Optical Properties of Nanostructure CuO Prepared by Different Stabilizing Agents

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The effect of using different stabilizing agents for the synthesis of CuO nanocrystals on the morphological structure was studied. Spec grad CuCl₂ and three different stabilizing agents LiOH, NaOH and kOH were used as starting materials. X-ray powder diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and UV-Visible absorption spectroscopy were used for characterizing the obtained powder samples. Surface morphologies of the obtained nanorods were found to depend on the used stabilizer. The breadth and length of the obtained nanorods were 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.

1. 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 morphologies 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 an indirect band gap of ~1.2 eV with interesting electrochemical, 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 morphologies of nanocrystal [5,6]. In the present article different stabilizing agent were used in order to study the effect of solute additions on the properties of the produced nanoparticles. The CuO nanostructure samples were obtained using different stabilizing agents of LiOH, NaOH and kOH.

2. Experimental

2.1. CuO Nanoparticles Preparation

Three powder samples of nanocrystalline CuO were prepared by dissolving 0.07M of cupper 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).

$$CuCl_2 + 2XOH \rightarrow Cu(OH)_2 \downarrow + 2XCl$$
(1)

where (X) is Li, Na and k.

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

$$Cu(OH)_{2} \leftrightarrow Cu^{2+} + 2 (OH)^{-}$$

$$Cu^{2+} + 2 (OH)^{-} \leftrightarrow CuO + H_{2}O$$
(2)
(3)

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.

2.2. Analytical Techniques.

The structure of the prepared samples were investigated (XRD) using (Philips PW3050/60, MPSS) diffractometer, with nickel- filtered Cu-K α radiation provided with a proportional counter. A scanning speed of 2 θ /min. and a chart speed of 10mm/min. was used in all cases. 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., Ldt UV/Vis double beam spectrophotometer (T80+) was used to record the UV-Visible absorption spectra of the as-prepared particles.

Results and Discussion. X-ray Powder Diffraction

The obtained XRD spectra were given in (Figs. 1 a, b and c) for the prepared samples using aqueous solutions of lithium, sodium and potassium hydroxides respectively. The X-ray diffraction patterns show that all CuO samples are of monoclinic tenorite structure. The XRD peaks of the copper oxide are in consistent with the data of the ICSD (Inorganic Crystal Structure Database) file, reference code (01-080-0076 [7], 00-048-1548 [8]. The peaks at 20 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, **111**, 111, **202**, 020, 202, **113**, 310, 220, 311, **222** of crystalline copper oxide, respectively. Which are in good agreement with recent observations [9, 10, 11].



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

In the absence of microstrains, the grain size of powder can be determined from the Scherrer equation [6] $d = \frac{0.941\text{\AA}}{\beta \cos\theta}$ where λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the peak and θ is the Bragg angle, In order to estimate the microstrains, one should apply the well known Williamson-Hall equation [12].

$$\beta \cos \theta = 4 \varepsilon \sin \theta + \frac{k\lambda}{D}$$

where θ is the diffraction angle, k the shape factor, λ the wavelength of X-ray, ε 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 together with calculated lattice constants in nanometer and Degree of crystallinity.

Figure 2 shows the Williamson-Hall plot of the prepared CuO samples. The estimated values of both ε and D, calculated from the above equation, are listed in Table 1. The obtained data reveal that both particle 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 Fig.(3, 4, and 5), where rod like structure is observed. In addition the TEM images shows collates of the formed rods.

 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 and Degree of crystallinity.

Stabilizing agent	TEM Particle		Band	x-ray Particle size			Lattice Constants (nm)			D.O.C
	size Breadth	(nm) Length	gap (eV)	Scherrer's (nm)	Williams on-Hall	Strain	а	b	С	%
LiOH	4 – 11	72 - 76	2.09	16.7 nm	20.2041	0.00234	0.469	0.344	0.512	59
NaOH	6 - 15	50 - 64	2.28	18.02 nm	31.0067	0.00265	0.469	0.343	0.512	78
KOH	3 - 7	11 - 76	2.64	37.3 nm	41.6216	0.00424	0.467	0.343	0.512	69
0.021 0.018 0.015										
0.0	09	1 2	1 4	1.6	1.8	2.0	22	2	4	2.6
0.0	16 -	• Cu	iO by Na	aOH	1.0	2.0				2.0
0.0 S										
ලු 0.0 ^ක 0.0	10 -	•								
0.0	 21]	1.2	1.4		1.6	1.8	ı	2.0	-	2.2
0.0	18 -									
හි 0.0 ස	15 -									
0.0	12 —	1.2	l	1.4	· · · · · · · · · · · · · · · · · · ·	6		1.8		2.0
4 sin θ										

Fig. (2): Plot of $\beta_{\alpha_{kl}} \cos \theta$ vs. 4 sin θ of the prepared CuO samples.

3.2. 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 (Figs. 3 - 5) indicate the nanostructure of CuO prepared using lithium and sodium hydroxides grown as nanorods morphology. It is clear from (fig. 3) that CuO nanorods prepared by using lithium hydroxide solution were clustered to form collate nanorods with breadth ranging from 4 nm to 11 nm with length ranging from 72 to 76 nm. However, the prepared sample by using NaOH solution (Fig. 4) shows 6 - 15 nm breadth and 50 - 64 nm length. Moreover, in the case of potassium hydroxide the breadth ranging from 3 to 7 nm length of 11 - 76 nm as shown in Fig. (5). Diffraction rings based on SAED images matches with the peaks in XRD patterns which proves the monoclinic structure of the prepared CuO particles.



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



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



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

3.3. Optical absorption spectra

UV-Vis absorption spectra of the prepared CuO samples were analyzed and presented in (Fig. 6) where the absorption peaks clearly observed at 218 nm, 220 nm and 222 nm for CuO nanostructures prepared by LiOH, NaOH, KOH respectively which attributes to direct transitions according to M. L. Cohen, et.al[13]. A straight line is obtained for all prepared samples (Fig. 7) by plotting $(\alpha hv)^2$ versus hv based on the relation $\alpha hv = A(hv - E_g)^{n/2}$, where α is the absorption coefficient, A is constant (independent on v) and n is the exponent depending on quantum selection rules for the particular 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 (Eg = 1.2 eV) [14] which is related to the decrease of particle size and hence the quantum confinement. The obtained Eg values are in fair agreement with the data obtained by Rakhshani [13] and Wang [15].



Fig. (6): UV-vis absorption spectra of nanostructure CuO prepared with different stabilizing agents.



Fig. (7): Tauc plot for CuO nanostructures prepared from different solutions

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