ANALYSIS OF TiO_2/ZnO LAYERS FOR PEROSKITE SOLAR CELLS: EXPLORING CRYSTALLINITY, CHEMICAL PROPERTIES, AND OPTICAL PERFORMANCE

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Abstract

The electron transport layer (ETL) was designed for perovskite solar cells (PSCs) using a sol-gel spin coating method on FTO glass substrates, including TiO2 and ZnO nanocrystals. Characterization using X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) implied the crystallinity and chemical properties of the FTO/TiO2/ZnO ETL layers. UV-Vis measurements revealed TiO2 absorption within the range of 211 nm-226 nm and ZnO absorption from 302 nm-387 nm. The energy band gap values of TiO_2/ZnO films showed their suitability as an ETL for PSCs. The study suggests that this ETL not only enhances electron transport and interfacial engineering but also holds promise as a light-harvesting layer in PSCs, attributed to its favorable crystalline quality, chemical characteristics, and optical performances.

Keywords: ETL, FTO, TiO2 /ZnO, Perovskite Solar Cells, XRD, FTIR and UV-Vis

Introduction

Since 2009, Lead halide perovskite materials were obtained. There has been a strong focus on solar cells (Sanglee, K, et al.,2022). Perovskite solar cells have rapidly reached a Power Conversion Efficiency (PCE) of 25.5% in the past few years (Drygała, A&Dobrzański, L.A,et al.,2016). Perovskite materials have unique photovoltaic properties, such as strong light absorption and long carrier lifetime. Optimizing the absorber layer and selecting suitable materials as electrodes are also important in improving the PCE. Surface engineering techniques, such as coating a thin layer on the electron transport layer (ETL) or hole transport layer (HTL) or surface modification, can significantly improve the electrical and optical properties, stability, and scalability of solar cells. Many studies have focused on the conventional (n-i-p) structure of PSCs. The electron transport layer (ETL) is a key component of a solar cell. ETLs protect the perovskite layer from direct contact with the transparent oxide and perovskite crystal structure, and play a crucial role in efficient transfer and transport. Among metal oxides, TiO2 can best serve as ETL in planar or mesoporous form. Surface modification of TiO2 has been carried out using different materials such as SnO2 (S. Casaluci, et al.2009), ZnO, MgO (Kojima, K. Teshima, &T. Miyasaka, et al.2009). Typical ETLs are titanium dioxide (2H, zinc) (Szewieczek, 0;. Zuo, C.; Zhang, L, et al.2023) or zinc-tin oxide (G. S. Han, H. S. Chung, et al.2015).In particular, perovskite solar cells with ETL from aged titanium sol revealed significant differences of short circuit current which is 8% higher than their counterpart with ETL from fresh sol (M.M. Tavakoli et al.,2015). Titanium dioxide can be deposited by chemical vapor deposition (G. San Vicente et al..2001) atomic layer deposition or sol-gel method (Liu H., Yang W., Ma Y., Cao Y.,et al., 2002), where the sol-gel is frequently used due to inexpensive, easy processing and high repeatability. Sol-gel method is low cost of necessary materials; TiO_2 is known to be the most widely used because of its mild reaction conditions and high purity and uniformity (Yu J.G.,& M. M. Ba-Abbad,et al.,2012). TiO_2 is an n-type wide bandgap semiconductor and has three crystalline phases, i.e. anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic) with band gap 3.02 eV (410 nm), 3.20 eV (387 nm) and 2.96 eV (419 nm), respectively. Among these three types, the rutile phase is most stable form while anatase and brookite types are

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metastable and possible to transform to rutile phase under high temperature of about 750°C. Synthesis of anatase, rutile and brookite of TiO_2 particle and thin film from $TiCl_3$ were reported by Leal J L *et al*. (Affa Rozana Abdul Rashid,et al.,2021), Considering ETL as an important part of perovskite-based solar cell we put more emphasis on examination of its impact on perovskite solar cell parameters.

Materials and Methods

Synthesis of Titanium Dioxide Films

In the present research, titanium trichloride ($TiCl_3$), hydrochloric acid (HCl) and ammonium hydroxide (NH_4OH) solutions were used as starting materials. All chemical reagents used in these experiments were of analytical grade, commercially purchase from chemical market used as received without purification. Deionized water (DI) was used as solvent. TiO_2 solution have been firstly prepared by using sol-gel method. Firstly, 20 ml of $TiCl_3$ was dissolved with 100 ml of Deionized (DI) water stirred for about 1hour on the magnetic stirrer. At that time, the color of solution was found to be purple. During stirring, the 40ml of ammonium hydroxide (NH_4OH) solution was added and it was found that the color of solution changed purple to dark black. The solution was stirred continuously about 15 minutes the color change to sky blues. After stirred at 15 minutes the color of this solution was changed to perfectly white. This procedure last totally about five hours. This solution reached the pH value in 10. During stirring, hydrochloric acid (HCl) was poured by using drop by drop in the mixture solution until to get a homogeneous solution and adjust pH levels to reach pH 7. The block diagram of TiO_2 films preparation was shown in Figure 1. Figure 2 showed the change in color of TiO_2 sol gel solution while the adjustment of pH level to reach 7.

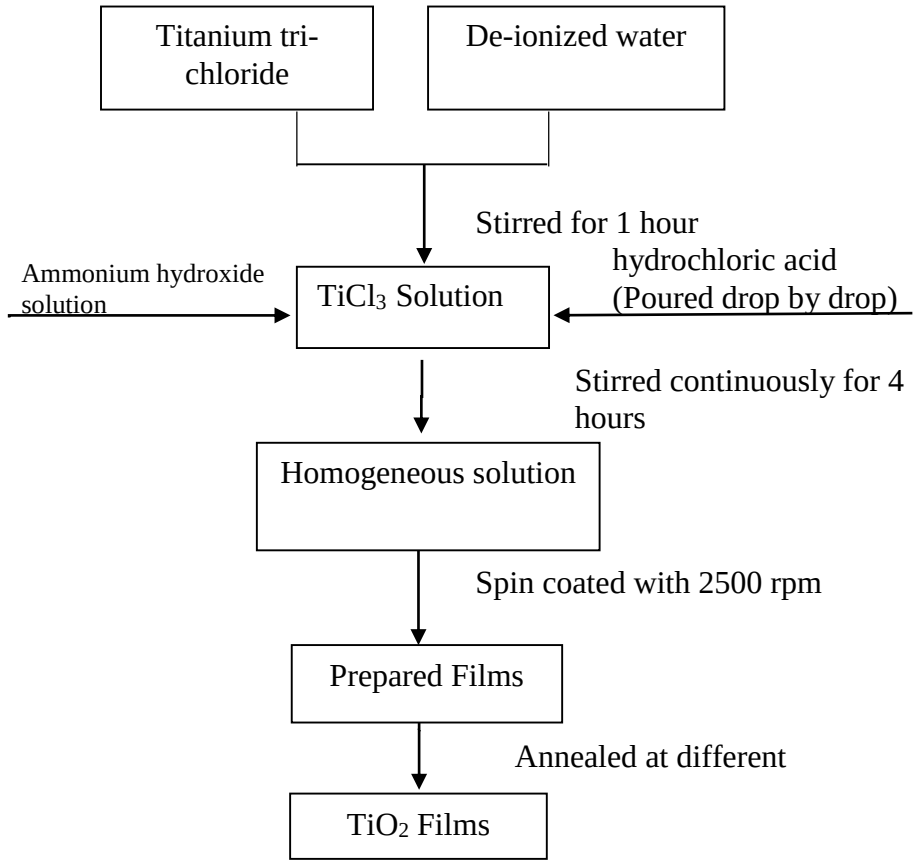

Figure 1 The block diagram of TiO_2 films preparation

Figure 2 Change in color of solution while the adjustment of pH level to reach 7

Synthesis of Zinc Oxide sol-gel solution

They were first agitated by a magnetic stirrer in various containers of 4g NaOH in 100ml DI water and 20.83 g $ZnCl_2.4H_2O$ in 100 ml DI water, and then stirred at room temperature for 15 min on a magnetic stirrer. Finally, the solution containing NaOH was slowly poured into a container of $ZnCl_2.4H_2O$ for three hours at 80°C with a magnetic stirring to obtain ZnO sol-gel solution.

Device Preparation of hybrid TiO_2/ZnO Electron Transport Layer

Firstly, the cutting Fluorine doped Tin Oxide glass substrates with a thickness of 1.1 mm and size of 1x1 cm^2 (11-20Ω) immersed by hydrochloric acid (HCl) and distilled water in the ratios 1:20 for 30 minutes to remove some impurities on the glass substrates. Secondly, these glasses were certainly washed by distilled water and were dried up at room temperature. And then, they were dipped in ethanol about 10 minutes and dried. After this process, these glasses were dipped in acetone for about 15 minutes and finally dried at room temperature. TiO_2 solution was coated on FTO glass substrates through spin coating machine with 2500 rpm for 30 s. After the deposition, the films were dried at 80 °C for 1 hour and allowed to cool slowly at room temperature. The prepared TiO_2 films onto FTO substrates were annealed at 400 °C, 450 °C, 500 °C, 550 °C and 600 °C for 2 hours respectively. Figure 4 showed TiO_2 solution was coated on FTO glass substrates. And then, ZnO solution was coated on the TiO_2 layer on FTO glass samples made at different temperatures by a spin coating machine at 2500 rpm for 30 seconds. The films were dried at 80 °C for 1 hour and cooled slowly to room temperature. The sample Preparation of hybrid TiO_2/ZnO Electron Transport Layer onto FTO glass substrates were annealed for 2 hours respectively shown in figure 3. The structural characterization of the deposited films was carried out by X-ray Diffraction and Functional groups and the vibrational energy of the molecules of sample were examined by Fourier transform Infrared Spectroscopy (FTIR). The optical properties of TiO_2/ZnO films were examined using UV-Vis spectroscopy.

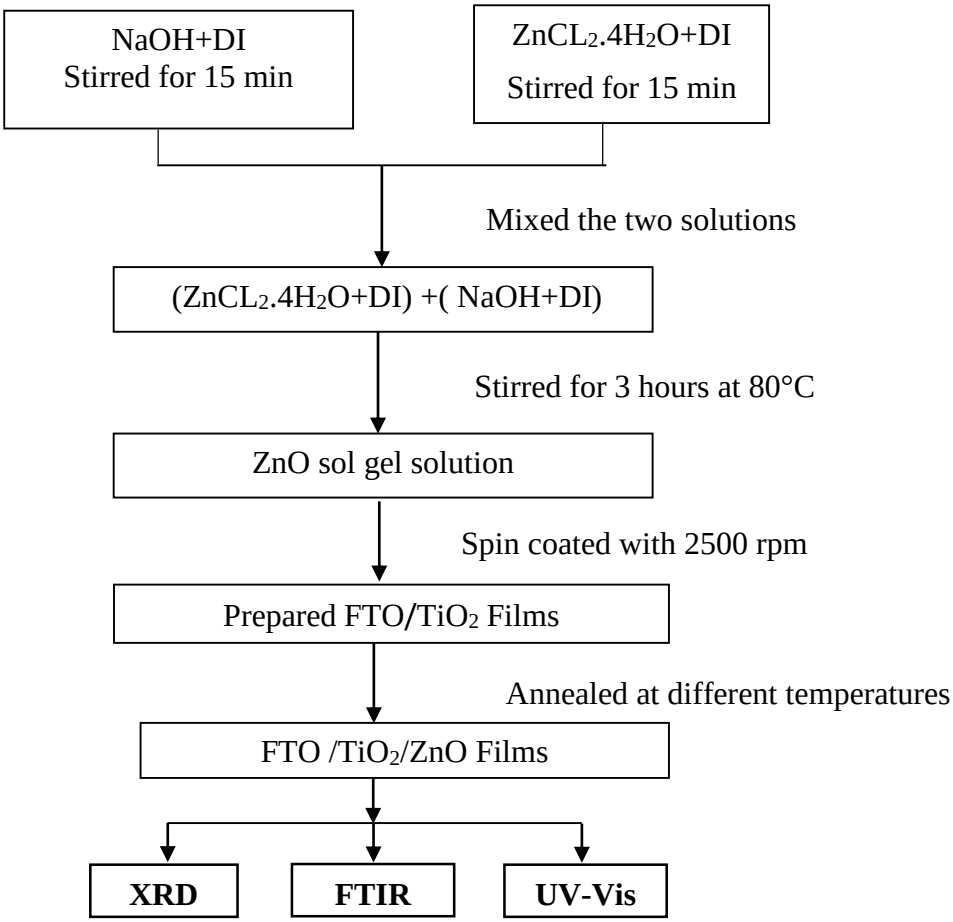

Figure 3 The block diagram of FTO/ TiO_2/ZnO preparation

Results and Discussions

XRD Analysis of TiO_2/ZnO Films

The structural properties of TiO_2/ZnO films were characterized by X-ray diffraction method. The tetragonal brookite phase of TiO_2 peaks were observed at (111), (201), (140) and (133) planes with their respective diffraction angles (2θ). JCPDS card number 00-003-0380 library file confirmed these diffraction peaks. For the ZnO, the distinct peaks were detected at (100), (002), (101) and (102) planes with their respective 2θ values. These results were in good agreement with of hexagonal crystal structure ZnO (Zincite) phases according to the JCPDS card number 00-001-1136. According to the XRD results, there were some minor peaks were also found. This may be the requirements of sample preparation and substrate cleaning process. All the XRD spectra of TiO_2/ZnO films compared in figure 4. The average crystallite sizes of TiO_2/ZnO films were calculated by Debye Scherrer formula. From the calculation results, the average crystallite sizes of TiO_2/ZnO films were 26.71 nm at 400 ^oC, 24.13 nm at 450 ^oC, 23.81 nm at 500 ^oC, 23.72 nm at 550 ^oC and 23.32 nm at 600 ^oC respectively. Table 1 tabulated the structural properties of TiO_2/ZnO films at different process temperatures. According to the XRD analysis, temperature conditions highly influenced the crystallinity during the thermal oxidation process. Increases oxidation temperature on TiO_2/ZnO films were decreased crystallite sizes.

Table 1. Structural properties of TiO_2/ZnO films at different temperatures

Distinct peaks (hkl)	Average crystallite size (nm)	Assigned structure
(111)	26.71 (400 °C) 24.13 (450 °C) 23.81 (500 °C) 23.72 (550 °C) 23.32 (600 °C)	TiO_2
(100)		ZnO
(002)		ZnO
(101)		ZnO
(201)		TiO_2
(140)		TiO_2
(102)		ZnO
(133)		TiO_2

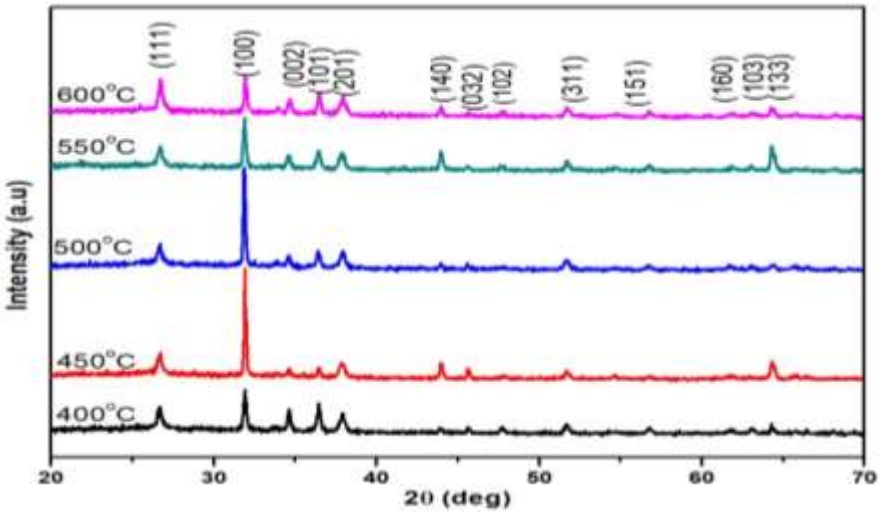

Figure 4 Comparison of XRD spectra for TiO_2/ZnO films at different temperatures

FTIR Analysis of TiO_2/ZnO Films

In this study, the chemical properties of the sol-gel synthesized TiO_2/ZnO films were examined by using FTIR spectroscopy. In these results, the absorption band at ~3368 cm^{-1} is related to O-H stretching vibration and ~1631 cm^{-1} to O-H bending representing the water as moisture. The peaks observed at ~1390 cm^{-1}-1500 cm^{-1} assigned to O-H bending vibration in carboxylic acid. The Ti-O stretching vibrations were detected at the wavenumbers ranges of 621 cm^{-1} -704 cm^{-1} [17]. The absorption peaks of Zn-O were observed at ~443 cm^{-1}- 448 cm^{-1} respectively. The existence of these characteristic bands in FTIR spectra confirms the successful formation of TiO_2 and ZnO. FTIR spectra comparison of TiO_2/ZnO films was shown in figure 5.

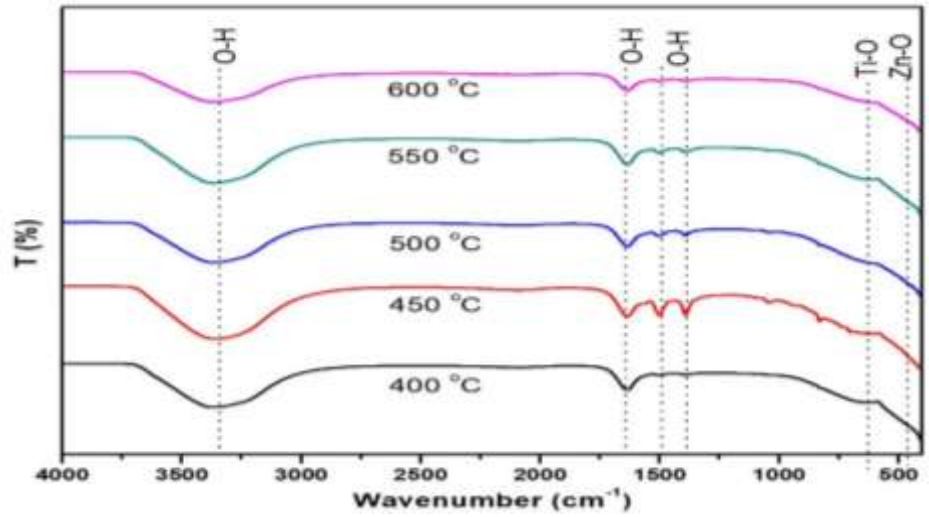

Figure 5 FTIR spectra comparison of TiO_2/ZnO films at different temperatures

UV-Vis Analysis of TiO_2/ZnO Films

The UV-Vis spectra of all TiO_2 films were obtained on Lambda 365 UV-Vis spectrometer in the range of 200 nm -700 nm. Figure 6 (a-e) showed that the UV-Vis absorption spectra with their corresponding energy band gaps of TiO_2/ZnO films at 400 ˚C, 450 ˚C, 500 ˚C, 550 ˚C and 600 ˚C. It was found that the maximum absorption of wavelength obtained by coating onto FTO is in the ultraviolet region. The maximum wavelength ranges of spectrum for all films laid between 200 nm to 400 nm. From the absorption spectra, the wavelength ranges 211 nm-226 nm was TiO_2 absorption and 302 nm-387 nm was ZnO absorption. The alternative method to observe the band gap is Tauc's plot method. On the characteristic curve, the extrapolating the straight line onto horizontal axis ($(\alpha h\upsilon)^2 = 0$) the values of band gap and the obtained films had a direct band gap shown in Table 2.

Table 2. Observed energy bandgaps and referenced energy bandgaps

Samples	**E_g (TiO_2/ZnO) (This study)**	**E_g (for TiO_2 only) (previous study)**	**References**
400 ºC	2.31 eV	3.94 eV	3.3-3.8 eV [18]
450 ºC	2.45 eV	3.92 eV	
500 ºC	3.50 eV	3.77 eV	
550 ºC	3.51 eV	3.74 eV	
600 ºC	3.86 eV	3.62 eV	

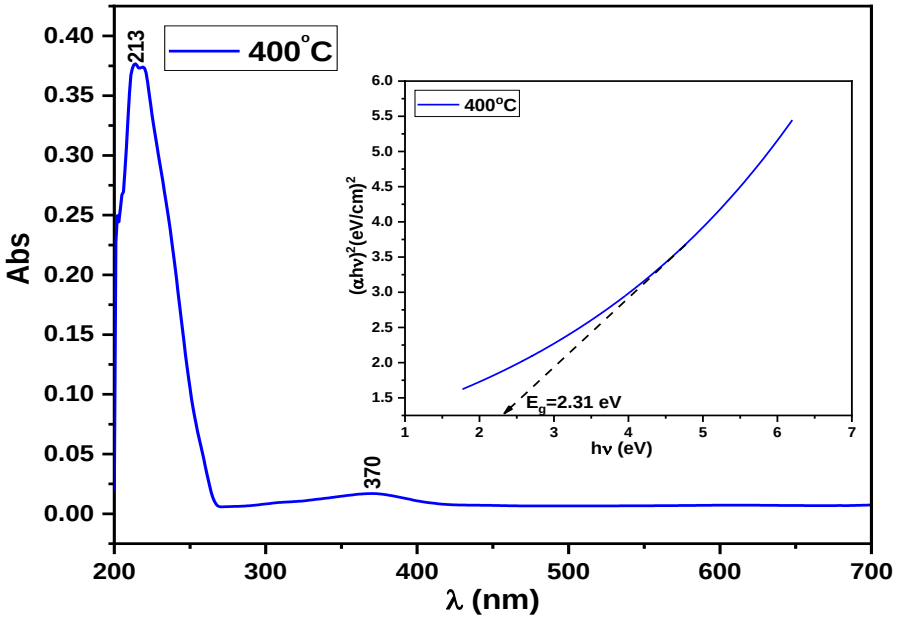

Figure 6(a) UV-Vis absorption spectrum and energy band gap of TiO_2/ZnO film (400 °C)

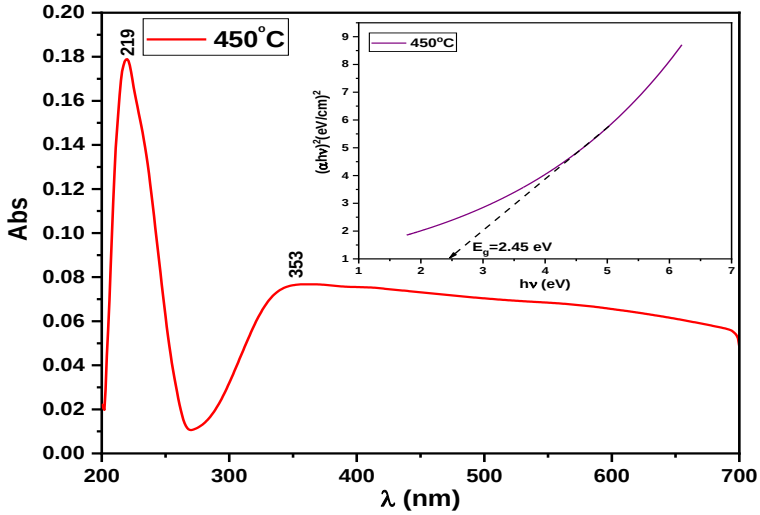

Figure 6(b) UV-Vis absorption spectrum and energy band gap of TiO_2/ZnO film (450 °C)

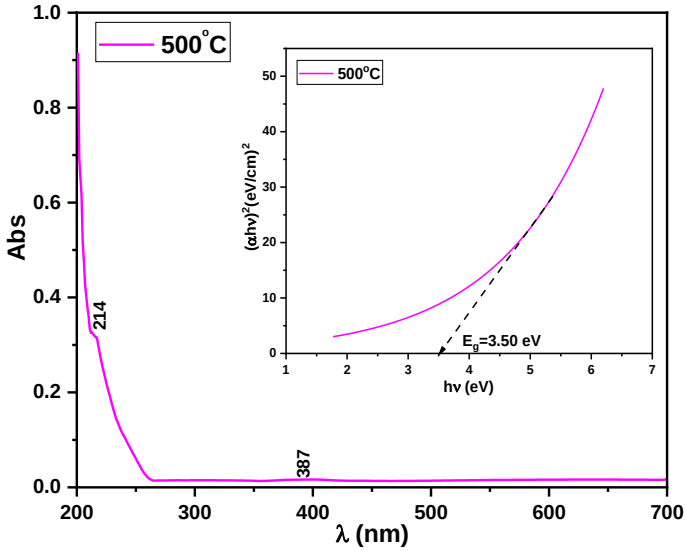

Figure 6(c) UV-Vis absorption spectrum and energy band gap of TiO_2/ZnO film (500 °C)

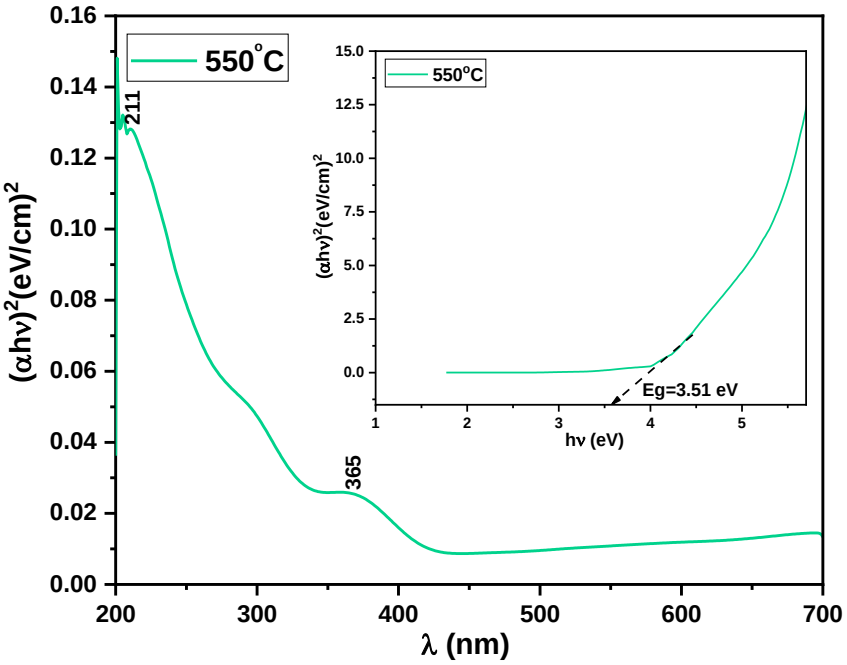

Figure 6(d) UV-Vis absorption spectrum and energy band gap of TiO_2/ZnO film (550 °C)

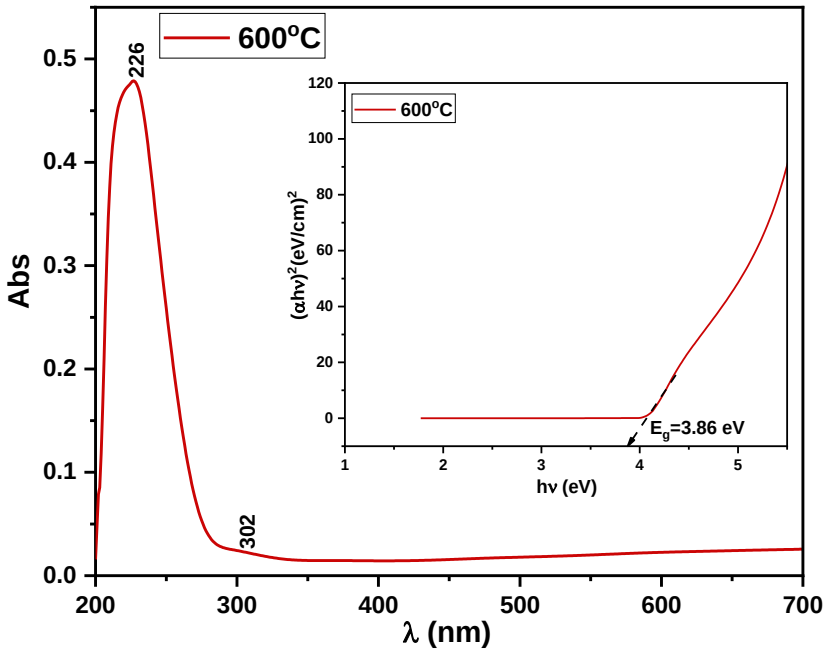

Figure 6(e) UV-Vis absorption spectrum and energy band gap of TiO_2/ZnO film (600 °C)

Conclusion

This study employed a sol-gel method to craft TiO_2/ZnO films at temperatures ranging from 400 °C to 600 °C. XRD and FTIR spectroscopy investigated the structural and chemical properties of FTO/TiO2/ZnO films, indicating temperature-dependent effects on crystallinity. XRD data resulted in a predominant alignment with TiO_2 and ZnO structures, with decreasing crystallite sizes at higher temperatures. FTIR analysis highlighted shifts in functional groups, including peaks indicating Ti-O and Zn-O bonds. UV-Vis spectrometry showcased maximum absorption in the ultraviolet region after coating onto FTO, and the energy band gap values

suggested suitability for use as an electron transport layer in perovskite solar cells. These findings spotlight the importance of optimized electron transport and crystalline quality for systematic perovskite layer growth.

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