



Effect of Natural Dye Extracts on the Absorbance Characteristics of TiO₂ in Dye-Sensitized Solar Cells

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Authors' contributions

This work was carried out in collaboration among all authors. Author PSC conceptualized the research and did the data collection and analysis. Author TEA proof read the work and interpreted the analysis. Author TTA Proof read the work and edited the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

Natural dye extracts from Chinese Ixora (*Ixora chinensis*) flower, Cassod flower (*Cassia Siamea*), Cassava leaf (*Manihot Esculenta*), purple heart (*Tradescantia Pallida*) and Copper leaf (*Acalypha Wilkesiana*) have been explored as sensitizers for the fabrication of dye-sensitized solar cells. The properties of the dyes were investigated using the FTIR and they all showed broad absorption bands in the 3800 to 3000cm⁻¹ wavelenght and strong presence of intermolecular H-bonds. The effect of dye extracts on the absorbance and transmittance features of TiO₂ was well studied by the UV-VIS and the absorbance peak was in the case of sensitization with Manihot Esculenta seen to radically improve above 1.0 at 350nm wavelength. Finally, the current and voltage characteristics of the DSSC were studied in sunlight and at a peak sunlight intensity of 601m/w², the Manihot and

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Cassod sensitized devices exhibited maximum voltage values of 115 and 84mV respectively and maximum current values of 4.32 and 2.99mA. These plants have shown great potential for application in fabrication of cost effective and environmentally friendly DSSCs.

Keywords: DSSC; solar; absorbance; current.

1. INTRODUCTION

As the global population is growing, energy resources are depleting at a similar pace. Although fossil fuels are the most abundant source of energy, by the next century, these fuel sources will have been depleted [1]. For a green and healthy environment, renewable energy resources are emphasized. Renewable resources such as solar and geothermal energy, wind power, etc. have been explored to satisfy the growing demand for energy and are poised to supply the world with a reliable, environmentally friendly, and sustainable energy system [2]. By the photosynthesis process, the sun is proven as the most efficient resource of energy for all living creatures [3].

Solar cells which are also called Photovoltaic cells play a crucial role in securing clean and green energy for consumption and utilization in wide sphere of applications. In case of solar energy, radiation obtained from the sunlight is capable of producing heat and light, causes photochemical reactions, and generates electricity. Research in this direction is focused on using suitable solar cell technologies to efficiently provide the world's daily need of energy consumption.

Dye -sensitized solar cell (DSSCs), a type of organic photovoltaic cell is a low-cost solar cell belonging to third-generation solar cells, which have higher efficiency than a thin film-based solar cell [4]. They are used to convert light energy into electrical energy using organic /inorganic dyes as photosensitizers, established on wide energy band semiconductor [5]. Research interests is focused on optimizing the redox couple [6]and dye absorbance [7], modifying semi-conductors with a wide bandgap as photo-electrodes [8] and developing high-performance counter-electrodes [9]. Moreover, natural and commercial synthetic dyes have been reported as a good replacement for transition metal coordination compounds (rutheniumpolypyridyl complexes) which are regarded as effective sensitizers but contain a costly heavy metal that posed environmental challenges [10]. Besides, the process of

synthesizing the complexes is complicated and expensive [11]. Since the performance of the DSSCs greatly depends on the dye used in that cell, to improve the performance of DSSCs with natural dye as a sensitizer, investigation on a wide variety of plants, fruits, and flowers will be carried out to determine their effectiveness as sensitizers in DSSCs.

In this work, natural dyes extracted from Chinese Ixora (*Ixora chinensis*) flower, Cassod flower (*Cassia Siamea*), Cassava leaf (*Manihot Esculenta*), purple heart (*Tradescantia Pallida*) and Copper leaf (*Acalypha Wilkesiana*) have been explored for the purpose of sensitizing solar cells.

2. MATERIALS AND METHODS

2.1 Extraction of Dyes from Selected Plants

Fresh leaves and flowers (Fig. 1) of Chinese Ixora (*Ixora chinensis*) flower, Cassod flower (*Cassia Siamea*), Cassava leaf (*Manihot Esculenta*), purple heart (*Tradescantia Pallida*) and Copper leaf (*Acalypha Wilkesiana*) were collected from the University of Port Harcourt, Abuja campus, Rivers state, Nigeria in November, 2023. The fresh samples were repeatedly washed with de-ionized water to remove every form of debris. Using a laboratory mortar and pestle, the samples were separately crushed (Fig. 2) to form fine paste. An electronic weighing balance was then used to measure 3g of the paste and immersed in 50ml of laboratory grade ethanol in an 250ml beaker. The beaker was first covered with place nylon (Fig. 3) before being left undisturbed in a dark environment for 24h. The solid residue was later filtered using wattman filter paper, leaving a beautiful colored dye which was then used as photosensitizer. The same process was repeated for all five samples.

2.2 Preparation of TiO₂ Paste and Photoelectrode

Commercial grade (Aigma Aldrich) TiO₂ was purchased and 1g of the powder measured into a laboratory mortar, 0.5ml nitric acid and 0.05g

polyethelene glycol all added into the mortar and mixed until a fine paste of TiO_2 was formed.

Indium Tin Oxided (ITO) glass was purchased from Sigma-Aldrich have sheet resistance of $9\ \Omega\text{cm}^{-1}$. The ITO glass was cut into 1cm X 1cm portions and then sonicated using distilled water and further sonicated with Acetone for 6h.

Using the Dr Blade method, the TiO_2 paste was uniformly deposited on the ITO by using masking tape to control the thickness of deposition in a procedure previously reported [12]

2.3 Preparation of Counter Electrode

Already sonicated ITO glasses were shaded using 4B pencils as described by Großerhode et

al. [13] to make the counter electrodes for the DSSC device.

2.4 Preparation of Electrolyte

A solid state polymer electrolyte was prepared by mixing 0.8g of KI crystals with 0.127g of Iodine as reported by Sathyajothi et al. [14].

2.5 Assembly of DSSC Device

The extracted dye solutions were put into five different petri dishes and the photoelectrode (TiO_2 coated ITO) was immersed into the dye for 1h to allow for absorbance. The electrodes were then rinsed with distilled water and ethanol and air dried for 24h.



Fig. 1. Flower harvested for extraction



Fig. 2. Crushed samples



Fig. 3. Samples soaked in ethanol and covered with black nylon and kept in the dark for 24 hrs

The sensitized photoelectrode and the counter electrode were then fixed to face each other and placed in such a way to give room for offset to allow for connections and properly held together with two crocodile clips. Using a burette, few drops of the electrolyte was passed between the two electrodes. Using sunlight as light source, the voltage and current of each cell was measured.

3. RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

The extracts from the five extracted dye samples were analysed as seen in Fig. 4, 5, 6, 7 and 8. In the dye from Chinese Ixora (CI), Peaks contained single bond area (2500-4000 cm^{-1}). A broad absorption band was found, informing there is hydrogen bond in the material. There is a sharp bond between 3400-3800 cm^{-1} , replying the existence of oxygen-related bonding which could be O-H or N-H. Peaks between 3000 and 3200 cm^{-1} was found, informing there is aromatic structure in the compound. Strong bond at less than 3000 cm^{-1} responded to the C-C bond. The presence of absorptions in the 3000 to 2850 cm^{-1} region indicates that there are hydrogens bonded to sp^3 -hybridized carbons in the compound. This indicates the presence of alkene in the

compound. Specific peak for aldehyde was found at between 2700 and 2800 cm^{-1} . Triple bond region (2000-2500 cm^{-1}) was not detected, informing the absence of $\text{C}\equiv\text{C}$ bond in the material. Regarding the double bond region (1500-2000 cm^{-1}). Peak at about 1851 cm^{-1} , informing there is $\text{C}=\text{O}$ bonding in the material indicating the presence of ketone or conjugated acid in the material. Peak at about 1608 cm^{-1} indicating the presence of an alkene (Fig. 4).

For the Manihot Esculenta, in the single bond area (2500-4000 cm^{-1}), several peaks were detected. Broad absorption band in the range of between 3850 and 3200 cm^{-1} , indicating hydrogen bond. Peaks at between 3000 and 3200 cm^{-1} , replying the aromatic ring. Peaks at below 3000 cm^{-1} , responding the single bond of carbon. The absorptions in the region of 3000 to 2850 cm^{-1} indicate the presence of H's bonded to sp^3 -hybridized C's. Aldehyde peak was not detected at between 2700 and 2800 cm^{-1} . Regarding the triple bond region (2000-2500 cm^{-1}), peak was not detected at 2457 cm^{-1} , informing absence of $\text{C}\equiv\text{C}$ bonding. In the double bond region (1500-2000 cm^{-1}), several peaks were detected: The strong absorption at 1855 cm^{-1} indicates the presence of an anhydride. A weak absorption band was also detected at 2446 cm^{-1} indicating the presence of carbon dioxide compound (Fig. 5).

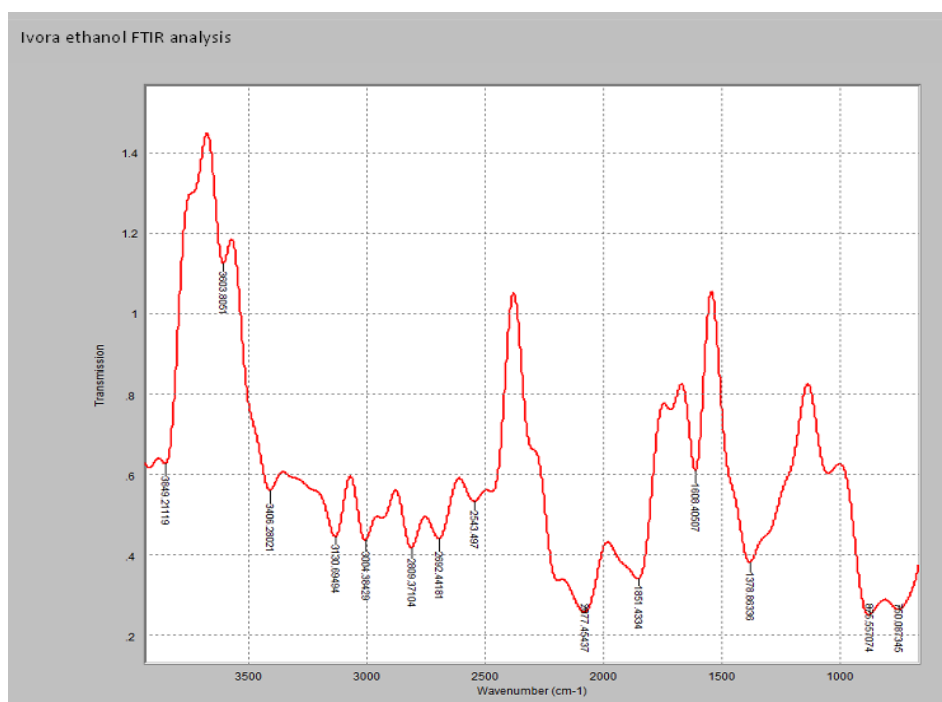


Fig. 4. FTIR analysis of chinese ixora extract

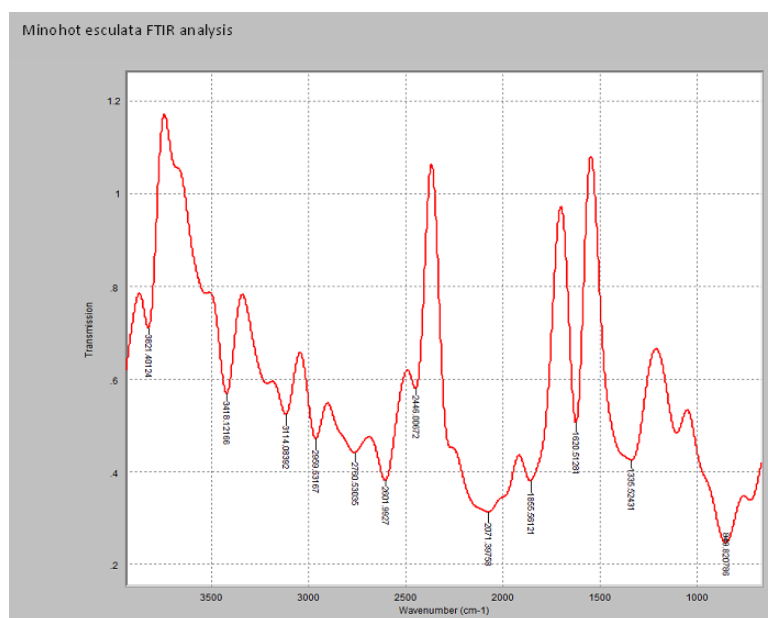


Fig. 5. FTIR Analysis of manihot esculenta extracted dye

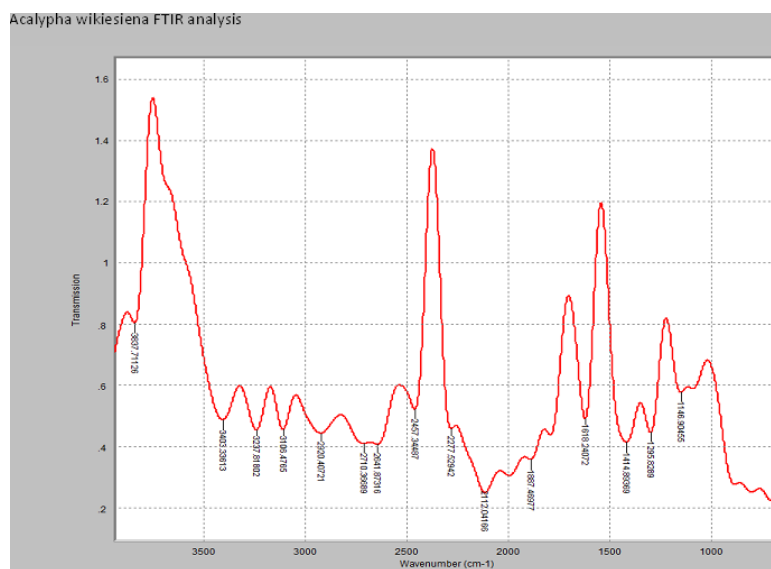


Fig. 6. FTIR analysis of acalypha dye extract

A Broad absorption band was found, at about 3806cm^{-1} in the Acalypha dye extract indicating there is hydrogen bond in the material with overtones at about 1414cm^{-1} . This indicated the presence of alcohol or phenol. There was no sharp bond at about 3500 cm^{-1} , replying the absence of oxygen-related bonding. There was a sharp peak between 3000 and 3200 cm^{-1} was found, informing there was an aromatic structure. Specific peak for aldehyde was found between 2700 and 2800cm^{-1} . No Triple bond region ($2000\text{-}2500\text{ cm}^{-1}$) was detected, informing the absence of a $\text{C}\equiv\text{C}$ bond in the material.

Regarding the double bond region ($1500\text{-}2000\text{ cm}^{-1}$), there was a peak at about 1618cm^{-1} indicating the presence of alkene in the sample. In the fingerprint region ($1500\text{-}600$), the peak was observed at about 1146cm^{-1} indicating the presence of phenol or aliphatic ether (Fig. 6)

In the Cassod dye extract, a broad absorption band was found (Fig. 7), informing there is hydrogen bond in the material. There is a sharp bond at about 3500 cm^{-1} , replying the existence of oxygen-related bonding. Peaks between 3000

and 3200 cm^{-1} was not found, informing the absence of aromatic structure. No narrow bond at less than 3000 cm^{-1} responded to the C-C bond. Specific peak for aldehyde was not found at between 2700 and 2800 cm^{-1} . Triple bond region ($2000\text{-}2500\text{ cm}^{-1}$) was not detected, informing absence of $\text{C}\equiv\text{C}$ bond in the material. Regarding the double bond region ($1500\text{-}2000\text{ cm}^{-1}$), there was a huge and sharp peak detected at about 1848 cm^{-1} . This informs some carbonyl double bond, which can be from ketones,

aldehydes, esters, or carboxyl. Since there is a specific peak for aldehyde at between 2700 and 2800 cm^{-1} the prospective peak for carbonyl should be from aldehyde. Peak at about 1624 cm^{-1} , informing there is $\text{C}=\text{C}$ bonding in the material with overtone at 901 cm^{-1} . Based on above interpretation, several conclusions can be obtained, including the analyzed material has hydrate component. This material has aldehyde-related component, double and triple bond in the material.

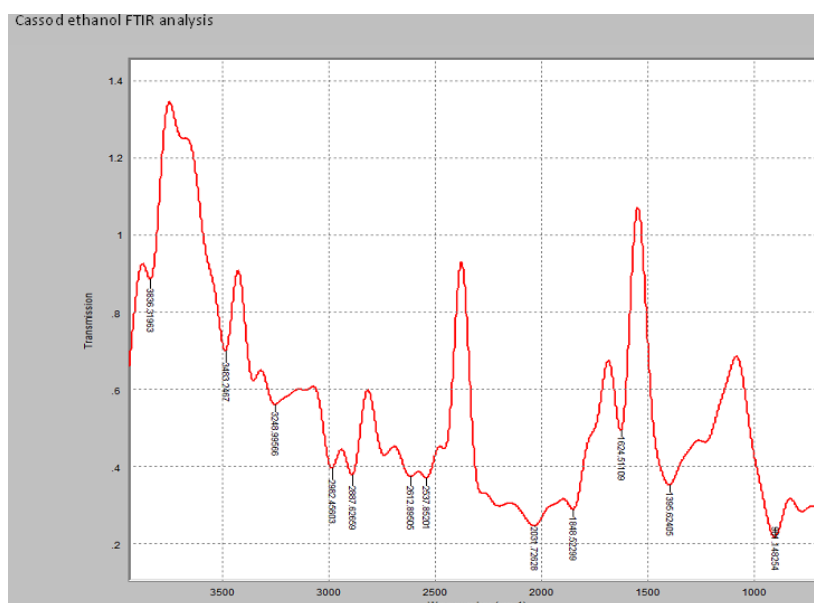


Fig. 7. FTIR analysis of cassod dye extract

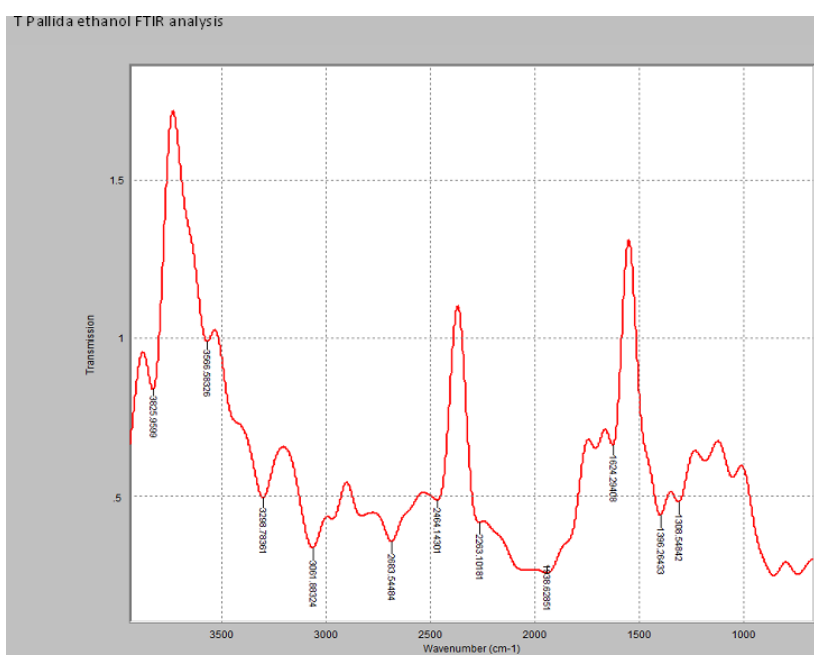


Fig. 8. FTIR Analysis of T. Pallida dye extract

For the T.Pallida dye extract, broad absorption band was found, informing there is no hydrogen bond in the material. There is a sharp bond at about 3500cm^{-1} , replying the presence of oxygen-related bonding with overtones at about 1396cm^{-1} . There was a sharp peak between 3000 and 3200cm^{-1} was found, informing there was an aromatic structure. No Specific peak for aldehyde was found between 2700 and 2800cm^{-1} . No Triple bond region ($2000\text{-}2500\text{cm}^{-1}$) was detected. Regarding the double bond region ($1500\text{-}2000\text{cm}^{-1}$), peak at about 1624cm^{-1} , informing there is $\text{C}=\text{C}$ bonding in the material (Fig. 8).

3.2 Ultraviolet –Visible Spectrometry (UV-VIS)

UV-VIS analysis was carried out on the TiO_2 paste before and after it was sensitized with the various dye extracts. Fig. 9, shows the before

analysis while in Fig. 10, the effect the different dye extracts had on the TiO_2 is obvious. From the plots, while Manihot Escullenta showed very poor transmittance capacity, Ixora showed the highest transmittance which as a consequence makes it poor in absorbance. Manihot Escullenta showed Moderately good absorbance value at about 0.9a.u improving the absorption characteristics of the semiconductor material. The highest impact on the absorbance was made by Cassod which raised the absorbance value of TiO_2 above 1.0 a.u . Peak absorbance values of all sensitized TiO_2 was measured at wavelength between 325nm and 350nm which corresponds to the value for TiO_2 nanoparticles. However, the effect of sensitization by the various dye extracts either reduced or increased its Absorbance characteristics with cassod dye extract raising the value above the 1.0au mark while maintaining its peak wavelength.

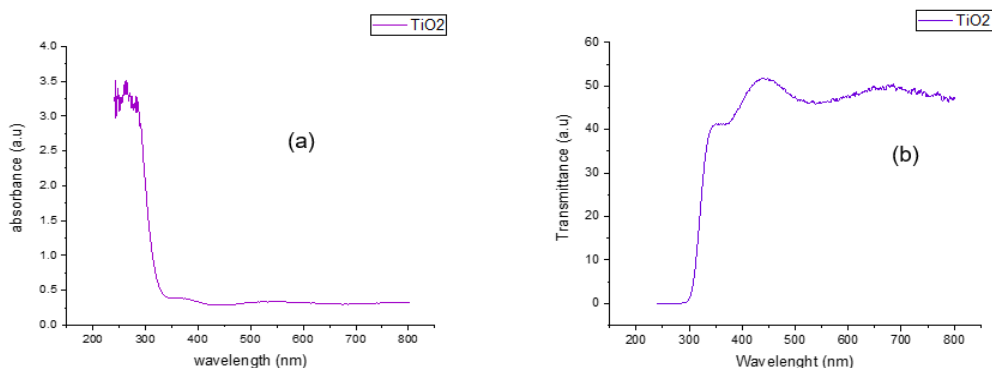


Fig. 9(a). Absorbance spectra of TiO_2 before it was sensitized with dye (b) Transmittance spectra of TiO_2 before it was sensitized with dye

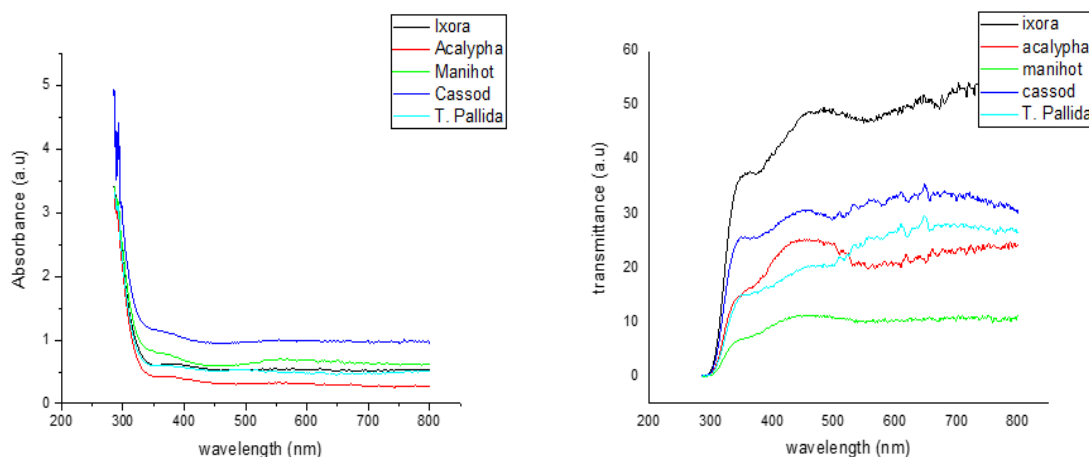


Fig. 10(a). Absorbance spectra of TiO_2 after it was sensitized with dyes (b) Transmittance spectra of TiO_2 after it was sensitized with dyes

Table 1. Voltage and current measurement of DSSC device

Intensity (w/m ²)	Voltage (mV)					Current (mA)					time
	Ixora	Acalypha	Manihot	Cassod	T.Pallida	Ixora	Acalypha	Manihot	Cassod	T.Pallida	
502	44	40	59	48	39	2.10	1.65	2.28	1.77	1.51	9.30
508	36	22	72	64	54	2.18	1.72	3.75	1.92	1.58	10.30
601	48	55	115	84	58	2.68	1.94	4.32	2.99	2.67	11.30
574	31	38	95	72	46	1.98	1.82	4.11	2.87	2.55	12.30
464	22	18	32	22	41	1.24	1.57	3.10	1.84	1.31	13.30
447	18	17	28	18	33	1.08	1.14	2.80	1.22	1.07	14.30
392	11	7	12	4	20	0.88	1.02	1.53	0.92	0.53	15.30

3.3 Current – Voltage Measurements of DSSC

The current and voltage of the device were measured in sunlight between 9.30am when the sun was bright and 15.30pm just the sun started to set as shown in Table 1. The devices sensitized the Manihot Esculenta and Cassod showed the best electrical properties with voltages of 115mV and 84mV and current of 4.32mA and 2.99mA respectively at an intensity of 601m/w² at 11.30am. Measurements for all devices were simultaneously repeated after every 1h interval until 15.30pm when the sun was observed to start setting.

Voltage and current vs time curves are presented in Fig. 9 and 10 respectively which shows the time of peak voltage and peak current.

4. CONCLUSION

In this work DSSC(s) have been fabricated and dye extract from five different plants used as photosensitizers. The dye extract from Manihot Esculenta has shown to produce more voltage and a higher peak current. Also the effect of the various dye extracts on the transmittance and absorbance features of TiO₂ applications as photoanodes in DSSCs have been established. This work has shown that Manihot Esculenta dye as well as other naturally occurring dyes presents an environmentally friendly, cost effective and efficient option for sensitizers in the development of dye sensitized solar cells (DSSCs).

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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