

Fabrication and Characterizations of TiO₂/ZnO Nanocomposite: Improving Dye-Sensitized Solar Cell Efficiency

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Abstract— In our study, TiO₂ doped ZnO nanoparticles were synthesized by sol-gel co-precipitation method applying different TiO₂ molar concentration ratios. The structural morphology, optical and electrical properties of the prepared nanocomposites were studied by various techniques including: high-resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), FT-IR, Raman spectroscopy, UV-diffuse reflectance (UV-DRS), photoluminescence (PL) and current-voltage (I-V) characteristics. The XRD results obtained showed that the TiO₂ deposition on the surface of the poly crystalline hexagonal wurtzite structure of ZnO is in conformity with HR-TEM, FT-IR and Raman spectroscopy results. Some modifications in the absorption and band gap emission, observed through UV spectra, exhibit red shifts compared to the undoped ZnO NPs and PL spectra that present blue shift to lower wavelength at about 310 nm. I-V measurements showed enhancement of the efficiency of dye-Sensitized solar cell (DSSC) from $1.26 \pm 0.08 \%$ for pure ZnO to $3.15 \pm 0.22 \%$ for TiO₂/ZnO NCs at the optimum doping (ZT1.0).

Index Terms— ZnO nanoparticles; TiO₂/ZnO nanocomposite; Dye-Sensitized Solar Cell; efficiency

I. INTRODUCTION

Many researchers have focused on enhancing the performance of dye sensitized solar cells (DSSCs) by using semiconducting metal oxides such as ZnO, TiO₂, CuO, and SnO₂ [1]; and metals such as Cu, Ni, Ti and Co etc.[2]. (DSSC) become a low-cost solar cell with highest efficiencies exceeding 11%. To date [3], DSSCs based on ZnO have attracted extensive attention in the academic research and industrial applications compared to the conventional semiconductor solar cells due to their high efficiency, low cost of fabrication, robust nature, environmental compatibility as well as rather simplicity of the fabrication process [4]. In DSSCs, the conversion of visible light to electricity is achieved by providing an effective path for the electron transport and a higher surface area for dye adsorption to maximize light absorption [5]. Zinc oxide, as a direct wide-band-gap semiconductor (3.37 eV) and higher electron mobility, making it frequently used in the production of DSSCs [6]. In fact, higher electron mobility in ZnO thin films

reduces the rate of back recombination of holes and electrons by making injection of photo excited electron into the conduction band became easier thus will enhance the performance of the solar cell [7]. Many methods, such as doping [8], metal modification [9] and coupling of composite semiconductors [10-12] have been investigated to reduce the rate of recombination between electrons and holes and increase the life time between them to improve absorbance efficiency for enhancing solar cell performance. In this respect, TiO₂ has been recognized as one of the most promising wide band gap semiconducting materials for dye-sensitized/quasi-solid-state dye-sensitized solar cells (DSSCs/QS-DSSCs) [13]. Thus, TiO₂ and ZnO have excellent properties and have similar band gap energy, this assist for many technological applications in solar cells fabrication [14], photo catalysis [15], gas sensors [16] and UV light-emitting devices [17]. In literature, there are several methods for preparations of ZnO and TiO₂ nano composites [18, 19]. Among of these, the sol-gel method showed many advantages such as good uniformity, high purity, low temperature synthesis, as well as, easily controlled reaction condition [18, 20].

In this direction, the effect of TiO₂ doping on ZnO NPs was studied to optimize its optical and electrical properties suitable for DSSCs applications. In this work, TiO₂ doping on ZnO NPs with different molar concentrations were prepared with sol gel co-precipitation method. The structural, optical and electrical properties have been investigated using X-ray diffraction (XRD), High-resolution transmission electron microscopy (HR-TEM), FT-IR spectra, Raman spectroscopy, UV-diffuse reflectance (UV-DRS) spectrum, photoluminescence (PL) spectra and I-V measurements to achieve the enhancement of DSSCs.

II. MATERIALS AND METHODS

2.1. Materials

The chemicals used are in the present work: zinc nitrate (Zn (NO₃)₂·6H₂O, Titanium (IV) isopropoxide [Ti (OCH (CH₃)₂)₄], Isopropanol [(CH₃)₂CHOH], NaOH, Lithium iodide (LiI), Eosin-Y and hydrogen hexachloroplatinate (IV) hydrate were obtained from Sigma-Aldrich company (USA) as a powder material of high purity of 98.85% or better. Iodine (I₂), Ethanol and Acetone were obtained from Honeywell.

2.2. Preparation of ZnO nanoparticles

ZnO nanoparticles were synthesized by co-precipitation method [21]. Typically, 7.44 gm Zinc nitrate Zn (NO₃)₂ was dissolved in 500 ml deionized water with stirring for 30 minutes at 100 °C, the pH = 6 by using 1M NaOH and keep

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stirring for one hour. The mixture was centrifuged at a speed of 4000 rpm and the precipitates were collected. The white powder obtained was washed several times with deionized water and ethanol; then drying at 80 °C in an electric oven and calcinated at 450 °C for 4 hours in air to remove any organic residues.

2.3. Preparation of TiO₂ doped ZnO nanocomposites

TiO₂ doped ZnO NCs were prepared by sol-gel co-precipitation method according to [22] with different molar concentrations (0.5, 1.0, 1.5, 2.0 and 2.5 mol. %) of TiO₂ precursors; the samples are denoted as (ZT_{0.5}, ZT_{1.0}, ZT_{1.5}, ZT_{2.0} and ZT_{2.5}) respectively. Two individual solutions were prepared: Solution A; ZnO NPs were prepared with the same procedure as given in sec. (2.2). Solution B; TiO₂ NPs was prepared by sol-gel method according to the recommendation given in [21]. Ti isopropoxide solution with specific molar ratios was added to isopropanol and then stirred for one hour. Then, solution A was added suddenly to solution B under continuous stirring at 250 rpm. The resultant solution was aged for 3 hours before it's centrifuged at 4000 rpm, washed several times with deionized water and ethanol and dried at 80 °C over night. Finally all prepared samples were calcinated at 450 °C for 4 hours in air.

2.4. Fabrication of DSSC electrodes

All the considered samples were deposited on quartz substrate coated with indium tin oxide (ITO) with thickness of 100-150 nm using Pulse Laser Deposition (PLD) at wave length of 1064 nm (Q-switched Nd:YAG laser). The prepared thin films are considered photo- electrodes of DSSCs. The prepared photo-electrodes were immersed in 0.04 g of Eosin-Y organic dye (C₂₀H₈Br₄Na₂O₅) dissolved in 100 ml acetone for 24 hours. The platinum-coated counter electrode was prepared by (4 mM hydrogen hexachloroplatinate (IV) hydrate, H₂PtCl₆.aq in ethanol solution depositing on ITO-glass and calcinated at 400 °C in the air for 1 hour. The redox electrolyte consisting of 0.3 M LiI and 0.03 M I₂ in polyethylene carbonate was injected into the inter-electrode space from the counter-electrode side through a predrilled hole .

III. EXPERIMENTAL TECHNIQUES

The phase of the prepared samples was examined by X-ray diffraction (XRD) using a diffractometer (Panalytical XPERT PRO MPD). CuK α radiation ($\lambda= 1.5418 \text{ \AA}$) was used at a rating of 40 kV and 40 mA. The morphology was investigated by High Resolution Transmission Electron Microscope (HR-TEM) - model JEM-2100, JEOL, Japan. The structural study of the prepared samples was investigated by Raman spectroscopy with laser source 532 nm and power 10 mW (model Sentera, Bruker, Germany). The functional groups were identified using a Fourier transform infrared spectrometer (FT-IR) model spectrum one (Perkin Elmer, USA) in the wave number range of 400–4000 cm⁻¹. The optical reflectance was recorded using a UV-Vis spectrometer (Perkin Elmer Lambda 1050). The photoluminescence spectra were recorded using a Perkin Elmer LS 50B luminescence spectrophotometer. The current–voltage (I-V) measurements of the fabricated DSSC were measured by using a solar simulator (Solar-Light (Science tech SS150W-AAA) and an electrometer (2400 Keithley Source Meter

SSIVT-60WC), while Air Mass 1.5-filtered light from the 150 W-Xenon lamp of the solar simulator shines the DSSC at a power density $P_i= 100 \text{ mW/cm}^2$.

IV. RESULTS AND DISCUSSION

4.1. Structural morphological characterization

4.1.1. X-Ray Diffraction (XRD) analysis

Fig. (1) represents the phase of the prepared samples (ZnO, ZT_{0.5}, ZT_{1.0}, ZT_{1.5}, ZT_{2.0} and ZT_{2.5}) as identified by XRD. The patterns of ZnO NPs (ZT_{0.0}) reveals the presence of polycrystalline hexagonal wurtzite structure of zinc oxide with diffraction peaks at angles (2 θ) of 31.36, 34.03, 35.86, 47.16, 56.26, 62.54, 67.64, and 68.79^o corresponding to the respective crystal planes of (100), (002), (101), (102), (110), (103), (200), and (112) , as evaluated from and matches with JCPDS data (file: 01-080-4199). The XRD pattern of sample ZT_{0.5} exhibits no major change from that of ZT_{0.0}, but sample ZT₁ shows a great change in structure that distinguishes the formation of heterojunction Zn-Ti confirmed with the data reported using Raman and IR patterns as we will be seen later. This heterojunction facilitates the charge separation of photogenerated carriers display excellent photocatalytic properties that confirmed b Uv and PL spectra. On other hand, the diffraction peaks of sample ZT_{1.5} demonstrated more degree of crystallinity beside that the existence of new diffraction peak appears at 40.5^o corresponding to (200) plane matched with ICDD data (ICDD file: 01-075-2545), confirming the presence of doped species. However, further increase of TiO₂ molar ratio (ZT_{2.0} and ZT_{2.5}) samples, the observed phase structure was mainly anatase TiO₂ crystalline phase due to that TiO₂ is too thicker to appear as a strong XRD signal.

The crystalline size of the prepared samples was calculated by using Williamson-Hull's formula [23]:

$$\beta \cos(\theta) = [K \lambda / D] + [4S \sin(\theta)] \quad (1)$$

where β is full width at half maximum (FWHM) in radians, λ is wavelength of X-rays used, θ is scattering Bragg angle, D is particle diameter, and S is the strain. The parameter K is the shape factor (taken as 0.94). The calculated particle sizes are listed in Table (1) for the considered compositions. The results indicated that the crystal size decrease with increasing the molar ratio of TiO₂ from 0.0 to 2.5 %.

Fig. (2) represents the most intense peaks of undoped ZnO and TiO₂ doped ZnO with molar ratio of 1.5%, a slight shift towards higher angles was observed in case of ZT_{1.5}, because of the ionic radius of Ti⁴⁺ ($r_{Ti^{4+}} = 68 \text{ \AA}$) [24] is smaller than that of ($r_{Zn^{2+}} = 0.74 \text{ \AA}$), implied the insertion of TiO₂ in the crystalline lattice of ZnO.

4.1.2. Transmission Electron Microscope (TEM)

The morphology of the prepared samples that investigated by HR-TEM are shown in Fig. (3). ZnO image shows an irregular hexagonal shape and large rectangular platelets of undoped ZnO nano particles. TiO₂ doped ZnO nanocomposite images show a spherical regular morphology with a good uniform particle size distribution and low agglomerate particles compared to undoped ZnO. The optimum regular spherical was obtained with ZT_{1.5} compared to the other molar ratios nonocomposites, this matched with the XRD patterns.

4.1.3. Fourier transform-Infra red (FT-IR) spectra

The FT-IR spectra of the investigated samples were recorded in the range of 400–4000 cm^{-1} and the obtained results are given in Fig. (4). The spectrum analysis of the samples revealed the presence of O-H ($\nu_{\text{O-H}}$ at 3367 cm^{-1}), symmetric C=O ($\nu_{\text{C=O}}$) at 1560 cm^{-1} and asymmetric C=O ($\nu_{\text{O-C-O}}$) at 1395 cm^{-1} . Here, a sharp strong band around 430 cm^{-1} was observed corresponding to the stretching mode of ZnO nanoparticles, in addition a new broad band between 500 and 700 cm^{-1} corresponding to Ti-O and Ti-O-Ti stretching mode of TiO₂-ZnO nanocomposites [26], which implied that TiO₂ was successfully doped ZnO NPs.

4.1.4. Raman spectroscopy

In fact, Raman spectroscopy of the prepared samples characterizes the vibrational modes of the crystallized phases to detect the incorporation of the dopant content. Fig. (5) shows the Raman Spectra of pure and TiO₂-doped ZnO NCs. The spectrum of pure ZnO exhibits significant peak of the E₂ (High) mode at 435 cm^{-1} represents wurtzite hexagonal structure of ZnO, associated with the motion of oxygen atoms in ZnO lattice [25]. Another peaks were observed at 322, 578, 1130, 1368 and 1525 cm^{-1} . The two peaks at 322 and 578 cm^{-1} are assigned to be (E_{2H}-E_{2L}) and A₁ (LO), respectively. Raman spectra of TiO₂ doped ZnO NCs compared to undoped ZnO, revealed that the intensity of some peaks decreased and vanished at (322, 435, 578 and 1130 cm^{-1}) with increasing doping content and additional peaks observed at around 133, 773 and 1905 cm^{-1} . The intensity of main peak of TiO₂ appeared at 133 cm^{-1} , increased with increasing TiO₂ doping, while other peaks decreased and vanished. According to literature, the additional modes are induced by host lattice defects; the host lattice defects in ZnO are activated and implied with doping content and then these modes appears [23]. The changes in the intensity of peaks confirm successfully doped ZnO.

4.2. Optical characteristics

4.2.1. UV- vis spectrum analysis

Diffuse reflectance spectra of the investigated samples were recorded to estimate the optical band gap of pure and TiO₂ doped ZnO NCs over the range of 200–800 nm using UV–visible optical spectroscopy. Fig. (6) shows the plot of the reflection percentage as a function of band energy (h ν) of prepared samples. The reflectance spectra of TiO₂-ZnO NCs showed a red shift compared with the pure ZnO NPs due to differences in the surface state of the ZnO/TiO₂ composites. The optical band gaps (E_g) of the samples have been estimated from the plots and listed in Table (1). The band gap of pure ZnO and TiO₂ are 3.32 eV and 3.20 eV, respectively, which are higher than the estimated band gap of the TiO₂ doped ZnO NPs. Table (1) declares that the band gap decreased with increasing the doping molar ratio of TiO₂ at (ZT_{1.0}) and further increasing doping molar ratio resulting increase the band gap. Consequently, ZT_{1.0} NCs represent the optimum doping. The band gap decreased due to the synergistic effect between the conduction band of TiO₂ and that of ZnO NPs, and also, related to both impurity and defect levels introduced to the forbidden band of TiO₂ due to the formation of some sub-bands [27]. The diagram of the energy band structure of TiO₂ with ZnO was shown in Fig. (7), the electrons in both valence bands (VB) could be excited to the conduction bands (CB) with simultaneous generation of the

same amount of holes in the VB. The charge carrier separation led to an increase in the carrier lifetime and enhanced the absorption efficiency. The previous results implied an evident enhancement of the ability of TiO₂ doped ZnO NCs to harvest UV light.

4.2.2. Photoluminescence (PL) spectroscopy

The room temperature PL spectra of the investigated were shown in Fig. (8), at excitation wavelength of 280 nm. PL spectrum of pure ZnO shows strong and broad UV emission band at 323 nm and the spectra TiO₂/ZnO NCs show blue shift to lower wavelength at about 310 nm, this may be due to the cooperation between ZnO NPs and dopant TiO₂ [28] resulting in decrease in the emission yield of TiO₂/ZnO. TiO₂ shows no UV emission, so the UV emission should come from the bottom ZnO, and weaken with the top TiO₂ layer. Some UV photons excited by ZnO NPs may have been absorbed by the coated TiO₂ NPs, and so TiO₂ NPs were excited by both the laser light and UV emission from the bottom ZnO NPs. These two excitation channels enhance the intensity of deep level emission of the TiO₂/ZnO NCs. The luminescence intensity of the optimum doped is observed at (ZT_{1.0}) has greatly enhanced, due to the interaction between the two semiconductors, which is an indication of the improvement in crystalline quality [29]. Moreover, for composite sample (ZT 1.0), the intrinsic defects that arise due to zinc vacancy, oxygen vacancy and interstitial zinc are less, which results in highly efficient (near band energy) NBE luminescence; these results show a great promise of the doped ZnO NPs in optoelectronics devices.

4.3. Current-Voltage characteristics:

The current-voltage (I-V) characteristics curves of DSSC based on ZnO NPs and DSSC based on TiO₂-doped ZnO NPs are shown in Fig. (9 (a)). The detailed photovoltaic (PV) parameters obtained from I-V curves, open circuit voltage (V_{oc}), short circuit photocurrent (J_{sc}), fill factor (FF) and efficiency (η) are summarized in Table (2) as a function of TiO₂ mol. %. A comparison between the performance of ZnO DSSC and that of TiO₂-ZnO DSSC, it revealed photovoltaic performance increasing of the short circuit photo current (J_{sc}) from 0.82 mA/cm² to 1.16 mA/cm², and fill factor (FF) from 32.25% to 67.87% and a small shift from 0.47 V to 0.40 V for the open circuit voltage (V_{oc}). Fig. (9(b)) shows the variation of efficiency (η) with TiO₂ precursor concentration (mol. %). The results indicate a clear enhancement efficiency of DSSC based ZnO from 1.26 \pm 0.08 to 3.15 \pm 0.22 % of DSSC based TiO₂-ZnO with ZT_{1.0}, which confirming with the results obtained from UV-DRS and PL spectra. The efficiency increase can be attributed to the energy barrier created, which reduces the rate of electron recombination back to dye molecules and electrolyte species [30-33]. Further increase of molar ratios (ZT_{1.5}, ZT_{2.0} and ZT_{2.5}) showed decrease in the efficiency of DSSC, may be attributed to the decrease of dye-adsorption efficiency of the ZnO film, screens by larger amount of doping particles [34], consequently, the light harvest rate and the electron injection rate decrease and this will be reflected by the decrease of both J_{sc} and η [35]. According to literature, contributed that the efficiency enhancement of cell revealed excellent long-term stability of the TiO₂-ZnO cell to be suitable for commercial DSSC application as shown in Table (3).

CONCLUSION

TiO₂ doped on ZnO (TiO₂/ZnO) nanocomposites have been synthesized by sol-gel co-precipitation method with different molar concentrations. XRD data reported the effect of doping , and a new peak at 40.5° was observed at (200) plane, IR spectra revealed the presence of new vibration mode around (500-700) which corresponding to Ti-O stretching mode in TiO₂-ZnONCs, Raman spectra showed blue shifted to lower frequencies due to increase of doping content. UV spectra of TiO₂-ZnO NCs had a red shift compared with pure ZnO NPs, PL spectra show blue shift to lower wavelength at about 310 nm. The current-voltage measurements show that an optimum doping (ZT1.0) enhanced the efficiency (η) from 1.26 ± 0.08 to 3.15 ± 0.22 %, these matched with (UV-DRS) and PL results. The results indicated that TiO₂ doped ZnO composite material had enhanced structural, optical and electrical properties and they are good promise for enhancement efficiency of DSSC applications.

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