Nanostructured CuO: Facile synthesis, optical absorption and defect dependent electrical conductivity

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ABSTRACT

Nanostructured CuO with different average crystallite sizes in the range ~11–48 nm is synthesized by thermolysis of carbonate precursor at different temperatures. Structural characterization of the samples is done using X-ray powder Diffraction and Transmission Electron Microscopy techniques. Analysis of UV–Visible absorption spectra of the samples reveal direct band gaps in the range 1.49–1.79 eV which is blue shifted in comparison with that corresponding to single crystalline CuO. DC electrical conductivity of the samples is found to increase with increase in crystallite size/decomposition temperature. The conduction mechanism is found to be defect dependent with holes associated with uncompensated Cu^{2+} vacancies being the charge carriers. A comparison of the DC electrical conductivities in vacuum and air ambience reveal that there is a decrease in the concentration of O^{2-} vacancies with increase in the decomposition temperature. X-ray photoelectron spectral studies confirm an increase in the concentration of Cu^{3+} ions in samples with higher electrical conductivity. Analysis of Raman spectra indicates a decrease in the concentration of O^{2-} vacancies with increase in the decomposition temperature confirming the proposed role of Cu^{2+} and O^{2-} vacancies in determining the electrical conductivity.

1. Introduction

Copper forms two stable oxides, viz., CuO (tenorite) and Cu_2O (cuprite) in which the cation valence states are +2 and +1 respectively [1]. In addition, a metastable oxide, Cu_4O_3 (paramelaconite) with tetragonal structure which is intermediate between the two stable oxides has also been reported [2]. Cu_2O which crystallizes with cubic symmetry is a semiconductor with a band gap of ~2.17 eV and is the most intensively studied material among the three copper oxides [3–5]. CuO has monoclinic structure and is a semiconductor with a direct band gap of ~1.2 eV [6–9]. In CuO, Cu^{2+} ions are in the $3d^9$ states with a single d hole per atom. Due to the Jahn-Teller stabilization of this well localized 3d hole, the degenerate $d_{x^2-y^2}$ and d_{z^2} orbitals of Cu^{2+} ions are displaced away from symmetry resulting in the monoclinic structure [10]. This distinguishes CuO from other transition metal monoxides such as NiO and CoO with slightly distorted cubic lattice. In CuO, each Cu^{2+} ion is coordinated with four close co-planar and two distant O^{2-} ions forming a distorted octahedron. Further, each O^{2-} ion is coordinated to four Cu^{2+} ions situated at the corners of a distorted tetrahedron [11,12].

CuO find potential application in many important fields such as sensors, solar cells, photo detectors, photocatalysts, nanofluids, field emission devices, superhydrophobic surfaces, water purification,

magnetic storage media, junction diodes, microwave dielectric materials, high temperature superconductors, p-n heterojunctions, electrochromic devices, rechargeable batteries, etc [9,13–15]. Polycrystalline samples of CuO have large value of dielectric constants (of the order of ~10^3 to 10^4) and are used in microelectronic devices such as stacked layer capacitors in Dynamic Random Access Memories (DRAMs) [16]. Further, CuO is also employed as transistor gate dielectric in complementary metal-oxide semiconductor (CMOS) field effect transistor (FET) logic devices [17]. For many of these applications, nanostructured CuO is preferred due to the large surface area to volume ratio and the possibility of tuning the optical and electrical properties. Many reports on the synthesis and properties of nanostructured CuO with different morphology and crystallite sizes have appeared in the literature and are comprehensively documented in a recent review article by Zhang et al. [9]. A perusal of the reported works on CuO in single crystalline, thin film, nanorod, nanowire, nanoparticle etc., forms leads to the inference that the synthesis routes and processing conditions significantly alter the physical and chemical properties. For instance, the optical band gap of nanostructured CuO is reported to depend on factors such as crystallite size, geometry, nonstoichiometry, etc [18,19]. Further, electrical conduction in CuO is extrinsic and both p-type and n-type conduction is possible depending on stoichiometry [9,19–22]. Most common type of defect possible in CuO is Cu^{2+} vacancies which

result in p-type behavior while an excess of O^{2-} vacancies may lead to n-type conduction [20–22].

In the present study, nanostructured CuO with different average crystallite sizes is synthesized through a facile chemical route. X-ray diffraction (XRD) analysis is used for ensuring phase purity and for estimating average crystallite size and unit cell parameters. The average particle size, particle size distribution and morphology are studied using Transmission Electron Microscopy (TEM). The absorption spectra in the UV–Visible region and temperature dependent DC electrical conductivity of the samples in vacuum and air ambience are studied in detail. X-ray photoelectron spectroscopy (XPS) and Raman analysis are employed for establishing the role of defects in determining the observed electrical conductivity.

2. Experimental

2.1. Synthesis of nanostructured CuO

Nanostructured CuO was synthesized through a two step process. In the first step, copper carbonate precursor was synthesized through a controlled chemical precipitation route using copper (II) nitrate $((CuNO_3)_2 \cdot 3H_2O)$ and ammonium carbonate $((NH_4)_2CO_3)$ as the starting materials. Ethylenedinitrilotetraacetic acid disodium salt dihydrate, EDTA ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$) was used as the stabilizer. All the chemicals used were of analytical (AR) grade and were used without further purification.

In a typical experiment, 20 ml of 0.3 M aqueous solution of $(CuNO_3)_2 \cdot 3H_2O$ and 20 ml of 0.2 M aqueous solution of $(NH_4)_2CO_3$ were simultaneously dropped at a slow rate into a beaker containing 140 ml of distilled water and 20 ml of 0.01 M aqueous solution of EDTA which was kept vigorously stirred using a magnetic stirrer. The reaction yielded copper (ll) carbonate hydroxide $(2CuCO_3Cu(OH)_2)$ as a blue precipitate. The reaction was carried out at room temperature and can be summarised as,

$3Cu \ (NO_3)_2 \cdot 3H_2O + 2(NH_4)_2CO_3 \rightarrow 2CuCO_3Cu(OH)_2 + 4NH_4NO_3 + 2HNO_3 + H_2O$
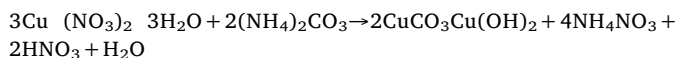
In order to understand the decomposition scheme of the carbonate precursor, Thermo Gravimetric Analysis (TGA) was carried out in a METTELER TOLEDO S R system in the range 50–700 °C (heating rate 5 °C/min) in air ambience. Result of TGA analysis is shown in Fig. 1(a). The rate of weight loss is very small at temperatures less than 210 °C. In the temperature range ~210–340 °C, 28.85% weight loss occurs with the maximum being at ~297 °C. No considerable weight loss is observed above 340 °C. From this observation it was inferred that the decomposition of the copper carbonate precursor occurs at temperatures greater than 210 °C. In the present work, the decomposition of the carbonate precursor was done at five different temperatures, viz., 250(C1), 300(C2), 400(C3), 500(C4) and 600 °C (C5) for two hours each. Sample codes which are given in brackets will be used for referring to the samples in the discussion of the results.

2.2. Characterization of nanostructured CuO

XRD pattern of the samples were recorded in the range $2\theta = 10$–$70°$ using a Philips X′pert PRO diffractometer with Cu Kα source ($\lambda = 1.54056$ Å). A JEOL 3010 High Resolution Transmission Electron Microscope (TEM) was employed for the Transmission Electron Microscopic analysis. The UV–Visible absorption spectra of the samples were recorded in a Shimadzu UV-2450 spectrophotometer in the range 200–800 nm with a step size of 0.1 nm. For the absorption measurements, the nanostructured samples were dispersed in distilled water using an ultrasonic bath.

DC electrical conductivity of the samples were measured under two different conditions – viz., (i) in vacuum (0.014 mbar) and (ii) in air

ambience, as a comparison of the conductivity values under two different atmospheres could reveal information regarding the conduction mechanism in the case of nanostructured transition metal oxides.

For conductivity measurements samples were consolidated in the form of cylindrical pellets having a diameter of 13 mm and thickness of about 1 mm by applying a uniform force of four tons for three minutes using a hydraulic press. Pelletization of all the samples was done under identical conditions. Conducting silver epoxy was painted on the circular faces of the pellets to ensure good electrical contact. The pellets were first air dried for twenty minutes and then dried at 40 °C for half an hour in a hot air oven. Electrical measurements in vacuum (0.014 mbar) as well as in air ambience were performed in a dielectric cell with provisions for evacuation, temperature measurement and control. Each pellet was heated to 413 K and then allowed to cool to 313 K and electrical measurements were done during cooling at 10 K intervals. The temperature of the pellet was maintained with an accuracy of ± 1 K during measurements. Electrical measurements were done using a KEITHLEY 2400 Source Meter. Voltage, V in the range 0–20 V was sourced and current, I was measured. The resistance of the samples were estimated from the slope of the linear V-I curve. DC electrical conductivity measurements of the samples in air ambience over the same temperature range were also done following the same procedure.

X-ray photoelectron spectra (XPS) of two representative samples, viz., C1 and C4 were recorded using a PHOIBOS HSA 3500 150 R6 X-ray photoelectron spectrometer using Al Kα source (1486.6 eV). Survey scan spectra were recorded in the range 1–1200 eV. Cu 2p and O 1s XPS measurements were carried out in the ranges 890–1024 eV and 526–536 eV respectively. Raman spectra of the samples in the range 50–1000 cm^{-1} were recorded using a Labram HR 800 micro Raman spectrometer employing 784 nm diode laser source.

3. Results and discussions

3.1. XRD analysis

The XRD patterns of the samples decomposed at different temperatures are shown in Fig. 1(b). In the case of each sample, all the peaks can be indexed with JCPDS-ICDD pattern no. 45-0937 corresponding to CuO with monoclinic structure. No peak corresponding to Cu_2O or Cu_4O_3 is present. This is in agreement with previous reports that only at very high temperatures, > 1000 °C, CuO gives off oxygen and transform into Cu_2O, and/or Cu_4O_3 [23,24]. Thus the scheme of the decomposition of carbonate precursor into CuO can be expressed as,

$2CuCO_3Cu(OH)_2 \rightarrow 3CuO + 2CO_2 + H_2O$
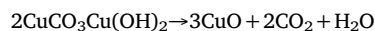
From Fig. 1(b), it is clear that the peaks in the XRD pattern of sample C1 are much broadened indicating smaller crystallite size. Also, with increase in the decomposition temperature, the peaks become narrower indicating an increase in the crystallite size. Crystallite sizes of the samples are estimated from the line broadening of the XRD peaks corrected for instrumental broadening using Scherrer equation, $t = k\lambda/\beta \cos \theta$ where t is the average crystallite size, k is a constant lying between 0.95 and 1.15, λ is the wavelength of X-rays used (1.54056 Å), β is the full width at half maximum (FWHM) of each peak and θ is the diffraction angle [25]. The average crystallite sizes of samples are estimated from nine diffraction peaks for each sample. The average crystallite size of the samples C1, C2, C3, C4 and C5 are ~11 ± 2, ~14 ± 4, ~19 ± 4, ~38 ± 7 and ~48 ± 9 nm respectively. The errors mentioned are the standard deviations among the values estimated from the nine characteristic diffraction peaks for each sample and hence is a measure of shape anisotropy. Thus from the XRD analysis, it can be concluded that the decomposition of carbonate precursor in the temperature range 250–600 °C results in the synthesis of phase pure nanostructured CuO samples with average crystallite size in the range ~11–48 nm.