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Synthesis and Structural Analysis of Different CuO Nano Particles

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Abstract: This investigation reports the synthesis of copper oxide nanoparticles using different feasible methods and their structural characterization. The synthesis process involved few innovative along with some established procedures by using different precursors to report a comparison study. The synthesized nano particles were characterize from X-Ray Diffraction (XRD) studies, Scanning electron microscopy (SEM) analysis and Energy dispersive X-ray analysis (EDX) for their shapes and sizes. The sizes of the synthesized nanoparticles are in nano scale with spherical structures irrespective of the techniques used. The calculated value of particle size is also confirmed from Debye Scherrer's formula. EDX spectrum shows the elemental composition of the samples. In addition, XRD peak-broadening analysis was used to evaluate the size and lattice strain from Williamson-Hall plots. Similarly, the band gap energy was evaluated for all the synthesized samples from UV-visible spectrophotometric analysis. Overall, the results of different synthesis methods have come up quite interestingly and appreciably.

Keywords: Energy dispersive X-ray analysis; X-ray Diffraction; Williamson-Hall analysis; Band gap energy.

1. Introduction

Nanotechnology is an interdisciplinary field of science with special interest in the area of materials. Nanomaterials can be obtained by using various techniques [1-3]. These materials are having extensive applications in many fields such as in medicines, solar cells, water purifications, opto-electronics, catalysis [4] etc. It has also been observed that many metals and their oxides in nano scale have extensive applications in different frontier areas due to their improved properties from bulk materials. Copper (ll)-oxide nanoparticles (CuO-NPs) with monoclinic structure has wide range of applications due to their unique physical and chemical properties like superconductivity, photovoltaic properties, relatively stable and the antimicrobial activity [5]. These nano particles are used as antioxidant [6], antibacterial [7], catalyst [8], and in batteries [9] as well as in solar cells [10]. They can also be utilized as burning rate catalyst in rocket propellant. However, nano-sized copper oxide shows superior catalytic activity and selectivity than that of the common copper oxide powder. Besides, comparatively low cost and easy synthesis is the added advantage of using copper oxide nano particles in various fields. There are different techniques for the preparation of copper oxide nano particles. The most promising methods for the synthesis of these nanoparticles are thermal decomposition [3], microwave radiation [11], sol-gel technique [12], chemical precipitation methods [13], and electrochemical methods [14-16], etc.

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In the present study, the copper oxide nanoparticles were synthesized by chemical precipitation methods, co-precipitation and powder synthesis technique using copper chloride dihydrate and copper sulphate pentahydrate as copper ion precursors. Other precursors are sodium and potassium hydroxides, sodium and potassium carbonates and ethanol etc. The synthesized products were characterized by different optical techniques and the results were explained on the basis of their structures and sizes. Efforts have been made to do a comparison study for the efficiency of the techniques employed.

The synthesis procedures were carried out by using few established procedures, though the concentration and amount of precursors were varied. In addition, few attempts have also been made to introduce some novel procedures to synthesize copper oxide nano particles. Synthesis techniques involving potassium hydroxide in aqueous and solid state media, potassium carbonate in co-precipitation reaction were some of the innovative steps that are quite rare in nano-literature.

2. Materials and Methods

Chemical Precipitation and powder technology are two prominent techniques for the synthesis of nanoparticles. In these techniques, usually a copper salt is used in presence of hydroxides and alcohols. All the reagents used for the synthesis were procured from Merck, India and were of analytic purity. These chemicals were used without further purification. Deionized double distilled water was used throughout the experiment.

2.1. Synthesis

Method-1

In this method, copper oxide nano particles were synthesized by using copper chloride dihydrate and sodium hydroxide pellets as precursors in aqueous media [17]. Efforts have also been made to take potassium hydroxide pellets in stead of sodium hydroxide. In both cases, 0.5g of copper chloride dihydrate was dissolved in 100ml deionized water with constant stirring. The temperature and pH of the solutions were maintained as 60^0C and 4, respectively. To these solutions, 1g of sodium hydroxide/ potassium hydroxide pellets was added to make the pH 11. Brownish-black precipitations of copper hydroxides were formed and the stirring was continued for one more hour to complete the precipitation reaction. The solutions were neutralized by adding few drops of hydrochloric acid. These precipitates were centrifuged and washed 3 to 4 times with deionized water to remove unreacted contents. These were dried in oven at 90^0 C for 4hour and kept overnight to get dried samples. These were then calcined at 400^0C for decomposition of hydroxides to oxide and were characterized for their properties.

Method-2

This synthesis method uses copper chloride dihydrate and sodium hydroxide in ethanol media [18]. Attempt has also been made to use potassium hydroxide for the synthesis. In both methods, accurately 3.0 g of copper chloride dihydrate was dissolved in 160mL of ethanol by constant stirring at room temperature. To this, 50 mL of 1N sodium hydroxide/potassium hydroxide dissolved in ethanol was added drop wise. The solutions were stirred continuously at room temperature to carry out the reactions. The colour of the solutions gradually changes from green to black precipitation of copper hydroxide. This stirring was continued for one more hour to complete the precipitation reaction. The samples were then centrifuged and washed 3 to 4 times

with deionized water for removal of unreacted contents. Obtained precipitates were dried in oven at 60^0 C for 4hour and kept overnight to get dried samples. These were calcined at 400^0C for decomposition of hydroxides to oxide.

Method-3

In this method, the copper oxide nano particles were prepared by a single step solid state reaction [19] where copper chloride di hydrate and sodium hydroxide/potassium hydroxide pellets were taken in 2:5 ratios to mix and grind in agate mortar pestle for 30 minutes. The color of the solid mixtures changed gradually from green to blue paste and finally to brown color solid. These brown solids were treated with ultrasonic waves for breaking the particles and were followed by centrifugation with deionized water to separate the residue. These were then washed with distilled water for 3 to 4 times followed by ethyl alcohol for removing the impurities and unreacted products to get hydroxides. Hydroxides were dried in oven at 60^0C for 6 hours and then calcined at 400^0C for decomposition of hydroxides to oxide.

During the synthesis of copper oxide nano particles, hydroxide ion plays an important role. Firstly, it is combined with cupric ion to form cupric hydroxide and this is decomposed to cupric oxide on heating. As heating is used to accelerate the reaction, there won't be any cupric hydroxide present in the products. Sodium and potassium hydroxides are strong electrolytes as a result they may neutralize the surface charges of the CuO nanoparticles, preventing them from possible crystalline aggregation. Apart from these, the use of high concentrated hydroxides helps in formation of diffusion layers on certain surfaces of CuO nanoparticles, and this may create an additional growth anisotropy allowing only energetically favourable crystallographic planes to grow [20].

$$CuCl_2 + 2NaOH/KOH \longrightarrow Cu(OH)_2 + 2NaCl$$

$$Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$$

Method-4

In addition to the above, one more simple method that follows the co-precipitation technique was also carried out [21]. In this technique, an aqueous solution of 0.01M Copper (II) sulfate pentahydrate and 0.4M of Sodium/Potassium Carbonate were dissolved in 300mL deionized water with constant stirring. The temperature and pH were maintained at 90^0C and 11, respectively. Brownish-black precipitations were instantaneously formed for both the cases, which were stirred continuously for one more hour to complete the precipitation reaction. These precipitates were centrifuged and washed for 3 to 4 times with deionized water to remove unreacted components. These were then dried in oven at 90^0 C for 4hour and were calcined at 400^0C for decomposition to get oxide.

$$2CuSO_4 + 2Na_2CO_3 + H_2O \longrightarrow Cu_2(OH)_2CO_3 + 2Na_2SO_4 + CO_2\uparrow$$

$$Cu(OH)_2CO_3 \longrightarrow CuO + CO_2\uparrow + H_2O$$

All the synthesized nano particles were characterized for their shapes, sizes and arrangement etc., from XRD, EDX, SEM and UV-visible spectrophotometric analysis.

3. Results and Discussion

For structural and crystalline size determination of nano particles, X-ray diffraction patterns were taken by using Rigaku smart lab X-ray Diffractometer using CuK alpha radiation (λ= 1.5405 Å) and X-rays generator operating at 40kv. The scanning range was maintained within 20-100deg with the scanning speed of $5^0 min^{-1}$. The XRD Patterns are shown in Figures 1 & 2. These patterns of CuO nano particles show the intensity and position of diffraction peaks, which confirm the presence of copper oxide in all the samples and the particles are of monoclinic crystal system (according to the literature, JCPDS, File No 01-080-1916)

The average crystallite size (D) has been calculated from the line broadening using the following Debye-Scherrer's relation and the average crystal sizes for different samples in nano scale have been presented in Table 1. Where K is Scherrer constant and accounts for the crystallite shape factor. The good approximation of K is 0.9, λ is the wavelength of X-ray, β is the "full width at half maximum (FWHM)" in radians of the X-ray diffraction peak and θ is the Braggs angle [22].

$$D = \frac{K\lambda}{\beta \cos\theta}$$

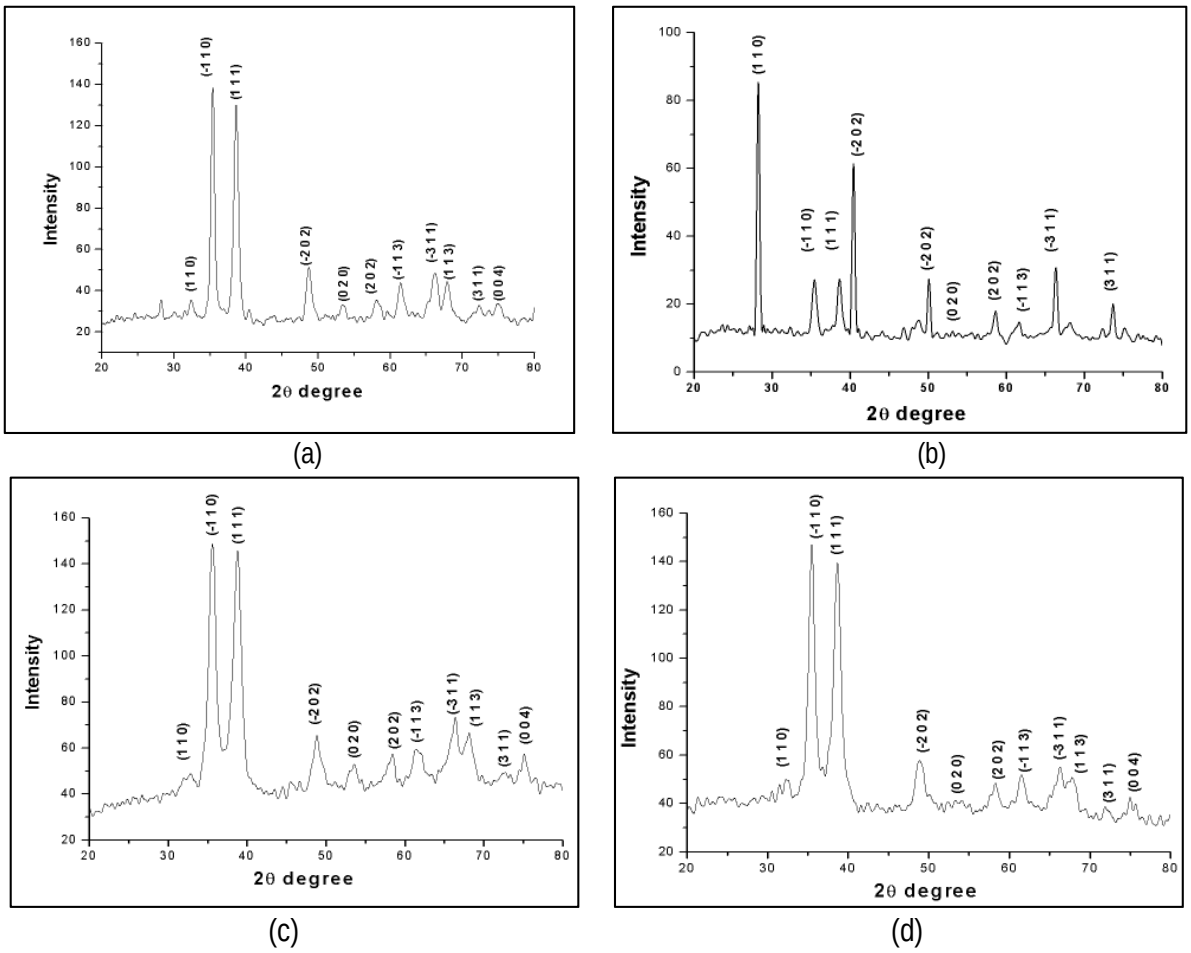

Figure 1. X-ray diffractograms of CuO NPs from (a) method 1 by KOH in aqueous media; (b) method 2 by KOH in ethanol media; (c) method 3 by KOH using solid state technique; (d) method 4 by K_2CO_3 using co-precipitation technique.

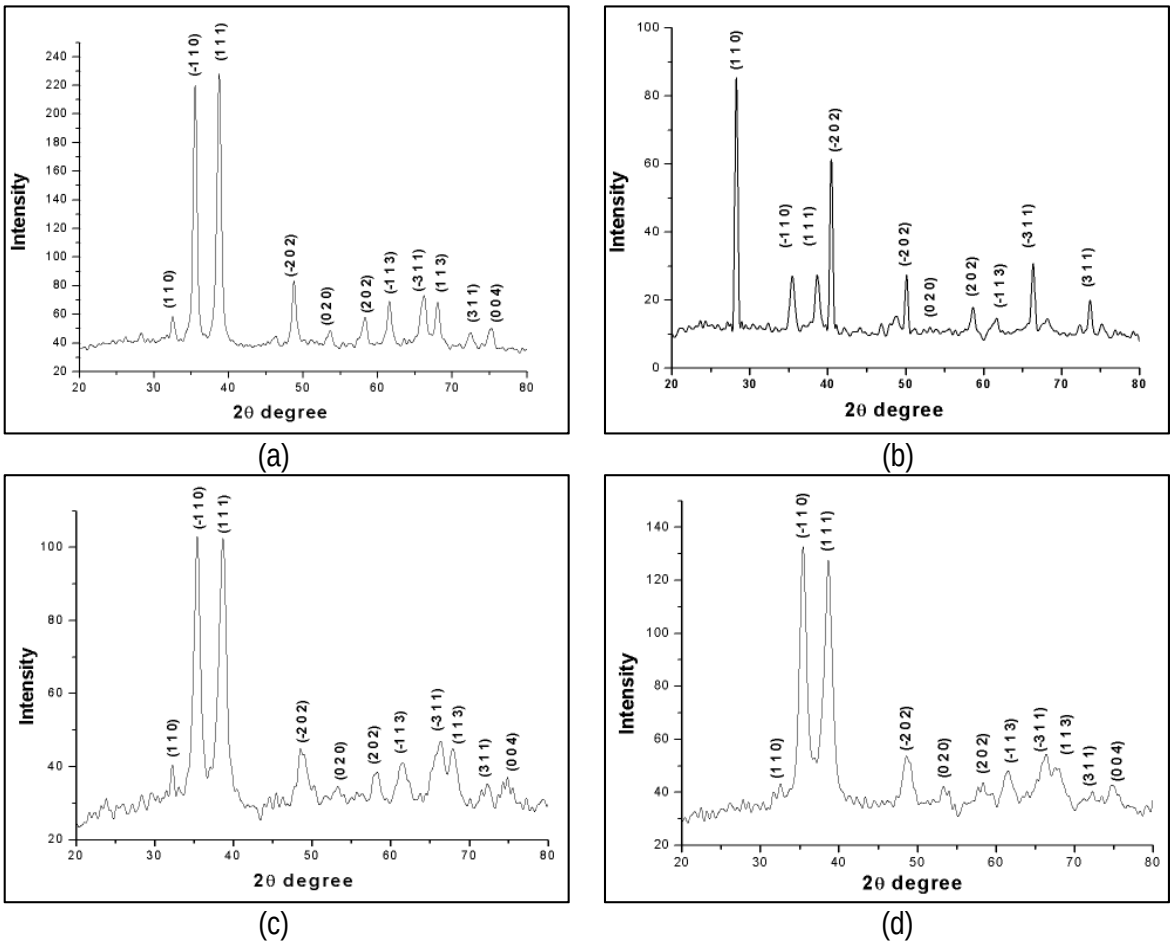

Figure 2. X-ray diffractograms of CuO NPs from (a) method 1 by NaOH in aqueous media; (b) method 2 by NaOH in ethanol media; (c) method 3 by NaOH using solid state technique; (d) method 4 by Na_2CO_3 using co-precipitation technique.

Besides, by using Williamson-Hall analysis (W-H), crystal sizes along with strain associated due to lattice dislocation can be determined from XRD data [23-28]. The proposal is an efficient method for separation of strain and size effects on broadening by looking at the peak width as a function of diffracting angle 2θ. The modified W-H is expressed as:

$$\beta\cos\theta = \left(\frac{K\lambda}{D}\right) + (4\varepsilon\sin\theta)$$

where, *D* is the average crystallite size and ε is the strain and assumed to be uniform in all crystallographic directions [29]. The above equation is in the form of straight line equation, where the term βcosθ was plotted against 4sinθ for the preferred orientation peaks of the prepared samples (see Figures 3 & 4). From Uniform Stress Deformation Model, USDM, the strain and slope are extracted. Accordingly, the slope and y-intercept of the fitted line represent strain and particle size, respectively. The average crystallite size and strain of the sample were presented in Table 1. In most of the cases, the crystallite sizes are matching with Debye Scherrer values with a positive strain, though very small. According to literature, less strain values show negligible effect on peak broadening [30].

Table 1. Average crystal size of copper oxide nano particles from XRD-analysis

Sl No.	CuO samples from different techniques		2Θ (degree)	Average Crystal size from Debye-Scherrer equation	William-Hall method	
					Crystal size	Micro Strain(%)
1	Method-1	With KOH	35.46	9.05	19.30	0.0202
		With NaOH	35.48	9.00	19.44	0.0202
2	Method-2 with Ethanol	With KOH	28.23	10.50	41.02	0.0186
		With NaOH	31.64	9.56	48.97	0.0241
3	Method-3 Powder Technique	With KOH	35.40	8.50	7.27	0.0210
		With NaOH	35.40	8.61	8.74	0.0209
4	Method-4 Co-precipitation	With K_2CO_3	35.40	8.61	8.50	0.0209
		With Na_2CO_3	37.25	8.06	1.51	0.0217

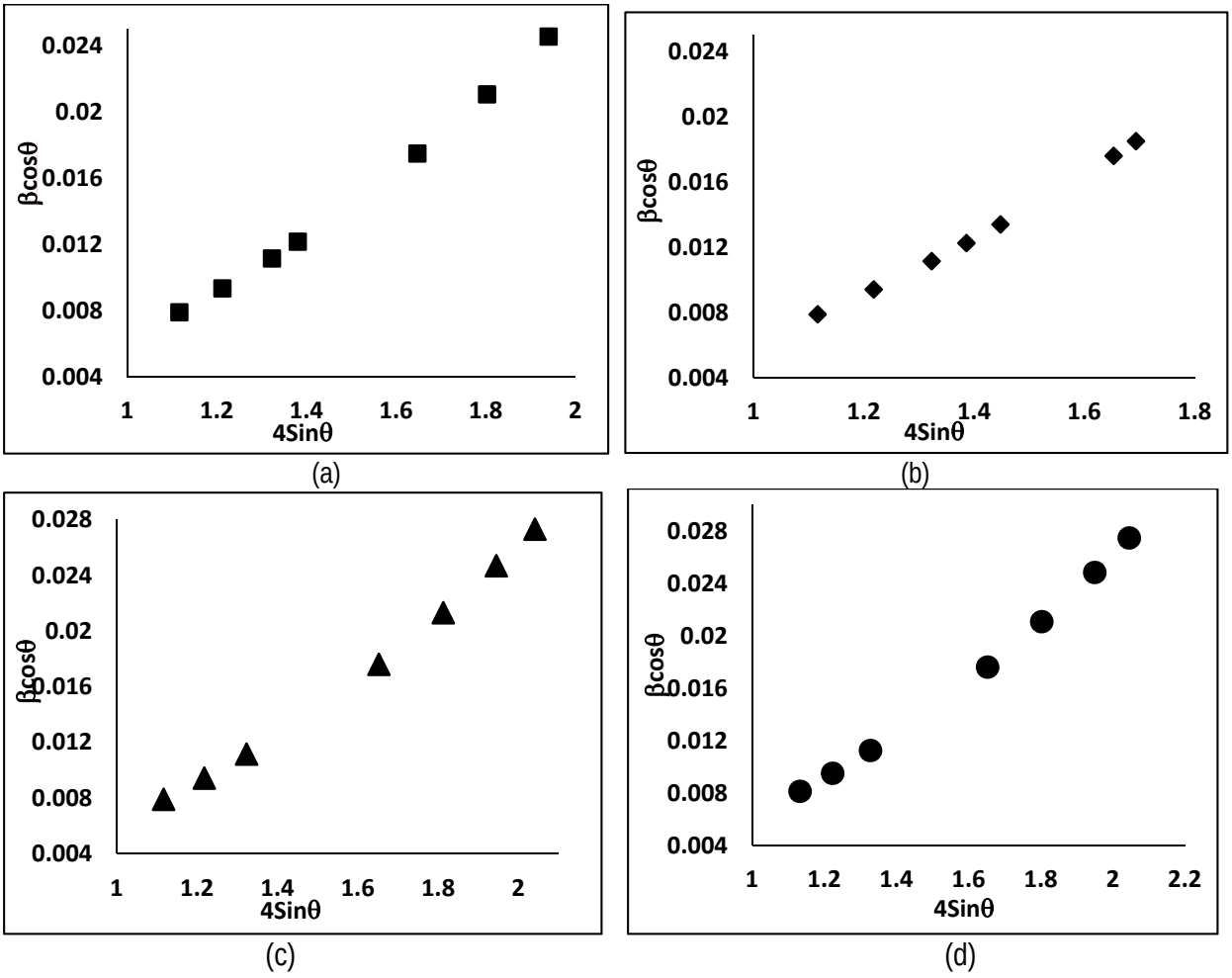

Figure 3. W-H plot for CuO nano particles from (a) method 1 by KOH in aqueous media; (b) method 2 by KOH in ethanol media; (c) method 3 by KOH using solid state technique; (d) method 4 by K_2CO_3 using co- precipitation technique.

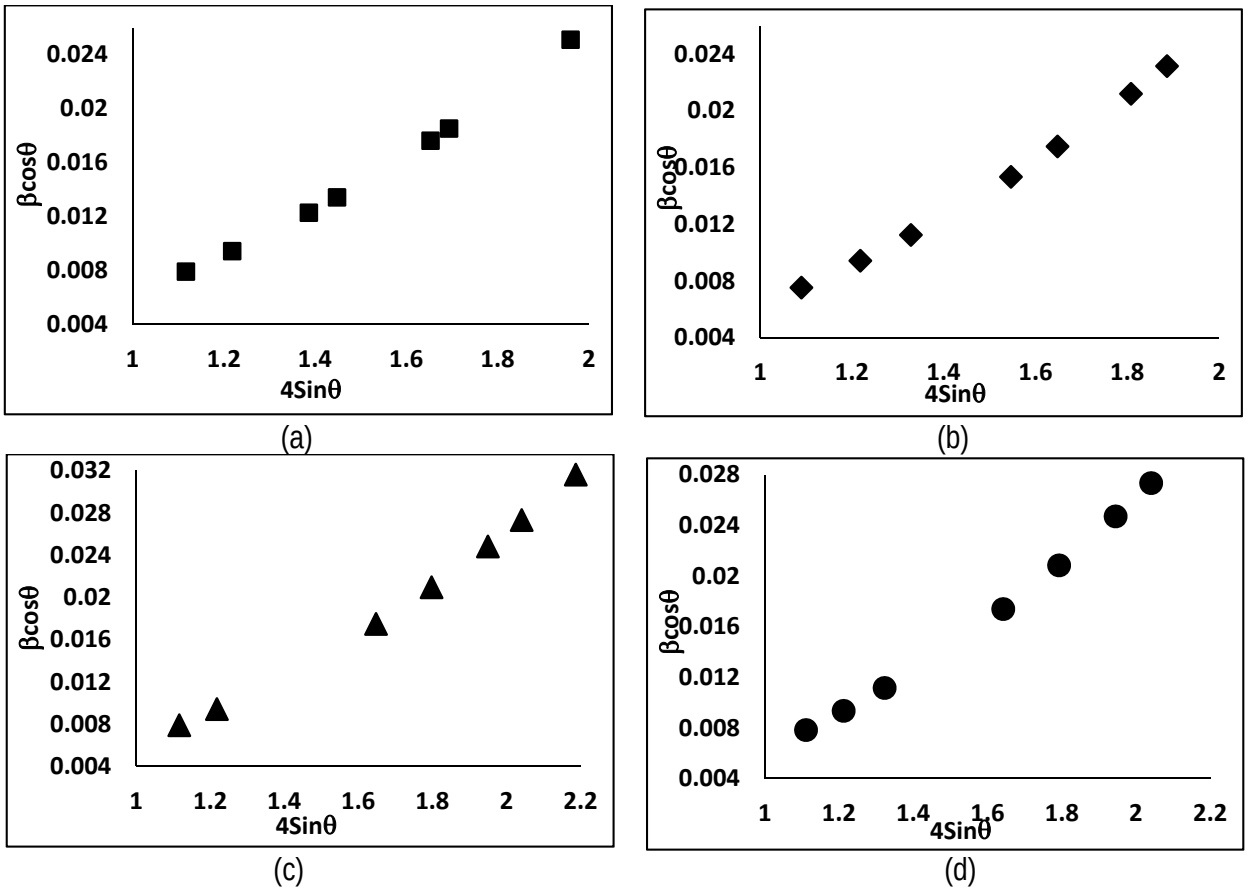

Figure 4. W-H plot for CuO nano particles from (a) method 1 by NaOH in aqueous media; (b) method 2 by NaOH in ethanol media; (c) method 3 by NaOH using solid state technique; (d) method 4 by Na_2CO_3 using co- precipitation technique.

The elemental composition of CuO nano particles have been studies from Energy Dispersive X-Ray Analysis (EDXA) using GEMINI ULTRA 55 instrument. The EDX images for all the samples have been presented in Figures 5 & 6. These images confirm the presence of copper and oxygen and the details of elemental composition of copper and oxygen are listed in Table 2. The elemental analysis for all samples shows the formation of CuO except few trace impurities like potassium and chlorides in the spectra and this is in good agreement with the results of XRD. However, the presence of trace impurities may be due to the use of potassium salts in some of the synthesis.

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The surface morphology of the synthesized CuO nano particles was analyzed using Scanning Electron Microscope (SEM) of GEMINI ULTRA 55 make instrument. Figures 7 & 8 show the SEM images for all synthesized particles. These morphologies are indicative of the sizes and shapes of CuO nano particles. In the present investigation, the synthesized particles are in nano scale with spherical shape irrespective of the techniques employed, though in some cases irregular

spherical shape for the particles have been observed. Details of sizes and shapes of CuO nano particles for all the synthesis techniques are listed in tabular form Table 3.

The UV-visible spectroscopic measurements were carried out at room temperature by using ELICO made SL-159 UV-visible spectrophotometer in the range 300-800nm to evaluate the band gap energy [Figures 9 & 10]. The absorption peaks were observed in between 310- 380 nm for all samples studied except few. The absorption peak is probably related to the electronic transition taking place from valence band to the conduction band due to quantum size of particles [31]. In this study a simple UV-Vis technique was used to calculate the optical band gap energy, E_g of synthesized CuO nanoparticles. This can be obtained by extrapolating the linear portion of the absorbance spectrum to zero to get λ and by using the following equation [32, 33].

$$E_g = h\nu$$

where h is the Plank's constant and ν is the frequency [$\nu = c/\lambda$] . In the present investigation, the E_g for all the synthesized particles are found to be in the range 2.32-3.11eV (see Table 4), whereas according to the literature [34-36], the E_g for bulk CuO is reported in the range 1.2-1.5eV. This blue shift in energy band may be explained due to the quantum confinement effect exerted by the nano sized crystals [30].

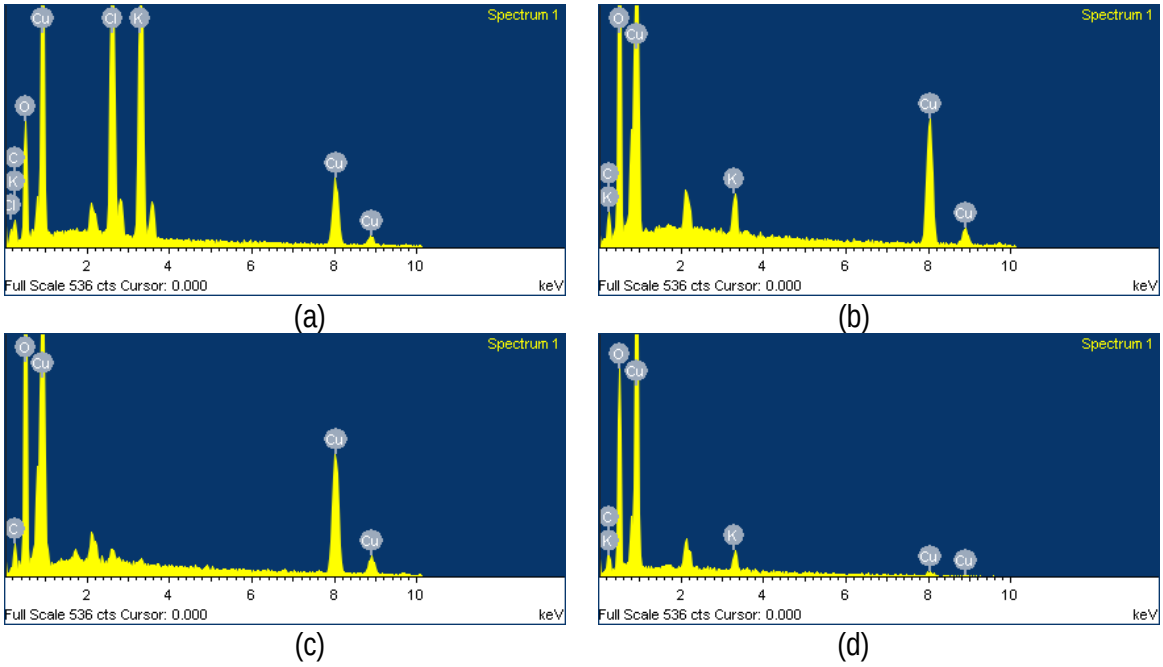


Figure 5. EDAX images of CuO NPs from (a) method 1 by KOH in aqueous media; (b) method 2 by KOH in ethanol media; (c) method 3 by KOH using solid state technique; (d) method 4 by K_2CO_3 using co-precipitation technique.

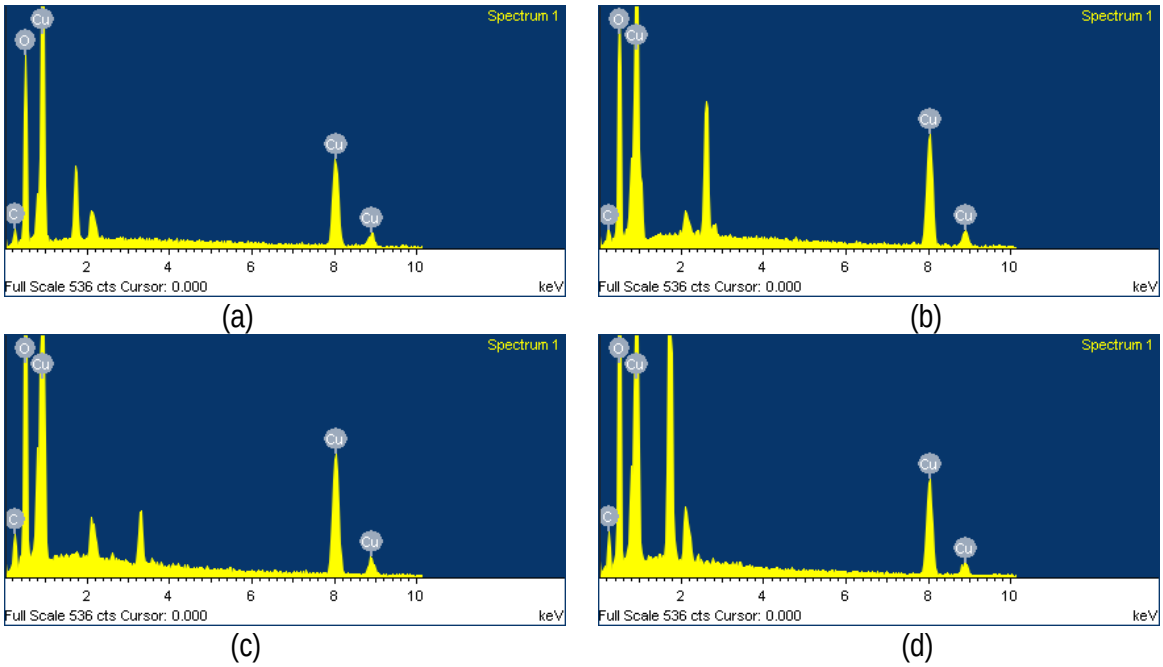
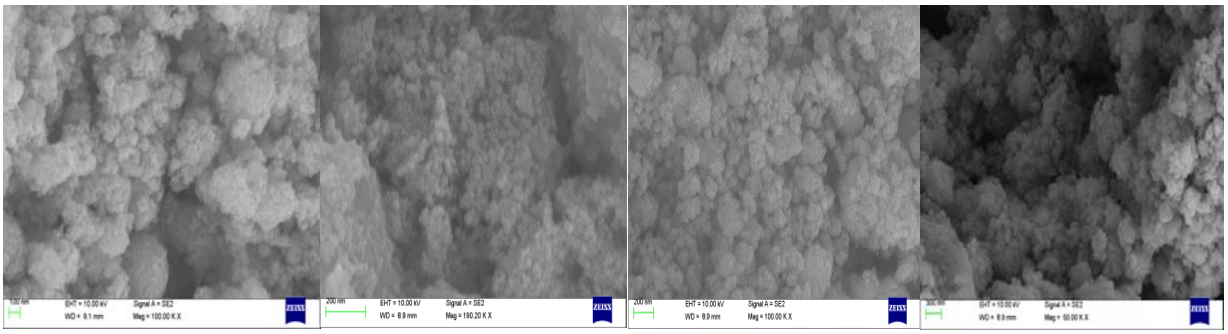


Figure 6. EDAX images of CuO NPs from (a) method 1 by NaOH in aqueous media; (b) method 2 by NaOH in ethanol media; (c) method 3 by NaOH using solid state technique; (d) method 4 by Na_2CO_3 using co-precipitation technique.

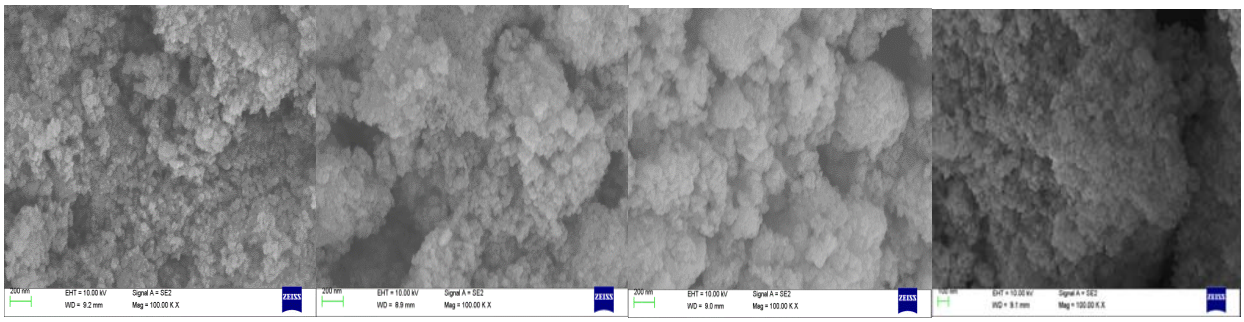
Table 2. Elemental compositions of copper oxide nanoparticles from EDX Analysis

Sl No.	CuO samples from different techniques		Cu Wt %	O Wt%	Cu At%	O At%
1	Method-1	With KOH	67.07	24.80	33.68	49.46
		With NaOH	67.73	25.60	33.09	49.68
2	Method-2 with Ethanol	With KOH	32.13	18.19	14.89	33.49
		With NaOH	71.41	23.60	37.28	48.94
3	Method- 3 Powder Technique	With KOH	68.39	25.09	33.77	49.20
		With NaOH	67.84	25.18	33.14	48.85
4	Method-4 Co-precipitation	With K_2CO_3	67.86	23.60	35.88	49.56
		With Na_2CO_3	65.81	25.59	30.90	47.72



(a) (b) (c) (d)

Figure 7. SEM morphologies of CuO NPs from (a) method 1 by KOH in aqueous media; (b) method 2 by KOH in ethanol media; (c) method 3 by KOH using solid state technique, (d) method 4 by K_2CO_3 using co- precipitation technique.



(a) (b) (c) (d)

Figure 8. SEM morphologies of CuO NPs from (a) method 1 by NaOH in aqueous media; (b) method 2 by NaOH in ethanol media; (c) method 3 by NaOH using solid state technique; (d) method 4 by Na_2CO_3 using co-precipitation technique.

Table 3. Particle sizes and shapes from SEM analysis for different CuO nano particles obtained from different techniques

Sl No.	CuO samples from different techniques		Particle Size range in nm	Shape
1	Method-1	With KOH	22-86	Spherical regular
		With NaOH	43-67	Spherical regular
2	Method-2 with Ethanol	With KOH	26-33	Spherical regular
		With NaOH	30-33	Spherical regular
3	Method- 3 Powder Technique	With KOH	38-45	Spherical regular
		With NaOH	57-142	Spherical regular
4	Method-4 Co-precipitation	With K_2CO_3	66-109	Spherical irregular
		With Na_2CO_3	27-49	Spherical irregular

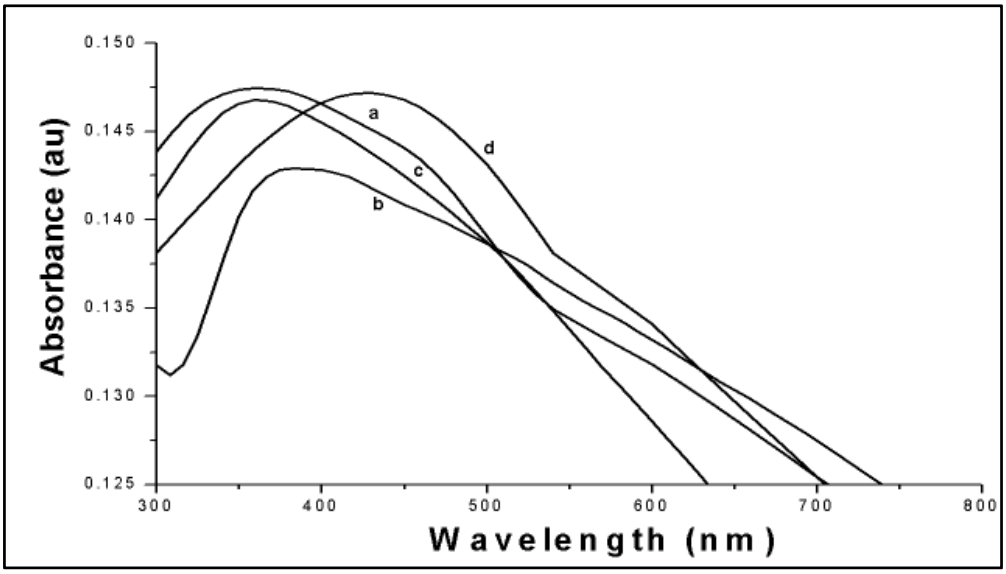


Figure 9. UV-visible absorption spectra from method 1 by KOH in aqueous media, (b) UV-visible absorption spectra from method 2 by KOH in ethanol media c) UV-visible absorption spectra from method 3 by KOH using solid state technique,(d) UV-visible absorption spectra from method 4 by K_2CO_3 using co- precipitation technique.

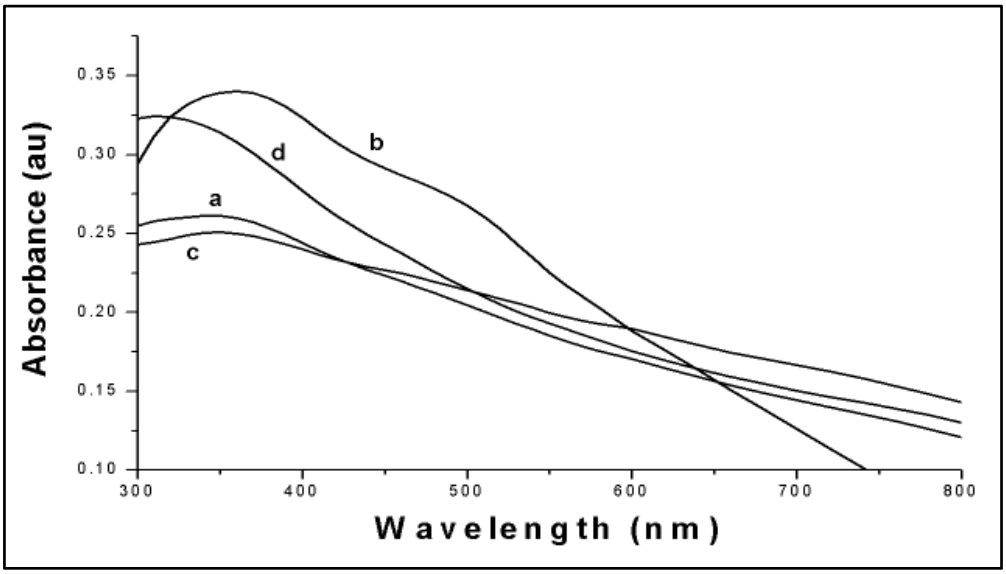


Figure 10. UV-visible absorption spectra from method 1 by NaOH in aqueous media, (b) UV-visible absorption spectra from method 2 by NaOH in ethanol media c) UV-visible absorption spectra from method3 by NaOH using solid state technique,(d) UV-visible absorption spectra from method 4 by Na_2CO_3 using co- precipitation technique.

Table 4. Band Gap Energy measured from UV-Visible Spectral Studies

Sl No.	CuO samples from different techniques		Band gap Energy(E_g) (eV)
1	Method-1	With KOH	2.99
		With NaOH	3.01
2	Method-2 with Ethanol	With KOH	2.77
		With NaOH	2.91
3	Method- 3 Powder Technique	With KOH	2.83
		With NaOH	2.32
4	Method-4 Co-precipitation	With K_2CO_3	2.47
		With Na_2CO_3	3.11

4. Conclusion

The present investigation provides different feasible techniques for the synthesis of copper oxide nanoparticles successfully. The synthesized samples were stable at room temperature and the size of the nanoparticles varies from 22 to 45nm except for few samples where the size varies between 50 to 150nm under scanning electron microscope. From the investigation it reveals that first two methods are quite suitable for synthesizing CuO nano particles less than 50nm. In addition, the shapes of all the samples show spherical shape irrespective of the techniques used. Though use of only sodium salts was there in the literature, efforts have been made to utilize potassium salts also. And surprisingly, in majority of cases, the results were found to be exceptionally high. However, in co-precipitation technique, sodium carbonate gave good result in comparison to potassium carbonate. Similarly in ethanol medium, elemental compositions for copper and oxides are more with sodium hydroxide precursor in comparison to other synthesis techniques.

The average crystallite sizes for all the synthesized particles were evaluated by both Debye-Scherrer and Williamson-Hall analysis. Except for few cases, the average sizes are quite matching. Apart from these, the band gap energy was also determined from UV-visible spectrophotometry, which was found to be enhanced from the respective bulk materials.

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