



Optical properties of nanostructure cuo prepared by different stabilizing agents

M.A.El-Sherbiny*, K.Abdullah, S.A.El-Khodary

Department of physics, Faculty of science, Al-Azhar University, Nasr city 11884 Cairo, (EGYPT)

Housing and Building National Research Center (HBRC), Dokki 12311, Giza, (EGYPT)

E-mail: SHERBINYP@YAHOO.COM

ABSTRACT

The effect of different stabilizing agents on size and shape of synthesized CuO nanocrystals is studied. Spec grad CuCl_2 and three different stabilizing agents LiOH, NaOH and KOH are used as starting materials. X-ray powder diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and UV-Visible absorption spectroscopy are used for characterizing the obtained powder samples. Size and shape of the obtained nanorods are found to be depend on the used stabilizer. The diameter and length of the obtained nanorods are also estimated. The optical band gap of the prepared samples were found to be 2.09, 2.28, and 2.64 eV for LiOH, NaOH and KOH respectively.

© 2015 Trade Science Inc. - INDIA

KEYWORDS

Copper oxide;
Nanostructure;
Nanowire;
Nanotube;
Stabilizing agent;
Band gap.

INTRODUCTION

It was established that, nanomaterial properties (mechanical, physical, chemical, electronic, optical and magnetic) differ from that of bulk counterparts. This is due to the high surface area to volume ratio as well as quantum confinement effects^[1]. Nanoparticles exist in several different shapes such as spheres, cylinders, rods, platelets, tubes, etc. Generally, they are designed with surface modifications tailored to meet the needs of given applications they are going to be used for^[2]. Oxides of transition metals are important class of semiconductors, because of their wide range of applications: magnetic storage media, solar energy transformation, electronics and catalysis^[3]. Cupric oxide (CuO) is a p-type semiconducting oxide with monoclinic crystal structure and direct band gap of ~1.2 eV with interesting electro-

chemical, photovoltaic, and catalytic properties. Various applications have been reported for nanostructured CuO such as heterogeneous catalysis, solar cells, gas sensors and magnetic storage media where it offers highly reactive surfaces, and improved optical, electrical, and catalytic properties compared to that of bulk crystals. Recently, the controlled shape synthesis of nanostructured CuO has attracted considerable attention where variety of CuO nanostructures (e.g. nanoneedles, nanoribbons, nanowires, nanorods, and nanosheet configurations) have been fabricated by pulsed laser ablation, sol-gel, hydrothermal processing and thermal oxidation^[4].

It was reported that there are different parameters such as temperature, time, pH value, pressure, concentration of chemical species and capping agent influence the morphology of nanocrystal^[5,6]. In the present

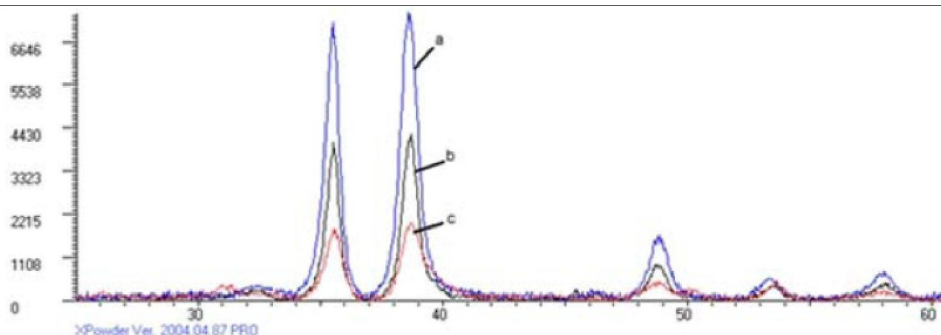


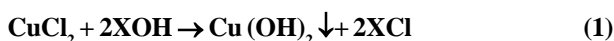
Figure 1: XRD spectra of prepared CuO nanostructures by using LiOH, NaOH and KOH (a, b and c respectively)

article different stabilizing agent are used in order to study the effect of solute additions on the properties of the produced nanoparticles. The CuO nanostructure samples are obtained using different stabilizing agents of LiOH, NaOH and KOH.

EXPERIMENTAL

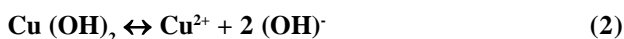
CuO nanoparticles preparation

Three powder samples of nanocrystalline CuO are prepared by dissolving 0.07M of copper chloride (S D Fine Chem. Limited, India) in 50 ml of distilled water under vigorous stirring for 20 minutes. Alkali solution of (X) OH were added to the Cu solution drop by drop with constant stirring at 57 °C until the pH value reaches 9 according to equation (1)



where (X) is Li, Na and k.

With the aid of hydrothermal process, part of the $\text{Cu}(\text{OH})_2$ colloids dissociate into Cu^{2+} and $(\text{OH})^-$ ions, and when the concentration of Cu^{2+} and $(\text{OH})^-$ reaches the supersaturation CuO nuclei will form according to the following reactions:



The obtained products were separated by centrifugation and washed thoroughly by distilled water, absolute ethanol and acetone in sequence to remove the possibly remaining ions. The ingots then dried in air at room temperature.

Analytical techniques

The structure of the prepared samples were investigated (XRD) using (Philips PW3050/60, MPSS) diffractometer, with nickel- filtered Cu-K α radia-

tion provided with a proportional counter. Transmission electron microscopy (TEM) images with selected area electron diffraction (SAED) pattern were recorded using (JEOL- JEM-1230) and accelerating voltage of 100 kV to get excellent imaging capabilities suitable for materials science applications. The prepared samples for TEM observation were dispersed in ethanol followed by ultrasonic vibration for 20 min, then one drop is placed onto a copper grid coated with a layer of amorphous carbon. For UV/Vis measurement, PG Instrument CO., Ltd UV/Vis double beam spectrophotometer (T80+) was used to record the UV-Visible absorption, prepared powder samples are dissolved in distilled water with same percentage (0.1 mg/mL) then treated with ultrasonic waves for 30 minutes.

RESULTS AND DISCUSSION

X-ray powder diffraction

The obtained XRD spectra are given in (Figures. 1 a, b and c) for the prepared samples. The peaks at 2θ values of 32.459, 35.52, 38.673, 48.816, 53.522, 58.136, 61.517, 66.178, 68.097, 72.300, 75.179 correspond to the crystal planes of 110, $11\bar{1}$, 111, $20\bar{2}$, 020, 202, $11\bar{3}$, 310, 220, 311, $22\bar{2}$ of crystalline copper oxide, respectively. These peaks are in consistent with the data of the ICSD (Inorganic Crystal Structure Database) file, reference code (01-080-0076^[7], 00-048-1548^[8]), and confirm that all CuO samples are of monoclinic tenorite structure. Which are in good agreement with recent observations^[9,10,11].

In the absence of microstrains, the grain size of powder can be determined from the Scherrer equation^[6] $d = \frac{0.941 \lambda}{\beta \cos \theta}$ where λ is the X-ray wavelength, β

TABLE 1: Grain size and microstrains of the prepared samples estimated from Scherrer equation and Williamson-Hall plot together with calculated lattice constants in nanometer

Stabilizing agent	TEM Particle size (nm)		Band gap (eV)	x-ray Particle size			Lattice Constants (nm)		
	Av. Diameter	Length		Scherrer's (nm)	Williamson-Hall	Strain	a	b	C
LiOH	8	72 - 76	2.09	16.7 nm	20.2041	0.00234	0.469	0.344	0.512
NaOH	10	50 - 64	2.28	18.02 nm	31.0067	0.00265	0.469	0.343	0.512
KOH	5	11 - 76	2.64	37.3 nm	41.6216	0.00424	0.467	0.343	0.512

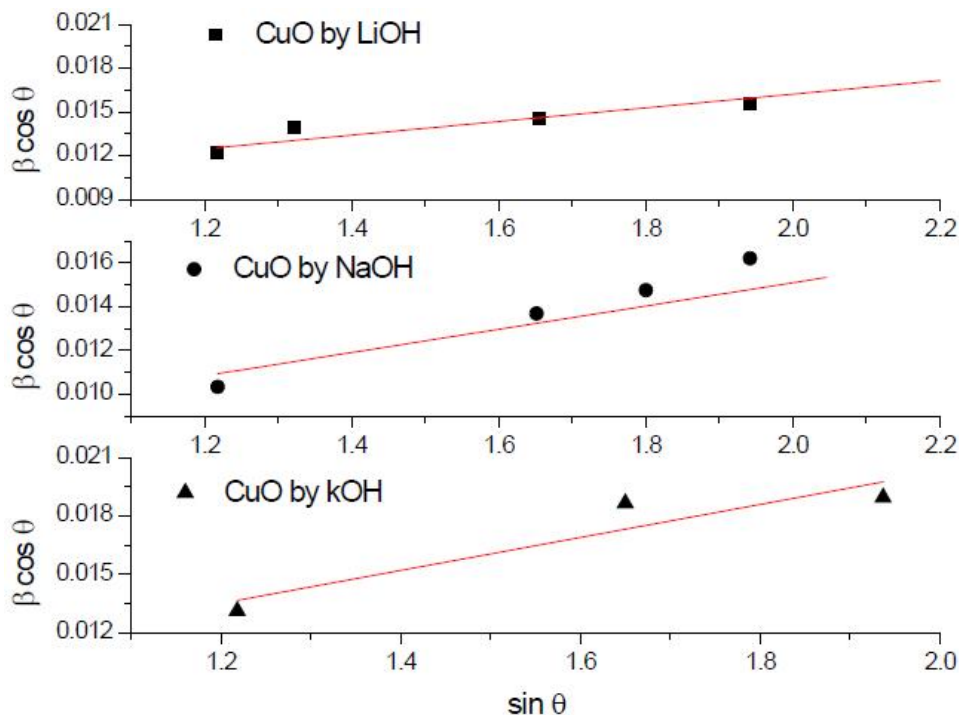


Figure 2: Plot of $\beta_{hkl} \cos \theta$ vs. $\sin \theta$ of the prepared CuO samples

is the full width at half maximum (FWHM) of the peak and q is the Bragg angle, In order to estimate the microstrains, one should apply the well known Williamson-Hall equation^[12]

$$\beta \cos \theta = \eta \sin \theta + \frac{k\lambda}{D}$$

Where q is the diffraction angle, k the shape factor, λ the wavelength of X-ray, η is the microstrains of the crystal lattice and D is the particle size. TABLE 1 shows the grain size and microstrains of the prepared samples estimated from Scherrer equation and Williamson-Hall plot.

Figure 2 shows the Williamson-Hall plot of the prepared CuO samples. The estimated values of both η and D , calculated from the above equation, are listed in TABLE 1. The obtained data reveal that both par-

ticule size and micro-strain increases by increasing the alkalinity of the alkali metals (Li, Na and k). TEM images of the prepared samples show in Figures 3, 4, and 5, where rod like structure is observed. In addition the TEM images shows bundles of the formed rods.

Transmission electron microscopy

The morphological surface characterization of the prepared samples were carried out by the transmission electron microscopy (TEM) equipped with the selected area electron diffraction (SAED) pattern. TEM images (Figures 3 - 5) indicate the nanostructure of CuO prepared using lithium and sodium hydroxides grown as nanorods morphology. It is clear from (figure 3) that CuO nanorods prepared by using lithium hydroxide solution were clustered to form bundle nanorods

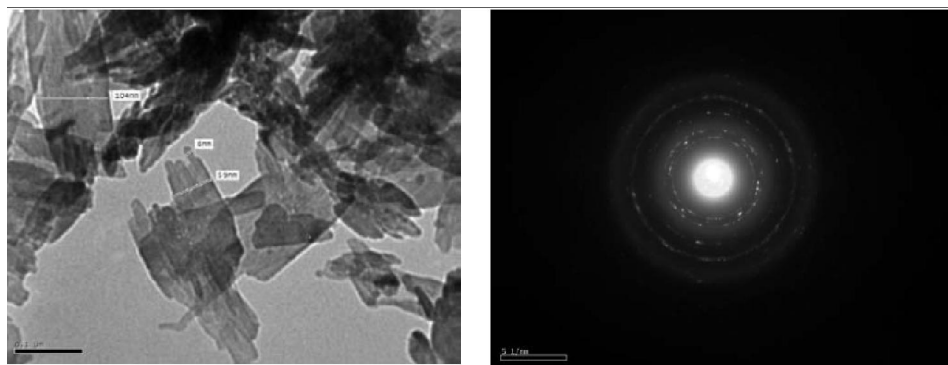


Figure 3: Transmission electron microscopy (TEM) images of CuO prepared with the use of lithium hydroxide stabilizing agent together with selected area electron diffraction pattern

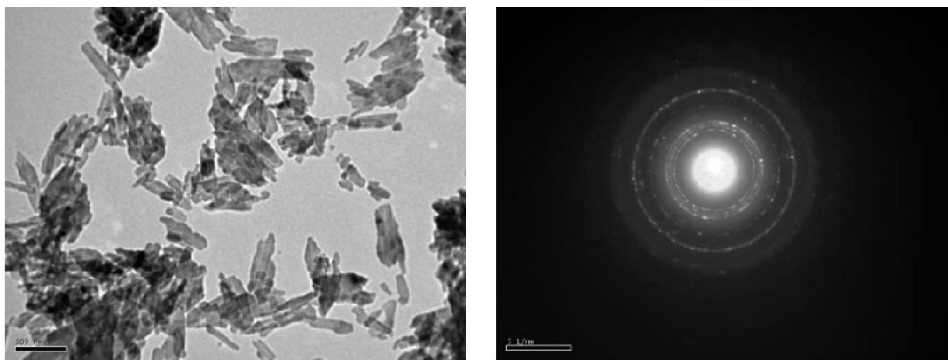


Figure 4: Transmission electron microscopy (TEM) images of CuO prepared with the use of sodium hydroxide stabilizing agent together with selected area electron diffraction pattern

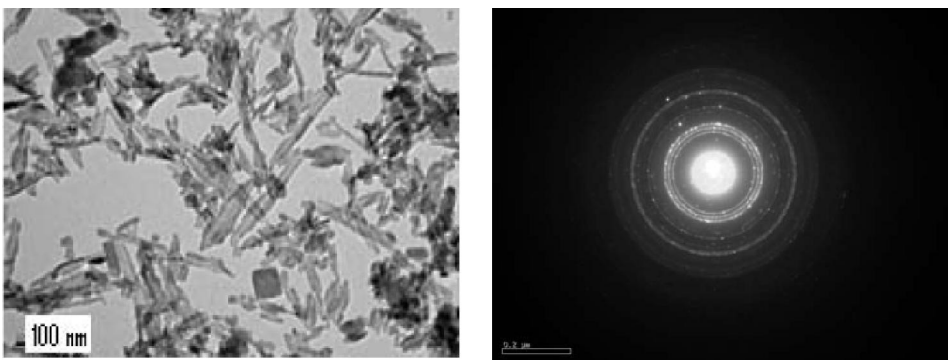


Figure 5: Transmission electron microscopy (TEM) images of CuO prepared with the use of potassium hydroxide stabilizing agent together with selected area electron diffraction pattern

with average diameter 8 nm with length ranging from 72 to 76 nm. However, the prepared sample by using NaOH solution (Figure 4) shows average 10 nm diameter and 50 - 64 nm length. Moreover, in the case of potassium hydroxide the diameter is about 5 nm length of 11 - 76 nm as shown in Figure 5. Diffraction rings based on SAED images matches with the peaks in XRD patterns which proves the monoclinic structure of the prepared CuO particles.

Optical absorption spectra

UV-Vis absorption spectra of the prepared CuO samples are analyzed and presented in (Figure 6) where the absorption peaks clearly observed at 218 nm, 220 nm and 222 nm for CuO nanostructures prepared by LiOH, NaOH, KOH respectively. A straight line is obtained for all prepared samples (Figure 7) by plotting $(\alpha h\nu)^2$ versus $h\nu$ based on the relation $\alpha h\nu = A (h\nu - E_g)^n$, where α is the absorption coefficient, A is constant (independent on ν) and n is the exponent depending on quantum selection rules for the particular

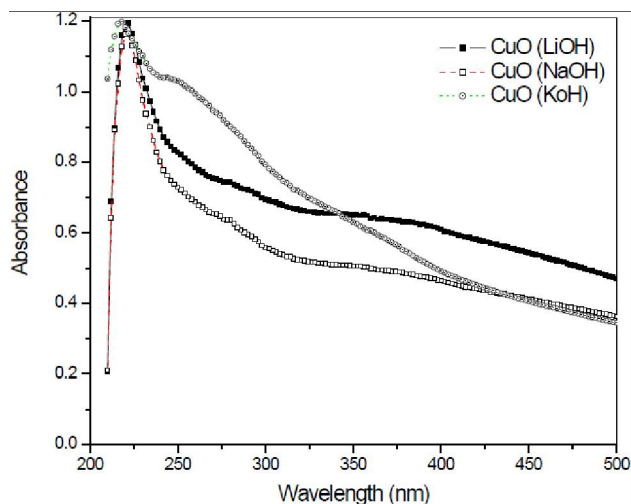


Figure 6: UV-vis absorption spectra of nanostructure CuO prepared with different stabilizing agents

material. This indicates that, the absorption edge is due to a direct allowed transition, such transitions are most probable in crystalline materials due to translation symmetry. TABLE 1 shows that the obtained band gaps of the prepared samples together with the particles size and shapes. It is clear also that the obtained band gaps are larger than the recorded value for the bulk CuO ($E_g = 1.2$ eV)^[14] which is related to the decrease of particle size and hence the quantum confinement. The obtained E_g values are in fair agreement with the data obtained by M. L. Cohen, et.al^[13] Rakhshani^[14] and Wang^[15].

REFERENCES

- [1] R.H.J.Hannink, A.J.Hill; "Nanostructure control of materials 2006" Woodhead Publishing Limited, Cambridge.
- [2] R.Nagarajan, T.Alan Hatton; "Nanoparticles: Synthesis, Stabilization, Passivation, and Functionalization, ACS Symposium Series", American Chemical Society, Oxford University Press. 996 (2008).
- [3] Wang Hui, Xu Jin-Zhong, Zhu Jun-Jie, Chen Hong-Yuan; Journal of Crystal Growth, **244**, 88 (2002).
- [4] Lee Jusang, I.Gouma Pelagia; Journal of Nano-materials, **2011**, 1 (2010).
- [5] S.M.Lee, S.N.Cho, J.W.Cheon; Adv. Mater., **15**(5), 441 (2003).

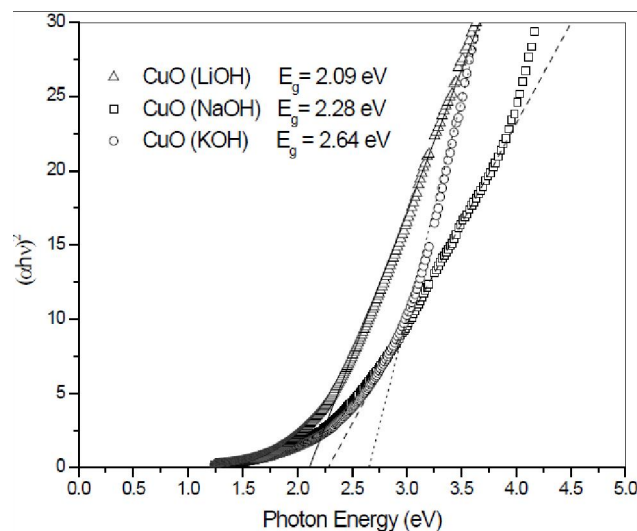


Figure 7: Tauc plot for CuO nanostructures prepared from different solutions

- [6] S.Yadav Raghvendra, C.Pandey Avinash; Physica E, **40**, 660 (2008).
- [7] O.Garcia-Martinez, R.M.Rojas, E.Vila, J.L.Martin de Vidales; Solid State Ionics, **63**, 442 (1993).
- [8] J.Langford, D.Louer; J. Appl. Crystallogr., **24**, 149 (1991).
- [9] Jenna Pike, Chan Siu-Wai, Zhang Feng, Wang Xian-qin, Hanson Jonathan; Applied Catalysis A: General, **303**, 273 (2006).
- [10] Zhou Kebin, Wang Ruipu, Xu Boqing, Yadong Li; Nanotechnology, **17**, 3939 (2006).
- [11] Yang Zeheng, Xu Jun, Zhang Weixin, Liu Anping, Tang Shupe; Journal of Solid State Chemistry, **180**, 1390 (2007).
- [12] V.D.Mote, Y.Purushotham, B.N.Dole; Journal of Theoretical and Applied Physics, **6**(6), 1 (2012).
- [13] M.L.Cohen, J.R.Chelikowsky; Electronic Structure and Optical Properties of Semiconductors, Springer-Verlag (1989).
- [14] A.E.Rakhshani; Solid-State Electron, **29**, 7 (1986).
- [15] Wang Hui; Journal of Crystal Growth, **244**, 88 (2002).