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ORIGINAL ARTICLE

Influence of Polyethylene Glycol (PEG) Surfactant on the Properties of Molybdenum-Doped Zinc Oxide Films

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ABSTRACT

In this work, the effect of dopant (molybdenum) concentration on the structural, morphological, elemental, and optical properties of surfactant (PEG)-assisted Mo-doped ZnO thin film which were synthesized using hydrothermal method were studied. The XRD and EDS characterizations showed separate and prominent peak stands for Mo which not observed in the control sample (undoped ZnO). The optical properties of the films, such as absorbance, transmittance, reflectance, and band gaps energy were determined by UV-Vis spectrophotometer. The samples recorded average absorbance in the visible region, which reduced towards the near-infrared region; with the 0.5 M sample recording the best absorbance property. Higher reflectance values were observed for PEG-assisted Mo-ZnO samples as compared with the undoped ZnO. As the concentration of the dopant (Mo) increases, the band gap energy of the PEG-assisted Mo-doped ZnO thin films decreases. The synthesized samples find potential application in solar cells and photovoltaic devices.

1 Introduction

Nanostructured materials have attracted considerable attention in fabricating nano-devices for several applications because of their unique properties. Nanomaterials have unique electrical, mechanical, chemical, and optical properties as a result of surface and quantum confinement effects occurs during size reduction [1]–[3].

Several studies have been reported on the synthesis and application of metal oxides such as TiO_2, SnO_2, ZnO, Co_3O_4, V_2O_5, NiO, and so on [4]–[7]. Recently, many researchers are interested in nanostructured ZnO materials because of their outstanding performance in the area of optoelectronics and photonics. Zinc oxide is a semiconductor with wide band gap energy (3.37 eV) and high exciton binding energy (60 meV) at ambient temperature. These properties make ZnO a potential candidate as photocatalyst, sensors, electrocatalysts, transducers [7]–[9], and for optoelectronic applications [10]–[12].

Different morphologies of nanostructured ZnO materials like nanorods, thin films, nanotubes, wires, hierarchical nanobranches, and nanocastles can be obtained using variety of synthesis techniques like chemical vapor deposition (CVD),

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sol-gel method, electrochemistry, thermal oxidation, and hydrothermal treatment [9], [13]. Among these synthesis strategies, hydrothermal technique is the easiest and most cost-effective routes to synthesis nanostructured ZnO in different morphologies. Zinc oxide (ZnO) contains specific energy levels that bring about various optical characteristics [14]. Visible light passes through zinc oxide (ZnO), and doping can boost its electrical or optical properties.

Doping is an efficient and simple means of altering the optical properties of the parent materials. Also doping will broaden the range of the base materials application. Doping is the process of adding a dopant to a semiconductor that leads to a shift in the Fermi levels [15], [16]. The Mo-doped ZnO thin films received much attention due to its low cost, non-toxic, highly transparent, and outstanding optoelectronic properties. Numerous research teams have developed ZnO thin films doped with different materials through different synthesis techniques, such as pulsed laser deposition, chemical vapor deposition, magnetron sputtering, hydrothermal, and sol-gel method techniques [17], [18].

Surfactants have molecular structure with two separate functional groups with different affinities inside the same molecule to demonstrate these two physical capabilities [18], [19]. Some examples of common surfactants such as Cetrimonium bromide (CTAB), Polyethylene glycol (PEG), Sodium dodecyl sulphate (SDS), Polyvinyl alcohol (PVA) and Polyvinyl pyrrolidone (PVP) [20]–[23].

The surfactants play an important role in nanoparticle synthesis by preventing aggregation of the synthesized nanoparticles and providing more stability in colloidal systems [23]. PEG is known to be non-poisonous, biodegradable, and can be chemically modified [24].

Liufu, Xiao, and Li investigated PEG adsorption on the surface of zinc oxide nanoparticles /polymer interface [25]. They obtained increased thickness at increasing concentrations and molecular weights due to variations in the zeta potential. Thirugnanam et al. have prepared zinc oxide films with PEG and PVP via sol-gel method [26]. Microcrystalline compact grains with pure phase structure formed.

Novel zinc oxide samples cross-linked with PVA/PEG blended membranes were fabricated by Dilshad et al. [20]. The membranes formed exhibited high permeability and selectivity. Zinc oxide nanocomposites were coated with Polycaprolactone/PEG by chemical precipitation method [27], [28]. Improved thermal stability, proper dispersion of the nanoparticles, and increased catalytic properties were observed upon addition of PEG.

In this work, we have investigated the structural, morphological, elemental, and optical properties of surfactant (PEG)-assisted molybdenum-doped ZnO thin films prepared at different concentrations of the dopant (molybdenum).

2 Experimental Details

2.1 Chemicals Used

All the reagents used in this work, such as Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), Hexamethylenetetramine ($C_6H_{12}N_4$), Molybdenum ($(NH_4)_6Mo_7O_{24}$) and Polyethylene Glycol (PEG) were of analytical grade (about 99.5% purity) and used without further purification. Distilled water (H_2O) was used throughout the experimental process.

2.2 Synthesis Process

Hydrothermal synthesis of the Zinc oxide (ZnO) thin films was carried out by mixing. In detail, the mixture of 0.2 M hexa-methylenetetramine (HMT) solution, 0.8 M zinc nitrate solution and 0.25 M polyethylene glycol (PEG) were prepared in three separate conical flasks. The mixtures were stirred at room temperature for 50 minutes to get a homogeneous solution. In this synthesis process, polyethylene glycol (PEG) was used as the surfactant to control the nucleation rate and rate of agglomeration [29]. Then, 0.3 M, and 0.5 M of ammonium heptamolybdate was added as dopant to the two flasks containing as-prepared solution and the flasks were labeled as control, 0.3 M, and 0.5 M. Each of the mixtures were ultrasonicated for 20 minutes and stirred for another 50 minutes. The solutions were transferred into a stainless steel autoclave and heated in an oven at 90 ℃ for 4 hours to allow the transformation of the precursors to the required oxide phases [13].

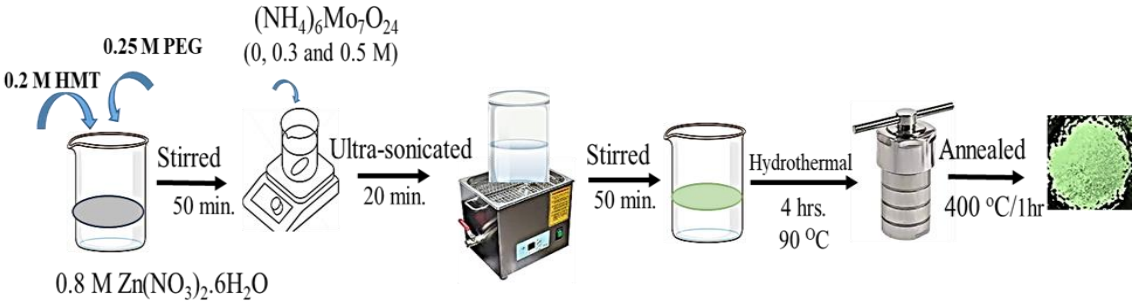


Figure 1: Synthesis route of undoped and Mo-ZnO nanoparticle using hydrothermal method

The resulting undoped and Mo-ZnO nanoparticles were cooled to a room temperature and annealed at 400 ℃ for 1 hour to minimize unwanted surface roughness and remove unwanted impurity [30], [31]. The glass substrates were treated with acetone and water for 15 minutes each in ultrasonication bath. The substrates were then sterilized in oven at 333 K for 24 hours before depositing the films. After all, the prepared nanomaterials were deposited on the glass substrates to fabricate ZnO thin films.

2.3 Characterizations

To understand the behavior of nanomaterials, several structural and chemical analyses were done. Crystal structures were determined by X-ray diffraction (XRD, Rigaku D/MAX 2400, λ¼0.1544 nm). The particle size of TiO_2 nanoparticle samples were calculated by using Debye's Scherer's equation, D=(kλ/β.cosθ) where D is particle size, K is Scherer's constant (0.94), λ is the X-ray wavelength, β is full width at half maximum of the diffraction peak, and θ is diffraction angle.

The surface morphology of as-synthesized thin films was characterized by SEM (Nova Nano-SEM450, 20 kV) and TEM (Tecnai G2 F20 S-Twin, 200 kV). The X-ray diffractometer (XRD) gave the structural property in accordance with SEM and TEM results of the deposited films. The chemical composition of the synthesized thin films was examined by energy dispersive X-ray spectroscopy (EDX, AMETEK). A UV-Vis spectrophotometer (756S UV-VIS) was used to investigate all optical properties of the thin films.

3 Results and Discussions

3.1 Structural Studies

The X-ray diffractograms of the PEG-assisted molybdenum-doped and undoped zinc oxide (ZnO) thin films are shown in Figure 2. Amorphous structures have been observed and could be because of proper alignment of the band levels of the materials. This means that the surfactant and dopant did not affect the crystal structure of the prepared zinc oxide films.

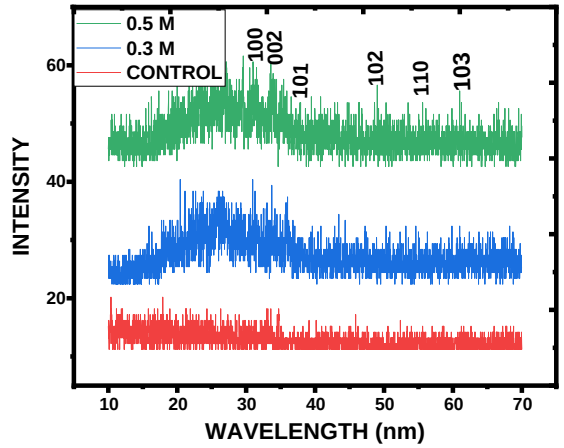


Figure 2: X-ray diffraction plots of the undoped, 0.3 M, and 0.5 M ZnO films prepared with PEG surfactant

The diffraction peaks observed in the XRD plots were 31.74°, 34.37°, 36.22°, 47.49°, 56.56°, 62.80°, and correspond respectively to hkl planes of (100), (002), (101), (102), (110), and (103). Average crystallite size was determined as 5.7 nm. The elemental composition of PEG-assisted molybdenum-doped zinc oxide thin films was estimated by the EDS technique as shown in Figure 3. The EDS spectrum evidently denoted the occurrence of zinc, carbon, and oxygen atoms in both undoped and Mo-doped thin films while just molybdenum atoms found only in the Mo-doped ZnO thin films. In addition, the percentage composition of Mo atom increases as the concentration of the dopant increase.

3.2 Surface Morphologies

The change in microstructure of PEG-assisted molybdenum-doped zinc oxide thin films is visualized by SEM images, owing to the variation in concentration of Mo in synthesis process. The SEM micrographs of PEG-assisted Mo-ZnO thin films are depicted in Figure 3(a–c). The SEM pictures of undoped ZnO displayed in Figure 3a, indicates microplates like architecture consisting of irregular shapes. The SEM morphology of PEG-assisted Mo(0.3 M)-ZnO thin films is shown in Figure 3b, the increased concentration of Mo thin film exhibits changes in morphology from dense microplates to micro flakes with warped edges exhibiting the ultrathin features. The SEM images were shown in Figure 3b indicated that the sample has a relatively uniform particles structure. Figure 3c displays an agglomerated grain-like morphology of PEG-assisted Mo(0.5 M)-ZnO thin films. It can be observed that an increased concentration of the dopant (Mo) alters the surface morphology of the thin films.

In addition, Figure 4 displays a selected area electron diffraction (SAED) pattern and transmission electron microscopy (TEM) images of the PEG-assisted Mo-doped ZnO thin films at 0 M, 0.3 and 0.5 M concentration of Molybdenum. The TEM micrographs displayed a grain-like morphology with irregular shapes while agglomerates were observed at increasing dopant concentrations. The TEM micrographs showed the effect of dopant (Mo) concentration on the morphology of the as-synthesized materials while the hkl indices can be observed from the SAED patterns.

3.3 Optical Characteristics

The plots of the absorbance against the wavelength of Mo-ZnO thin films are shown in Figure 4b(i) in the wavelength range between 400 nm – 1100 nm. The PEG-assisted Mo-ZnO films exhibited significant absorbance in the visible region of the electromagnetic spectrum (0.2 M concentration of dopant being the exception) with gradual drops within the visible region and very low absorbance towards the NIR region.

Average absorbance (about 35%) within the visible region decreased to about 15% towards the NIR region while the highest absorbance was recorded by the 0.5 M sample. The transmittance plots as shown in Figure 4b(ii) recorded high transmittance in the visible region which increased at increasing wavelength towards the near-infrared region.

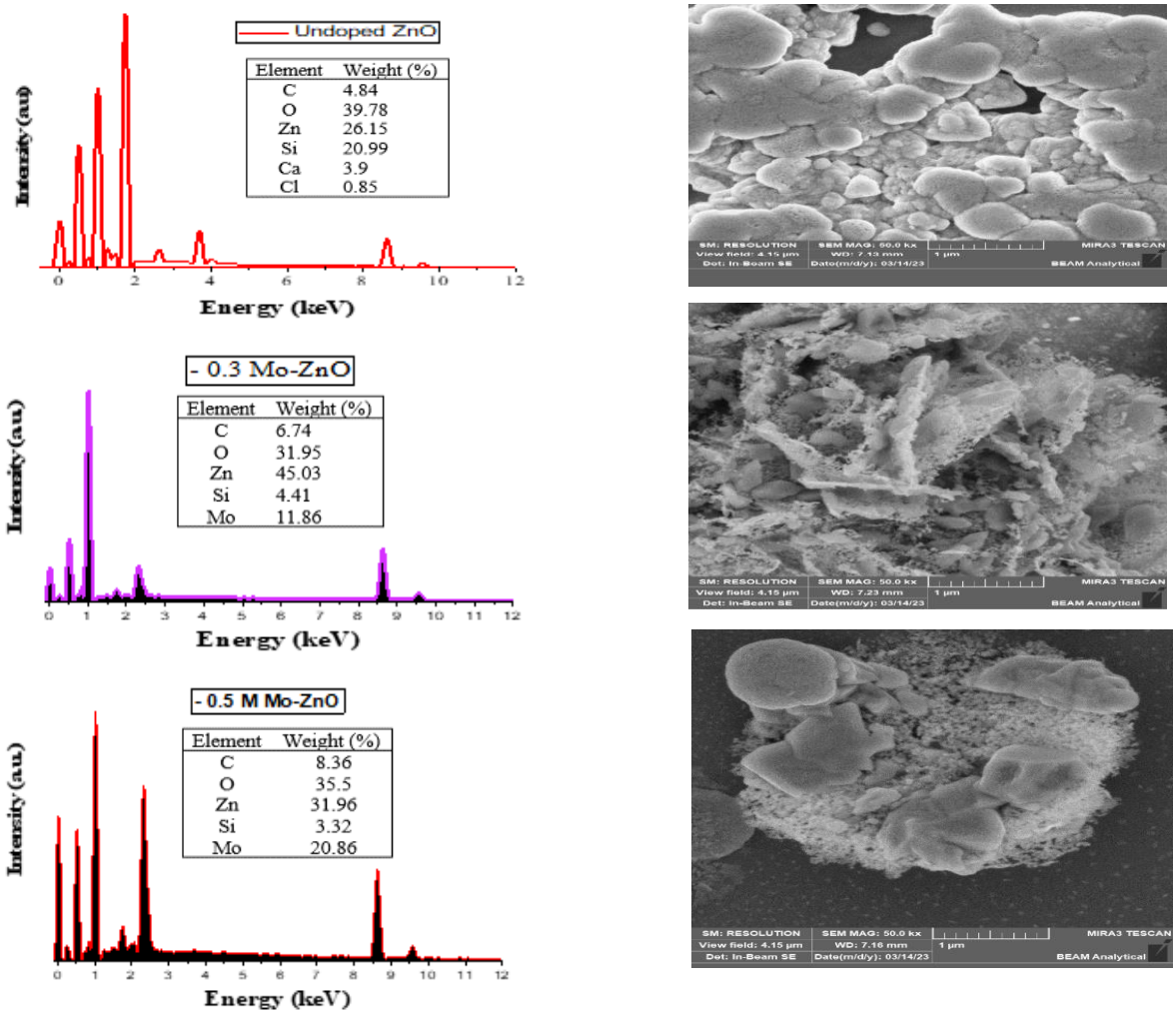
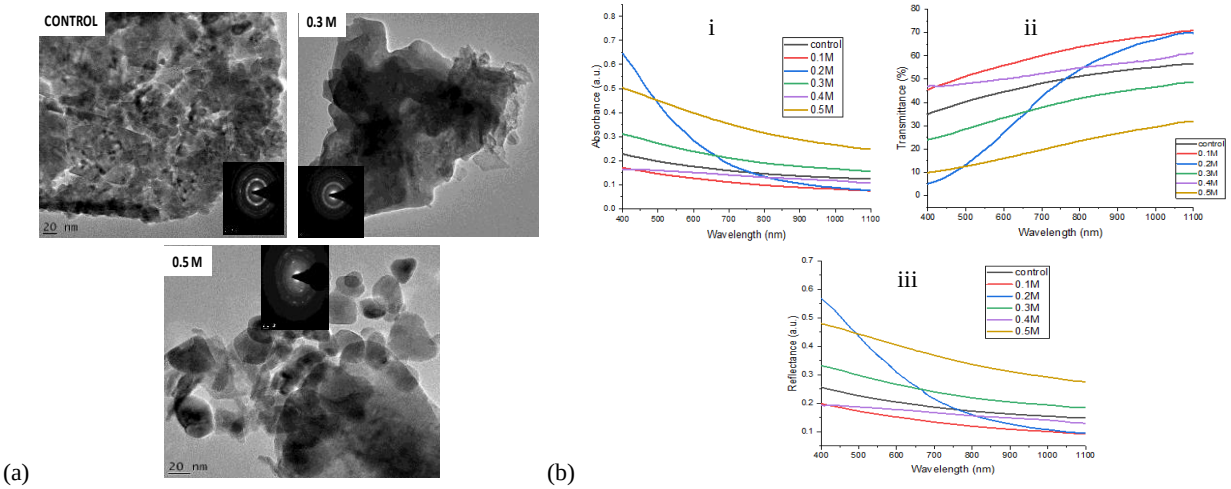


Figure 3: The Energy dispersive spectroscopy (EDS) elemental composition analysis plot and SEM image of PEG-assisted molybdenum-doped zinc oxide thin film



(a) (b)

Figure 4: a) TEM and SAED Image of the PEG-assisted molybdenum-doped zinc oxide thin films b) (i) Absorbance, (ii) transmittance, and (iii) reflectance plots of the undoped and Mo-doped ZnO samples

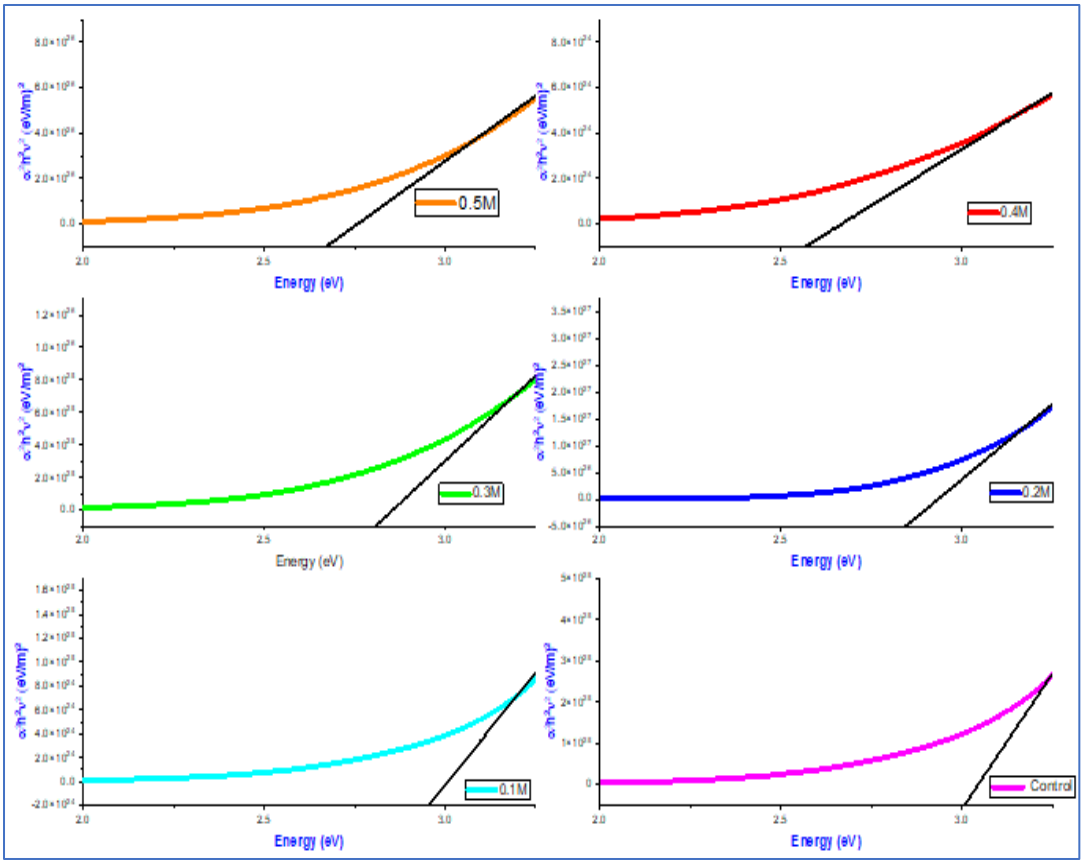


Figure 5: Plots of $\alpha^2(hv)^2$ versus photon energy (hv) for the PEG-assisted doped ZnO thin films

High optical transmittance is a desirable feature in optoelectronic devices. The high optical transmittance in the NIR region makes them suitable for infrared sensors and optical displays [27]. The reflectance plots are shown in Figure 4b(iii) and reveal decreasing reflectance in the visible region of the spectrum.

Plots of $\alpha^2(hv)^2$ versus photon energy (hv) as seen in Figure 5 have been used to determine the band gap energies of the surfactant-assisted Mo-ZnO thin films. The Control (undoped ZnO) film recorded the highest band gap energy with a band gap energy of 3.02 eV, which is comparable to that of pure Mo-ZnO (~3.2 eV) [19]. Band gap energies of 3.02, 2.94, 2.84, 2.80, 2.56 and 2.67 eV were obtained for the 0, 0.1, 0.2, 0.3, 0.4, and 0.5 M samples respectively.

The band gap energy values of the films decreased at increasing dopant concentrations of Mo. This is because the dopant introduced energetic carriers that reduced the energy needed by the carriers for band-to-band transition.

4 Conclusion

PEG-assisted Mo-doped ZnO thin films were synthesized via hydrothermal technique. The as-synthesized materials were characterized using XRD, TEM, SAED, EDS and optical method. The XRD results of the synthesized nanoparticles showed amorphous nature of the ZnO samples. The EDS characterization showed separate and prominent peaks for the prepared samples. Optical properties of the films, such as absorbance, transmittance, reflectance, and band gap energies were determined using UV-Vis spectrophotometer.

The samples recorded good absorbance and reflectance features in the visible region of the spectrum. The sample with 0.5 M of Mo concentration displayed lowest transmittance values because of the film thickness. Increasing the concentration of the dopant (Mo) reduced the band gap energies of the ZnO thin films. The dopant and PEG-surfactant improved the optical properties of the prepared zinc oxide samples.

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Declaration of Competing Interest

Authors have declared that there is no existing conflict of interest.

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