FABRICATION OF TiO_2/DYE-SENSITIZED SOLAR CELLS (DSCs) USING DYE EXTRACTS AND THEIR MIXTURE AS PHOTOSENSITIZERS

ABSTRACT

In this work we have reported an investigation on *Hibiscus sabdariffa and Delonix regia* dye extracts and their mixture as natural sensitizers for *TiO_2/DSCs*. A shift in the absorption maximum toward the lower energy of the ultraviolet-visible spectrum was observed for the dye mixture and a shift in the absorption maximum towards the higher energy of the ultraviolet-visible spectrum was observed for the dye extracts. The optical band gaps obtained at the point where the absorption spectra showed strong cut offs range from *1.79eV* to *2.40eV*. Also, we have used TiO_2 thin films of thickness *5.2μm* and the Light Harvesting Efficiencies (*LHE*) of the dye extracts and the dye mixture adsorbed onto TiO_2 surface were close to unity. The average diameter of the *TiO_2* films obtained from SEM is in the range of *25-40nm* reflecting that the *TiO_2* films are transparent and suitable for DSC application. The XRD pattern revealed the TiO_2 films to be of anatase form and the structure type is tetragonal with *3.53217Å* as the *d-spacing* for the most prominent peak, *$2\theta=25.2139^o$* (*ICDD* data file: *01-075-8897*). Three (*3*) DSCs each of *0.52 cm^2* active area were assembled and subjected to current-voltage characterization using a standard overhead Veeco viewpoint solar simulator equipped with *AM 1.5* filter to give a solar radiation of *1000 W/m^2* and coupled to Keithley source meter (model *4200SCS*). The photoelectrochemical performance of the fabricated DSCs showed open-circuit voltages (V_{oc}) varied from *0.42* to *0.53* V, the short-circuit current densities (J_{sc}) ranged from *0.10$mAcm^{-2}$* to *0.90$mAcm^{-2}$* and the fill factors (*FF*) varied from *12* to *38%*. The best overall solar power conversion efficiency of 0.13% was obtained, under AM *1.5* irradiation and a maximum short circuit current density of *0.90$mAcm^{-2}$*. Nevertheless, pure *Hibiscus sabdariffa and Delonix regia dye extracts* proved to be rather poor sensitizers as can be seen by the low spectra absorption at lower energies with current densities of *0.17$mAcm^{-2}$* and *0.10$mAcm^{-2}$* respectively. The solar power conversion efficiencies for *Hibiscus sabdariffa and Delonix regia* dye extracts were *0.01%* and *0.02%* respectively. In our earlier studies, we highlighted an established fact that raw natural dye mixtures exhibit better performance than pure dye extracts. Thus, the power conversion efficiency of *0.13%* observed for the dye mixture sensitized *TiO_2/DSC* corresponds to an increment in the neighborhood of *85%* to *92%* over the pure dye extracts sensitized *TiO_2/DSCs*.

Keywords: Natural dyes, dye mixture, light harvesting efficiency, molar extinction coefficient, TiO_2-DSC, optical band gap, power conversion efficiency.

1.0 INTRODUCTION

The power conversion efficiencies of natural dye-sensitized solar cells are low compared to solar cells sensitized with inorganic and synthetic dyes [1, 2, 3]. This is due to weak bonding between the natural dyes and TiO_2 surface which ultimately leads to low short circuit current density deliverable by the solar cells [4]. Other reasons include transformation of the natural dye functional groups from a more stable state (flavilium state) to an unstable state (quinoidal state) upon attachment to the TiO_2 surface which is as a result of high pH values [5, 6, 7]. This unstable state is usually characterized by long bond length functional groups that prevent dye molecules from arraying effectively on the TiO_2 film thereby causing low electron transfer from the dye

molecules to the conduction band of TiO_2. Finally, the masking and agglomeration effects of natural dyes which limit the light harvesting efficiency to ultraviolet and the onset of the visible light spectrum [5, 7, 8, 9, 10].

Several research efforts have been made to improve the interaction between the natural dyes and TiO_2 surface in order to achieve high power conversion efficiency. These include the use of appropriate extraction solvents, synergistic effect of dyes derived from single species such as algal derived photosynthetic pigments, organic acids and mixed dyes [11, 12, 13, 14, 15, 16, 17, 18, 19]. Thus, it was established that mixed dye system would account for many possible types of interactions between dyes with various constituents present, but this is yet to be thoroughly understood [20]. Although, there could be more possible ways to increase the efficiency of solar cells sensitized with natural pigments but it is evident from the equation for power conversion efficiency [equation (1) below] that high values of short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and fill factor (*FF*) lead to high efficiency in any solar cell. As such, it is necessary to improve these three parameters in order to raise power conversion efficiency of a DSC.

In our previous studies, we developed and characterized DSC based on TiO_2 nanoparticles coated with Hibiscus sabdariffa (Zobo) and the overall solar power conversion efficiency of 0.033% and a maximum current density of $0.17 mAcm^{-2}$ were obtained [21]. Typically, low peak absorption coefficient, small spectra width and very low power conversion efficiency of this DSC boosted additional studies oriented; on one hand, to the use of a new natural sensitizer (Delonix regia) in addition to Hibiscus sabdariffa and their mixture as a promising strategy for harvesting more light in the higher wavelengths. On the other hand, we hope to increase the extent of Light Harvesting Efficiency (LHE) within the TiO_2 electrode by depositing a blocking layer sequentially to enhance the surface area of TiO_2, to favor cluster formation in TiO_2 nanoparticles for effective anchorage of the natural dye extracts and their mixture and to improve interconnectivity among TiO_2 nanoparticles for enhancement in the short circuit current density. Sequel to this, three (3) DSCs each of 0.52 cm^2 active area were assembled by sandwiching a surlyn polymer foil of 25 μm thickness, as spacer between the photoelectrode and the platinum counter electrode and characterized using a standard overhead Veeco viewpoint solar simulator equipped with AM 1.5 filter to give a solar radiation of 1000 W/m^2 and coupled to a Keithley source meter (model 4200SCS) which was connected to the computer via GPIB interface for data acquisition.

2. MATERIALS AND METHODS

Titanium isopropoxide, Titanium nanoxide, acetylacetonate, ethanol, isopropanol, fluorine doped tin-oxide (FTO) conducting glass [$11.40\ ohm/m^2$, $(1.00 \times 1.00) cm^2$], electrolyte (iodolyte-AN-50), sealing gasket (surlyn-SX1170-25PF), and screen-printable platinum catalyst, (Pt-catalyst T/SP) all were obtained from SOLARONIX. Dye extracts were obtained from the natural products *(Hibiscus sabdariffa* and *Delonix regia).* A mixture of 0.3M of titanium isopropoxide, 1.2M acetylacetonate and isopropanol was spin coated three (3) times with different concentrations sequentially as blocking layer on the pre-cleaned fluorine doped tin-oxide (FTO)

conducting glasses and sintered at 150^{o}C for four minutes each time the deposition was made. Subsequently, a paste of titanium nanoxide in propanol in the ratio 1:3 was screen printed on the three (3) fluorine doped tin-oxide (FTO) conducting glasses and allowed to dry at 125°C in open air for 6 minutes.

The FTO/TiO_2 glass electrodes were sintered in a furnace at 450°C for 40 minutes and allowed to cool to room temperature to melt together the TiO_2 nanoparticles and to ensure good mechanical cohesion on the glass surface. Dried leaves of *Hibiscus sabdariffa and Delonix regia* were crushed into tiny bits and boiled in 75ml of deionized water for 15 minutes. The residue was removed by filtration and the resulting extracts were centrifuged to further remove any solid residue while a mixture in the ratio 50:50 by volume of the dye extracts was made. The dye extracts and the mixture were used directly as prepared for the construction of the DSCs at room temperature. A scattering layer of TiO_2 was also deposited on the TiO_2 electrodes before the electrodes were immersed (face-up) in the natural dye extracts and their mixture for 18h at room temperature for complete sensitizer uptake. This turned the TiO_2 film from pale white to sensitizer colour. The excess dye was washed away with anhydrous ethanol and dried in moisture free air.

The thickness of TiO_2 electrodes and the deposited scattering layers was determined using Dekker Profilometer. Surface morphology of the screen-printed TiO_2 nanoparticles was observed using EVOI MA10 (ZEISS) multipurpose scanning electron microscope operating at *20kV* employing secondary electron signals while the corresponding Energy Dispersive Spectra (EDS) were obtained using characteristic x-rays emitted by TiO_2 nanoparticles. The X-ray diffraction (XRD) pattern of the screen-printed TiO_2 nanoparticles at room temperature was recorded using X-ray Diffractometer; Panalytical Xpert-Pro, *PW3050/60*, operating at *30mA* and *40kV*, with monochromatic *Cu-Kα* radiation, of wavelength $\lambda = 1.54060\text{Å}$. A scanned range *3–80.00553º 2θ*, with a step width of *0.001º* was used. The pattern was analyzed and the peaks were identified using *ICDD* data file (*01-075-8897*). The UV-Visible (*UV-Vis*) absorption measurements of the dye extracts, their mixture and the dye extracts and their mixture on the screen printed TiO_2 electrodes were carried out with *Avante UV-VIS* spectrophotometer (model-*LD80K*). From these measurements, plots for the absorbance, Light Harvesting Efficiency (*LHE*) and molar extinction coefficient versus the wavelengths of interest were obtained using the relevant expressions from [4].

Three (*3*) DSCs each of $0.52cm^2$ active area were assembled by sandwiching a surlyn polymer foil of *25μm* thickness, as spacer between the photoelectrode and the platinum counter electrode and then hot-pressed at *80°C* for *15s*. A drop of liquid electrolyte was introduced into the cell assemblies via pre-drilled holes on the counter-electrodes and sealed using amosil sealant. In order to have good electrical contacts, a strip of wire was attached to both sides of the FTO electrodes. Finally, the DSCs were subjected to current-voltage characterization using a standard overhead Veeco viewpoint solar simulator equipped with *Air Mass 1.5* (AM 1.5) filter to give a solar radiation of 1000 W/m^2 and coupled to *Keithley* source meter (model *4200SCS*) which was connected to the computer via *GPIB* interface for data acquisition. Subsequently, the working electrode and counter electrode of the DSC were connected in turn to the positive and negative terminals of the digital *Keithley* source meter respectively. The bias was from short circuit to open circuit and was obtained automatically using LabVIEW software from National Instruments Inc, USA. From the data, *I-V* curves were plotted in real time for the DSCs under

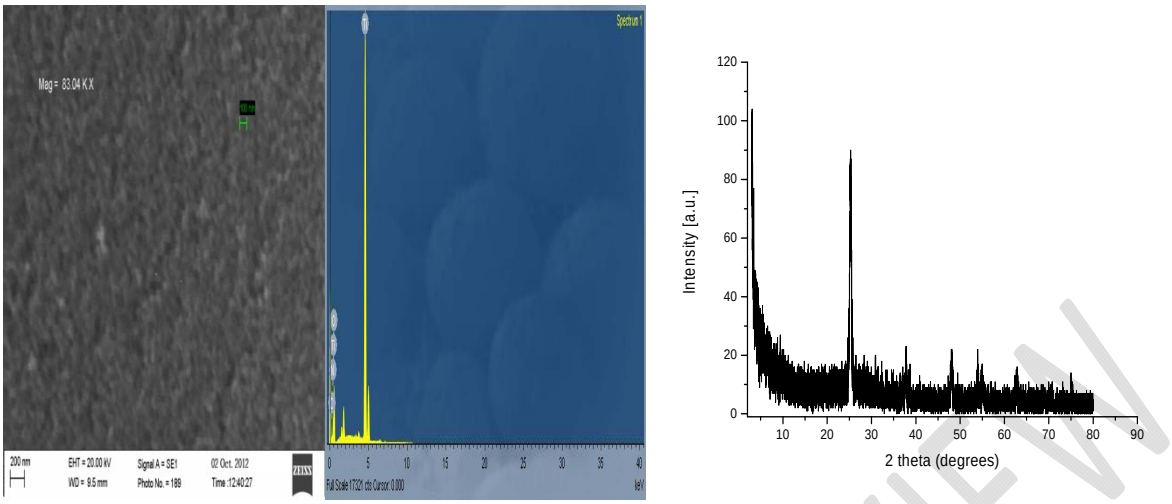
illuminated condition. Following this, the photovoltaic parameters viz; the open circuit voltage (V_{oc}) and short circuit current (I_{sc}) were obtained from the *I-V* curves for the cells. The fill factor (*FF*) and the power conversion efficiency for the cells were obtained using the following relations:

$$FF = \frac{P_m}{V_{oc} \cdot I_{sc}} \text{ and } \eta = \frac{FF \cdot V_{oc} \cdot J_{sc}}{I_{in}} \quad (1)$$

3.0 RESULTS AND DISCUSSION

The image presented in Figure 1 obtained using characteristic x-rays emitted by TiO_2 nanoparticles was observed at a magnification of 83.04kX. The uniform contrast in the image revealed TiO_2 to be practically isomorphic with titanium and oxygen being the dominant elements with concentration of about 99.9% as depicted in the EDS spectra (Figure 1b). The morphology of TiO_2 nanoparticles is such that the particles are closely parked and spherical in shape. The average diameter of the particles is in the range of 25-40nm reflecting that TiO_2 nanoparticles are transparent and suitable for DSC application. The thickness of TiO_2 on the FTO conducting glass determined using Dekker Profilometer was found to be 5.2μm for each photoelectrode and that of the deposited scattering layers was found to be 1 μm. The XRD pattern revealed the compound name for the TiO_2 electrode to be anatase syn., and the structure type is tetragonal with *3.53217Å* as the *d-spacing* for the most prominent peak, *2θ=25.2139°* (ICDD data file: *01-075-8897*). Other prominent peaks occur at *2θ= 37.7883°, 48.0463°, 53.9110°, 55.0481°, 62.7104° and 75.1376°* with *d-spacing d= 2.38075 Å, 1.89370 Å, 1.70073 Å, 1.66826 Å, 1.48160 Å and 1.26338 Å.*

In figure 2, the dye extracts and their mixture exhibit absorption maxima slightly above *400nm* and the most prominent shoulders occur slightly above *500nm*. But upon sensitization on TiO_2, there was reduction in absorption maxima and the prominent shoulders for the dye extracts while an enhancement in the absorption maximum with a shift toward high wavelengths (*450nm – 600nm*) was observed for the dye mixture and the prominent shoulder broadened toward the higher wavelengths (*750nm – 900nm*) with reduced absorption intensity for the mixture.



(a) (b) (c)

Figure 1: TiO_2 structural characteristics: (a) Surface morphology, (b) Energy Dispersive Spectra and (c) XRD pattern for the screen printed TiO_2.

Chemisorption of anthocyanins on TiO_2 was been reported by [22] to be as a result of alcoholic bound protons which condense with the hydroxyl groups present at the surface of nanostructured TiO_2. Such attachment to the TiO_2 surface stabilizes the excited state, thus shifting the absorption maximum towards the lower energy of the spectrum. In our study, a shift in the absorption maximum towards the lower energy of the spectrum was observed for the dye mixture adsorbed on TiO_2 and a shift in the absorption maximum towards the higher energy of the spectrum was observed for the dye extracts adsorbed on TiO_2. This observation suggests that there was effective adsorption of the dye mixture onto TiO_2 surface which could be attributed to the low *pH* value and the short bond length of the *OH* groups present in the dye mixture. These *OH* groups favour the formation a strong bond with the oxide surface and also good arraying to the TiO_2 film effectively. The shift may also be attributed to the changing of the anthocyanin molecule from the unstable quinoidal state to the more stable flavilium state to upon chelation.

It is an established fact that the light absorption by a dye monolayer is small since the cross section for photon absorption of most photosensitizers is much smaller than the geometric area occupied on the semiconductor surface, but with thin film semiconductor the obtainable LHE is usually close to unity [23]. In this work, we have used TiO_2 thin film of thickness 5.2µm and the LHE of the dye extracts and the dye mixture adsorbed onto TiO_2 surface is close to unity.

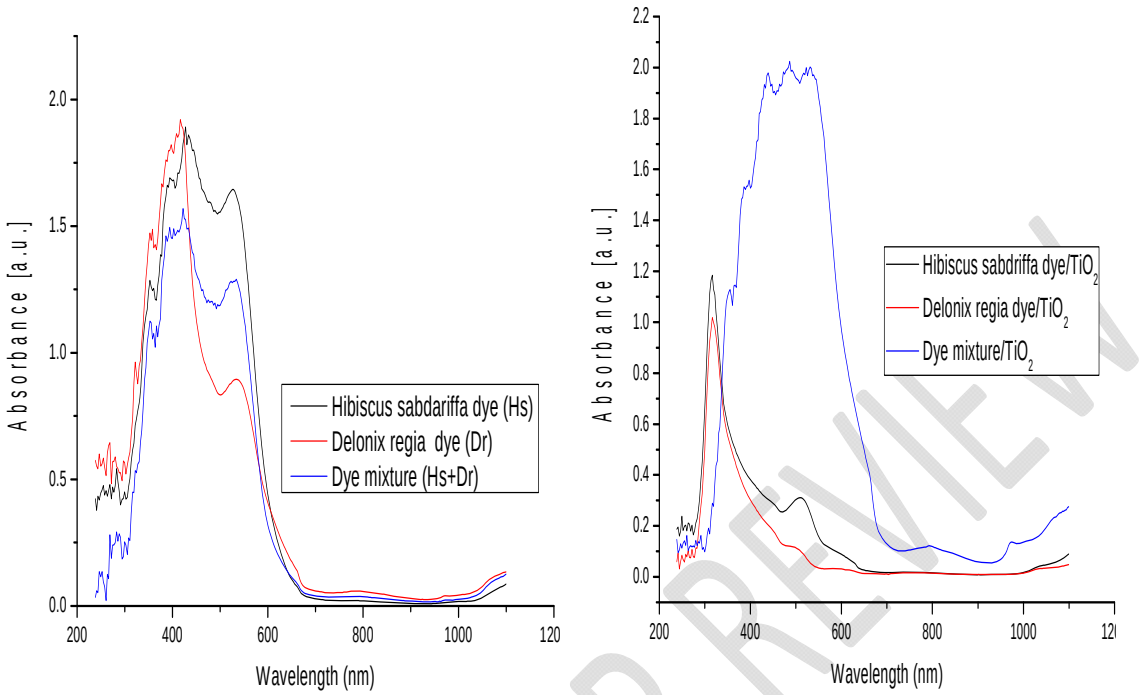


Figure 2: UV–VIS absorption spectra for (a) Hibiscus sabdariffa dye extract, Delonix regia dye extract and Mixture of dye extracts and (b) Hibiscus sabdariffa / TiO_2, Delonix regia/TiO_2 and Mixture of dye extracts/TiO_2.

The light harvesting efficiency values obtained are plotted against wavelengths as shown in figure 3. The absorption band of the dye extracts after sensitization on TiO_2 becomes a bit discrete after sensitization but quite broad for the dye mixture after sensitization. Whilst the molar extinction coefficients are very high for the dye extracts and the mixture, it turned out that only small areas are being covered by the solar irradiance spectrum for the dye extracts but an increase in the area was observed for the dye mixture. Most notably, the spectra bandwidth is within the range of *150nm* to *200nm* for the dye extracts but an increase in the vicinity of *400nm* to *500nm* was observed for the dye mixture. This increase in the spectra bandwidth significantly enhances the photocurrent density for the dye mixture/TiO_2-*DSC* as evident from current-voltage characterization.

Current density and power versus voltage characteristics of the DSCs are plotted and shown in figure 4. The photovoltaic parameters are determined and tabulated in Table 1. The current density ranges from $0.17 mAcm^{-2}$ to $0.90 mAcm^{-2}$, the open circuit voltage ranges from *0.42V* to *0.53V*, the fill factor from 12% to 38% and the power conversion efficiency ranges from *0.01%* to *0.13%*. Thus, it is evident from *table 1* that high values of J_{sc}, *and* V_{oc} are responsible for the higher efficiency obtained for the dye mixture/TiO_2-DSC compared to those of the parent dyes. In our previous studies, we developed and characterized DSC based on TiO_2 nanoparticles coated with Hibiscus sabdariffa (Zobo) and the overall solar power conversion efficiency of

0.033% and a maximum current density of $0.17mAcm^{-2}$ were obtained [21].This boosted additional studies oriented to the use of dye mixture (Hibiscus sabdariffa plus delonix regia) leading to an enhancement in the light harvesting efficiency and hence the photocurrent density which is owed to the high peak absorption coefficient and large spectra bandwidth.

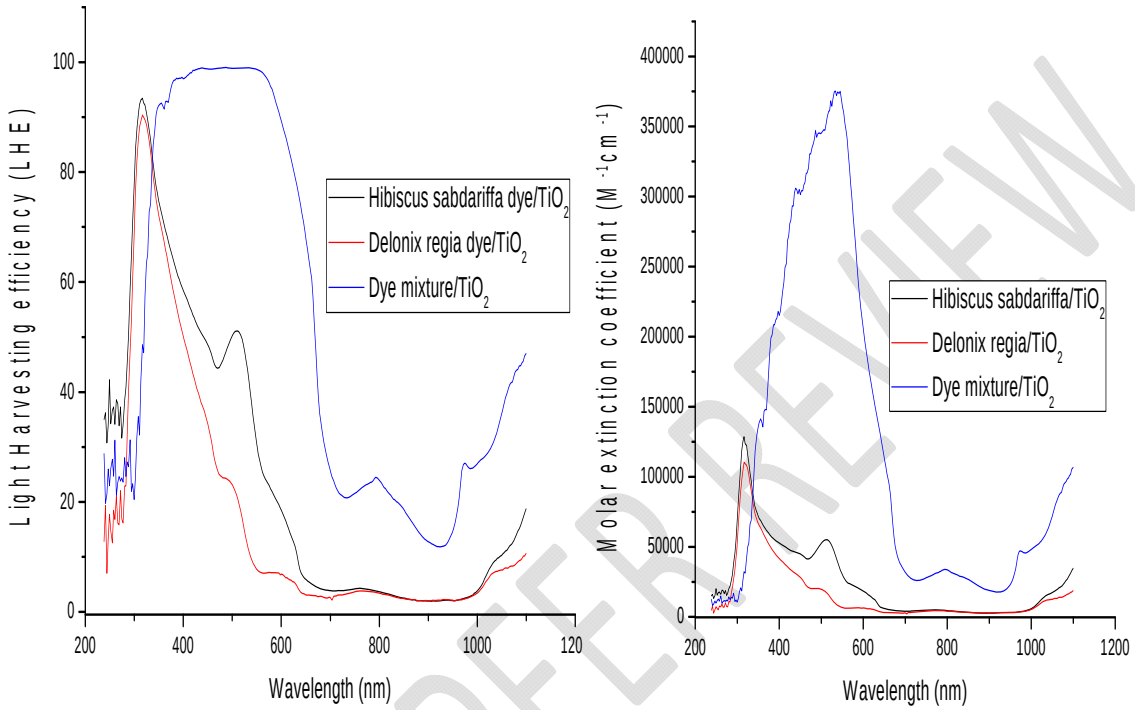
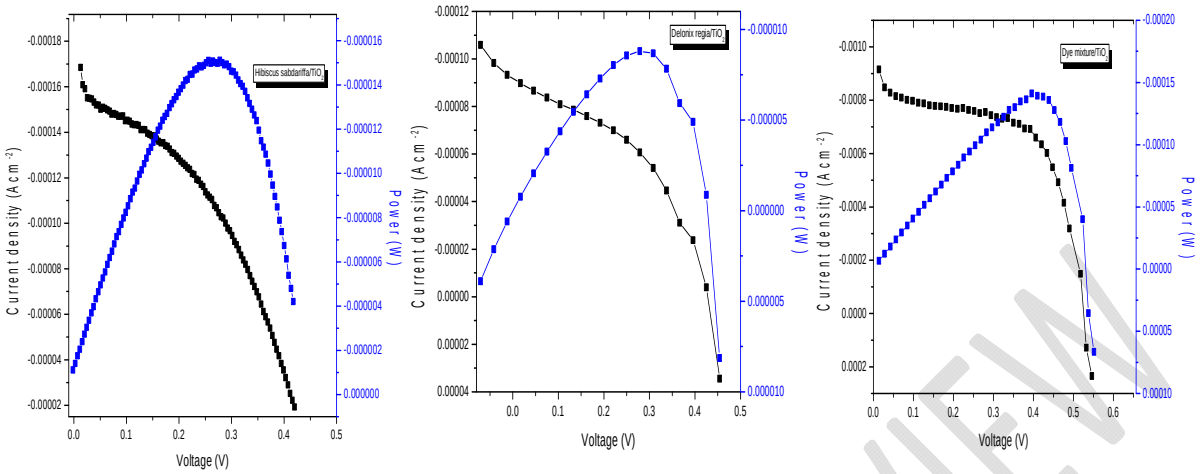


Figure 3: Light Harvesting Efficiency (LHE) for (a) Hibiscus sabdariffa / TiO_2, Delonix regia/TiO_2 and Mixture of dye extracts/TiO_2 and (b) Hibiscus sabdariffa / TiO_2, Delonix regia/TiO_2 and Mixture of dye extracts/TiO_2.

Table 1: Photovoltaic parameters of the DSCs sensitized with *Hibiscus sabdariffa dye, Delonix regia dye and their mixture*

DSC	$J_{sc}(mAcm^{-2})$	V_{oc} *(V)*	*FF*	*η (%)*
H. sabdariffa /TiO₂	*0.17*	*0.42*	*0.12*	*0.01*
Delonix regia /TiO₂	*0.10*	*0.45*	*0.38*	*0.02*
Dye mixture /TiO₂	*0.90*	*0.53*	*0.28*	*0.13*



(a) (b) (c)

Figure 4: Current density and Power versus voltage for (a) TiO_2-DSC sensitized with *Hibiscus sabdariffa dye,* (b) TiO_2-DSC sensitized with *Delonix regia dye* and (c) TiO_2-DSC sensitized with dye mixture.

In this work, it was discovered that TiO_2 band gap was reduced upon sensitization with the extracted dyes and their mixture. The optical band gaps were obtained at the point where the absorption spectra showed a strong cut off, when the absorbance values are minimum. The values range from *1.79eV* to *2.40eV*. The band shifts could be attributed to molecular transitions that take place when the dye molecules chelate with TiO_2. Typically, anthocyanin dyes exhibit π - π^* orbital transition which is attributed to the wavelength range between *500nm* to slightly above *650nm*. In this work, the cut off wavelength for the spectra ranges between 600*nm* to slightly above 700*nm*. Finally, it is well known that proton adsorption causes a positive shift of the Fermi level of the TiO_2, thus limiting the maximum photovoltage that could be delivered by the cells [22]. Nevertheless, the dye mixture proved to be a better sensitizer compared to pure *Hibiscus sabdariffa and Delonix regia* that exhibited low spectral absorption at lower energies. However, no deviation from this trend was observed when the duration of continuous stimulated sunlight illumination was increased for several hours.

4.0 CONCLUSION

In this work we have reported an investigation on *Hibiscus sabdariffa and Delonix regia* dye extracts and their mixture as natural sensitizers of *TiO_2/DSCs*. The best overall solar power conversion efficiency of *0.13%* was obtained, under *AM 1.5* irradiation and a maximum current density of *0.90mAcm^{-2}*. Nevertheless, pure *Hibiscus sabdariffa and Delonix regia dye extracts* proved to be rather poor sensitizers as can be seen by the low spectral absorption at lower energies with current density of *0.17mAcm^{-2}* and *0.10mAcm^{-2}* respectively. The solar power conversion efficiency for *Hibiscus sabdariffa and Delonix regia* dye extracts are *0.01%* and *0.02%* respectively. In our earlier studies, we highlighted an established fact that raw natural dye

mixtures exhibit better performance than pure dye extracts. Thus, the power conversion efficiency of 0.13% observed for the dye mixture corresponds to *92%* and *85%* increment over the pure dye extracts sensitized *TiO_2/DSCs*. This could be related to the specific pools of ancillary molecules present in the dye mixture of (*i.e.,* alcohols, organic acids, *etc.*) which act as coadsorbates, suppressing recombination with the electrolyte, reducing dye aggregation and favouring charge injection. Although the efficiencies obtained with this natural dye extracts and the dye mixture are still below the current requirement for large scale practical application, the results are encouraging and may boost additional studies focused on the modification of solar cell components compatible with the dye mixture. In view of this, we are currently exploring the possibility of increasing the power-conversion efficiency of the *DSCs* based on *TiO_2* using modified *TiO_2* and counter electrodes and *Delonix regia*.

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