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Zinc and Titanium Oxide Composite for Galena and Turmeric Dye-Based Sensitized Solar Cell

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ABSTRACT

Ruthenium (Ru)-complex dyes are the widely used materials as photosensitizers in Dye-sensitized solar cell (DSSC) devices fabrication for a long time. This work considered the use of alternative natural mineral dyes to the effective but expensive Ru-complex dye and also modified the photoanode used. The modified photoanode has improved properties both structural and optical-wise, over the TiO_2-based photoanode film. The energy gap obtained for both the Turmeric and Galena dye are 2.27 eV and 1.70 eV respectively. The I-V characteristics of the TiO_2-based cell show 340 mV and 32 µA for the generated open-circuit voltage (V_{oc}) and short circuit current (I_{sc}) respectively, while V_{oc} and I_{sc} of 510 mV and 25 µA for the modified photoanode cell was obtained. The Galena as the natural mineral dye shows a promising alternative to the challenge of quick degradation of plant dyes in DSSC.

1. Introduction

The world population increase has called for a rise in the energy demand, greatly, in this digital age. The use of electronic devices, among others, actually necessitated this more. Different sources of energy have been employed for this purpose. Part of this is the solar energy. The global concern over climate change due to anthropogenic activities as a result of the use of some of these energy sources calls for a search for an alternative route to power this age more healthily and efficiently [1]. Out of the available environmentally friendly sources of energy on earth, solar energy is highly perceived to eventually play a key role as a potential energy source. This births the importance of developing a relatively cheap device for solar energy conversion to electrical energy. Hence, further research on DSSC have caught the attention of the material scientists of this century, as a promising substitute to the relatively expensive silicon-based photovoltaics. DSSC is such that is categorized as belonging to the third generation of photovoltaic technology. In 1991, it was credited to the work of two scientists known as Michael Gratzel and O'Regan [2]. Extensive and intensive study has not ceased on this seemingly new photovoltaic technology for its suitability for commercial use. A typical DSSC is made up of four major parts namely; the dye, the photoanode, the counter electrode (as back contact) and the liquid electrolyte. This prototype has produced good performance over time, except the durability challenge posed by the type of dye used. The process involved in producing this cell is flexible and relatively cheap when compared with silicon-based cell fabrication procedures. Since the use of Ru-based dyes in DSSC has been faced with the unsatisfactory challenges of cost and degradation, further research is focusing on alternative photosensitizers to address these issues. Hence this research is centred on studying the effectiveness of a natural mineral dye (Galena) as a photosensitizer in fabricating DSSC and also to modifying the photoanode to improve the photon transmission into the dye for faster electron injection unto the conduction band of the photoanode, all geared towards the prospective enhancement of the cell's efficiency and stability.

2. Materials and Methods

2.1 Materials

The natural mineral dye material used, known as galena, was gotten in a community market in Ilorin, Nigeria. Figure 1 shows it in its unprocessed state while the turmeric spice root shown in Figure 2 was used as the natural plant dye material. A mortar and pestle was used to crush the plant dye while an electric crusher was used to grind the natural mineral to powder. The following reagents were used: Titanium dioxide (TiO2) powder (LOBA Chemie Laboratory Reagents and Fine chemicals, TiO2 M.W. 79.89, Minimum assay – 98%); Zinc Oxide (ZnO) powder (BURGOYNE Laboratory Reagents, India, ZnO M.W. 81.38, Min. 99%), Polyethylene Glycol 6000 (Qualikems Laboratory Reagents). For the fabrication of the cells, transparent conducting oxide (TCO) glasses were used as the electrodes.

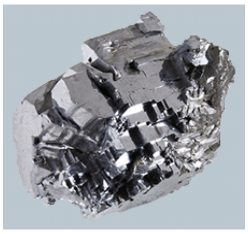


Figure 1: Raw galena [3]

Figure 2: Turmeric plant root

2.2 Methods

After being crushed appropriately into achievable small sizes, the dye materials were soaked separately in beakers with ethanol for 24 hours, for the extraction of the dye content in them. The extracted dye was gotten for characterizations by making use of the decantation method [3].
The optical properties of the dyes were obtained by the use of a UV-visible spectroscopic technique (with VWR: UV-6300PC Double Beam Spectrophotometer).
The chemical compositions of the mineral dye were achieved by using the Gas Chromatography-Mass Spectrometry approach (GC-MS) and the maker of the facility used is the Agilent Technologies – 5975C Inert MSD. The library database of the National Institute of Standards and Technology (NIST) was made used and compared for accurate elucidation of the organic chemical compositions. The doctor blade technique was used for the deposition of the TiO2/ZnO film on the TCO glasses. The electrode produced was finished by heat-treating it in an electric oven for one hour at 100 0C. This electrode was immersed in the dye solutions for a few hours. The nomenclature given to Zinc Oxide-Titanium Oxide Composite is *ZTO*. The liquid electrolyte solution (Iodide/tri iodide) was used for producing the redox couple in the fabricated DSSC. I-V characteristics of the cells were obtained by using Sourcemeter (named NEWPORT Keithley Sourcemeter) and solar simulator (ORIEL Sol 1A) at AM1.5. The expressions given in equations (1) and (2) were eventually used for estimating the cells' efficiencies.

Fill Factor (F.F) = $\frac{V_m J_m}{V_{OC}\ I_{SC}}$ [4] (1)

Efficiency = $\frac{J_{SC} V_{OC}}{P_{in}} F.F \times 100\%$ [5] (2)

The maximum open-circuit voltage and maximum current density are V_m *and* J_m, respectively while the J_{SC} and V_{OC} are the short circuit current density and open-circuit voltage respectively. The input power is P_{in}.

3. Results and Discussion

3.1 Optical properties of Dyes

Figure 3 presents the comparative absorption of light by the two dyes used.

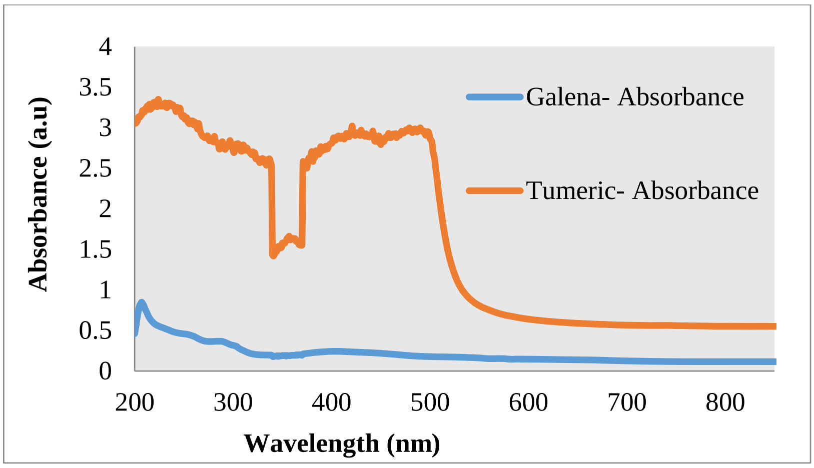


Figure 3. Absorbance plots of both dyes used (Galena - blue; Turmeric - red)

The dyes are also referred to as photosensitizers because they are expected to absorb photons from sunlight, especially in the visible region. Figure 3 shows that the dyes absorb in the visible region of electromagnetic radiation, which ranges from 380 nm to 800 nm. Although few absorption peaks were seen in the ultraviolet region (which is from about 270 nm to 379 nm). This can be attributed to the presence of components like flavonoids in the plant dye in particular. Table 1 shows the summary of values of absorption peaks with their respective wavelength in the visible region, with the highest observed in the natural plant dye, though. The absorption of light by the natural mineral in the visible region promises a potential alternative material as a photosensitizer.

Table 1: Absorption peaks and wavelengths values for the dyes

Dye	Wavelength (nm)	Absorbance
Galena	405	0.243
Turmeric	424	2.903

Ru-complex dye has an embedded form of charge transfer referred to as ligand-centred. It is characterized by π–π^* transitions in it. Also, there is another charge transfer known as metal-to-ligand, and this is mostly known for 4d-π^* transitions. There are known absorption bands at the lower energies, which represent the metal-to-ligand transfer and the ones with higher energies which relate to the ligand-centred [3]. The natural mineral dye used has higher energetic transitions, according to the plot presented in Figure 3, which corresponds to the ligand-centred transfer, hence favouring its absorption of solar radiation for the operation of a photovoltaic device.

3.2 Optical band gap

The band gaps of the dyes used were obtained using the expression given in (3)

Band gap, $E_g = hc/\lambda$ (3)

The Planck's constant is represented by 'h' and the 'λ' is the threshold wavelength, which is also referred to as offset absorption wavelength. The 'c' is the speed of electromagnetic radiation [6].
Table 2 presents the calculated band gap for the dyes. It was observed from the results that an increase in the threshold wavelength results in the narrowing of the optical band gap of the dyes. As the offset absorption wavelength approaches the infrared region, the gap narrows more and hence is expected to cause an increase in the fabricated cell's efficiency [7].

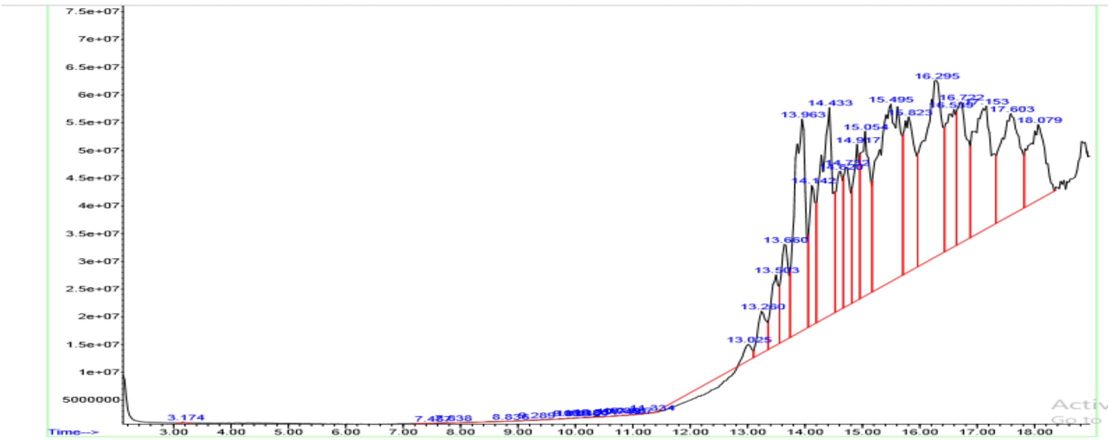
Table 2: Optical band gap of dyes with respective offset absorption wavelengths

Dyes used	**Offset Absorption wavelength (nm)**	**Band gap (electron Volt)**
Galena	725	1.70
Turmeric	407	2.27

The dye with higher absorption of photons of sunlight has a narrower band gap and carries better potential in being a good photosensitizer.

3.2 Chemical properties of the dyes

The chemical composition of the galena dye was studied by the results of the GC-MS. Figure 4 presents the chromatogram of the mineral dye. The organic structure of the compositions present in it was analyzed by using a comparative approach. The library database of the NIST was compared with spectra obtained from the dye and presented in Table 3. This is done to confirm the presence of functional groups already known to contribute to the absorption of solar radiation in a liquid substance.



RT (Mins.)

Figure 4. Chromatogram of the natural mineral dye

The presence of ester, which is for the carbonyl stretching absorption, is confirmed in the mineral dye by the propanediol ester family. Also, the hydroxyl group in the dye is attributed to the 2,3,4,6 –tetrachlorophenyl present. The 4-Dibenzofuranamine is most likely to be the root of the amine group in the substance, which favours good absorption of solar radiation. The three functional groups; amine, carbonyl and hydroxyl, all contribute to photons absorption in a natural compound, especially a liquid.

Table 3: Summarized results of chemical compositions in galena

Dye name	**Compound abundance**	**Retention time for galena dye**	**Retention time (RT) in the library**	**Compounds in the dye**
Galena	5.7E+7	13.963	13.975	i. Dodecanoic acid, 1,2,3 – propanetriyl ester ii. 4-Dibenzofuranamine
	5.8E+7	14.433	14.426	i. Dodecanoic acid, 2,3,4,6-tetrachlorophenyl ester ii. Fumaric acid, 2,3–dichlorophenyl hexyl ester iii.4-Dibenzofuranamin

3.3 Structural Properties of Zinc and Titanium Oxide (ZTO) Composite

In other to maximize the properties of both ZnO and TiO2 as the photoelectrode in the fabricated DSSC, a composite of the two is obtained. The X-ray diffraction pattern of the composite is shown in Figure 5. Distinct peaks of Rutile, the tetragonal structure seen for the TiO2 and the wurtzite, hexagonal structure for the ZnO confirmed the perfect blended composite obtained which makes it possible to harness the electrical and structural properties of the two for better performance in a photovoltaic photoanode [8]. JCPDS Card numbers 36-1451 and 21-1276 for ZnO and TiO2 respectively, were used for comparing the obtained pattern with the International Centre for Diffraction Data (ICDD) database.

3.4 Optical properties of TiO2 and ZTO

TiO2 and ZTO films produced on glass substrates were subjected to optical characterization and the transmittance within the visible region is presented in Figure 6.

The materials characterized show high transmission of light in the region considered, which 400 nm to 800 nm is. This can be taken as a good material for transparent conducting oxide in solar cells and electronics device production. 70 % transmission of light is observed in the ZTO, which is higher than what was obtained in TiO2 (Figure 6 clearly shows this). There is an improved transmission of light given by ZTO when compared with TiO2 and this is also expected to enhance good electron mobility, hence higher conductivity in the produced photoelectrode.

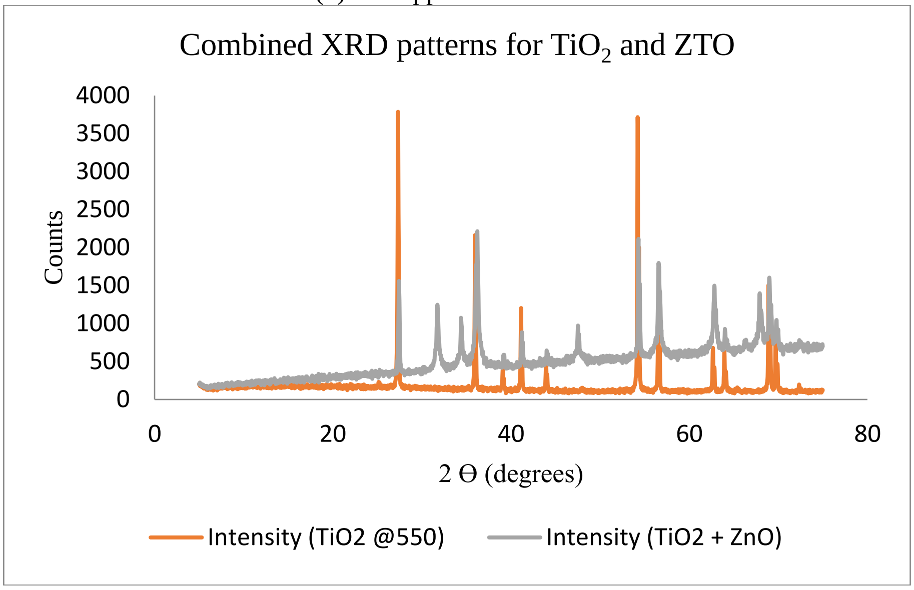


Figure 5. X-ray diffraction patterns for TiO_2 and ZTO compared

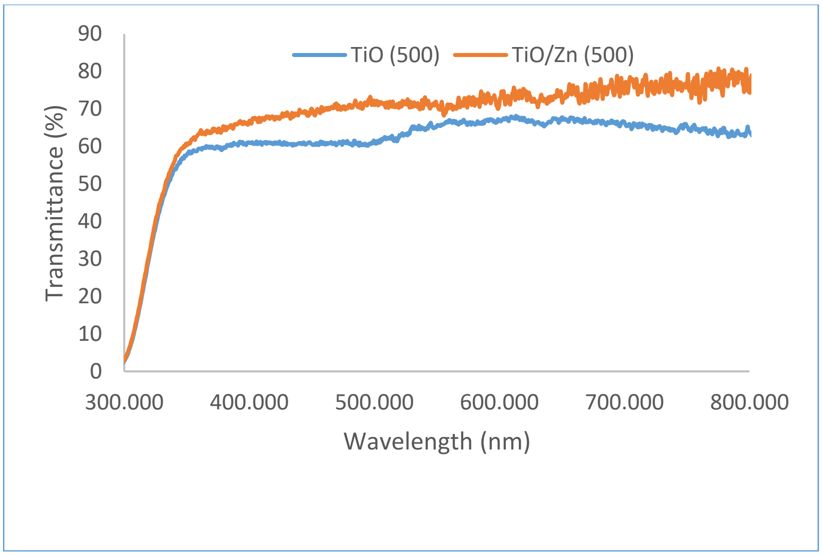


Figure 6. Transmittance of both TiO_2 and ZTO

3.5 Electrical characteristics and power conversion efficiency of the Fabricated DSSC

The electrical properties and the cells' efficiency were obtained. The power of the simulated light supplied to the cells is 100 mW/cm2. GAN is given to the galena-based cell while TM is for the turmeric-based cell. Tables 4 and 5 show the summarized results of the DSSC produced. Equations 1 and 2 mentioned earlier were employed to obtain the cells' efficiency. Figures 9 and 10 present the I-V curves of the fabricated cells.It was observed that the efficiencies of the cell are dependent on the fill factor in Figures 9 and 10. The TiO2 GAN-based cell low fill factor is suspected to be due to high sheet resistances which could be created by the coarse nature- of the dye material on the glass substrates used as TCO. Although TM-based DSSC generated the highest efficiency in this research, which is 0.52 %, the relatively quick degradation challenge of the natural plant dye calls for sourcing alternative natural dye, hence the promotion of natural mineral dye [9]. Figure 7 and Table 4 present the degradation percentage of the plant dye versus the natural mineral dye. It is seen that plant dye degrades faster than mineral dye.

Slower degradation occurs in the galena dye than in the turmeric dye. This is suspected to be a result of the high hydrophilic tendencies and hydroxyl functional group of the plant material for turmeric dye. For good durability and stability of photosensitizer, its periphery is expected to be hydrophobic. The percentage degradation was calculated by using the open-circuit voltage generated after two weeks from the day of fabrication. This was achieved by the expression in equation 4.

$$Percentage\ degardation,\ \%\,D = \frac{V_1 - V_2}{V_1} \times 100\% \quad (4)$$

V_1 is the initial open-circuit voltage while V_2 is the final.

Table 4: Degradation study of fabricated cells

Cell Type	**V_{oc1} (mV) (DAY 1)**	**V_{oc2}(mV) (after two weeks)**	**I_{sc1} µA (DAY 1)**	**I_{sc2} µA (after two weeks)**	**Degradation Percentage (%)**
GAN_TiO_2	340	250	32	24	26. 50 %
TM_TiO_2	500	250	25	8	50.00 %

The encouraging stability of galena dye in terms of degradation could be based on its compositions as studied by the GC-MS mentioned earlier and also on its metal compositional content. This research brings to light the promising potential of natural minerals, like galena, as alternative photosensitizers to be explored more in DSSC fabrication.

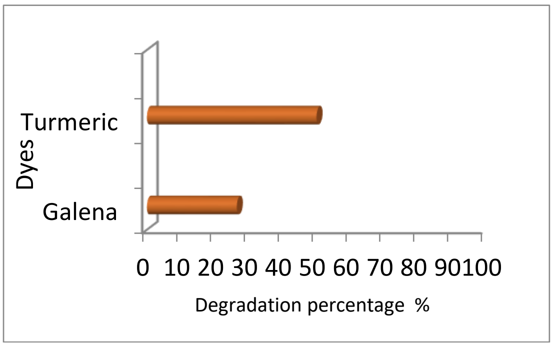


Figure 7. Degradation of the dyes

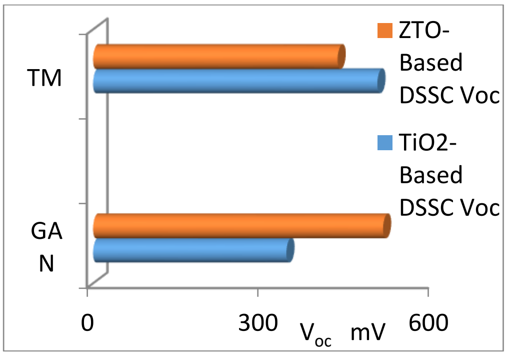


Figure 8. Performance of DSSC V_{oc}

The modified semiconductor (ZTO)-based DSSC performs better for the galena as dye, than the ordinary TiO_2-based cell. Table 5 and Figure 8 present this in a concise manner.

The improved performance of the ZTO-based cells as seen in the increased open-circuit voltage (compare Tables 4 and 5) may be due to the high electron mobility of ZnO combined with the fast electron injection properties of TiO_2 in the produced composite for photoanode [10].

Table 5: Estimated performance of the modified ZTO-based DSSC produced

DSSC names	Open-circuit voltage (mV)	Short-circuit current (μA)	DSSC Fill Factor (%)	Cell Efficiency (ŋ) (%)
GAN_ZTO	510	25	27	0.03 %
TM_ZTO	430	120	10	0.52 %

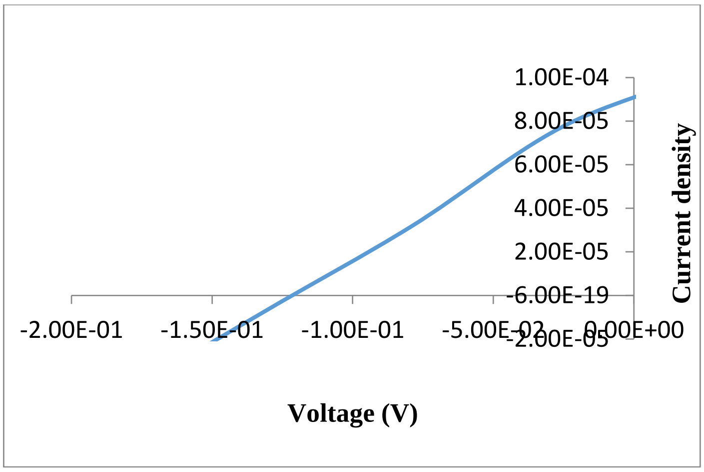


Figure 9. I-V plot of the ZTO_Turmeric DSSC

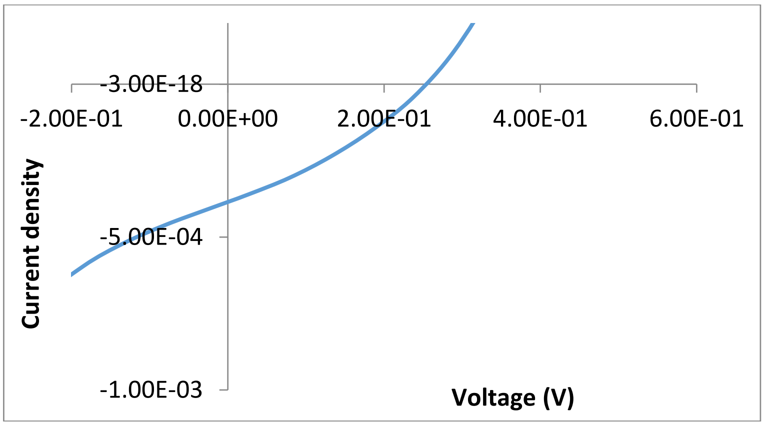


Figure 10. I-V plot of the ZTO_Galena DSSC

4. Conclusion

In this work, a modified Zinc and Titanium Oxide composite Based- DSSC has been fabricated with both Galena (a natural mineral) and Turmeric (plant) dye as photosensitizers. The turmeric-based DSSC generated 500 mV and 25 μA open-circuit voltages and short-circuit currents respectively, while the galena-based DSSC gave 340 mV and 32 μA open-circuit voltages and short-circuit currents respectively. The degradation studies of the fabricated cells showed that the mineral dye is more stable, with a degradation percentage of 26.5 %, than the plant dye. Also, the ZTO-based cell performed better than the ordinary titanium oxide-based cell for the mineral dye as the photosensitizer.

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