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Effect of Doping with Carbon Nanotubes on Structural and Optical Properties of Nanostructured Zinc Oxide Thin Films

This research aims to study the effect of doping with carbon nanotubes on the structural and optical properties of zinc oxide films. Nanocomposite films of carbon nanotubes (ZnO:CNTs) with different weight ratios were produced using a vacuum deposition method on glass substrates. The structural, morphological and optical characteristics of the prepared thin films were studied. The prepared ZnO:CNT thin films showed polycrystalline structures with different CNT concentrations. The dominant orientation of these thin films produced in the hexagonal phase is (002). For pure ZnO thin films and ZnO thin films doped with 7% CNT, the typical crystallite sizes are 18.98 nm and 26.86 nm, respectively. As for the optical properties, it was observed that there was a decrease in the energy gap values when grafting with carbon nanotubes.

Keywords: Zinc oxide; Optical properties; Carbon nanotubes; Nanocomposite
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1. Introduction

Due to their uses in solar cells [1], light-emitting diodes [2], photodetectors [3], gas sensing, and corrosion protection [4], semiconducting thin films have garnered a lot of attention. The remarkable applications of zinc oxide (ZnO) in various disciplines, including electronics and optics, have generated a lot of attention [5]. Consequently, to achieve greater absorption of input photon energy and unique optical qualities, many researchers have focused their attention and work on the structure of zinc oxide at the micro- and nano-scale. It is well-known that zinc oxide has an energy gap of 3.37 eV and shows negative conductivity, so it can be used in the manufacture of transparent electronic devices, optoelectronic devices, and sensors [6]. The importance of mixing zinc oxide with another material helps in obtaining better magnetic, electrical, and optical properties for the devices [7-10]. Introducing carbon nanofibers (CNTs) into zinc oxide structure provides an easy route to produce a modified energy gap that can be used in UV detectors and light-emitting diodes [11-13].

In this research, thin films were prepared using the vacuum evaporation deposition technique on a glass substrate. Zinc oxide and carbon nanotubes (ZnO: CNT) are combined to produce thin films with varying weight percentages of CNT (0, 7 wt.%) of the produced powders. This study also presents the effects of CNTs concentration on the optical, morphological, and structural properties of thin films prepared from the produced compounds.

2. Experimental Work

Powders of zinc (Zn) and carbon nanotubes (CNTs) with a high degree of purity were used in this work, and CNTs were used as an additive in proportions (0, 7 wt.%) of the mixture. After adding the CNTs to the zinc, the ingredients are mixed in an agate grinder for 30 minutes. The mixture is then placed in a cylindrical steel mold with a diameter of 1 cm and pressed for 5 minutes at a pressure of 8 tons/cm^2. Undoped and CNTs-doped zinc samples were deposited on glass substrates located on the sample holder inside the vacuum evaporation chamber. After that, the materials were heated in a tungsten boat under a pressure of about 5x10^{-5} bar, and the films were extracted after deposition and then placed in a thermal oxidation furnace at a temperature of 400°C for 30 minutes to obtain undoped ZnO films as well as CNTs-doped ZnO films. The prepared samples were characterized using UV-visible spectrophotometry, x-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM).

3. Results and Discussion

The structures of undoped and CNTs-doped ZnO thin films were examined using XRD analysis using 1.5406Å x-ray source and scanning range from 7° to 80°. The characteristic peaks of undoped ZnO appeared in the crystallographic directions (100), (002), (101), (110), (103), (112), and (004) with an average crystallite size of 18.98 nm, while it was 26.86 nm for the CNTs-doped ZnO films as the distinctive peaks of ZnO were clearly observed [14,15]. As can be seen in Fig. (1), these results match the COD ID: 00-230-0450 [16]. Some results are indicated in table (1).

No distinct diffraction peaks corresponding to CNTs were observed at $2\theta \approx 26°$, 45°, and 54° because of the low concentration of CNTs in the tested samples [12,17,18]. The typical XRD patterns for the undoped and CNTs-doped ZnO films confirm the wurtzite phase. The decrease in the full-width at half maximum (FWHM) of the diffraction peaks indicates an increase in the crystallite size from 18.98 to 26.86 nm for the ZnO:0.07% CNTs thin films, as calculated from the Debye-Scherrer's formula. This doping level has increased the surface area due to the formation of a thin layer of ZnO around the CNTs, as shown by SEM images. The formation of this thin layer with application of oxidation temperature led to an increase in the crystalline arrangement of the ZnO material. These factors has resulted in an increase in the intensity of ZnO peaks in the XRD pattern. Figure (2) displays the SEM images of the prepared thin films, as the formation of porous films is shown.

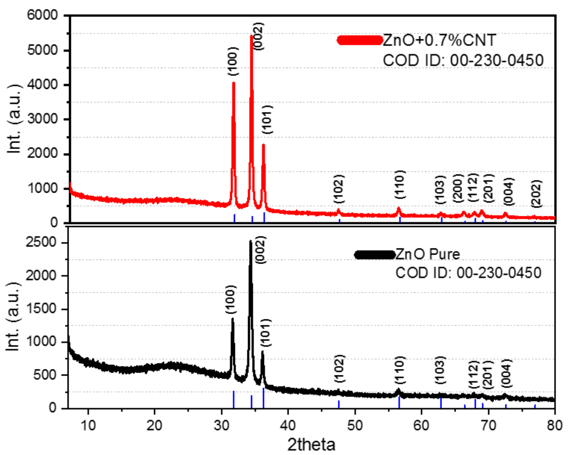
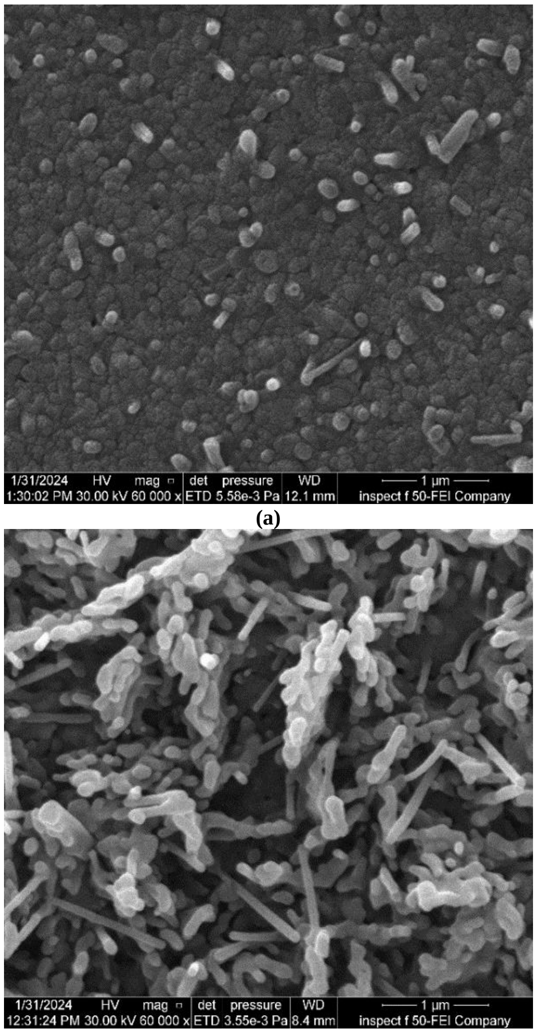


Fig (1) XRD patterns of undoped ZnO film and ZnO doped with 7 wt.% CNTs film sample

Table (1) Some X-ray diffraction parameters

Sample	2θ (deg)	FWHM (deg)	Crystallite Size (Å)
Undoped ZnO	31.6241	0.2972	277
	34.3115	0.1956	425
	36.0946	0.3742	223
	56.4660	0.6974	129
	65.6816	2.5176	37
	68.2971	2.8281	33
	72.4403	0.6791	144
7 wt.% CNTs-doped ZnO	31.6487	0.212	442
	34.2907	0.2779	297
	36.0818	0.3133	297
	47.3823	0.3048	313
	56.4126	0.3627	189
	62.7148	1.5339	34
	66.1883	0.7268	80
	67.740	0.4763	192
	68.9017	0.5493	122
	72.4199	0.7621	77
	76.7142	0.1821	386

It is possible to compare the increased porosity of ZnO thin films doped with 7 wt.% CNTs with the lower aggregation seen in undoped ZnO thin films. This illustrates how the ZnO has totally encased the CNTs particles. The lower aggregation in the doped thin film is ascribed to the fact that CNTs prevent ZnO nanoparticles from aggregation. This result is in good agreement with the findings of other work [19]. Figure (3) shows the AFM analysis of undoped and doped ZnO thin films, and the 3D images show distinct vertical hierarchical particles with the films. It is observed that the ZnO layer has a surface roughness of 15.88 nm, which could be due to minimal material aggregation. The surface roughness increases by 120.3 nm (root mean square value) after doping.



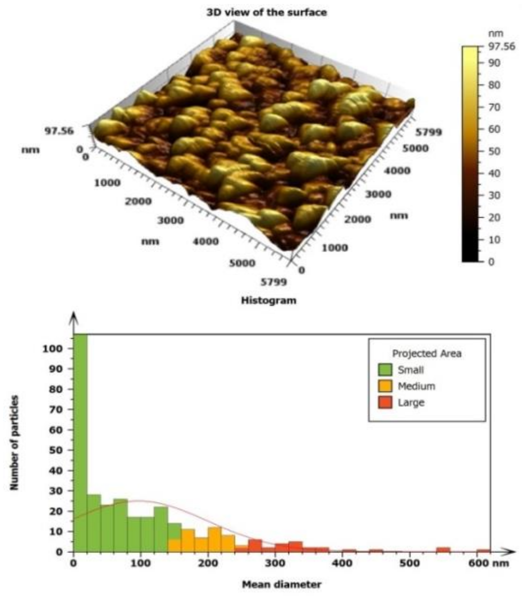
(a)

(b)

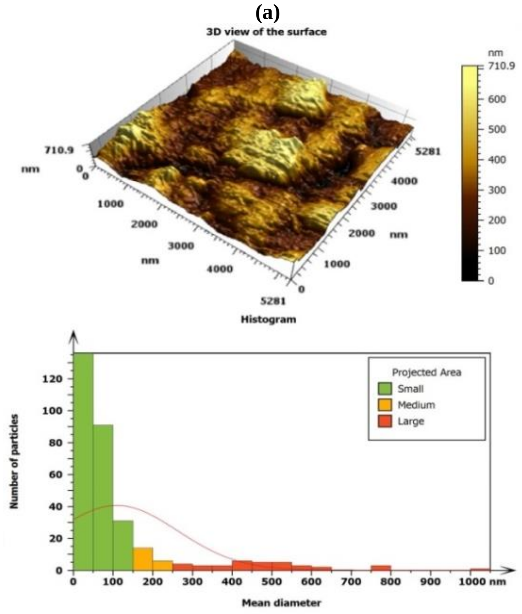
Fig. (2) SEM images of (a) undoped ZnO film, and (b) ZnO doped with 7 wt.% CNTs film sample

The SEM and 3D AFM results show that the surface layer of ZnO completely envelops the CNTs and is almost uniformly distributed over the surface.

Figure (4) shows the UV-visible absorption spectra of undoped and CNTs-doped ZnO films. It can be noted that the optical energy gap of the undoped ZnO film is 3.25 eV at 386.8 nm wavelength, while the optical energy gap of the ZnO doped with 7 wt.% CNTs is 3.18 eV at 397.58 nm. This is due to the increased absorption of incident photons and their ability to excite electrons from the valence band to the conduction band.



(a)



(b)

Fig. (3) AFM results of (a) undoped ZnO film, and (b) ZnO doped with 7 wt.% CNTs film sample

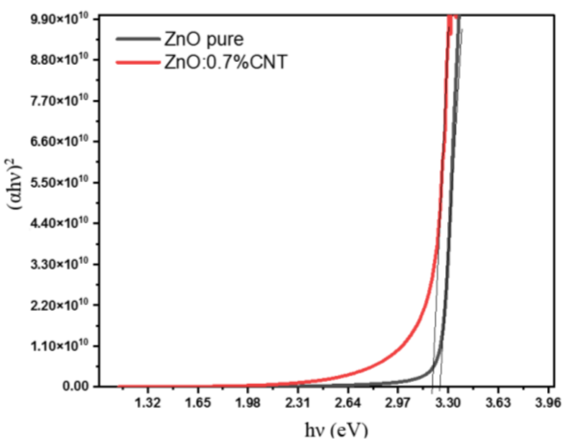


Fig. (4) Determination of optical energy gap values for undoped ZnO film and ZnO film doped with 7 wt.% CNTs

4. Conclusions

In summary, this study provides valuable insights into ZnO thin films doped with carbon nanotubes. It has been observed that increasing the doping ratio of CNTs enhances the adsorption of the prepared films, which serves their applications. Increasing the doping level to 7 wt.% results in a decrease in the energy gap. In addition, as the doping causes a disturbance in the original crystal form of the material. The results also showed that the doping had a clear effect on the characteristics of the hosting nanoparticles.

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