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Effect of Titanium Oxide (TiO_2) on Natural Dyes for the Fabrication of Dye-Sensitized Solar Cells †

Isioma M. Ezeh [1], Omamoke O. E. Enaroseha [1,*], Godwin K. Agbajor [1] and Fidelis I. Achuba [2]

1 Department of Physics, Delta State University, Abraka 330105, Nigeria; ezehmiriam@gmail.com (I.M.E.); gkagbajor@delsu.edu.ng (G.K.A.)
2 Department of Biochemistry, Delta State University, Abraka 330105, Nigeria; achuba@delsu.edu.ng
* Correspondence: enarosehaomamoke@gmail.com; Tel.: +234-8036204434

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Abstract: Titanium oxide (TiO_2) is the most widely used white pigment because of its brightness and very high reflective index, traits surpassed by only a few other materials; it has gained adequate ground in the fabrication of solar cells due to its wide band gap of 3.32 eV. Various natural dyes such as laali plant dye, zobo leaf dye and tomato seed dye act as sensitizers. This research intends to explore the effect of this titanium oxide on enhancing sensitivity in light harvesting by using dye-sensitized solar cell fabrication. Indium tin oxide, one of the transparent, conducting optical glasses, was chosen for the photoanode, on which the prepared titanium powder and the extracted dye were coated using the screen printing method. TiO_2 was screen printed over the TCO (ITO) or plain glass slide and annealed at 4000 °C for 3 min; then, the dyes were injected drop by drop and analysis was carried out for XRD and UV–optical. From the XRD results obtained for the laali dye, the XRD showed no prominent peaks and when improved by introducing titanium oxide, it showed the peaks as having a rutile nature which enhances light harvesting. The optical properties showed a transmittance edge at 350 nm which gradually increased as the wavelength increased with no visibility on the absorbance graph. For the tomato dye, a visible peak was observed and this increased with the addition of titanium oxide, while transmittance rose at 380 nm and fell at 550 nm, with no absorbance. The zobo dye showed no evidence of visible peaks and little change in the peak visibility with the addition of TiO_2 was observed, with the transmittance edge at 350 nm, maximum at 390 nm and constant with TiO_2 enhancement, and showing no visible absorbance properties. Laali and zobo are good transmittance materials, unlike the tomato dye which is a good absorbance material. Conclusively, TiO_2 is effective in dye-sensitized solar cell fabrication since there were visible changes within the scientific environment which further enhanced light harvesting.

Keywords: adhesion; annealed; dyes; fabrication; titanium oxide; light harvesting

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1. Introduction

Titanium oxide (TiO_2) is produced in varying particle sizes, oil and water dispersible and with varying coatings for the cosmetic industry. This pigment is used extensively in plastics and other applications for its UV-resistant properties where it acts as a UV absorber, efficiently transforming destructive UV-light-energy to heat. TiO_2 is found in almost every sunscreen as a physical blocker because of its high refractive index, its strong UV-light-absorbing capabilities and its resistance to discoloration under ultraviolet light. Due to its wide band gap characteristics and unique photoelectric properties, it is one of the most promising semiconductor materials for the preparation of photoanodes for a dye-sensitized solar cell (DSSCs) [1].

The IUPAC name is titanium dioxide, titanium (IV) oxide, titania, in rutile, anatase, and brookite states. In order to further discuss the nature of titanium dioxide, a previous work is noted as follows: recently, porous, thin film electrodes composed of one dimensional nanomaterials were demonstrated to provide direct electron conducting channels to the electrodes and enhance solar cell efficiency [2]. The anatase titania nanorods prepared from commercial Degussa P25 powdered TiO_2 by the alkaline hydrothermal method were applied to fabricate composite TiO_2 photoanodes for DSSCs which further enhanced the dye-sensitized solar cell efficiency by 7.6%. The purpose of this study, therefore, is to ascertain the effect of the powdered TiO_2 on the natural dye sensitizer in enhancing the efficiency of the operation of dye-sensitized solar cells. Structural and optical characterization will be employed to ascertain this. TiO_2 is frequently used in paints, toothpaste, and sunscreen because of its stable and nontoxic nature. Nanoparticles, nanorods, nanowires, nanotubes, and nanosheets are among the morphologies that can be synthesized. TiO_2 exists in three crystalline forms in nature: rutile, anatase, and brookite. Rutile has a thermodynamic advantage over other forms due to its thermodynamic stability. Each TiO_2 phase has distinct physical properties and, as a result, distinct functions. Rutile's high refraction index allows it to scatter white light more efficiently than anatase. It is often used in paints as a white pigment. Because of its surface chemistry and greater band gap, anatase is preferred in photocatalysis [3].

The optical properties of the TiO_2 anatase phase have been extensively studied using the electrostatic spray deposition method [3]. Due to its light scattering feature, rutile TiO_2 offers an advantage in dye-sensitized solar cells in terms of effective light harvesting. The band gap for anatase TiO_2 is roughly 3.2 eV and 3.0 eV for rutile TiO_2, as illustrated in Figure 1. The energy required to transfer electrons from the valence band to the conduction band is known as the band gap. The material's band gap controls which wavelengths of the solar spectrum it can absorb.

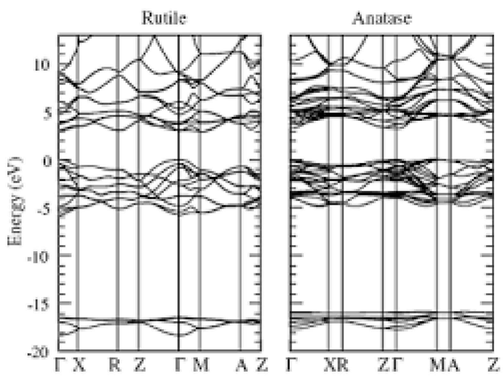

Figure 1. Band gap of anatase and rutile TiO_2.

Natural dyes are locally sourced as sensitizers for light harvesting in the fabrication of dye-sensitized solar cells, due to their availability and accessibility. Using dye as a sensitizer in solar cell manufacturing has become the most practical solution for power generation. The sensitizers, including laali stem bark (Lawsonia inermis, isoplumbagin dye), tomato fruit (lycopene dye), and zobo leaves (anthocyanin dye), were chosen for their unique red coloration as it is within the ultraviolet region of the solar spectrum, which helps to enhance light harvesting. These sensitizers are discussed in detail in the following paragraphs.

Lycopene (Lycopersicon esculentum) is a red carotene and carotenoid pigment and physiochemical found in tomatoes and other red fruits and vegetables, such as red carrots, watermelons, and papayas, and is derived from the neo-Latin Lycopersicon. Despite its molecular similarity to carotene, lycopene has no vitamin A action. It also contains mostly trans-lycopene (35–96 percent of total lycopene content) and only a small amount of cis-lycopene (1–22 percent of total lycopene content). Figure 2 shows the Chemical structure of lycopene dye [4].

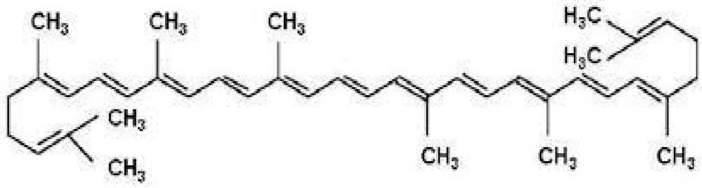

Figure 2. Chemical structure of lycopene dye [4].

Lycopene is the pigment principally responsible for the characteristic deep-red color of ripe tomato fruits and tomato products. Its importance as an antioxidant, arising from its physicochemical and biological characteristics, cannot be overemphasized [4]. Adenike et al. conducted research into the application of dye extracts of natural origin on solar cells made with an enhanced dye of ITO/TiO_2/ZnO/dye sensitizers [5]. A comparison was made between zobo and tomato dyes [6]. The photosensitizer laali stem bark was used to investigate the potential properties of a solar cell with an optical origin [7]. Marcus and Villy examined the kinetics of electron ejection and recombination in dye-sensitized TiO_2 particles in another investigation [8]. Similar research was carried out by Enaroseha et al. to analyze 2.9 µm holmium-doped potassium lead bromide (Ho:KPb2Br5) for transition to diode laser applications [9].

Dyes are important components in DSSCs because they aid in the harvesting of light for photoelectron production and electron transfer [10–15].

Anthocyanins as the dye pigment of the zobo leaves, are a vast family of flavonoids found in plants that are responsible for many of the natural colors seen in fruits and flowers. Anthocyanins have sparked renewed interest due to their potential health benefits and as natural colorants. Anthocyanins can also be used in chemotaxonomic and ecological research. They have vibrant, appealing colors and are water soluble. Acylated anthocyanin pigments have better processing and storage stability. It is thought that the presence of acylated groups in the structure of anthocyanin protects the oxonium ion from hydration, preventing the production of hemiketal (pseudo base) or chalcone forms [16]. Anthocyanin pigments, like all others, are made from two separate streams of chemical raw materials in the manufacturing process.

The process for producing the amino acid is one of the streams. From a C2 unit, the other stream creates three molecules of a C3 unit. As shown in Figure 3, these streams meet and are coupled together by enzyme chalcone syntheses, which produce an intermediate-like compound via a folding mechanism similar to that found in plants [17].

Zobo, also known as roselle, has been shown to contain anthocyanin. The botanical name for this plant is hibiscus sabdariffa, which is also known as red sorrel. The Malvaceae family includes zobo, which is a branching or erect annual shrub with reddish stems that can grow up to 3.5 m tall. Anthocyanin with a surface area of 1.54 cm^2 is found in zobo dye. Anthocyanin has a peak absorbance of 216AU and an optical absorbance of 283–516 nm [10]. A similar application was used in Utility of Magnetic Nanomaterials for Theranostic Nanomedicine [18]. The Chemical structure of anthocyanin dye is shown in Figure 3 [19].

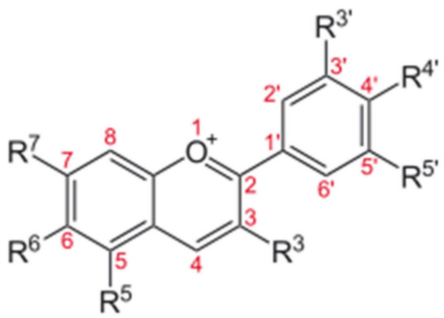

Figure 3. Chemical structure of anthocyanin dye [19].

Isoplumbagin is the physiochemical property obtained from the bark of the stem of the plant known as laali (Lawsonia inermis) and the Chemical structure of isoplumbagin dye is shown in Figure 4. Laali, as it is popularly called, is grown in the savannah region of West Africa [5] and used as the coloring material in the designing of fashionable tattoos on human bodies. Lawsonia inermis (laali) is a very popular natural dye used in coloring fingers, hands, nails and hair amongst the Hausas in the Northern part of Nigeria. The color wavers between reddish brown or light green since the dry powdered leaves soaked in water turns reddish brown but the soaked stem bark appears to have a light green coloration.

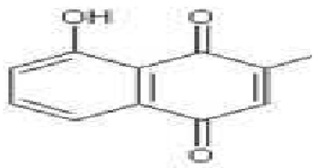

Figure 4. Chemical structure of isoplumbagin dye [5].

2. Materials and Methods

2.1. The Hydrothermal Preparation of TiO_2 Thin Film

A measure of 6 g of powdered TiO_2 was weighed and placed in a mortar for grinding, and 0.1 M of acetic acid was made as shown in Figure 5a–e. The following are the steps that were taken:

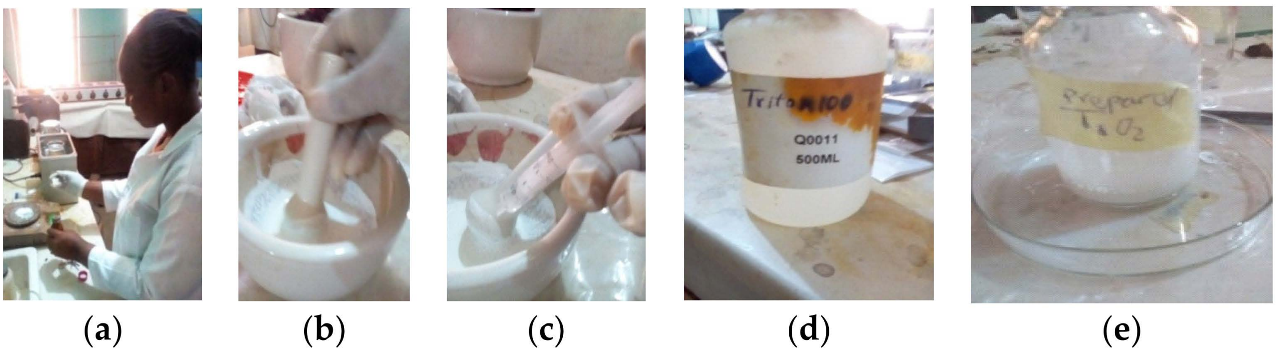

Figure 5. (**a**–**e**): Preparation of TiO_2.

Acetic acid, 0.06 mL, was mixed with 9 mL pure water. The diluted acid was in this prepared solution. Then, 7.5 mL of the prepared diluted acid solution, 20 mL at a time, was poured into the powdered TiO_2 inside the mortar. It was ground until it took on the shape depicted in Figure 5c.

A sample of 1 mL water was vigorously mixed with a drop of Tritaniod (Triton X-100) as shown in Figure 5e. This solution was also added to the ground TiO_2 powder to produce a floppy whitish solution similar to that seen in Figure 5c. The solution of TiO_2 was now poured into a bottle ready for use as shown in Figure 5d.

2.2. Preparation of TCO (ITO) Glass

TCO glass comes in two varieties, fluorine-doped tin oxide FTO and indium-doped tin oxide ITO so due to its availability, the ITO (indium-doped tin oxide) was chosen for this research, as shown in Figure 6. To remove contaminants, the glass was carefully cleansed with acetone solution then placed in a beaker filled with distilled water which was placed inside an ultrasonic machine for about 15 min before being removed and placed in the dry oven.

Figure 6. The ITO glass.

2.3. Preparation of TiO_2/Dye Composite

After a drop of the already prepared titanium oxide solution was deposited on the four slides and screen printed evenly, a drop of (a) laali, (b) tomato, and (c) zobo dye solution as shown in Figure 7a–c were added to it and annealed at 400 °C with a time lag of 3 min and left to cool.

(**a**) (**b**) (**c**)

Figure 7. (**a**–**c**): ITO/TiO_2/dye deposition process.

3. Presentation of Results and Discussion

Characterization of TiO_2 and Its Composite Film

The optical characterization was carried out using the SHIMADZU UV-1800 spectrophotometer found at the Energy Research Centre, University of Nigeria, Nsukka, as shown in Figure 8 below; the structural X-ray diffraction (XRD) analysis was carried out at the South Africa Science Laboratory. The image of the SHIMADZU UV-1800 spectrophotometer shows the equipment and the inner chamber where the slides are inserted and under illumination; the graph is displayed on the computer screen. The results obtained are displayed in Figures 9–16 and while the XRD results are displayed in Figures 17–23.

Figure 8. SHIMADZU UV-1800 spectrophotometer.

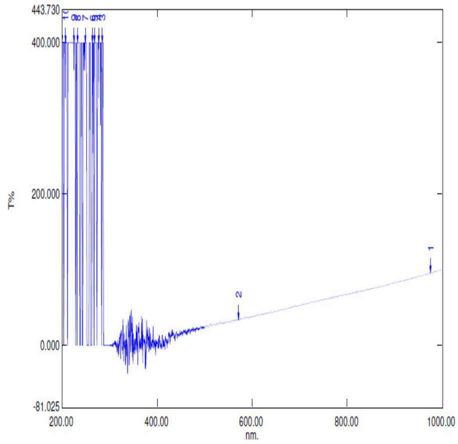

Figure 9. Transmittance of TiO_2.

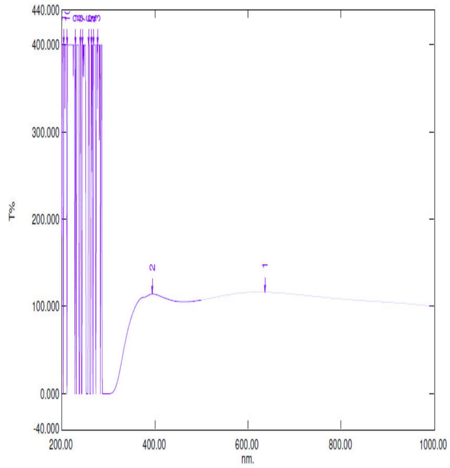

Figure 10. Transmittance of ITO plain glass.

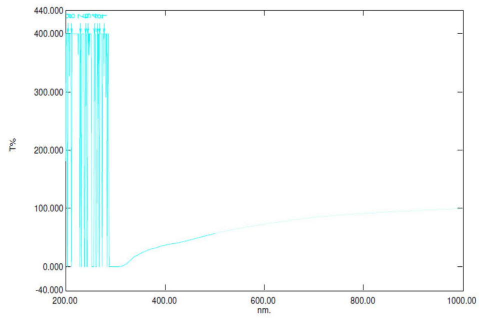

Figure 11. Transmittance of laali dye.

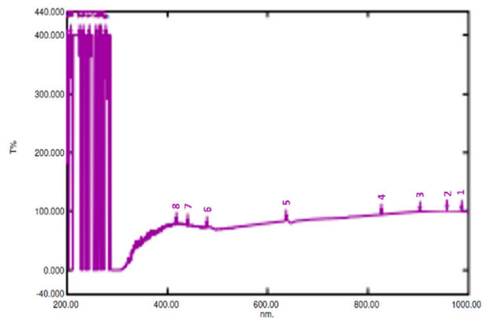

Figure 12. Transmittance of ITO/TiO_2/laali dye.

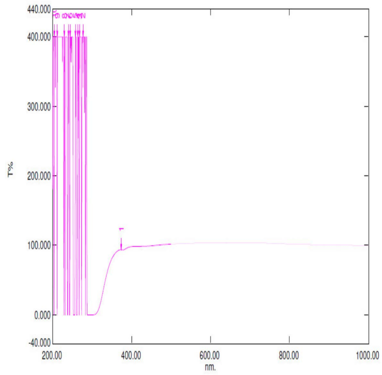

Figure 13. Transmittance of zobo dye.

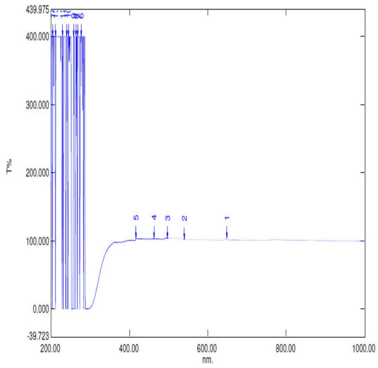

Figure 14. Transmittance of ITO/TiO_2/zobo dye.

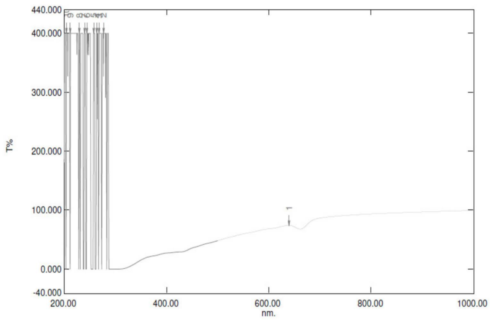

Figure 15. Transmittance of tomato dye.

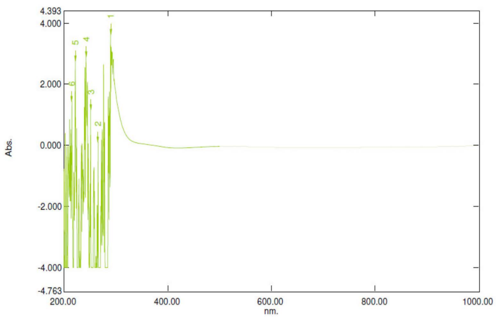

Figure 16. Absorbance of ITO/TiO_2/tomato dye.

From the results obtained in Figures 9–16, TiO_2 enhanced the performance of the sensitizers in the light-harvesting process. It was observed that laali and zobo dyes are good transmitters of light while tomato dyes are good for absorbance, as shown in Figures 15 and 16. Titanium oxide enhances the absorbance property of tomato and likewise the transmittance properties of laali and zobo dye. With the high reflective index of TiO_2 and its transformation of destructive UV-light energy into heat, when cells are fabricated, it will speed up the generation of electricity. This was achieved when multiples of these dye-sensitized solar cells were arranged in series, exposed to sunlight at 2.92 volts and lighted a 2.0 volt diode bulb [20]. The optical property of laali showed 30% transmittance between the 380 and 1000 nm wavelengths; as the TiO_2 was introduced, there was an improvement of 80% transmittance in the same wavelength range of 380–1000 nm.

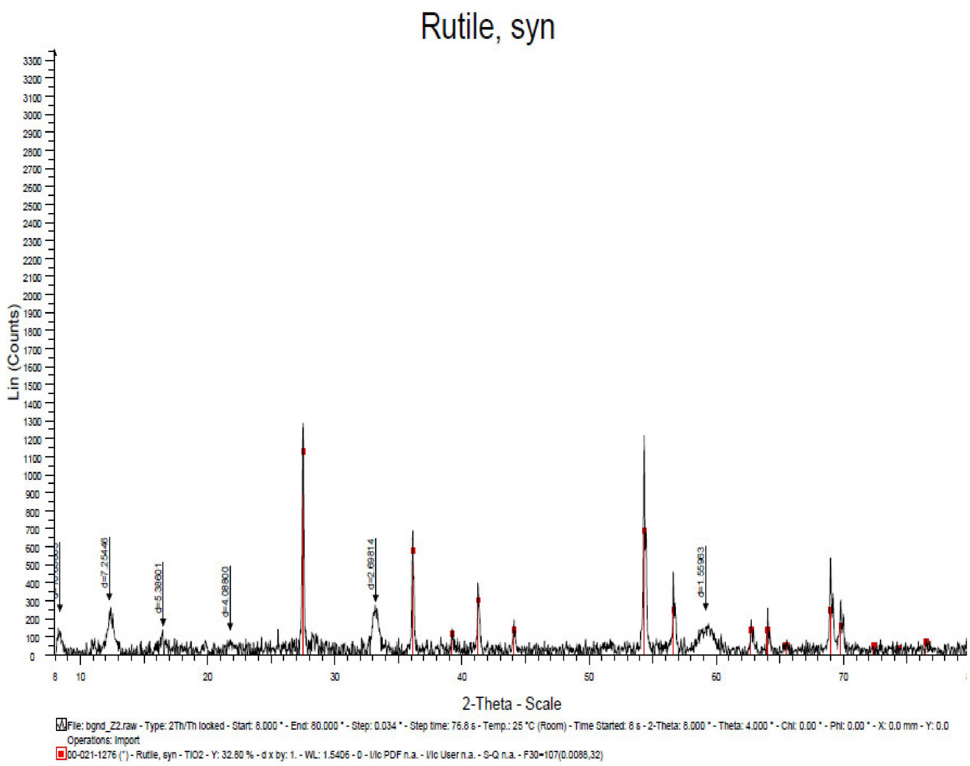

Figure 17. XRD of TiO_2.

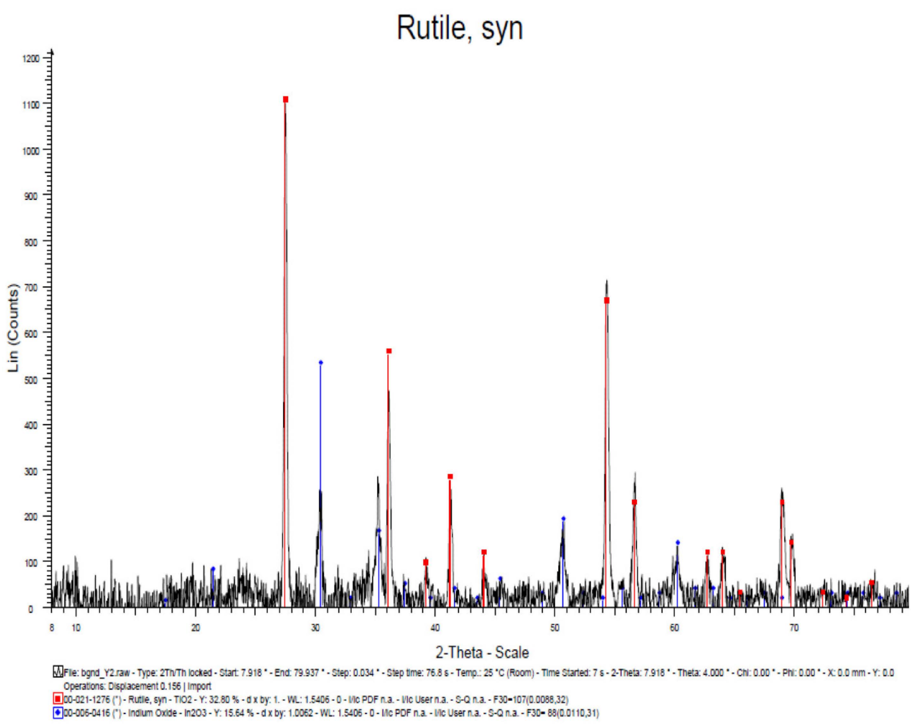

Figure 18. XRD of ITO /TiO_2/laali dye.

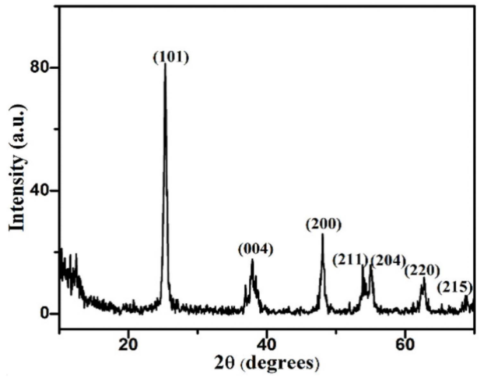

Figure 19. XRD OF TiO_2 nanoparticles [21].

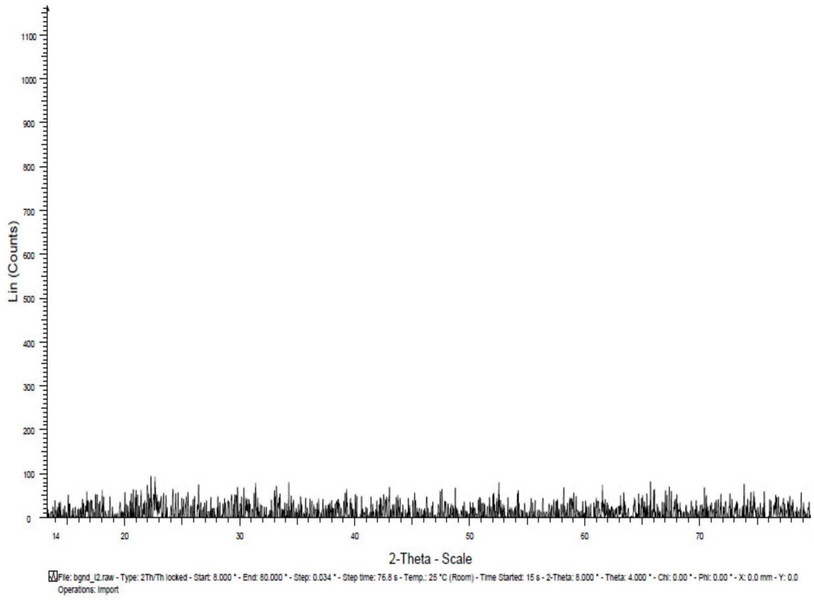

Figure 20. 1.14: XRD of zobo dye.

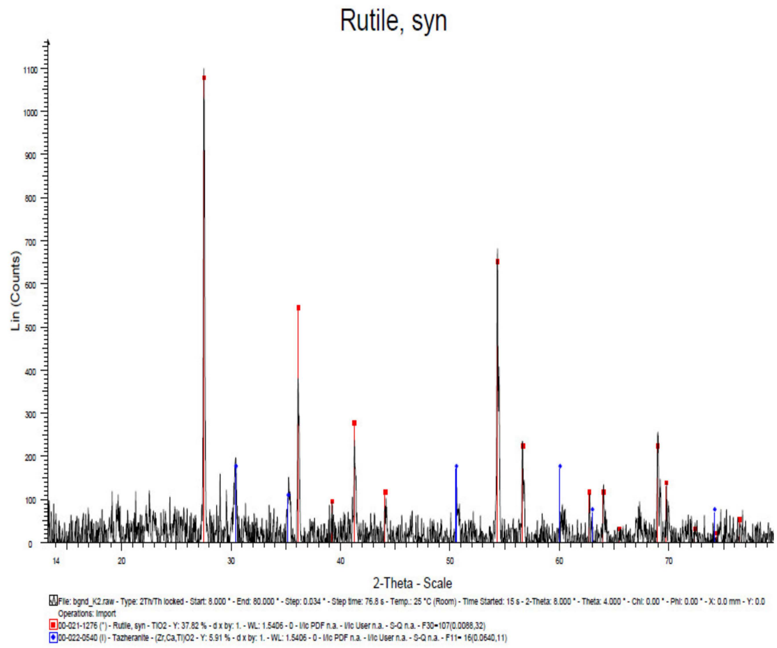

Figure 21. XRD of ITO/TiO_2/zobo dye.

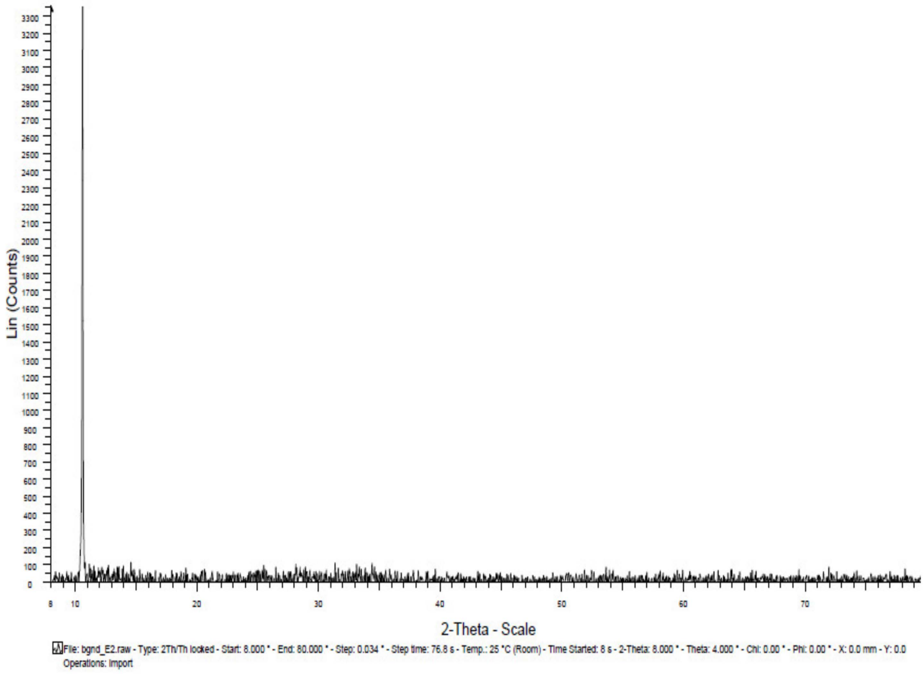

Figure 22. XRD of tomato dye.

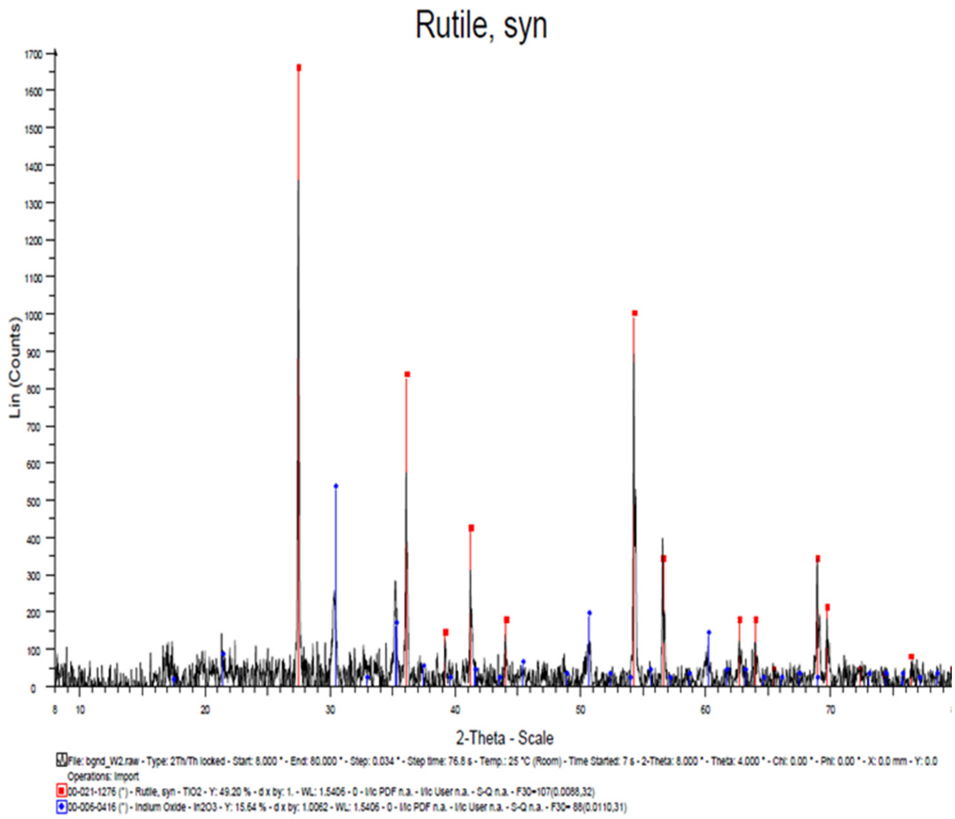

Figure 23. XRD of ITO/TiO_2/tomato dye.

From the X-ray diffraction analysis, it was observed that titania enhanced peak formation and thereby enriched the light-harvesting properties of the DSSCs.

The XRD peaks of titanium dioxide TiO_2 we found are similar to those of Sanjay et al. [22], with two prominent peaks, as shown in Figure 18 above, which show the anatase structure with a band gap of 3.2 eV and also the optical properties of titanium dioxide, which show 100% transmittance between wavelengths of 450 and 900 nm.

In considering TiO_2 with the laali (isoplumbagin) dye, the XRD showed no significant peaks, but when the metallic oxide TiO_2 was added alongside indium tin oxide ITO, three distinct peaks appeared, indicating that the dye and the metallic oxide share an electron interaction. In the XRD of zobo (anthocyanin dye), there were no visible peaks, but with the addition of TiO_2, about three prominent peaks were observed, indicating an electron interface. It was observed that the XRD of tomato (lycopene dye) revealed just one strong peak, but when TiO_2 was added, two more prominent peaks formed, indicating an electron interface.

The optical property, an 80% improvement from 30%, showed the importance of TiO_2 in the fabrication of dye-sensitized solar cells for electricity generation, likewise the X-ray diffraction property in the increase in visible peaks.

4. Conclusions

We have successfully deposited TiO_2 on indium tin oxide using a screen printing method and extracted dyes using a simple deposition process. The simplicity and cost effectiveness of the overall fabrication process, the widespread availability of the dyes and easy extraction of the dye renders it a novel and inexpensive solar cell application. From the results, it can be deduced that TiO_2 enhances the free flow of electrons within the photosensitizers by improving the transmittance from 30% to 80% and establishing an increase in the peaks indicating the free flow of electrons within the anode and the cathode in the cells for the performance of light harvesting.

Author Contributions: I.M.E. carried out the design of the problem with the draft preparation, and O.O.E.E. did the literature review and the methodology. G.K.A. did part of the writing, while F.I.A. plotted the graphs, analyzed it. All authors have read and agreed to the published version of the manuscript.

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