Journal of
Materials Sciences and Applications

JScholar
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Research Article Open Access

Simple and low cost growth of flower-like ZnO onto ITO/PET and FTO substrates through hydrothermal process for photoelectrochemical applications

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Received Date: March 21, 2022 **Accepted Date:** May 19, 2022 **Published Date:** May 21, 2022

Citation: Yousra Litaiem, Donia Dridi, Miguel Mollar, Bernabé Marí and Radhouane Chtourou (2022) Simple and low cost growth of flower-like ZnO onto ITO/PET and FTO substrates through hydrothermal process for photoelectrochemical applications. J Mater sci Appl 6: 1-9.

Abstract

In this study, both of ZnO/FTO and flexible ZnO/ITO/PET photoelectrodes have been synthesized through a simple wet hydrothermal route. Morphological, structural, optical and photoelectrochemical properties of elaborated photoelectrodes have been investigated. Scanning electron microscopies (SEM) investigation reveal homogenous and uniform particles for ZnO/ITO/PET and for ZnO/FTO. Only the size which differ between hexagonal shaped particles. X-ray diffraction (XRD) analysis demonstrates that ZnO was crystallised in hexagonal wurtzite structure. The band gap energy of ZnO deposited onto ITO/PET was found to be 3.273 eV closer to that found for ZnO/FTO which is about 3.27 eV. PL Results exhibit a strong UV emission peak around 380 nm which could be attributed to the near-band-edge (NBE) in the ZnO. ZnO/FTO sample shows a weak broad emission in the visible range 450- 650 nm and assigned to the electronic states situated in the band gap which are related to the intrinsic defect of ZnO. ZnO/FTO exhibit a current of about 3 μA at 0.6 V which is four orders higher than that obtained for ZnO/ITO/PET. ZnO/ITO/PET flexible photoanode was demonstrated to generate photoelectrochemical photocurrent. Consequently, it could be used as best candidate for the generation of flexible and stretchable hybrid photoelectrochemical solar cells.

Keywords: ZnO, ITO/PET, FTO, Hydrothermal, DRX, SEM, PEC

Introduction

Over the last few decades, stretchable transparent electronics based on the deposition of transparent conductive oxide semiconductor on flexible substrates are one of the most crucial technologies for the next generation of optoelectronic devices. These transparent electronics have attracted substantial attention due to their low cost, light weight, and semi-transparency as compared with well-established rigid substrate-based electronics. This vital and innovative branch open the door for many novel applications such as flat panel displays, home electronic appliances and photovoltaics.

Thanks to its exclusive features, namely its wide band gap, its large exciton binding energy, and its high transparency, ZnO has gained huge interest as one of the strongest candidate for several promising applications including solar cells [1,2], gas sensors [3-6], transducers [7], UV photodetectors [8-11]. Photoelectrochemical solar cells (PEC) provides the conversion of photons into storable chemical energy through water splitting reaction giving rise to electron-hole pairs [12,13]. Over other well studied photoanodes based on metallic oxide like TiO_2, SnO_2 and $BaTiO_3$, ZnO has emerged as best photoelectrode for PEC solar cells thanks to its exclusive properties such as excellent electrochemical stability and electron mobility [14], its low cost of synthesis [15]. Further, in PEC process, when the ZnO/electrolyte junction was illuminated by solar light, electron-hole pairs (HPs) have been generated by photons absorption. These generated EHPs have been separated by the electric field in the depletion region. The excited electrons move through the bulk region to the counter electrode, where reduction takes place and the generated holes transport towards semiconductor/electrolyte interface, where oxidation occurs [16]. Nanostructured ZnO could be deposited on diffrent polymer substrates such as polymer substrates employed for thin film deposition such as polycarbonate (PC) [17], Poly Ethylene Terephthalate (PET) [18-19], Poly Propylene Adipate (PPA) [9] and Poly Tetra Flouro Ethylene (PTFE) [10] suffer from distortions at high temperatures [11] and the film deposition should be carried out at low temperatures. PET offers exclusive mechanical features, high transparency with high transmittance in the visible light range, low permeability of gas and water vapor, and higher heat resistance than other polymers such as polycarbonate and polyphthalamide. In this way, indium tin oxide (ITO) coated polyethylene terephthalate (PET) substrate (ITO/PET substrate) has been mostly used for a wide range of application fields thanks to its superior electrical conductivity and good flexibility with light weight. ZnO thin films could be produced by several techniques such thermal evaporation [20], chemical vapor deposition [21], radiofrequency (RF) magnetron sputtering [22-24], spray pyrolysis [19], pulsed laser deposition [25, 26], sol-gel-dip-coating [27-31], electrodeposition [19,32-33] and hydrothermal [34-38]. Especially, hydrothermal method has gained much interest due to its unique advantages including its simplicity, low temperature (60–100 °C) and a more controllable process. Further, it was considered as one of the most widely used methods for obtaining nanostructures.

In this context, indium tin oxide (ITO) coated polyethylene terephthalate (PET) and FTO substrates was used as substrates for preparing ZnO/PET/ITO and ZnO/FTO photoanodes for PEC solar cell through a wet synthesis route. Then, a detailed investigation of structural, morphological, optical and photoelectrochemical properties of synthesized ZnO photoanodes.

Experimental Details

ZnO thin films were fabricated by one-step using hydrothermal method. All reagents were from analytic grade and used without further purification. 0.5 g hexamethylene tetramine and 0.90 g zinc nitrate ($Zn(NO_3)_2$) were dissolved in deionized water. The pH solution was adjusted by adding citric acid until pH solution 7. The final mixtures were transferred into a 100 ml Teflon- lined stainless steel autoclave for hydrothermal reaction. Indium tin oxyde Polyethylene terephthalate (ITO/PET) sheet (= 188 μm) free from scratches was purchased from (DuPont Teijin Films, USA). Fluorine doped tin oxide (FTO) was purchased from Asahi Company (10- 15 Ω/square). ITO/PET and Fluorine doped tin oxide (FTO) substrates were cut into 2 cm ×3 cm square pieces and ultrasonically cleaned for 5 min in acetone, 5min in absolute ethanol, and finally rinsed with distilled water.

The ZnO growth process is shown by the chemical reactions listed as follows [39]:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 4NH_3 + 6HCHO \quad (1)$$

$$NH_3 + H_2O \rightarrow NH^+ + OH_4^- \quad (2)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (3)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (4)$$

The reactions were performed at 90 °C for 20 h and then cooled down to room temperature naturally. All simples was washed with distilled water and absolute ethanol and dried in air for further studies.

Photoluminescence measurements of prepared samples were performed at room temperature (300K). The PL was excited with the 266 nm line of a laser source. The signal was detected through a 250 mm Jobin-Yvon monochromator by a GaAs photomultiplier associated with a standard lockin technique.

The morphology and microstructure of the synthesized ZnO micro-particles were characterized using scanning electron microscope (FE-SEM) (ZEISS UL TRA55) at acceleration voltage 10kV. Structural analyses of the ZnO thin films were characterized using the X-ray diffraction apparatus (Rigaku Ultima IV diffractometer in Bragg-Bentano (θ-2θ) configuration and using CuK_{α} radiation 1.5418 Å).

Key Findings

Morphological properties

ZnO thin films deposited onto ITO/PET and FTO glass have good adherence and they have a white color. Figures 1(a) and 1(b) show the SEM pictures of ZnO thin films

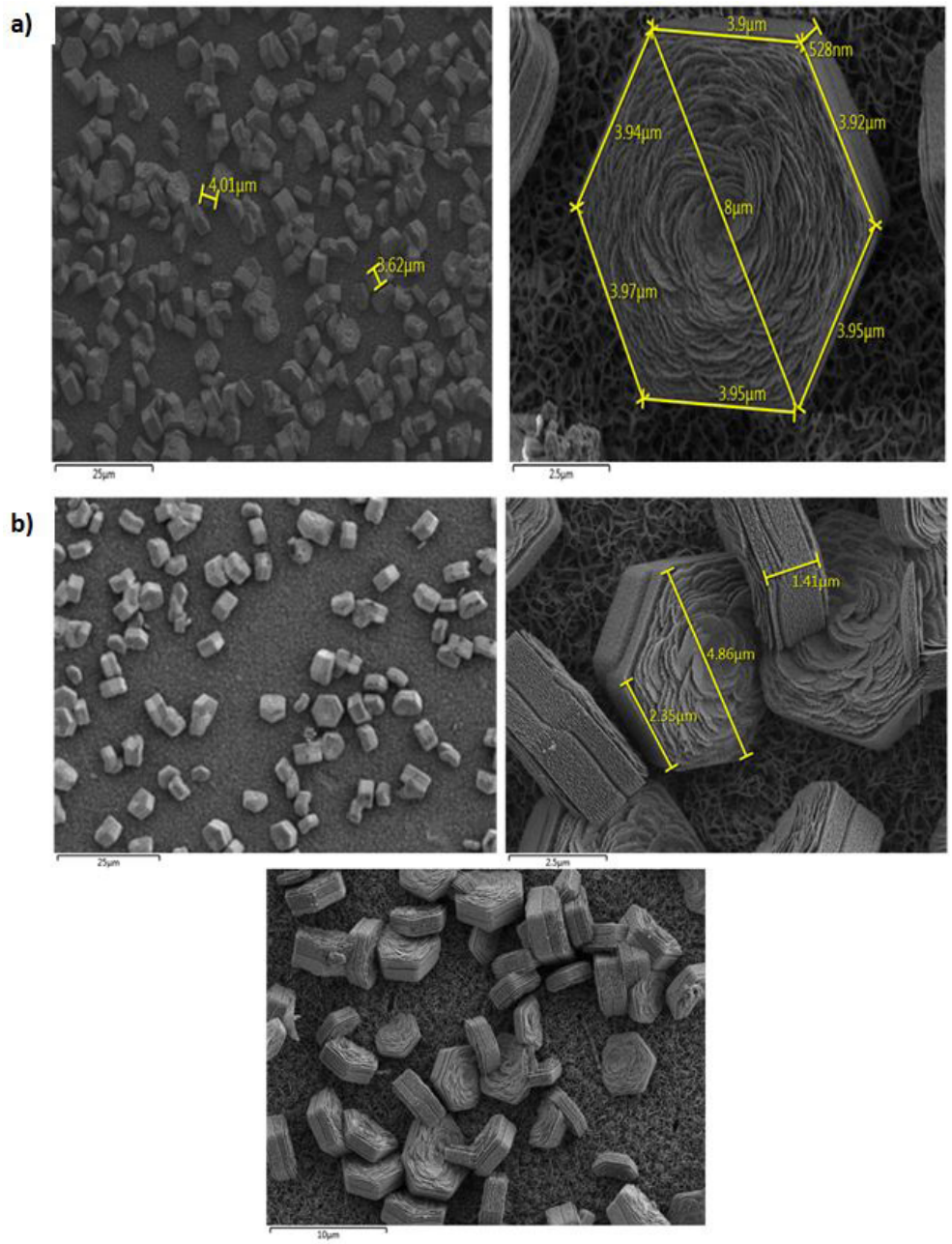


Figure 1: SEM micrographs of micro-structures based ZnO grown through hydrothermal process on ITO/PET (a) and FTO (b) substrates.

deposited onto ITO/PET at different scales. ZnO thin films morphology shows the presence of micro- particles covering the entire surface of the sample. These particles are homogeneous, uniform and their shape like hexagonal flowers. At higher magnification, we can deduce that edge length of the hexagon flower is equal to 4 μm. In the same way, ZnO thin films deposited on the FTO substrate exhibit micro-particles with the same morphology as compared to those deposited in ITO/PET substrate. The only difference was the size of the particles that were smaller on the glass substrate which is of the order of 3μm. Similar Morphology was found by Sun et al [40] in their twinned flower-like ZnO structures synthesized through hydrothermal method at a low- temperature as 90 °C.

Structural properties

Fig. 2 (a) shows the X-ray diffraction spectrum of the ZnO thin film grown onto ITO coated PET substrate. We note the existence of very larger peaks which are characteristic peaks of the flexible substrate. These later are located at angle position 29.95°, 46.89° and 53.77°. All the diffraction peaks are in good agreement with those of the hexagonal wurtzite structure of ZnO (JCPDS card 01-089-7102). No other diffraction peaks are found, indicating that the products are pure ZnO.

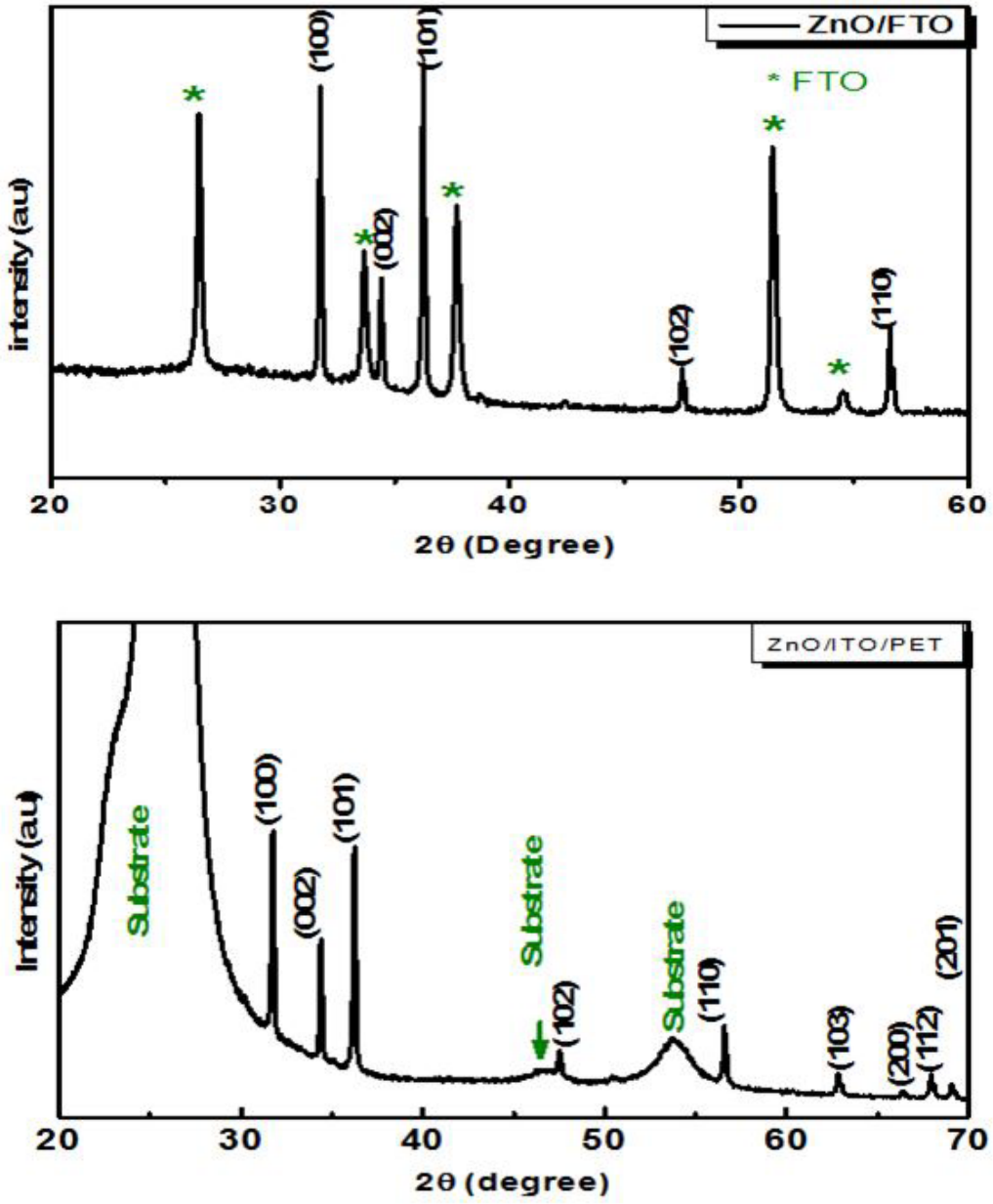


Figure 2: X-ray diffraction patterns of the micro-structured ZnO thin films deposited onto FTO (a) and ITO/PET (b) substrates.

Fig. 2(b) shows the XRD patterns of ZnO thin films deposited on glass substrates. Ten peaks were found at position 2θ ≈ 31.802 °, 34.489 °, 36.355 °, 47.553 °, 56.586 °, 62.931 °, 66.440 °, 68.007 ° and 69.127 ° witch respectively corresponding to hkl planes (100), (002), (101), (102), (110), (103), (200), (112) and (201) and witch in agreement with the "Zincite, syn" phase.

ZnO/FTO thin films show slightly better Crystallinity than that deposited onto PET substrates. Similar observation was reported by Kulkarni et al [41] in their ITO films deposited onto polymer and glass substrates. ZnO thin films deposited on glass substrate show a preferred (101) orientation, which corresponding also to the preferential orientation observed on the JCPDS file (01-089- 7102). However, in ITO/PET substrate is not evident to confirm the orientation for the films deposited due the largest characteristic pics of the polymers.

Optical properties

Optical transmittance spectra of ZnO/ITO/PET and ZnO/FTO thin films were shown in Fig. 3(a). This Figure indicates that both films are absorbers in UV region and exhibiting a high transmission (T (%) ≥ 65%) in the visible region (400-800 nm). Such transparency may be due to low scattering and absorption losses. The elaborated films exhibited sharp absorption edges in the ultraviolet region (360-400 nm). The optical band gap values of synthesized films could be determined from Tauc' s relation (Eq. (8)) for permitted direct transitions [29]:

$$ahv = A\ (hv - E_g)^n$$

where hν is the photon energy, A is a constant, E_g is the band gap energy of the prepared material and n is an integer and equals to 1/2. From the estimated values of the absorbance coefficients, the plots of hν versus $(\alpha h\nu)^2$ are plotted in Fig. 3(b).

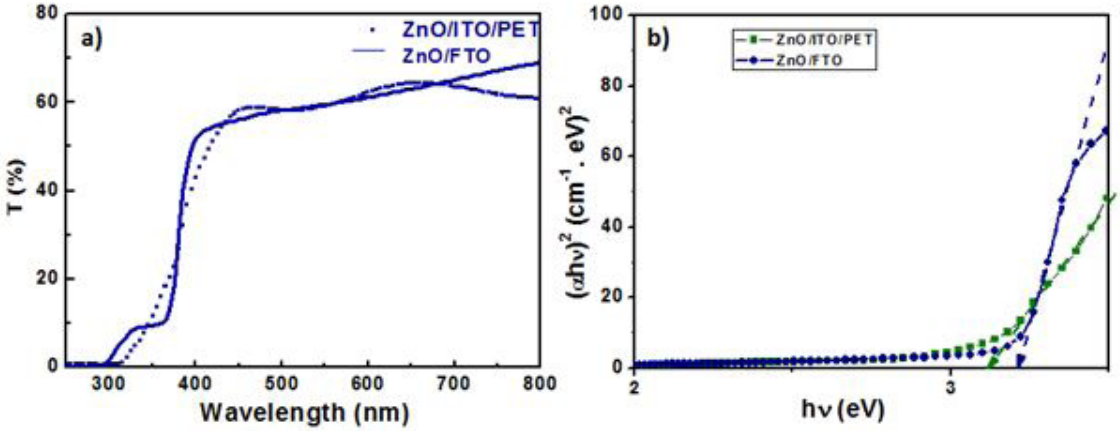
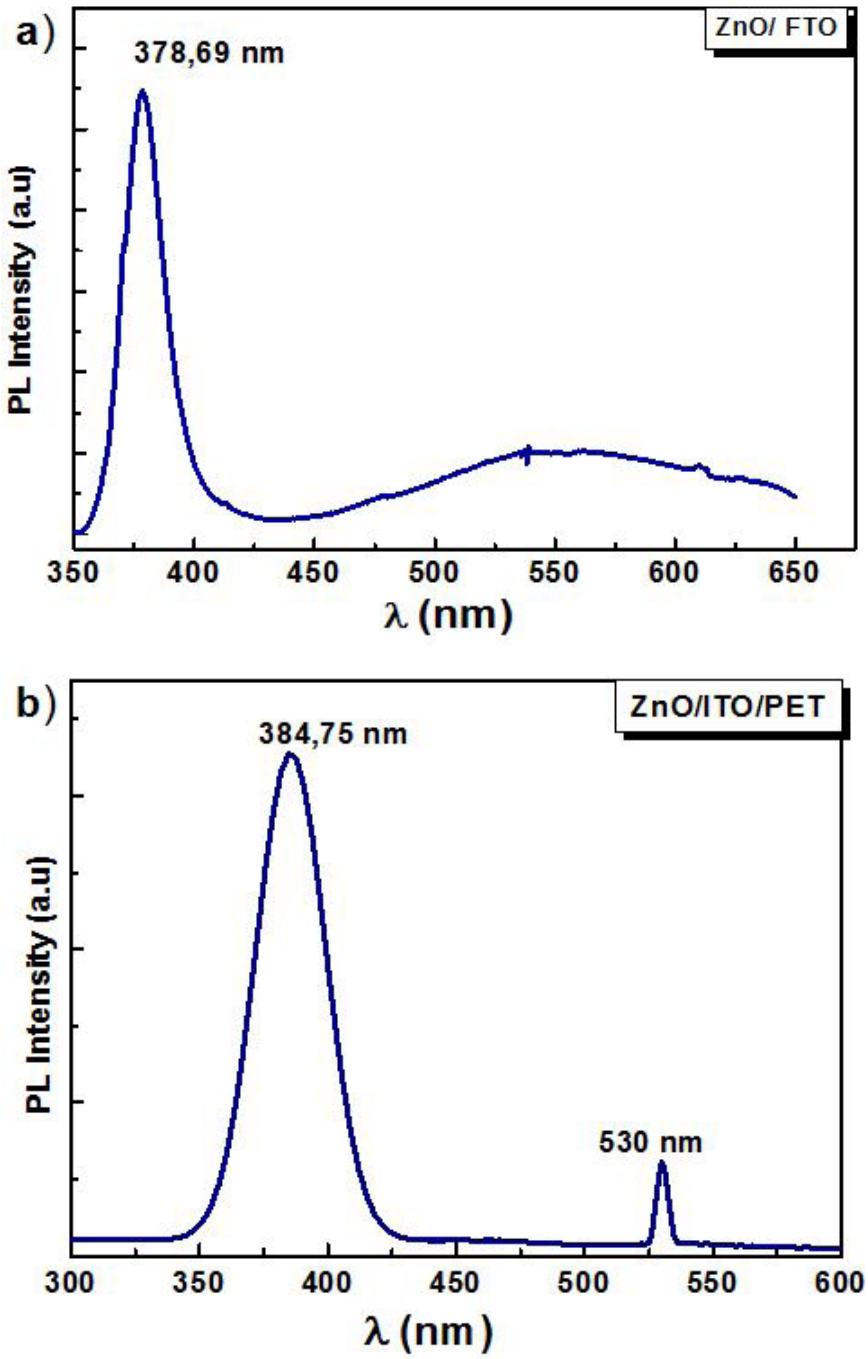


Figure 3: UV–vis transmittance spectra of ZnO thin films grown on FTO and ITO/PET substrates (a) and optical band gap estimation for ZnO thin films grown onto FTO and ITO/PET substrates (b).

The sharply increased absorbance coefficient could be assigned to band to band transition due to electron transfer from valence band to conduction band. The intersection points of the linear portion of the graph to the X-axis give the band gap energy of the synthesized materials. The band gap energy value of ZnO thin layer deposited onto ITO/PET and FTO glass substrates is found to be 3.273 eV and 3.270 eV respectively [29]. The estimated band gap values were much closer with previous reported values.

In addition, room temperature photoluminescence (PL) spectra of the grown ZnO thin films onto different substrates are also measured and shown in Fig. 4. Results indicate that these two spectra exhibit strong UV emission peak at around 380 nm. Only ZnO thin films grown onto FTO substrate exhibited a weak broad emission in the visible range between 450nm and 650 nm. The UV emission peak could be attributed to the near-band-edge (NBE) in the ZnO whereas the visible band emission was assigned to the electronic states into the band gap which are related to the ZnO's intrinsic defects. The decay of the NBE intensity of ZnO involves the high intrinsic defects density within the gap which acts as a trap or recombination center for the photogenerated electron\hole pairs.



Photoelectrochemical properties

In order to evaluate the charge transport and electrical properties of the elaborated ZnO thin films, the photoelectrochemical responses were evaluated under artificial illumination (100 mW/cm^2) in an aqueous solution of sodium sulfate (0.5 M, at a pH of 7). As shown in the insert of Figure 5, dark linear sweep voltammetry (LSV) scans from -0.6 V to 0.6 V vs. Ag/AgCl showed a small current in the range of 0.3 μA/cm2. This behavior could generally be correlated with the open circuit voltage or surface states modifications. Under illumination, ZnO thin films grown on the different used substrates have a non-linear rectification behavior corresponding to the diode characteristics. It is commonly known that the threshold of the photocurrent at $V=V_{on}$ could be attributed to the measure of the flat band potential V_{FB} [29]. From the PEC measurements, the flat band potential of the ZnO deposited on FTO and ITO/PET substrates are in the range of - 0.47 V and - 0.6753 V respectively.

The forward current of ZnO thin films deposited on FTO substrate is about 3 μA at an applied potential of 0.6 V. This current was higher than that obtained for ZnO thin film deposited on ITO/PET by about four orders. This difference

in current values was probably related to the difference in crystallinity and in carrier density. In fact, Ismail et al [10] have studied the photoresponse of ZnO (space between of and ZnO) thin films on Au, ITO and FTO substrates and have concluded that an increase in photoresponse was attributed to the high crystallinity as well as the high surface area [35-39].

The photocurrent response of the synthesized samples under illumination light intensity of 100 mW/cm^2 at an applied potential of 0.6 V vs. Ag/AgCl is shown in Figure 6. The photocurrent of the samples appeared immediately upon irradiation then fastly returned to a steady state when the illumination was cut off. This behaviour was related to the n-type semiconductor.

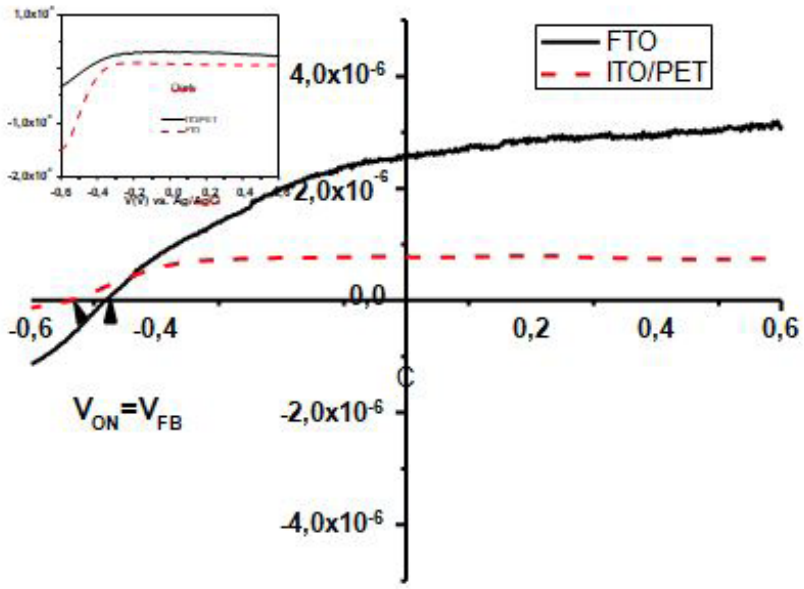


Figure 5: Photocurrent density of ZnO thin films deposited onto FTO and ITO/PET substrates under illumination and in dark displayed in the inset graph.

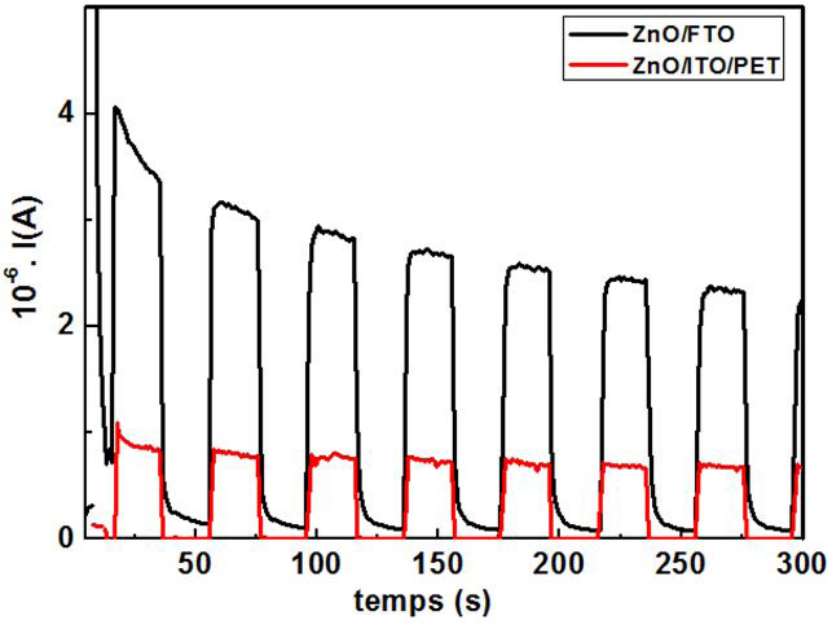


Figure 6: Photocurrent-time plots of ZnO/FTO and ZnO/ITO/PET photoanodes under illumination (100 mW/cm^2) at an applied potential of 0.6 V (vs Ag/AgCl) during 300 seconds.

Conclusions

In this paper, both of ZnO/FTO and flexible ZnO/ITO/PET photoelectrodes have been elaborated via a simple wet hydrothermal route. Morphological, structural, optical and photoelectrochemical properties of elaborated photoelectrodes have been investigated. Scanning electron microscopies (SEM) investigation reveal homogenous and uniform particles for ZnO/ITO/PET and for ZnO/FTO. Only the size which differ between hexagonal shaped particles. The X-ray diffraction (XRD) analysis demonstrates that ZnO was crystallised in hexagonal wurtzite structure. The band gap energy of ZnO deposited onto ITO/PET was found to be 3.273 eV closer to that found for ZnO/FTO which is about 3.27 eV. PL Results exhibit a strong UV emission peak around 380 nm which could be attributed to the near-band-edge (NBE) in the ZnO. ZnO/FTO sample shows a weak broad emission in the visible range 450- 650 nm and assigned to the electronic states situated in the band gap which are related to the intrinsic defect of ZnO. ZnO/FTO exhibit a current of about 3 μA at 0.6 V which is four orders higher than that obtained for ZnO/ITO/PET. ZnO/ITO/PET flexible photoanode was demonstrated to generate photoelectrochemical photocurrent. Consequently, it could be used as best candidate for the generation of flexible and stretchable hybrid photoelectrochemical solar cells.

Author Contribution Statement

The wide majority of the work has been carried out by Yousra Litaiem, assistant professor in laboratory of nanomaterials and systems for renewable energies (LaNSER). Dr Dridi Donia, post doc research assistant in LaNSER has played an essential role during research and redaction phase of the paper, Professors Miguel Mollar and Bernabé Marí have played essential roles during research part. Finally, Professor Radhouane Chtourou, director of Resaerch and technology center of energy has played an essential role in results discussion.

Data Availability Statement

This manuscript has no associated data or the data will not be deposited. [Authors' comment: There is no external data associated with the manuscript.].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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