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Structural and Morphological Study of CuO Nanostructure Synthesized by Chemical Route

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ABSTRACT

Cupric oxide (CuO) nanostructure was prepared by chemical route using copper acetate [Cu(CH $_3$COO)$_2$-H $_2$O] and sodium hydroxide(NaOH) at different concentrations . Different morphologies: nanowires, flower-like nanostructures were observed at different material concentrations. The x-ray results, confirm the presence of cupric oxide monoclinic crystal structure, with calculated crystallite sizes between14.5-12.2 nm and 15.9-18.4 nm for different concentrations of chemical materials. The FTIR was also confirm the presence of CuO phase and the calculated band gap 2.1eV.The product were characterized by X-ray diffraction (XRD) ,Scanning electron microscope (SEM), Fourier transform infrared (FTIR) spectrum analysis and ultra-violet UV-Vis spectrophotometer.

1. Introduction:

Nanostructured materials have attracted much scientific attention due to their interesting size-dependent chemical and physical properties and potential technological applications. Cuprous oxide (Cu_2O) is also a p-type semiconductor having a band gap of approximately (2.1-2.6 eV) and having a cubic crystal structure. Cupric oxide (CuO) is a p-type semiconductor with a narrow band gap (1.2-1.5 eV) and having monoclinic crystal structure [1].Much larger band gap value for copper oxide has also been reported (2.43eV),which is larger than that in bulk [2].For example, the UV-visible absorption spectrum studies showed that the band gap of CuO nanoparticles (Eg ¼ 2:43 eV) is much larger than that in bulk CuO (Eg 1:85 eV) [3,4]. The advanced structures of CuO with various shapes have been obtained, such as nanowires [5], nanorods [6, 7], nanoslices [8], nanoflowers [9],nanocrystals[10] and nanobundles [11].CuO has received considerable attention due to its potential applications in many fields ,such as catalyst [12], gas sensors[13,14], semiconductors, solar cells [15], nanofluids [16] ,solar energy storage [17] ,and it has also been used in wet cell batteries as a cathode electrode [18,19].Several methods have been used for cupric oxide nanostructures preparation , such as, chemical method [20,21] , thermal decomposition [22,23] , aqueous precipitation method [24], hydrothermal method[25], sol-gel rout [26] , thermal evaporation [27] and thermal oxidation [28-32] .

In the present work, we have synthesized CuO nanostructures by chemical route to study the effect of material concentrations on the structure and morphology of the growth product. Copper oxide nanowires and flower like nanostructures were observed at two different chemical concentrations used.

2. Experimental

In this work ,we used two different materials concentrations of Copper acetate monohydrate [Cu (CH_3 COO) $_2$ -H_2O] and sodium hydroxide [NaOH] for cupric oxide (CuO) synthesis by chemical route.0.5M and 0.2M of aqueous copper acetate are prepared by dissolving 0.99g and 0.39g of copper acetate in 10 ml of deionized water respectively. Similarly, 5M and 2.5M of aqueous sodium hydroxide are prepared by dissolving 2g and 1g of sodium hydroxide in 10ml of deionized water

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respectively. 10ml of the prepared aqueous sodium hydroxide is mixed rapidly with 10 ml of aqueous copper acetate. After a reaction of 1minute the black precipitate is formed. Stirring is continued for 15 minutes, and then the mixture is separated by centrifuge process, and washed with deionized water . It is then dried in air at 100°C for 2 days.

Centrifugation is done to collect the precipitate, chemical reaction between copper acetate and NaOH is performed according to the following equation:

$Cu(CH_3COO)_2 . H_2O + NaOH \rightarrow CuO + 2Na\ (CH_3COO) + H_2O$ (1)

Where (2Na (CH_3COO)) is soluble in water .Therefore, the sediment was washed several times with deionized DI water.

3. Characterization:

X-ray Diffraction (XRD) analysis of the product was carried out on Shimadzu XRD-6000. X-ray diffractometer equipped with Cu Kα radiation (λ = 0.15406 nm),employing a scanning speed of 12° min^{-1} and 2θ ranges from 20° to 50°. The morphology of the produced nanostructure was investigated using Scanning Electron Microscope - SEM (Tescan Vega II-Cheek).The Fourier transform infrared analysis was carried out using (Shimadzu / ARAffinity-1) in the range of 500-4000cm^{-1} . UV –Vis spectrophotometer was also used to calculate the band gap energy of synthesized CuO nanostructure and compared with value of bulk CuO.

4. Results and Discussion

4.1. XRD Analysis

The XRD pattern of synthesized samples is presented in Fig. 1. All the peaks of XRD pattern can be indexed to that of monoclinic CuO according to the journal committee of diffraction standared (JCPDS, File No.5-661) Fig. 1a and (JCPDS, File No.41-0254) Fig.1b . The XRD results reveal that relatively sharp peaks which indicate the enhancement of CuO crystallinity. The broadening of the peaks is indicative of small crystallite size. There is no additional impurity from cubic Cu_2O indicating the phase purity. The detailed analysis of the XRD for the present samples compared with standard data are given in the Tables (1) and (2).There are two different crystal orientations related to the resulted nanostructures observed.

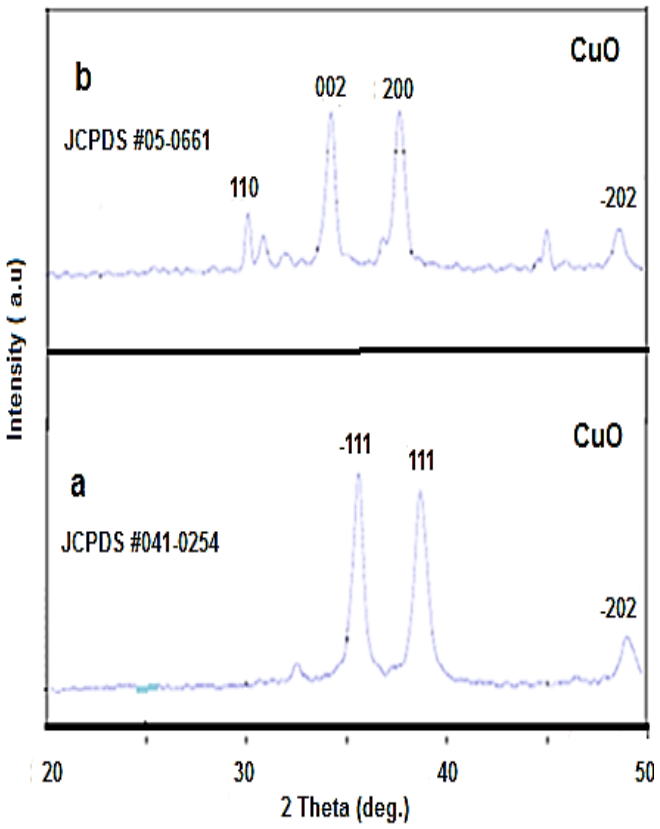


Fig. 1. The XRD pattern of the as prepared CuO nanostructure at different concentrations , (a) Cu $(CH_3COO)_2$-H_2O(0.5M) and NaOH (5M), (b)Cu$(CH_3COO)_2$_H_2O(0.2M) and NaOH (2.5M)

The crystallite size (D) of the samples was estimated from XRD peak broadening using Debye-Scherrer's formula.[33]:

$$D = 0.9\lambda / \beta \cos \theta \quad (2)$$

Where λ is the wavelength of X-Ray (0.15406 nm), β is the full width half maximum in radian (FWHM°Xπ/ 180), θ is the diffraction angle. The calculated crystallite sizes (D) are shown for both nanostructures are shown in Table (1) and (2). The D values for CuO nanowires are 12.2nm and 14.5nm for reflection planes (-111) and (111) respectively. The D values for CuO flower-like nanostructure are15.9nm-18.4nm for reflection planes (002) and (200) respectively .There is no much difference between the calculated D values for the two nanostructures.

Table 1. X-Ray data of the strongest peaks for CuO nanowires

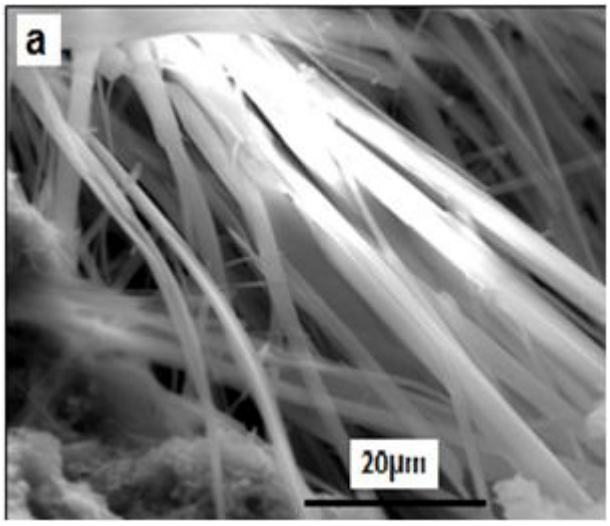
Present Work				JCPDS Card No. 05- 0661			
$2\theta°$	d_{hkl}	$I/I_o\%$	$D(nm)$	$2\theta°$	d_{hkl}	hkl	$I/I_o\%$
35.6027	2.51964	100	14.5	35.551	2.523	-111	100
38.7405	2.32248	92	12.2	38.729	2.323	111	92

Table2: X-Ray data of the strongest peaks for CuO flower-like nanostructure.

Present Work				JCPDS Card No.041-0245			
$2\theta°$	d_{hkl}	$I/I_o\%$	$D(nm)$	$2\theta°$	d_{hkl}	hkl	$I/I_o\%$
35.6764	2.51461	98	18.4	35.437	2.531	002	98
38.8580	2.31573	100	15.9	38.940	2.311	200	100

4.2. SEM Analysis

Figure.(2) represents the SEM image of the as-synthesized CuO nanostructures at different concentrations. The morphology of CuO samples shows the formation of CuO nanostructure The figure (2.a) is similar to the SEM image of CuO nanowiresshown in reference [34] .



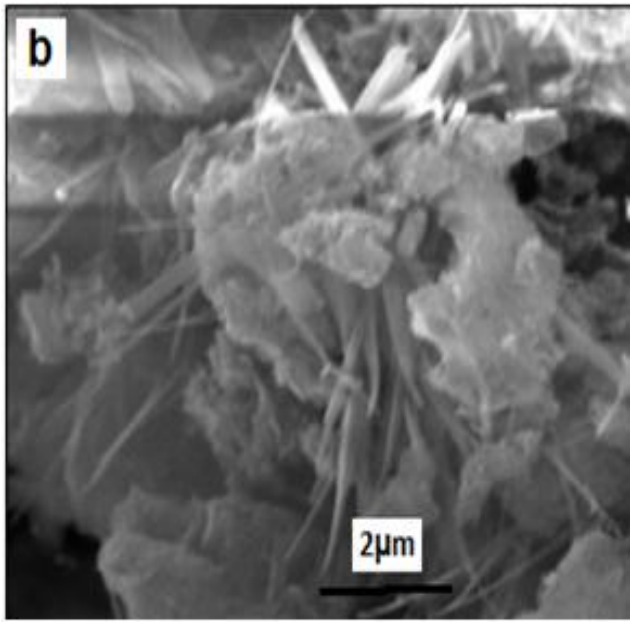


Figure 2: SEM image of (CuO) nanowire at concentration(0.5M) of Cu(CH3COO)2-H2O ;(5M) of NaOH (a) and(CuO) flower- like nanostructure at concentration(0.2M) of Cu(CH3COO)2-H2O; (2.5M) of NaOH (b)

4.3. FTIR Analysis

FTIR analysis was carried out to understand the chemical and structural nature of the synthesized CuO and the effect of the chemical used in the synthesis of CuO nanostructure. Figure (3) and (4) represents the FTIR spectrums of CuO nanostructure at two different concentrations were recorded in the range of 500 to 4,000 cm^{-1} .In figure (2),the three characteristic band observed at 424.3 cm^{-1} ,501.4 cm^{-1},601.7 cm^{-1} ,while in experiment two ,the three characteristic band observed at 432cm^{-1} ,497.6cm^{-1} ,603.7cm^{-1} can be assigned to the Cu-O stretching vibration and 3458 cm^{-1}can be assigned to the O-H stretching vibration . Both are confirm the formation of CuO single phase ,which is in good agreement with XRD Results .These result are found in a good agreement with others workers [20].

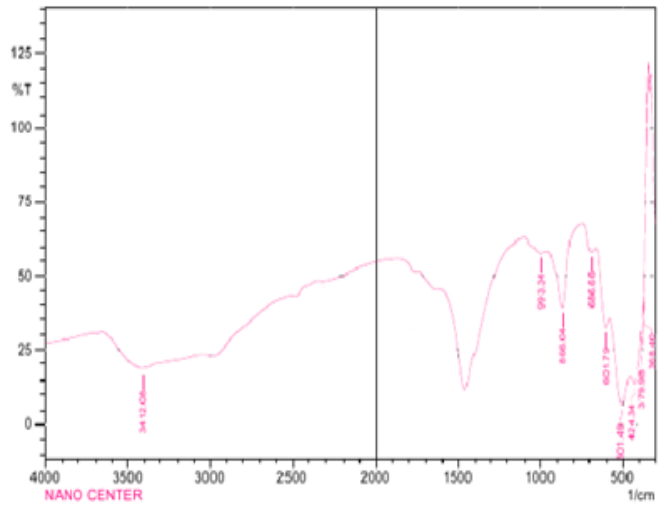


Figure (3): The FTIR spectrum of the as-synthesized CuO nanowires at concentration Cu (CH3COO)2-H2O(0.5M) and NaOH (5M)

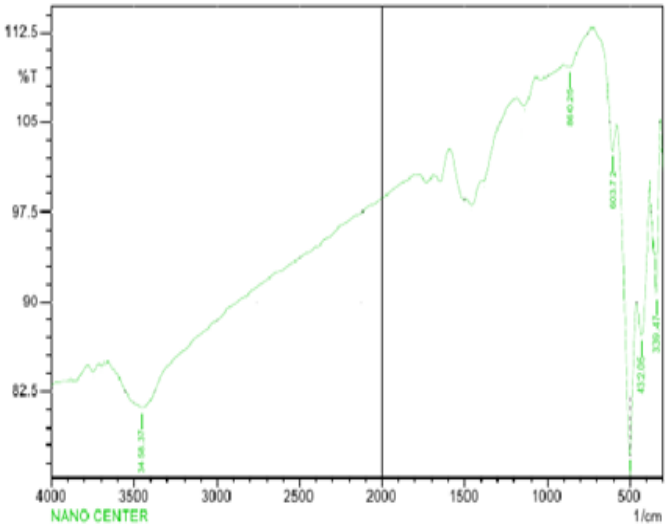


Figure (4) :The FTIR spectrum of the as-synthesized CuO flower-like nanostructure at concentration Cu (CH3COO)2-H2O(0.2M) and NaOH (2.5M)

4.4. UV-Visible Analysis

The optical characterization of the sample was recorded on UV-Vis absorption spectrophotometer in order to determine the Band gap energy of CuO nanostructure.In this study a simple UV-Vis technique was used to calculate the band gap energy of synthesized CuO nanowires and compared with value of bulk CuO. The absorption band gap E_g can be determined by the following equation [35]:

$$(\alpha\, h\nu)^n = B(h\nu - E_g) \qquad (3)$$

where $h\nu$ is the photo energy, α is the absorption coefficient, B is a constant relative to the material and n is either 2 for a direct transition or 1/2 for an indirect transition. This equation gives the band gap energy E_g in terms of eV. When straight portion of $(\alpha h\nu)^2$ against $h\nu$ plot extrapolated to the point α=0 as shown in fig. 5. The band gap of CuO nanowires was calculated to be 2.1eV, CuO band gap value has been reported for nanowires 2.03 eV [36] .

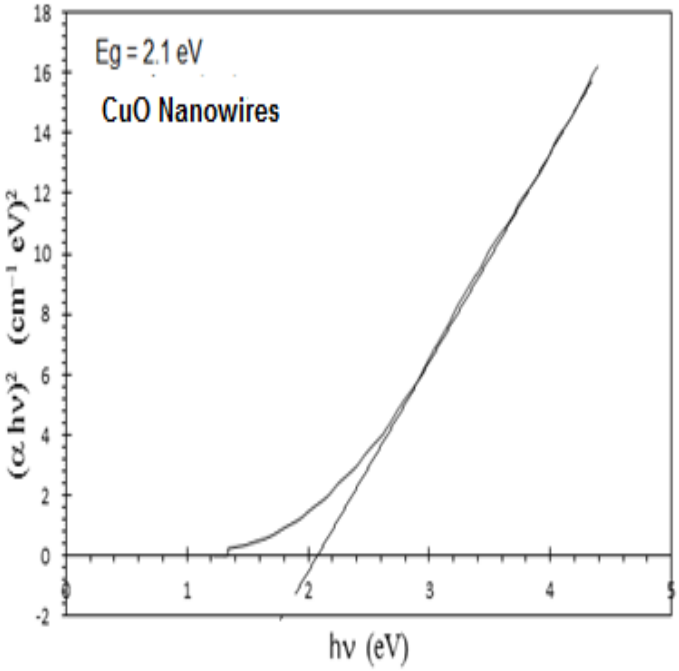


Fig. 5. Shows plot of $(\alpha h\nu)^2$ versus hν (eV) for CuO nanowires.

5. Conclusion

Copper oxide nanostructures were successfully synthesized by chemical route. It was found that two different concentrations of chemical materials exhibit nanowires and flower –like structures. XRD shows the monoclinic structure of CuO phase only with calculated crystallite size range between 12-18nm. FTIR confirm the presence of CuO. The morphology of as prepared CuO shows nanowires and flower-like nanostructures as results of different concentrations.

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دراسة تركيبيه و مورفولوجيه للتركيب النانوي ل (CuO) المصنع بالطريقة الكيمياوية

فائق حماد عنتر عبد القادر داوود فيصل مروة عبد الكريم

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ألخلاصه :

تم تحضير التركيب النانوي لأوكسيد النحاس بالطريقة الكيمياويه وذلك باستخدام خلات اوكسيد النحاس المائية [Cuo(CH3Coo)2− H2O] وهيدروكسيد الصوديوم (NaoH) وبتراكيز مختلفة. مورفولوجيات مختلفه للاسلاك النانويه والتراكيب النانويه لشبه الزهرة قد تمت ملاحظتها عند تراكيز مختلفه. نتائج حيود الاشعه السينيه (XRD) أكدت وجود أوكسيد النحاس بتركيب بلوري أحادي الميل وبأحجام بلوريه محسوبه بين (14.5−12.2) نانومتر و(18.4 15.9−) نانومتر ولمختلف التراكيز للمواد الكيمياويه. طيف الاشعه الحمراء (FTIR) أكد ايضا وجود طور (CuO). تم حساب فجوة الطاقه و مقدراها 1−2 ev. تمت دراسة العينات بأستخدام حيود الاشعه السينيه (XRD) والمجهر الالكتروني الماسح (SEM) وطيف الاشعه الحمراء لتحولات فوريه (FTIR) ومطياف الاشعه الفوق البنفسجيه – المرئيه (UV−vis).