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Influence of Thermal Treatment on the Optical Properties of Zinc Oxide and Titanium Oxide for Dye-Sensitized Solar Cell Application

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Abstract

The optical properties of one of the components of a Dye-sensitized solar cell (DSSC) were reported using a photoanode prepared with zinc oxide (ZnO) and titanium oxide (TiO_2) in conformity with Doctor Blade's technique. The prepared photoanodes were characterized with UV-vis spectroscopy. The ZnO and TiO_2 photoanode exhibits high transparency (≥ 60 %) to photons. The modified photoanode, with ZnO-TiO_2(ZTO) composite, revealed an improved light transmittance over TiO_2. The energy band gaps obtained for ZnO thin films as-prepared and annealed are 3.93 eV and 3.98 eV, respectively, and 4.08 eV and 4.14 eV, respectively, for the TiO_2 as-prepared film and the annealed film. The ZTO composite lowers the absorption in the visible region. The results obtained provide improved photoanode for DSSC application, compared to using unannealed semiconductors.

Keyword: Annealing, Photoanode, Zinc Oxide, Titanium Oxide, Dye-sensitized solar cell

1. Introduction

The global rise in population has appreciably necessitated an increase in the world's energy demands in this century. Alternative energy sources such as radiation from the sun, wind energy, and hydropower are being investigated widely. Access to energy is not the only drive to move away from reliance on fossil fuels. There is a severe concern over change in our climate due to different anthropogenic activities, which increase the concentrations of what is known as greenhouse gases, like carbon dioxide (CO_2), in the earth's atmosphere (Wills, 2014). The reduction of crude oil and rising consciousness of the impacts of its use on the environment has awakened nations to reconsider the weight of maximizing renewable energy sources like solar energy. Out of the available renewable energy sources, solar energy is limitless and pollution-free. (Evbogbai *et al*., 2009). This energy from the sun should be appropriately and efficiently harnessed for human use. However, even though silicon-based solar cells have been developed to harness solar energy efficiently, they are not yet economically handy compared with fossil fuels. This is mainly due to the high production costs (Zhang, 2011). Developing cost-effective solar energy devices with realistic efficiency is becoming a concern for many. As renewable energy-based systems gain pace, Venkatraman *et al*. (2018) reported that there has been a focus on capturing solar energy while making it useable and cost-effective. Silicon, polymer, quantum dots, dye-sensitized, and, more recently, perovskites-based solar cells are among the technologies that turn sunlight into energy. Grätzel cells, also known as dye-sensitized solar cells (DSSCs), have sparked much interest among

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these researchers (Hagfeldt *et al*., 2010; Clifford *et al*., 2011). Hence, Dye-Sensitized Solar Cell (DSSC) have been brought to the glare of publicity as an essential substitute to silicon photovoltaic due to their stimulating features like low fabrication cost, simple fabrication process, improved operation at higher ambient temperature, ability to work with diffuse light. DSSC is a device that belongs to the recent generation of photovoltaic devices, as introduced by Regan and Grátzel in 1991 (Agarkar, 2014). Since the invention of DSSC, it has experienced intensive study and is currently undergoing broad and swift growth for commercial use.

A distinctive DSSC consists of four components: a photoanode of morphologically porous Titanium dioxide (TiO_2) or Zinc Oxide (ZnO) semiconductor film of wide energy band gap, dye molecules as a photosensitizer, an electrolyte containing I^- /I^{3-} and a conductor-coated transparent conducting glass as back contact. Such an archetype has produced good performance over time. According to Agarkar (2014), coupling the cell allows for a flexible and relatively cheap processing method. This involves employing a simple film deposition method like Doctor Blade. A good number of sensitizers used in DSSC are synthetic dyes; an example is the Ruthenium-complex dyes, which are toxic and expensive, with low annual yield and limitation in large-scale production of DSSC, though with the best power conversion efficiency when compared with other types of sensitizers. (Tomar, *et al*., 2020).

The unsatisfactory discrepancy between the output of silicon-based solar cells and that of DSSC reveals that something significant must be done to improve the situation. One of the pertinent issues to consider is the electron mobility, electron injection capacity, and recombination rate of holes and electrons in the semiconductors to be sensitized by the dye in a DSSC. The first two properties aforementioned are premised on the nature and properties of the photoanode used. For instance, Jamila *et al*. (2020) used a nanocomposite of Ag-TiO_2 as a photoanode using a natural dye from the flame tree flower (*Delonix regia*) from the flamboyant tree. The photoconversion efficiency of the unmodified cell was 0.36 %, whereas the upgraded DSSC exhibited a photoconversion efficiency of 0.71 %. Hence, this work focuses on the study of necessary modifications, like the effect of annealing and composite on a semiconductor for photoanode, with the expectation of improving the overall power conversion efficiency (PCE) of DSSC.

2. Materials and Methods

The following materials and reagents were used in preparing the studied photoanode without further purification: titanium dioxide (TiO_2) powder (LOBA Chemie Laboratory Reagents and Fine chemicals, TiO_2 M.W. 79.89, Minimum assay—98%); Zinc Oxide (ZnO) powder (BURGOYNE Laboratory Reagents, India, ZnO M.W. 81.38, Min. 99%); Polyethylene Glycol (PEG) 6000 (Qualikems Laboratory Reagents); and microscope glass as substrate.

The glass substrates were precleaned before use. They were first washed with detergent and water. Acetone, isopropyl alcohol, and ethanol were also used to clean the glasses with an ultrasonic cleaner (model VWR) for efficient removal of any dirt or contaminant. This was done for 30 minutes. Polyethylene Glycol was also mixed with the TiO_2 and ZnO for good adherence of the film on the substrate. The photoanode films were prepared using the Doctor blade's method. The films were annealed in an electric furnace at C.

The prepared photoanode was subjected to optical characterization using a UV-vis spectrophotometer (model: Avantes, Avalight-DH-5- BAL) to investigate the optical properties of TiO_2 and ZnO thin films in the wavelength range of 239 to 999 nm.

3. Result and Discussion

3.1 Characterization of Zinc Oxide (ZnO) thin film

3.1.1 Transmittance of Zinc Oxide (ZnO) films

The optical transmittance spectra of ZnO thin films was obtained from the UV-vis spectroscopy analysis in the wavelength range of 239 nm to 999 nm. Figures 1 and 2 show the as-prepared and the annealed transmittance spectra of ZnO thin film respectively.

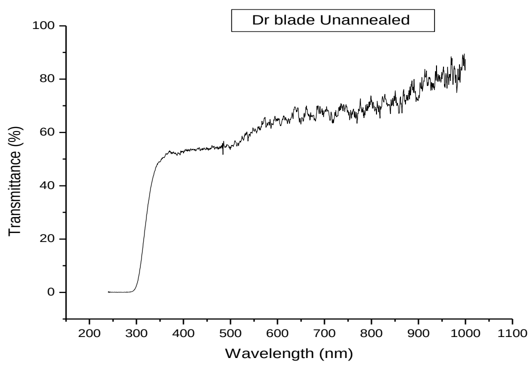


Fig. 1: As-prepared ZnO thin film

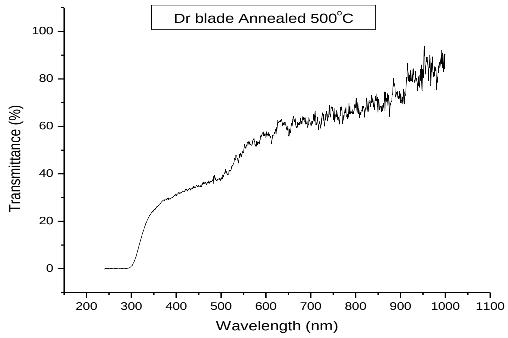


Fig. 2: Annealed ZnO thin film at 500 ^{0}C

Several transmittance peaks are observed in the wavelength region of visible light considered. There is an appreciable high transmittance of about 65 % for the as-prepared and 60 % for the annealed around 600 nm, within visible region (380 nm – 800 nm) of electromagnetic radiation. This can be attributed to the photoanode film thickness. Material of such allows photons to pass through to reach the dye for absorption in order to enhance excitation of electrons in it. Annealing slightly reduces the percentage transmission of light in the ZnO material in the region of consideration for application in DSSC.

3.1.2 Absorbance of Zinc Oxide films

The absorption spectra of the ZnO thin films were determined from transmittance results, using the formula in equation 1 and presented in Figures 3 and 4.

$$A = 2 - Log(T\,\%) \qquad (1)$$

A sharp decrease in the transmittance is observed at about 330 nm and 350nm for as-prepared and annealed respectively, which is considered to be due to the band edge absorption. This strong absorption means that the incoming photons have the enough energy to move electrons from the valence band to the conduction band at shorter wavelengths (λ < 400 nm).

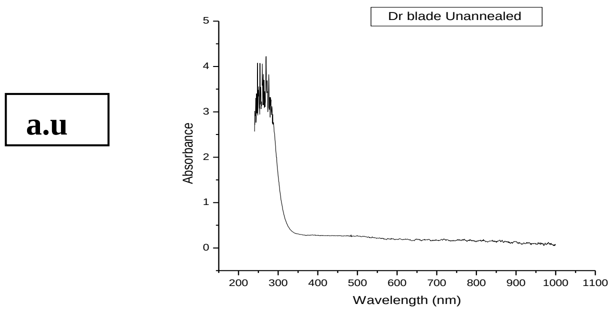


Fig. 3: Absorption spectra of As-prepared ZnO thin film

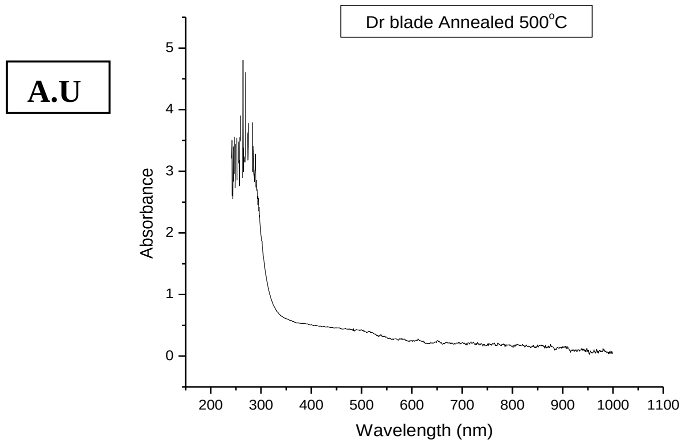


Fig. 4: Absorption spectra of Annealed ZnO thin film

The fall in the absorption of light in the visible region is confirming the fact that the material is indeed a good transparent semiconductor which allows photons to pass through to the desired end. This observation is typical of transparent conducting oxide (TCO), which is sine qua non for use in photoanode in a DSSC.

3.1.3 Energy Band Gap

To obtain the band gap energy of the material, the dependency of absorption coefficient on photon energy in high absorption regions is investigated. The following relationships are used to assess the optical band gap of the films:

$$E = hf \qquad (2)$$

hf is the absorption photon energy, h is Planck's constant which is 6.63 x 10^{-34} Js

$$(\alpha hf)^2 = A\,(hf - E_g) \qquad (4.6)$$

$\alpha = Absorption\ \ coefficient$. Equation 2 is referred to as Tauc's Relation.

$(\alpha hf)^2$ is shown as a function of photon energy to determine the value of the direct optical band gap.

It has been observed that the plot of $(\alpha hf)^2$ vs (hf) is linear (from Figures 5 and 6) over a wide range of photon energies indicating a direct type of transitions.

The energy band gaps obtained are 3.93 eV and 3.98 eV for ZnO thin films as-prepared and annealed respectively. The widening of the band gap beyond the theoretical value of 3.37 eV for ZnO is suspected to be as a result of the addition of PEG which was used in the preparation of the films for good adherence to the substrate. The widening of band gap attributed to PEG used in the formation of the film could be as a result of the addition of foreign atoms (impurities) from the polymeric material; ethylene glycol used in the PEG.

The energy gap of the annealed sample widened as a result of the annealing procedure, which reduced crystal defects, increased crystallization, and so increased the gap between the valence band and conduction band of the material, resulting in a material suited for TCO usage. The band gap widening can be attributed to the larger downward shift of the valence band. The widened band gap observed could also be as a result of the presence of vacancies, probably due to the effect of the annealing, in the ZnO nanostructure. This is in agreement with the report of Kamarulzaman, *et al.*, (2015). Band gap is a very important physical feature of materials which affect their electrical behaviour.

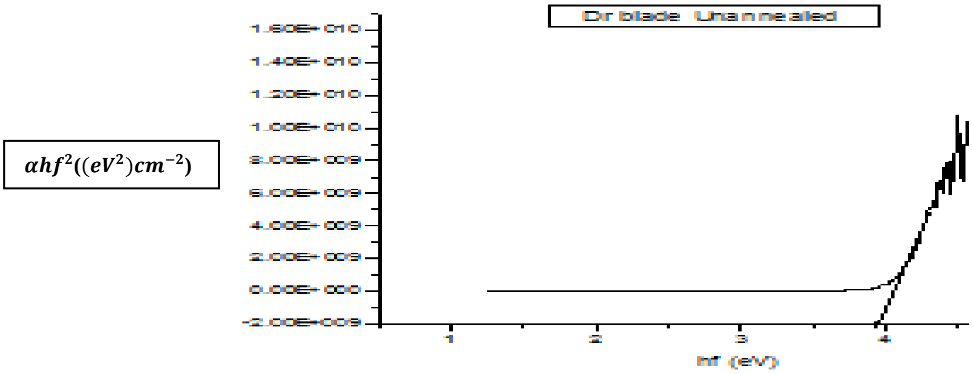


Fig. 5: Energy band gap of As-prepared ZnO thin film

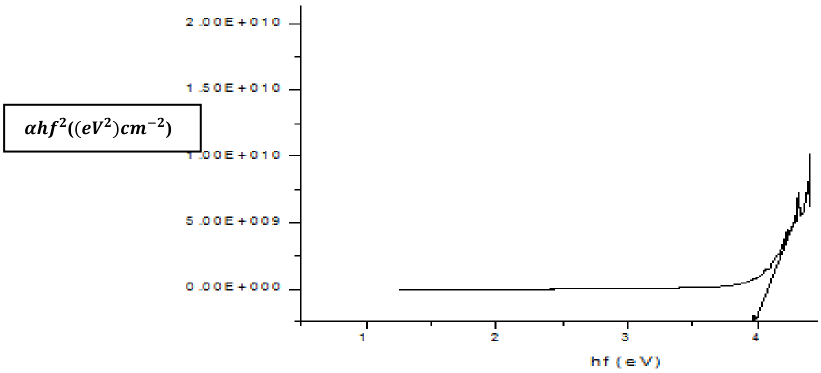


Fig. 6: Energy band gap of annealed ZnO thin film at 500 ^{0}C

3.2 Characterization of Titanium Oxide and ZTO

The optical properties of the deposited TiO_2 film and the zinc oxide and titanium oxide composite named ZTO were obtained by using the UV-Vis spectroscopy. The transmittance and absorbance spectra were presented in Figures 7 and 8 respectively. The percentage transmission obtained is around 70 %. This is a bit higher than that of ZnO (as discussed earlier). TiO_2 is more transparent than ZnO. ZTO has an improved transmission of light and ZnO in it will also enhance good electron mobility, and hence higher conductivity.

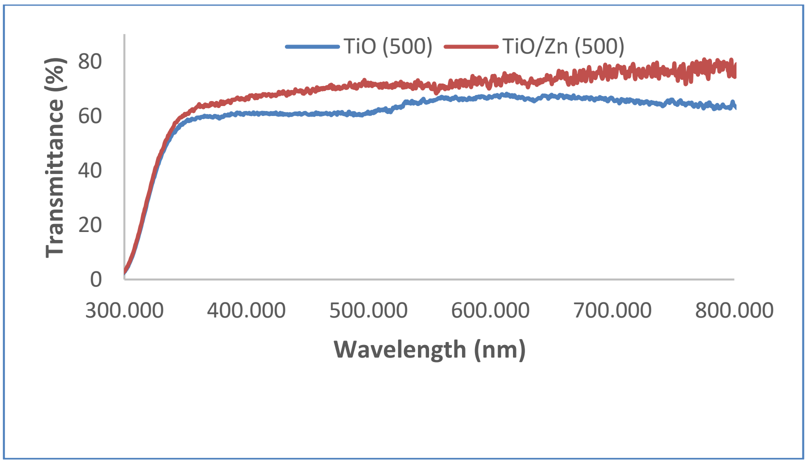


Fig. 7: Comparison of transmission spectra of TiO2 and ZTO

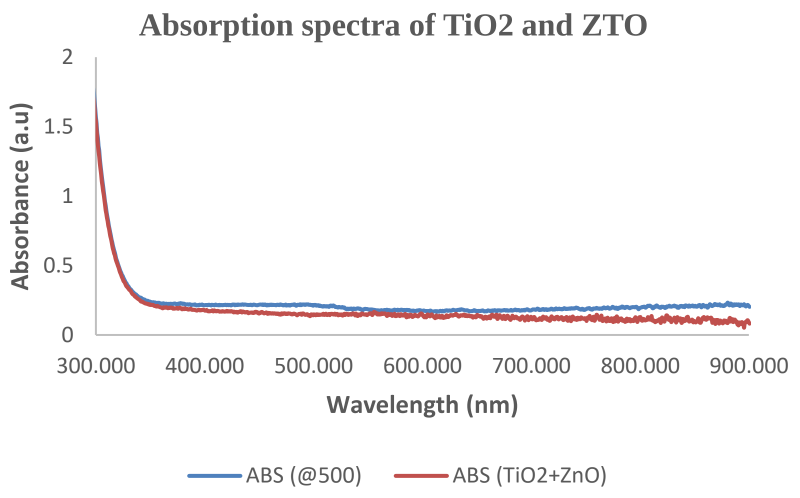
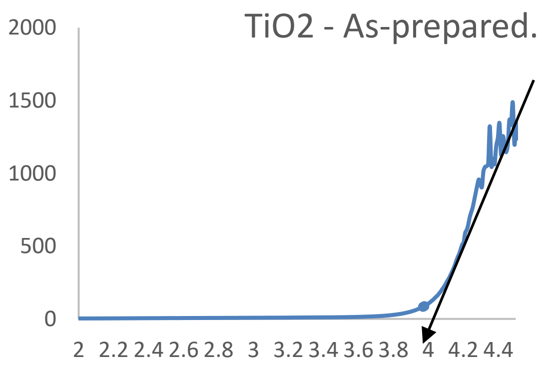


Fig. 8: Absorption spectra of TiO_2 and ZTO

There is significantly low absorption in the visible region which is inversely a result of high transmittance. Also, the composite lowers the absorption, and hence increases transmission, especially between 400 nm and around 550 nm where solar radiation peaks in a day.

3.3 Energy Band Gap

The energy gap of the TiO_2 and ZTO films were obtained from the absorbance values derived from the spectroscopic analysis carried out. It is expected that the energy of the photons is greater than band gap of the material for separation of charges to take place for its application in photovoltaic device. The energy band gaps of the as-prepared and annealed films were given in Figures 9 and 10 respectively. The values were estimated to be 4.08 eV and 4.14 eV respectively for the as-prepared film and the annealed film. Annealing raises the band gap slightly, probably due to the heat treatment effect on the crystallinity of the semiconductors and hence widening the energy band gap.



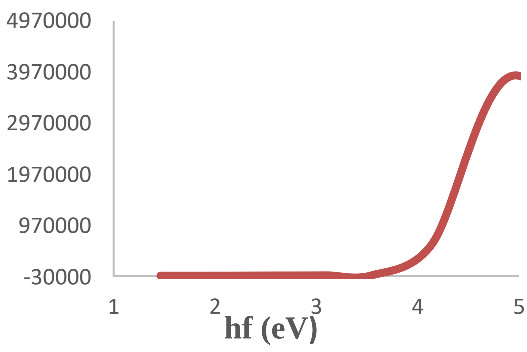


Fig. 9: Energy band gap of TiO2 **Fig. 10**: Energy band gap of Annealed TiO2

A sufficiently wide band gap for a semiconductor to be suitable as a TCO is obtained (which is 4.14 eV), as compared to the theoretical band gap of about 3.2 eV, according to Dachille *et al.*, 1968. The widening is probably attributed to the introduction of the PEG. There is no huge difference between the band gap of TiO2 and ZTO as shown in Figure 11.

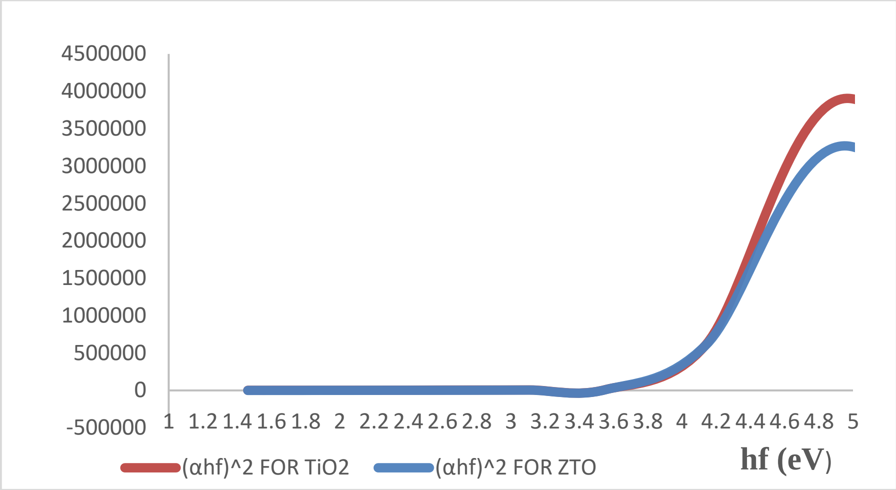


Fig. 11: Comparison of energy band gap of TiO_2 and ZTO

4. Conclusion

This work reported the effect of annealing on the optical properties of ZnO, TiO_2, and their composite. ZnO and TiO_2 films have their energy band gap increase slightly due to the introduction of polymeric material. The materials deposited as the photoanode exhibit high transparency () to photons, making it suitable as a semiconductor for light-passage medium for fabricating dye-sensitized solar cells. The modified photoanode, with ZnO-TiO_2 composite, revealed an improved transmittance of light of about 70% over 60% for ordinary TiO_2. It is evident from the results obtained that thermal treatment produced enhanced optical properties and consequentially promising electrical properties in a photoanode for application in DSSC.

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