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Pi-pi* orbital transitions and photo-degeneracy of *C.acuminata* sensitized solar cells

T Abodunrin[1], A Boyo[2], M Usikalu[1], L Obafemi[1], O Oladapo[1], L Kotsedi[3], Z Yenus[3] and M Maaza[3]

[1]Covenant University, Canaanland, Nigeria
[2]Lagos State University, Ojo, Nigeria
[3]iThemba Labs, Western Cape, South Africa

E-mail: Temitope.Abodunrin@covenantuniversity.edu.ng

Abstract. Dye-sensitized solar cells (DSSCs) have acquired great prominence as favourable low-cost photovoltaics due to their ease of fabrication, all- year -availability, ease of obtaining raw materials and adjustable optical properties like transparency and colour. These advantages coupled with the ability to work under poor lighting makes them a suitable candidate for next generation of research. In this research, *C.acuminata*-sensitized photo anodes play an important role for achieving high performance since the porous metal oxide films provide a large specific surface area for dye loading and the possibility to extend the absorption threshold of past studies of sensitizers. The doctor blade method and high-temperature sintering were some of the methods used in the fabrication of the photo anode. A study of the performance of the *C.acuminata*-DSSCs with four different electrolyte sensitizers based on iodide redox mediator is determined. The result is DSSCs that exhibit a maximum power output of 39.37 W, fill factor of 0.7 and a power conversion efficiency of 0.6% under unfavourable sunlight intensity conditions and photo-degradation of about 37.5 % in absorbance after 425 suns.

1. Introduction

The Kola nut (Kola) a tropical African genus belonging to the *Sterculiaceae* family, has about one hundred and twenty-five species. The most prominent among the species are Cola acuminata (*C.acuminata*) and Cola nitida (*C.nitida*) due to their economic importance. Both are planted for their edible seed, *C.acuminata* is polycotyledonous while *C.nitida* is a dicotyledon fruit. *C.acuminata* and *C.nitida* contain caffeine, kolanin, and theobromine which make them natural stimulants. Aside from its chemical constituent, Kola is rich in phenol thus, it is an astringent.

These two species bear a striking resemblance, however, *C.nitida* is of higher commercial importance due to the higher demand both locally and export [1]. The molecular formula of *C.acuminata* is $C_8H_{10}N_4O_2$ this provides details of spontaneous redox chemical reactions. Since the first report of DSSC in 1991, remarkable progress has been recorded through the use of electrolytes, photo anode materials and choice of a sensitizer. The sensitizer has an influence on the power conversion efficiency of the DSSC and is crucial in the determination of the stability of the cell thus; this property is the objective of our inquiry. All through the developmental process, practical reforms using different dyes have been employed, but only ruthenium polypyridyl complexes gave reasonable outcomes. Ruthenium dyes, however, require elaborate purification during their preparation process

and are very expensive. In order to avoid this setback, research focus has shifted to easily accessible and cheaper light harvesting molecules. All plants possess systems that harvest light using a conjugation of chlorophyll molecules for competent energy conversion. In natural chlorophylls are derivatives of modified bacteriochlorin units, this is the principle underlying several inorganic dyes which have been based on TiO_2 as photo anode in DSSC [2]. In this work, we report DSSC studies of organic *C.acuminata* dye based on TiO_2 photo anode. This framework is modified by amino groups bonding firmly with the TiO_2 matrix. In order to enhance light –harvesting chromophores, iodine base is added to four different DSSCs. Iodine redox reactions such as (I/I^-, I/Br^-, I/MnO^2, I/Cl^-), displace the amino functional group in a substitution to produce suitable and efficient DSSCs. The photoelectric parameters give the I-V plot, the incident photon to conversion efficiency (IPCE), maximum power (P_{max}), fill factor (FF) for the different electrolytes [4].

2. Materials and Method

C.acuminata leaves were harvested and air-dried until it assumed constant weight. The mass of the leaves was determined with Ohaus electronic balance before milling. This solid mass is aerated for 3-4 hours to discourage bacterial growth. 71 Kg of crushed leaves was soaked in 2,500 ml of methanol for 11 days. Liebig rotary evaporator was used to concentrate the *C.acuminata* dye for further use. Dye-sensitized solar cells were made by the doctor blade method of applying TiO_2 Anatase paste purchased from Solaronix onto indium doped tin oxide (TCO) glass substrate from Sweetmans Ltd of specification (75 mm X 25 mm) and resistivity 10 Ω/m^2. The wet TiO_2 paste was air dried for 1h, after which the active area of exposure (25 mm X 4.5 mm) was sintered at a temperature of 300^0C for 1h until TiO_2 cake turns brown and then white again. Initial preparation steps included; cleaning ITO in detergent solution and rinsing with distilled water. Concentrated HNO_3 was blended uniformly in TiO_2, in the molar ratio of 5:3, respectively, until the consistency of TiO_2 paste is like cake icing. Then the resulting colloidal suspension was applied to the conductive side of the ITO. The counter anode was coated with a thick layer of soot over a naked Bunsen flame. This procedure was repeated for KBr, KI, $KMnO_4$, and $HgCl_2$ electrolyte respectively [4].

The Genesys spectrophotometer (10S series) was used to obtain the UV/Vis spectrographs. The molar concentration of the sample was 1:100 g of *C.acuminata* dissolved in methanol of 99.8 % purity. Shimadzu FTIR spectrophotometer was used to determine the values for the Fourier transform in infrared within a range of 491-3821 cm^{-1}. The molar ratio used for the analysis was 1:100 [3,4].

3. Result and discussion

3.1. Phytochemical screening

C.acuminata reveals the presence of tannins, alkaloids, steroids, volatile oils, glycosides, saponin and cardiac glycosides. Alkaloids, tannins, steroids, glycoside and saponin glycosides high presence suggests a strong availability of materials for charge transport.

3.2. Photoelectric Result

The highest and lowest values of Isc were observed for KCl and KBr respectively. The same trend is repeated in the V_{oc} and ŋ. However, the fill factor has the highest value of 0.70 for the KBr sensitized DSSC while KCl sensitized solar cell has FF value of 0.23. The V_{oc} in KCl is about 20 % more that obtained from KBr electrolyte as shown in Table 1. In this experiment, it is observed that the Cl^- is preferentially discharged for charge transport; this is due to favourable reaction with the iodine from I^-. Although the quality of The KCl cell is comparatively less than the KBr, the efficiency is higher by over 30 %. The factors responsible for the low FF could be the leaking electrolyte creating a high internal resistance and several trap and recombination sites within the titania framework consequently lowering the quality of the KCl/DSSC figure 1 in comparison with KBr/DSSC. The low values observed for KBr and KI is as a result of unfavourable chemical reaction and differential displacement of Br^- and I^- in the interface.

3.3. UV/Vis Spectroscopy

Figure 2 illustrates reveal wavelength peaks and highest absorbance in the near-ultraviolet region, the highest peak is within 650 to 660 nm wavelength corresponding to an absorbance index of 4.00 a.u; a π to π^* molecular orbital transition, this lies in the blue region of the electromagnetic spectrum. This is characteristic of porphyrin dye in the Q-band [3]. Table 1 shows the Cl^- causes the highest displacement. However, Br^- finds it difficult to overcome the chemical potential barrier but has a better quality (shown by the FF). The Vis region shows a loss in the initial activation energy (A.E) between 575 and 630 nm. A small peak at 625 nm shows a second π to π^* transition for an obvious minimum potential barrier, this indicates a strong C-H bond at this absorption peak (FTIR analysis). In the infrared region, *C.acuminata* reveals no observable spectral response in the far infrared region. Wavelength 525 to 575 nm shows rapid spectral responses which do not actually lead to an orbital jump for molecules of *C.acuminata* for 0-1 a.u, it may, therefore, be a gradual build-up of energy that was eventually responsible for the high peak. The absorbance of *C.acuminata* is about 0.4 a.u in the blue region; least within the infrared region; less than 0.1 a.u as illustrated in figure 2.

3.4. FTIR spectroscopy

C.acuminata contains the C-X bond in peaks 491.6 nm, 580.59 nm, 719.47 nm and 1166.97 nm, the functional group is the alkane, and the suffixes are iodine, bromine, chlorine and fluorine respectively; this affirms the CH_3 group in figure 1. The range of intensity for the four peaks is 22.01; the area indicates a medium appearance in which concentration of fluoroalkanes is highest of the four despite its relatively low intensity.

These represent surfaces for articulation either with other bonds or the Titania framework. Wavelength peaks 837.13 nm, 896.93 nm and 974.08 nm represent vinyl C-H bonds which vary from medium to strong appearance as shown by the intensity; it is higher than the C-X bond. The functional group, in this case, is alkene. Many essential molecules like amino acids and neurotransmitters are amine based with application in drug modelling and preparatory materials for dyes. Depending on how they are attached, they cause the desired lowest unoccupied molecular orbital (LUMO) to highest occupied Molecular Orbital (HOMO) transition. The aldehydes (C=O) that consist of ketones occur at 1722.49 nm are the most important functional group because of their influence of conjugation. Esters and Lactones comprising of derivatives of carboxylic acids appear at a wavelength of 1735.99 nm, occur in association with amides and serve as surfactants and phase transfer catalysts [4].

3.5. Surface Morphology

The framework in which *C.acuminata* dye lies is shown in figure C under an accelerating voltage of 15.0 KV and display magnitude of 500 reading through a diameter of 12.7 mm, the zinc oxide film has a thickness of 200 μm. The leaf-like structures show centers of nucleation and reaction around the interface. Figure 4 shows a contrast, there is a cluster of rods, cones from titanium reacting with the *C.acuminata* with the same sensitizer; KI. This facilitates the π to π^* transition of the methyl group in the visible region and an unidentified or a mixture of various bonds in the ultraviolet region; this could explain the several reaction spots (Figure 3), the summation of their individual Eigen value catalyses into the high-energy peak. Howbeit, charge transport could be impeded by the sites acting as traps or recombination sites resulting in the low output efficiency.

3.6. Photodegeneracy of C.acuminata dye

The rate at which *C.acuminata* decays or degenerate is determined as a function of the decrease in the absorbance of the dye over a given period of study. The rate of degeneracy may be faster or slower due to factors such as; increased ambient temperature, pH, and exposure to ultraviolet radiation. In *C.acuminata* dye, these conditions were kept constant, the only variable was time. The formula used for determining the rate of degeneracy expressed in percentage is given by equation 1.

$$D = \frac{A - A_o}{A} * 100$$

(1)

Where:

D: rate of degeneracy

A: Initial Absorbance

A_0: Final Absorbance

From Figures 2 and 5, the rate of degeneracy is 37.5% in 24 months.

Table 1. Photoelectric parameters of *C.acuminata* with four different electrolytes

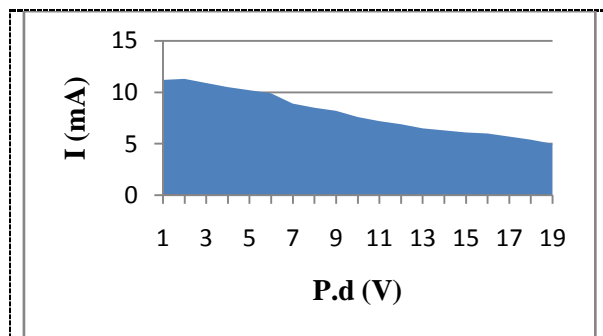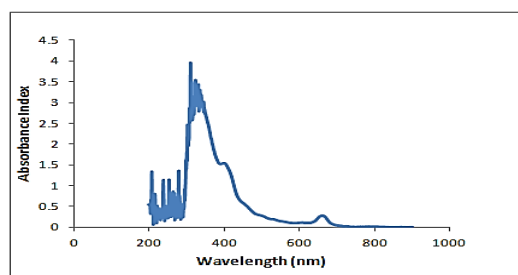| Electrolyte	I_{sc} (mA)	V_{oc} (V)	Pmax	Ŋ (%)	Fill Factor
KCl	1.666	101.4	39.368	0.566	0.23
KBr	0.112	5.0	0.392	0.018	0.70
KI	0.214	14.5	1.165	0.028	0.38
HgCl$_2$	0.653	11.0	2.242	0.043	0.31

Figure 1. I-V of *C.acuminata*.

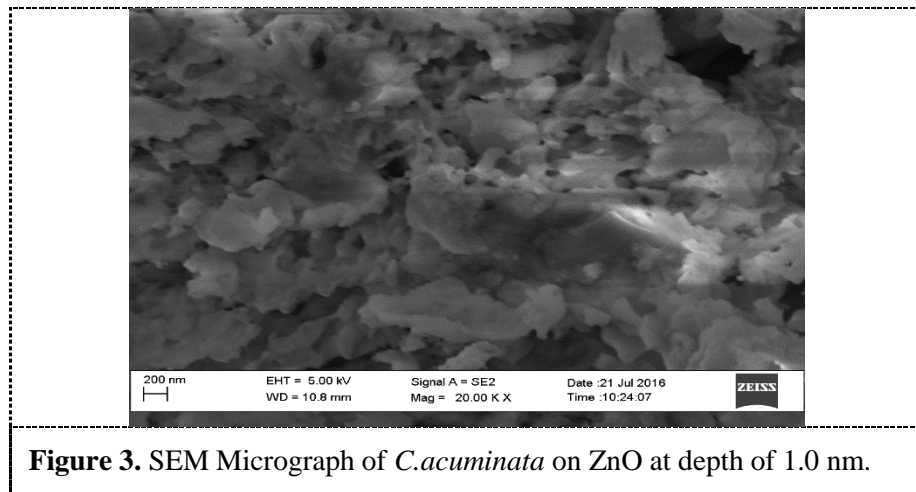**Figure 2.** UV/Vis of *C.acuminata* @ Feb.2014.

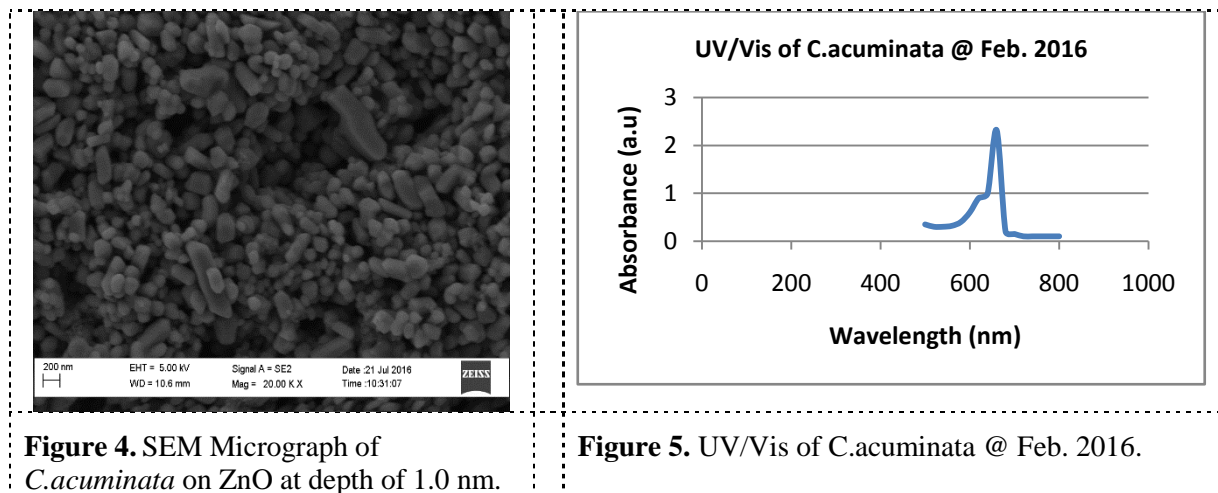**Figure 3.** SEM Micrograph of *C.acuminata* on ZnO at depth of 1.0 nm.

Figure 4. SEM Micrograph of *C.acuminata* on ZnO at depth of 1.0 nm.

Figure 5. UV/Vis of C.acuminata @ Feb. 2016.

Table 2. The Fourier Transform in Infrared (FTIR) of *C.acuminata* in charge transport.

No.	Peak	Type of bond	Intensity	Corr. Inte	Base (H)	Base (L)	Area	Corr. Are
1	491.86	Iodoalkanes	82.077	0.731	493.79	482.22	0.955	0.033
2	580.59	Bromoalkanes	80.298	0.274	632.67	578.66	4.464	0.096
3	719.47	Chloroalkanes	76.334	4.079	727.19	690.54	3.055	-0.025
4	837.13	Para-disub. benzene	74.529	8.374	871.85	786.98	8.29	1.539
5	974.08	Monosub. alkenes	62.335	9.337	995.3	925.86	10.442	1.281
6	1082.1	Aliphatic amines	64.058	3.305	1103.32	1057.03	8.316	0.409
7	1166.97	Fluoroalkanes	60.067	7.64	1203.62	1132.25	13.844	1.738
8	1247.99	Ethers	58.769	8.093	1292.35	1217.12	14.709	1.64
9	1722.49	Aldehyde	45.794	7.877	1728.28	1683.91	10.039	0.799
10	1735.99	Esters and lactones	49.3	4.239	1830.51	1730.21	10.793	-6.087
11	2727.44	Ammonium ions	69.274	1.94	2750.58	2715.86	5.338	0.196
12	3421.83	Primary amines	47.622	0.82	3429.55	3417.98	3.678	0.031
13	3821.11	Secondary amines	84.135	5.153	3824.97	3813.4	0.665	0.1

Acknowledgments

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