLES AND A STUDY ON PROPERTY VARIATION WITH SYNTHESIS TEMPERATURE

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Abstract: Metal-oxide (CuO) nanoparticles were synthesized by hydrothermal method within a self-designed stainless-steel autoclave, sealed and heated at various temperature. X-ray diffraction analysis (XRD) revealed the single-phase monoclinic structure of CuO nanoparticles with an average grain size of 25, 33, and 66 nm at 105, 120, and 150 ^{0}C temperature respectively. Fourier Transform Infrared (FTIR) spectroscopy identified the representative bands of copper oxide nanoparticles at 609.51 & 507.28 cm^{-1}, 519.15 & 605.65 cm^{-1} and 518.85 & 611.43 cm^{-1} for temperature of 105, 120 and 150 ^{0}C respectively. UV-Vis spectroscopy determined a broad characteristics absorption band of CuO nanoparticles near about 300 nm for three different temperatures. CuO nanoparticles prepared at highest temperature (150 ^{0}C) exhibited the most transmittance among the three. By using Tauc plot, Bandgap was calculated of 1.55, 1.60 and 1.88 eV for three samples prepared in 105, 120, and 150 ^{0}C respectively. Electrical properties of CuO nanoparticles exposed that the resistivity decreases by increasing the temperature which was in accordance with the well-known semiconductors. Impedance analyzer revealed that dielectric constant and Q-factor of CuO nanoparticles were increased along with the increasing temperature. Shape and size of CuO nanoparticles were varied with preparation temperature. Moreover, the adding temperature of solution of NaOH and $CuCl_2.2H_2O$ had an important influence on the shape and size of CuO nanocrystals. The as-synthesized CuO nanoparticles can be potential candidate to be used in electronic devices, including solar cell applications.

Keywords: CuO nanoparticles; hydrothermal method; autoclave; optical properties; resistivity; dielectric constant; bandgap

1. Introduction:

Metal oxides nanoparticles have become an indispensable tool in modern science and technology because of their unique properties and wide range of applications in electronics, environmental conversion, solar cells, medicine, biosensors etc. [1]. Among them, copper oxide (CuO) nanoparticle is receiving increasing consideration due to its brilliant optical, electrical, physical, and magnetic properties. The CuO nanostructure exhibit excellent performance comparing to its bulk counterpart. As a consequence, various CuO nanostructures have been manufactured in the form of nanowire, nanorod, nanoneedle, nanoflower and nanoparticle [2]. In the recent years, synthesis of inorganic materials with infrequent and unique morphologies has appealed considerable devotion because of potential applications as catalysts, medicine, electronics, ceramics, pigments, and cosmetics [3]. Many synthesis route have already been established for the various nanostructure preparation. Nanowires [4], Nanotubes, Nanorings, have been synthesized by chemical vapor deposition method [5], thermal evaporation method [6], sol-gel method [7], co-precipitation method [8], hydrothermal method [9-13], electrodeposition method [14], and chemical bath deposition method [15]. The hydrothermal method is a synthesis technique to grow crystals and nanocrystals using reactions in water at elevated temperatures and pressures. There are numerous advantages of the hydrothermal method including aggregate reduction resulting in monodispersity, ability to morphological control of the final products, and crystalline product [16]. In the current studies, CuO NPs were prepared by using hydrothermal process to control over size. The whole process was maintained within a self-designed stainless-steel autoclave at different temperatures. The as-prepared CuO nanomaterials were characterized by XRD, UV-Vis Spectroscopy and FTIR to know its structural, optical and chemical properties respectively. The electrical properties were also investigated by using impedance analyzer.

2. Materials and methods:

2.1. Materials:

Copper (II) chloride ($CuCl_2$. $2H_2O$) with ACS grade reagent was purchased from Merck (Germany) had purity 99.0%. Distilled water was obtained from water distillation apparatus from Department of Chemistry, JU (Savar, Dhaka). Sodium Hydroxide (NaOH) pellets with 97.0% was also purchased from Merck (Germany). Acetone and all of the other reagents which were used in this experiment were purchased from local market. All of the reagents had analytical grade purity level used in the experiment.

2.2. Sample preparation:

In the experiment all the reagents that were used of analytical grade purity. Hydrothermal method was used to prepare CuO nanoparticle with sodium hydroxide as precipitating agent. In a beaker solution of copper precursor was prepared by addition of 0.2 M $CuCl_2.2H_2O$ and 0.4 M of sodium hydroxide dissolved in 40 ml of distilled water. Under constant stirring the solution of aqueous NaOH was mixed drop wise into the above solution. Final solution was maintained pH value of 10. The final solution was moved into the stainless steel autoclave. The hydrothermal synthesis was maintained at 105,120 and 150ºC for 12 hours. Obtained black precipitate was washed several times with deionized water and acetone to remove all the impurities. After completing the reaction, final products were filtered and dried at 75^0C for 6 hours is drier [17]. A schematic diagram of synthesis of CuO nanoparticle by hydrothermal method has been shown below:

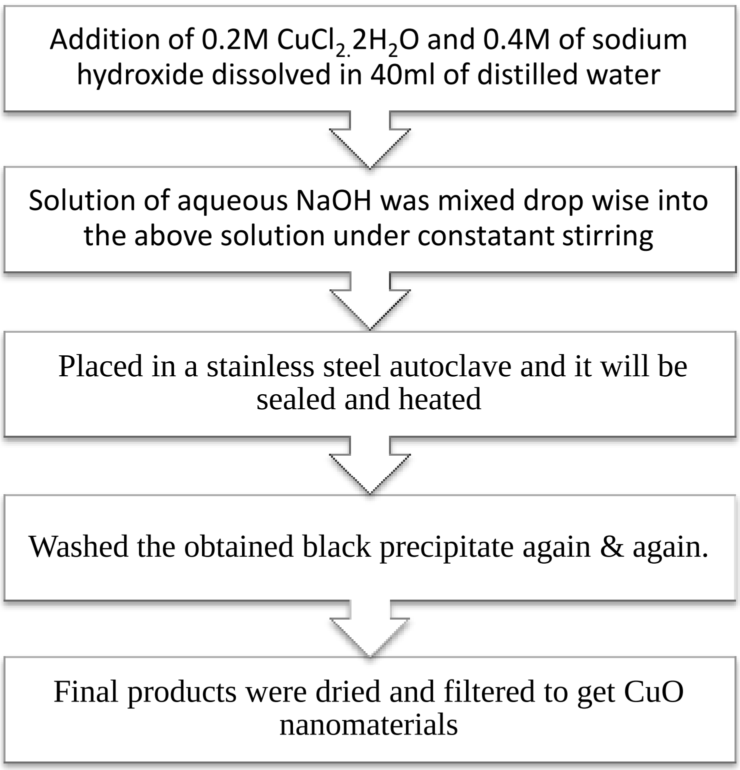

Figure 1: Flowchart for synthesis of CuO nanoparticle.

2.3. Characterization techniques:

CuO nanoparticles were prepared at three different synthesis temperatures (105, 120 and 150 ºC) in a hydrothermal process. The characterization of the as-prepared nanoparticles was completed by X-Ray diffraction (XRD), UV-Vis Spectroscopy and Fourier Transform Infra-Red (FTIR) Spectrometer to know its structural, optical, electrical properties respectively. The electrical properties of was also investigated by using an Impedance Analyzer.

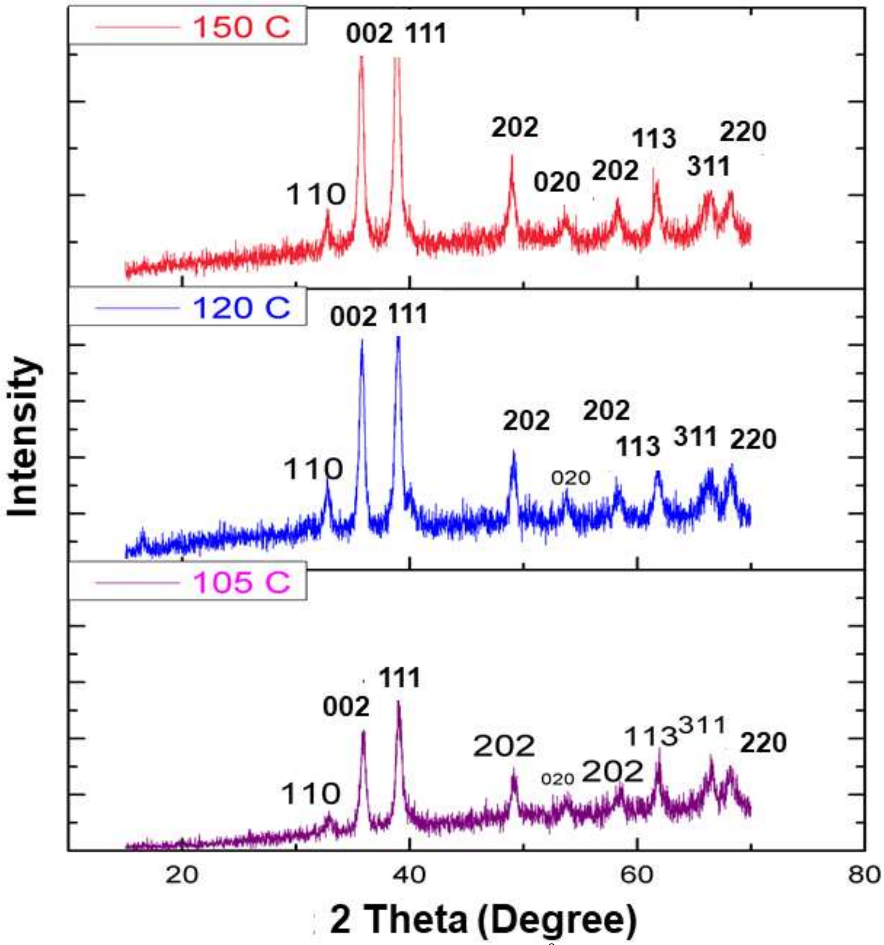

Figure 2: XRD pattern of CuO nanoparticles for 105, 120 and 150^0 C.

3. Results and discussion:

3.1. Structural properties of CuO NPs:

3.1.1. X-ray diffraction analysis:

The crystal structure and purity of the synthesized CuO nanoparticles were determined by powder XRD shown in Figure 2. The intensities and positions of observed diffraction peaks were good agreement with the reported values in the JCPDS file No. 45-0937 [3] that identified a single-phase of CuO nanoparticles with monoclinic structure. The good resolution of the main diffraction peaks reflected the good crystallinity of the CuO nanoparticles [3]. The crystalline size was calculated using Debye Scherrer equation

$$d = \frac{0.9\,\lambda}{\beta cos\theta}$$

Where d was the average crystallite size (nm), K was the grain shape factor (0.9), $\boldsymbol{\lambda}$ was the X-ray wavelength (0.15406 nm), β was the full width at the half maximum (FWHM) intensity in radians, and θ was the Bragg diffraction angle of the 2θ peak. The average crystalline sixe was found in the range 8.28-38.73 nm for the CuO nanoparticles prepared in temperature 105 ^{0}C. XRD pattern of CuO nanoparticles prepared at temperature 120 and 150 ^{0}C revealed the average crystalline size in the range of 14.77 to 116.38 nm and 12.93 to 355.32 nm respectively. The preparation temperature effected the size of CuO nanoparticles. The average size of CuO nanoparticles were 25.17 nm, 32.93 nm, and 66.05 nm prepared at temperature 105, 120 and 150 ^{0}C respectively. The grain size was increased along with the elevated operating temperature.

3.2. Optical properties of CuO NPs:

3.2.1. Absorbance and transmittance:

UV-Vis spectroscopy determined a broad characteristics absorption band of CuO nanoparticles near about 300 nm for three different temperatures [18]. CuO nanoparticles prepared at highest temperature (150 ^{0}C) exhibited the most transmittance among the three. Figure 3 showed the UV-Vis absorption spectra for three set of copper oxide prepared at three different temperature 105, 120 and 150 ^{0}C.

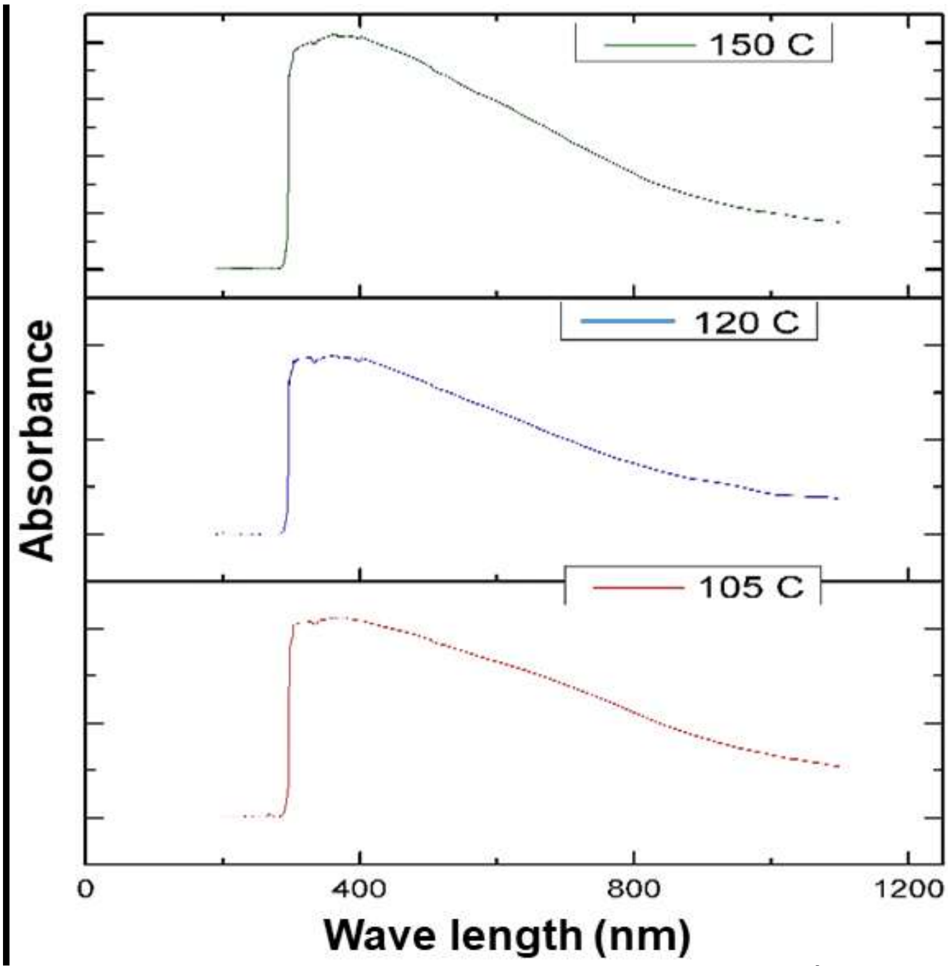

Figure 3: UV-Vis absorption spectra of CuO nanoparticles prepared at 105,120 and 150^{0}C.

Figure 4 revealed the variation of with wavelength λ (nm) in the wavelength range 190-1100 nm for three sample of CuO nanoparticles prepared at different temperature. The maximum transmittances within the visible region of the spectrum (400-700 nm) were 22.5, 62.5, and 65. It was found that the transmittance was increase with the increasing light wavelength for all samples. In the infrared region of the spectrum of CuO exhibited 2, 10.6, and 18.5 minimum transmittances for 105, 120 and 150 ^{0}C temperature respectively. Therefore, CuO nanoparticles prepared at 105 ^{0}C can be a good absorber.

3.2.2. Band gap measurement:

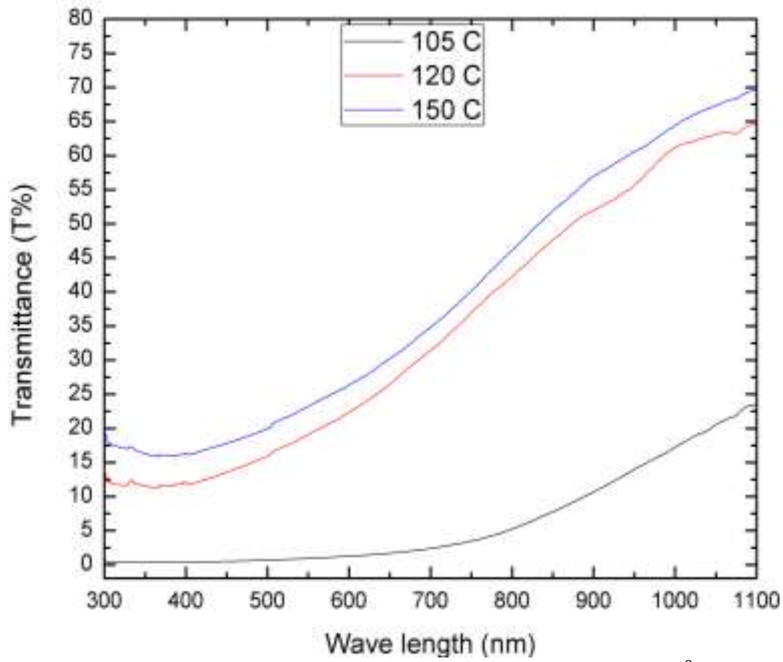

Figure 4: Transmittance spectra of CuO nanoparticles prepared at 105, 120 and 150^0 C.

The optical transition involved in the as-synthesized nanoparticles can be determined on the basis of the dependence of α on hϑ by using the Tauc relation.

$$\alpha h\vartheta = B\left(h\nu - E_g\right)$$

Where, E_g was the optical energy gap between the bottom of the conduction band and the top of the valance band, the value of B was a constant and n was the index which was assumed to be 0.5 for indirect transition and 2 for direct transition.

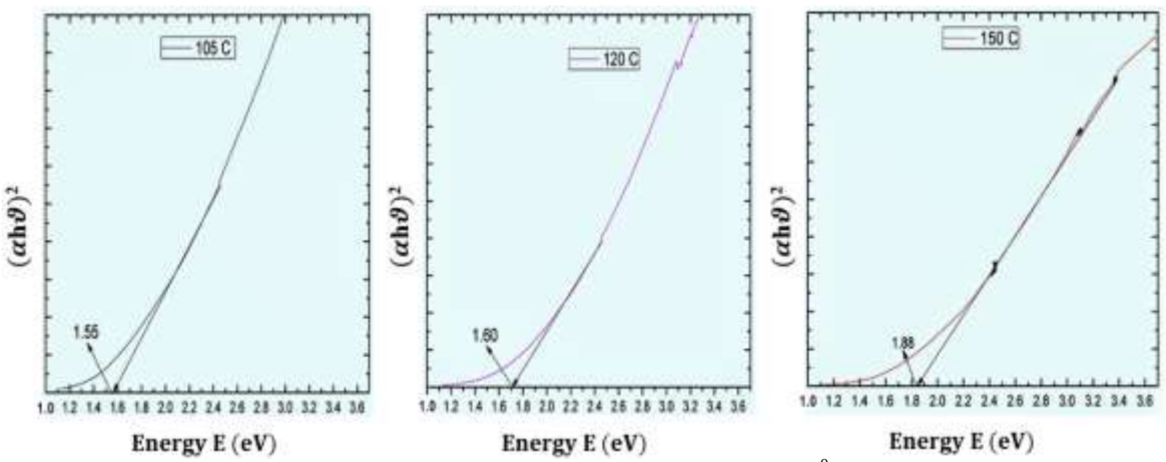

Figure 5: Bandgap energy of CuO nanoparticles prepared at 105 ,120 and 150 ^{0} C.

It was observed that the bandgap of CuO nanoparticles was varied along with the different operating temperatures. The estimated bandgap was found to be about 1.55, 1.60 and 1.88 eV for three different operating temperatures 105, 120 and 150 ^{0}C respectively [18]. The bandgap was lowest for 105 ^{0}C and highest for 150 ^{0}C. For CuO nanoparticles at 150 ^{0}C significant bandgaps was observed. From the Table 1, it was found that the bandgap energy of CuO nanoparticles 150 ^{0}C was comparable to the light energy in the infrared region and it can absorb more light than other two CuO nanoparticle samples. So, it was presumed that CuO nanoparticles prepared at elevated temperature can be a potential candidate to be used in optoelectronics devices.

Table 1: Band gap values for CuO nanoparticles for different temperature.

Sample nanoparticles	Temperature (^{0}C)	Band gap (eV)
CuO	105	1.55
CuO	120	1.60
CuO	150	1.88

3.3. Fourier transform infrared (FTIR) spectroscopy:

FTIR analysis was carried out to understand the chemical and structural nature of the synthesized CuO nanoparticles. Figure 6 represents the FTIR spectrum recorded for the CuO nanoparticles in the range of 400 to 4000 cm^{-1}. Three characteristic bands were observed at about 418 cm^{-1}, 518 cm^{-1}and 611 cm^{-1} in all the three spectra of CuO nanoparticles synthesized at different temperatures. The absorption bands at 418 cm^{-1} were attributed to the (Cu-O symmetric stretching) while the peaks at 518 cm^{-1} (Cu-O assymetric stretching) and 611 cm^{-1} (Cu-O wagging) identified the presence of metal oxide group in the sample [19]. The vibration peaks at 3446 cm^{-1} indicated the presence of hydroxide group within the sample due to the water attached to the surface of the CuO nanoparticles, which can be removed by further heating. The metal oxygen bonds at 1645 cm^{-1} (M-O rocking out of plane) identified the formation of CuO nanoparticles by hydrothermal method [19].

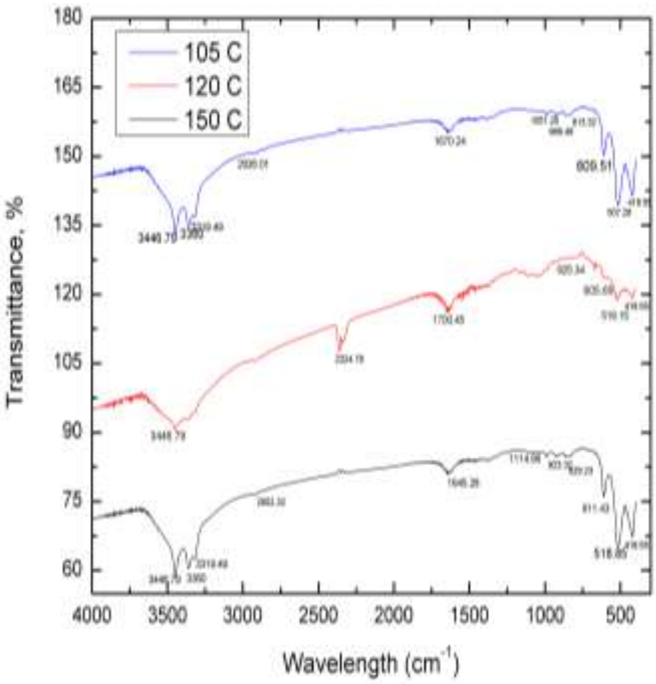

Figure 6: FTIR spectra of copper oxide nanoparticles at three different temperature.

3.4. Electric properties analysis:

The as-synthesized CuO powders were mixed with 5% polyvinyl alcohol (PVA) as a binder and uniaxially pressed into pellets (8.4mm × 2.4mm) at a pressure of a 10 kN. The compacts were then successively sintered in a muffle furnace in air at a temperature 100 ^{0}C for 2 hours and finally furnace cooled at room temperature. Then electric properties of the samples prepared at three different temperatures 105, 120 and 150 ^{0} C had been studied by Wayne Kerr 6500B Impedance Analyzer (UK).

3.4.1. Electric resistivity:

Electric resistivity, Quality factor, loss tangent and dielectric constants have been investigated at different frequencies.

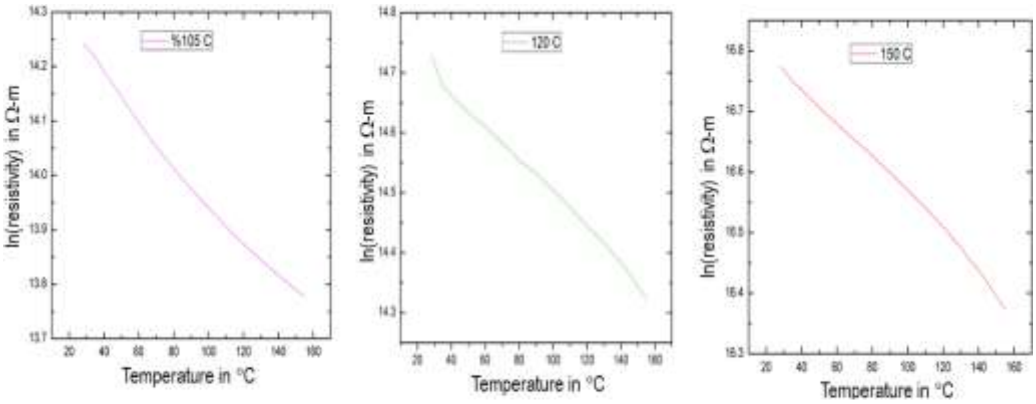

Figure 7: Variation of resistivity as a function of operating temperature.

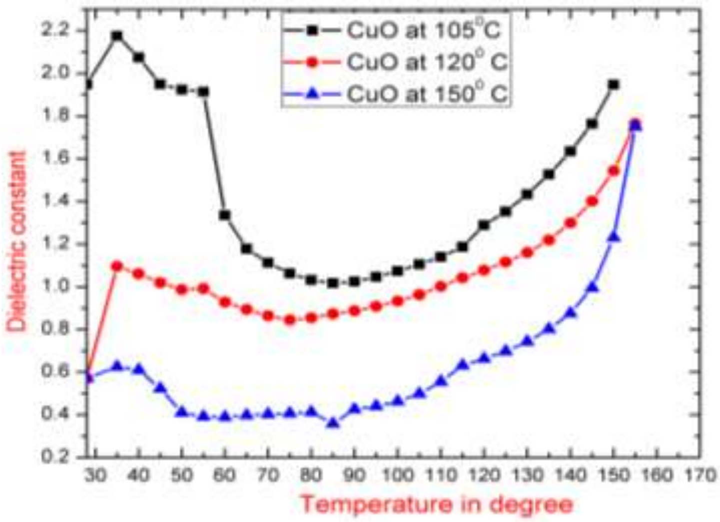

Figure 8: The variation of dielectric constant of CuO nanoparticles as a function of temperature.

From the Figure 7 it was found that resistivity of CuO nanoparticles prepared at temperature 105, 120 and 150 ^{0}C was decreased with increasing temperature which was in accordance with the well-known nature of semiconductor. The decrease in resistivity along with the increasing temperature verified the negative temperature coefficient of resistance of CuO nanoparticles as a wide bandgap semiconducting material.

3.4.2. Dielectric properties:

The consequence of temperature on dielectric constant of CuO nanoparticles was deliberate using temperature in need of impedance spectroscopy. Fig. 8 depicted the variation of dielectric constant as a function of temperature. Below 100 ^{0}C temperature for every sample of CuO nanoparticles, dielectric constant ($\in$) was decreased with increase of temperature. But above 100 ^{0}C, dielectric constant ($\in$) was increased with the elevated temperature [20]. The reason of increasing dielectric constant ($\in$) was vibration of atoms in the samples. The increase in dielectric constant with the increase in temperature can be explained as the temperature increased, the dipoles relatively became free and they responded to the applied electric field. The polarization and dielectric constant were increased with the increasing temperature.

3.4.3. Quality factor:

From the practical point of view quality factor (Q-factor) determines the merit of a material. The Q-factor of CuO nanoparticles at different temperature (105, 120, and 150 0C) as a function of log of frequency ranging from 100-100k Hz had been shown in Figure 9. Figure 9 exposed that Q-factor of CuO nanoparticles was increased with increasing temperature. But for CuO nanoparticles prepared at temperature 105 0C, the quality factor was not increased as much as 120 and 150 0C. Moreover, the Q-factor increases rapidly with increasing frequency. So, a perfect frequency band can be identified at which the as-synthesized nanoparticles to be used as a good semiconductor.

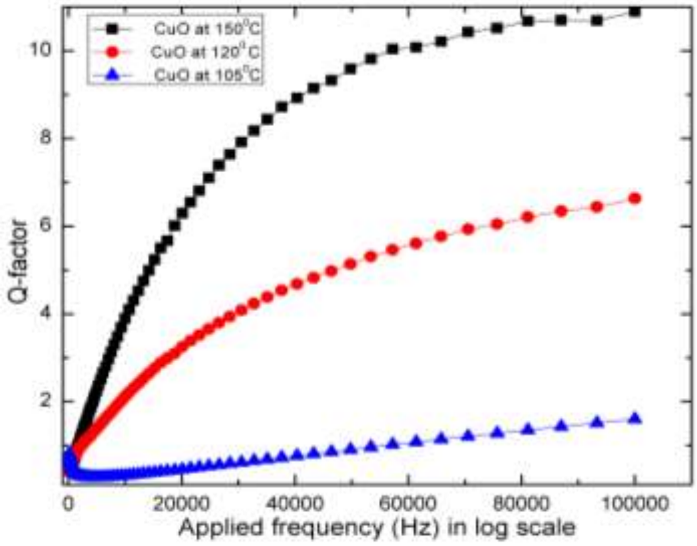

Figure 9: The variation of Q- factor of CuO nanoparticles as a function of temperature.

4. Conclusion:

Metal-oxide (CuO) nanoparticles were successfully synthesized by hydrothermal method within a self-designed stainless-steel autoclave, sealed and heated at various temperature. The optical, structural, chemical bond and electrical properties were studied in detail for three different preparation temperatures. X-ray diffraction analysis (XRD) revealed the single-phase monoclinic structure of CuO nanoparticles with an average grain size of 25, 33, and 66 nm at 105, 120, and 150 ^{0}C temperature respectively. Fourier Transform Infrared (FTIR) spectroscopy identified the representative bands of copper oxide nanoparticles at 609.51 & 507.28 cm^{-1}, 519.15 & 605.65 cm^{-1} and 518.85 & 611.43 cm^{-1} for temperature of 105, 120 and 150 ^{0}C respectively. UV-Vis spectroscopy determined a broad characteristics absorption band of CuO nanoparticles near about 300 nm for three different temperatures. CuO nanoparticles prepared at highest temperature (150 ^{0}C) exhibited the most transmittance among the three. By using Tauc plot, Bandgap was calculated of 1.55, 1.60 and 1.88 eV for three samples prepared in 105, 120, and 150^{0}C respectively. Electrical properties of CuO nanoparticles exposed that the resistivity decreases by increasing the temperature which indicated well-known negative temperature coefficient of resistance, completely in accordance with the semiconductors. Impedance analyzer revealed that dielectric constant and Q-factor of CuO nanoparticles were in increasing order along with the increasing temperature. Overall results depicted that the shape and size of CuO nanoparticles were varied along with the preparation temperature. The results also showed that the adding temperature of solution of NaOH and $CuCl_2.2H_2O$ had an important influence on the shape and size of CuO nanocrystals. Absorption spectra of CuO nanoparticles demonstrated the broad absorption bands and wide bandgap energy of the as-synthesized nanoparticles calculated by using Tauc plots. Impedance analyzers identified the formations of CuO nanoparticles with very good semiconducting properties. Hence all the studies exhibited that the as-synthesized CuO nanoparticles can be a potential candidate to be used in electronic applications including solar cell. CuO nanoparticles had been synthesized without any organic solvents, which has made this synthesis route very easy, cost effective, and environment friendly Green Technique.

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