



## Structural, optical and morphological properties of ZnO/MWCNTs nanocomposite photoanodes for Dye Sensitized Solar Cell (DSSC) Application

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### ABSTRACT

Zinc Oxide (ZnO) and ZnO/ multiwalled carbon nanotubes (MWCNTs) nanocomposites were prepared by direct blending procedure. The pure ZnO and ZnO/MWCNTs nanocomposite films were coated on Indium Tin Oxide (ITO) coated glass substrate by doctor blade method followed by annealing. The MWCNTs were functionalized by mixed acid treatment before incorporation into ZnO matrix and the presence of the carboxylic group was confirmed by Fourier Transform Infrared Spectra (FTIR). Electrical properties of these films were investigated by means of Current-Voltage (I-V) characteristics. Structural, Morphological and optical properties of the nanocomposite films were examined by means of X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FE-SEM) and UV-Vis spectroscopy respectively. The incorporation of functionalized MWCNTs (f-MWCNTs) in ZnO matrix provides better separation of ZnO particles and hence prevents aggregation. SEM analysis confirms the increase in porosity of the ZnO films after incorporation of MWCNTs which enhances the absorption of light in photoanode of solar cells. It makes these films a better candidate for use as working electrode for Dye Sensitized Solar Cells (DSSCs).

**Keywords:** ZnO, ZnO/MWCNTs, Nanocomposites, DSSC, Photoanode

### INTRODUCTION

The exhaustion of accessible fossil fuels and incessantly rising global energy demands; seek for alternative energy sources, predominantly renewable solar energy, has turned out to be very important.<sup>1</sup> As photovoltaic devices offer clean energy that is proficient to lessen global dependence on conventional energy sources.<sup>2</sup> Since major breakthroughs in 1991, dye-sensitized solar cells (DSSCs) have acquired more and more research attention over the past two decades and penetrated public sight.<sup>3</sup> Dye-sensitized solar cells are a promising low-cost solar device, which has been intensively studied and a potential alternative to conventional solid state devices.<sup>4-9</sup> Though a typical DSSC device uses nanocrystalline TiO<sub>2</sub> as a photoanode material but decent performance of this device with another wide band gap metal oxide semiconductors, for instance ZnO and Nb<sub>2</sub>O<sub>5</sub>

prepared as porous electrodes have also exhibited in the similar manner.<sup>10-12</sup> Due to higher electronic mobility (more favorable for the collection of photoinduced electrons) and identical conduction band energy levels, Zinc Oxide (ZnO) is a potential alternative to TiO<sub>2</sub>. In addition, the relative ease of manufacturing extremely crystalline ZnO with a range of morphologies, it has been used more than TiO<sub>2</sub> in DSSCs.<sup>13-15</sup>

Carbon nanomaterials such as fullerenes, graphene and carbon nanotubes are presently being intensively studied in solar cell purposes due to their huge surface area, exclusive electrical properties, amazing chemical and mechanical constancy.<sup>16-18</sup> Electron transport in the semiconducting nanostructured film and enhancement in light absorption can be increased by incorporating carbon nanomaterials into the matrix of the photoanode material. Particularly, one dimensional (1D) carbon nanotubes have large metallic conductivity similar to metals and display huge electron-storage capacity such as one electron for every 32 carbon atoms.<sup>19,20</sup>

In this study, films of ZnO and ZnO/MWCNTs nanocomposite were prepared by using direct blending procedure and coated on Indium Tin Oxide (ITO) coated glass substrate by doctor blade method. These films were then characterized by various techniques meant for their use in DSSCs working electrode material.

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## EXPERIMENTAL DETAILS

Zinc Oxide (Himedia, India), multi walled carbon nanotube (>95%) (Sigma Aldrich, USA), Polyethylene glycol (PEG<sub>20000</sub>) was purchased from Himedia (India) and Indium Tin Oxide (ITO) coated glass (15 Ω/sq) was taken as a substrate material. Throughout the experiments de-ionized water was used and all the chemicals were used with no further purification. First of all, ITO substrate was cleaned with acetone, ethanol and de-ionized water respectively for 30 minutes in an ultrasonic bath. Then the working region of the substrate was defined by means of Scotch tape. The MWCNTs were functionalized by acid treatment method.<sup>19</sup>

ZnO nanopowder and PEG<sub>20000</sub> (to avoid aggregation) were grounded in a mortar using de-ionized water for one and half hour to attain a thick and sticky paste. This paste was coated on ITO coated glass substrate by doctor-blade method to obtain ZnO film. Another paste having 0.3 wt% of functionalized MWCNTs (f-MWCNTs), ZnO, PEG<sub>20000</sub> and de-ionized water was also prepared and coated on the ITO in the same manner to get ZnO/MWCNTs nanocomposite film. After drying at room temperature, films were gradually annealed at 450 °C in a furnace to improve the crystallinity of these films and removal of organic substances present in the paste. These films were found to be 8 μm thick as measured by digital micrometer screw gauge having least count 1 μm. The crystal phases of these films were recorded by X-ray diffraction using Rigaku (Miniflux-II diffractometer) with Cu Kα radiation in 2θ range 20–60 ° at room temperature at 2 °/min scanning rate. The absorption spectra of these films were recorded by means of Varian UV-Vis spectrophotometer (Cary 5000). The morphological studies of the films were revealed by FESEM using TESCAN (MIRA II LMH). The current- voltage (I-V) measurement of these films was recorded with a semiconductor device analyzer from Agilent Technologies (Model B1500A).

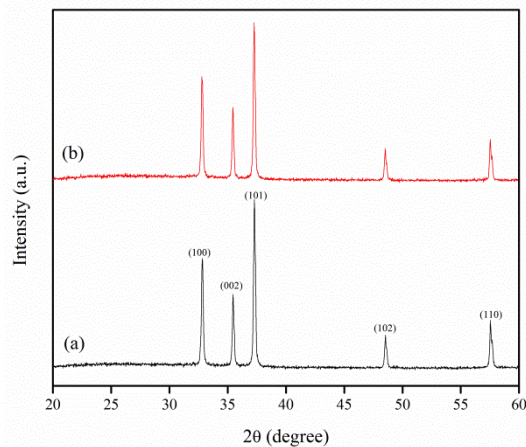
## RESULTS AND DISCUSSION

### 3.2 Structural Analysis

The XRD patterns of ZnO and ZnO/MWCNTs nanocomposite films coated on simple glass substrates are shown in Figure 1. On comparisons of these two spectra; it is found that there is no visible change in the shape and position of peaks but a slight increase in peak intensity in case of nanocomposite film. Five orientation peaks are observed for both the films at 2θ = 32.7°, 35.4°, 37.2°, 48.5° and 57.5° corresponding to (100), (002), (101), (102) and (110) planes of ZnO.<sup>7</sup> Though, the typical peak of MWCNTs around 2θ = 26.3° is not observed in the XRD spectra of ZnO/MWCNTs film. It may be due to very low concentration (0.3 wt %) of MWCNTs present in the nanocomposite film which is incapable to produce noticeable peaks for MWCNTs. No additional peak related to impurity is identified in the spectrum.

The mean crystallite size for these films is calculated by means of Debye-Scherrer equation as:

$$D = 0.9 \lambda / \beta \cos \theta$$



**Figure 1.** XRD spectra of (a) ZnO film (b) ZnO/MWCNTs nanocomposite film

Where, D is the mean crystallite size, λ be the wavelength of CuKα line, β represents FWHM (full width at half maximum) of the peak and θ stands for Bragg angle. The mean crystallite size for these films are given in the Table 1

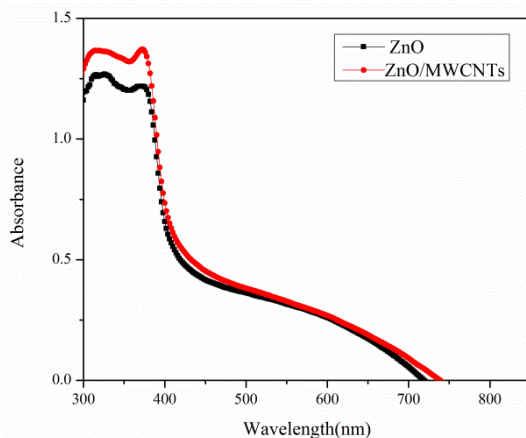
**Table 1.** Mean Crystallite size (D) for ZnO and ZnO/MWCNTs film

Sample film	D (nm)
ZnO	56.40
ZnO/MWCNTs	56.51

It can be seen from above table that the mean crystallite size is increased slightly in case of ZnO/MWCNTs nanocomposite film as compared to pure ZnO film.

### 3.2 Optical studies

UV-Visible Absorption spectra of the ZnO and nanocomposite films are revealed in Figure 2.



**Figure 2** UV-Visible absorption spectrum of ZnO and ZnO/MWCNTs nanocomposite films

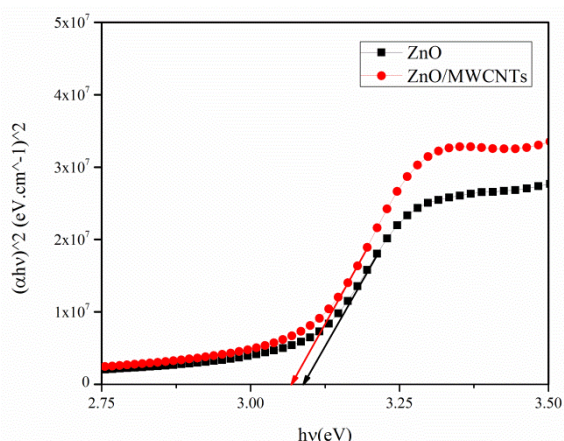
It can be concluded clearly from the absorption spectra that nanocomposite films have higher absorption in UV-region as compared to the pure ZnO film. The absorption in case of nanocomposite film is found to 8.66% more than ZnO film. Hence it indicated the more dye absorption characteristic of

the nanocomposite film which proves these films a potential candidate for DSSCs application.

The optical band gap for both the films is calculated using Tauc plot as shown in Figure 3. As the optical absorption edge is investigated by the following relation

$$\alpha h\nu = B (h\nu - E_g)^m$$

where  $\alpha$  represents the optical absorbance,  $B$  is a constant,  $E_g$  stands for optical band gap and  $m$  has the value  $\frac{1}{2}$  and  $2$  for direct and indirect transitions respectively.<sup>21</sup> It is observed that the plot of  $(\alpha h\nu)^2$  versus  $h\nu$  is linear designating direct type of transitions for both films. The band gap is calculated by extrapolating the linear portion of the curve to the energy axis. The band gap values for these films are shown in table 2.



**Figure 3** Tauc plot for ZnO and ZnO/MWCNTs nanocomposite films

**Table 2.** Effect on band gap values with MWCNTs incorporation into ZnO

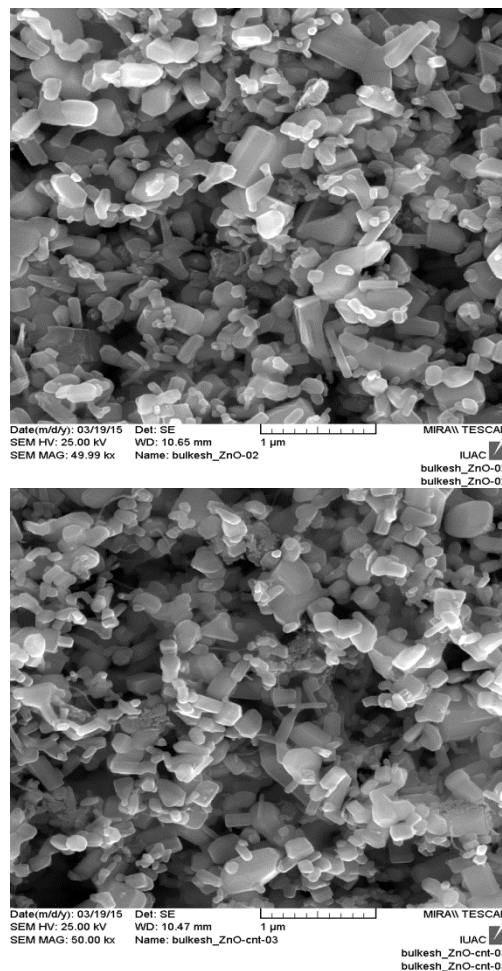
Sample film	Band Gap (eV)
ZnO	3.10
ZnO/MWCNTs	3.07

The incorporation of MWCNTs in ZnO leads to decrease in the band gap from 3.10 eV to 3.07 eV. It broadens the absorption range towards high wavelength region. Figure 2 also show an increase in absorption range from 400 nm to 410 nm which enhances the performance of solar cell due to relatively higher photon to electron conversion efficiency.

### 3.3 Morphological properties

The FE-SEM micrograph of ZnO and ZnO/MWCNTs are shown in Figure 4.

It can be seen from figure 4 micrograph that f-MWCNTs are entrenched in the ZnO nanoparticle arrangement. It is eminent that the exterior of ZnO nanoparticles particles have a lot of hydroxyl groups which strongly interact with the carboxylic groups attached on f-MWCNTs surface lead to better dispersion of MWCNTs.<sup>7</sup> Furthermore ZnO/MWCNTs nanocomposite film possesses more porous structure than pure ZnO film. The porous character of the film supports its use in DSSCs due to large specific area (1000 times more than bulk) available for dye adsorption as

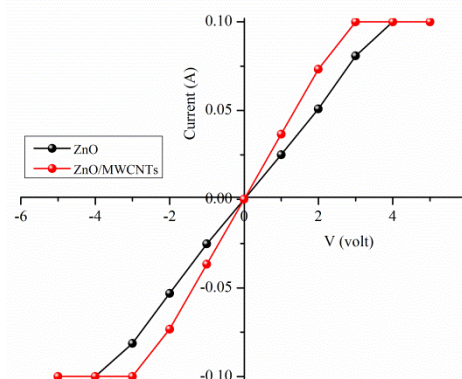


**Figure 4** FE-SEM images of (a) ZnO film (b) ZnO/MWCNTs nanocomposite film

well as electrolyte diffusion.<sup>22</sup>

### 3.5 I-V Characteristics of films

The measured I-V characteristics in -5 V to +5 V sweeps of the films under UV-illumination are shown in Figure 5.



**Figure 5** I-V curves of ZnO and ZnO/MWCNTs nanocomposite films

The non-linear behavior in the I-V curves were observed for ZnO and ZnO/MWCNTs nanocomposite films. The current at a given voltage is higher for the ZnO/MWCNTs

nanocomposite film under UV-illumination than that of pure ZnO film. This shows that the production of electron-hole pairs is more in the nanocomposite film as compared to ZnO film.<sup>23</sup> The effect of the light on the films indicates that the nanocomposite film are more favorable to be used as electrode materials in DSSCs than pure ZnO films.

## CONCLUSION

ZnO and ZnO/MWCNTs nanocomposite films were successfully prepared through direct blending method and the crystallite size of ZnO/MWCNTs nanocomposite film was found to be slightly increased. It is observed that structural and optical properties of nanocomposite film were enhanced by means of MWCNTs inclusion in ZnO matrix. SEM analysis revealed that ZnO/MWCNTs film was highly porous as compared to pure ZnO film so it is favorable for more dye adsorption and the MWCNTs were uniformly distributed. Also f-MWCNTs having -COOH terminal groups could improve the solar electron compilation owing to better interconnection between ZnO nanoparticles and functionalized MWCNTs. The I-V measurements were also in support that more current is generated in nanocomposite film than pure ZnO film under UV-illumination. These outcomes concluded that efficiency of DSSCs can be enhanced considerably via MWCNTs inclusion in ZnO matrix as compared to pure ZnO nanoparticles film photoanodes.

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