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Extracts of *Cola acuminata*, *Lupinus arboreus* and *Bougainvillea spectabilis* as Natural Photosensitizers for Dye-Sensitized Solar Cells

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Abstract**—**Organic dyes from *Cola acuminata* (*C. acuminata*), *Lupinus arboreus* (*L. arboreus*) and *Bougainvillea spectabilis* (*B. spectabilis*) leaves and their mixtures were used as sensitizers to manufacture dye-sensitized solar cells (DSSC). Photoelectric measurements of *C. acuminata* showed a short circuit current (J_{sc}) of 0.027 mA/ cm^2, 0.026 mA/ cm^2 and 0.018 mA/ cm^2 with a mixture of mercury chloride and iodine ($Hgcl_2$ + I); potassium bromide and iodine (KBr + I); and potassium chloride and iodine (KCl + I) respectively. The open circuit voltage (V_{oc}) was 24 mV, 25 mV and 20 mV for the three dyes respectively. *L. arboreus* had J_{sc} of 0.034 mA/ cm^2, 0.021 mA/ cm^2 and 0.013 mA/ cm^2; and corresponding V_{oc} of 28 mV, 14.2 mV and 15 mV for the three electrolytes respectively. *B. spectabilis* recorded J_{sc} 0.023 mA/ cm^2, 0.026 mA/ cm^2 and 0.015 mA/ cm^2; and corresponding V_{oc} values of 6.2 mV, 14.3 mV and 4.0 mV for the three electrolytes respectively. It was observed that the fill factor (FF) was 0.140 for *C. acuminata*, 0.3198 for *L. arboreus* and 0.1138 for *B. spectabilis.* Internal conversions of 0.096%, 0.056% and 0.063% were recorded for three dyes when combined with (KBr + I) electrolyte. The internal efficiency of *C. acuminata* DSSC was highest in value.

Keywords**—**Dye-sensitized Solar Cells, Organic dye, *C. acuminate*, *L. arboreus, B. spectabilis,* Dye Mixture.

I. INTRODUCTION

THIRD generation solar cell fabricated by [1] has drawn a lot of research interest as a result of its relative cheaper cost of production, eco-friendliness, and ability to transform solar energy photons to useful electricity in terms of quantum efficiency. This represents about 10% of incident photons that can be converted to electricity in the sensitization with electrolytes because of the wide band gap of semiconductor dyes [2].

Dye "depth" [3] in the nanostructure presents high chance that a photon will be absorbed, and that the dye will be able to convert them to electrons. Dye films must be thick to accommodate sufficient path length of insolation and absorption by dye. The DSSC uses the same basic principle as plant photosynthesis to generate electricity from sunlight [4]. Each plant leaf is a photo-chemical cell that converts solar energy into biological material. Although only 0.02 - 0.05% of the incident solar energy is converted by the photosynthesis process, the food being produced is 100 times more than what is needed by the plant, and the rest is stored for mankind. More so, their low dielectric constants [5], weak intermolecular forces and small polymers and molecules bring about higher concentration of photo excited states. Sensitization of wide band gaps is attributed to presence of natural pigments extracted from leaves, flowers or some other parts of plants. In a DSSC or photo electrochemical cell, mesoporous titanium oxide ($TiO_{2)}$ is used as anode for the sensitized complex organic dye in an organic solvent.

Transport of charges occurs at boundary of semiconductor when electrons are ejected by incident photons causing a transition of electron from a lower valence band; Lowest Unoccupied Molecular Orbital (LUMO) to higher conduction band; Highest Occupied Molecular Orbital (HOMO) [1] of semiconductor to the charge collector. DSSC's Performance [6], [7] is influenced by the dye used as sensitizer, absorption spectrum of the dye and covalent bond of dye with TiO_2. The Green colour of *C. acuminata* falls within the range of 500 nm to 800 nm; the wavelength considered in this research is between 200 nm and 900 nm. Most flowers, leaves and fruits contain various pigments rich in chlorophyll that can be extracted and used to manufacture solar cells. In this study, *C. acuminata* flavonolic extracts, *L. arboreus* and *B. spectabilis* extracts and their mixtures were used as dye-sensitizers for preparing DSSC's.

C. acuminata belongs to the family '*Malvaceae'*, sub-family; 'stercutioideae' of genus 'Cola' from the fruit tree bearing kola nut. It is a native of tropical West African forests, with about forty different species, most popular of which are *C. acuminata* and *C. nitida*. Cola contains caffeine and is used for flavouring a lot of beverage [8] drinks. The economic significance comes from its ability to act as a concentrated stimulant of the central nervous system (CNS) and may be used to relieve migraines [9]. Phytochemical analysis results show that *C. acuminata* has [10] more alkaloids (2.22%), tannin (6.46%) and saponin (8.06%) than *Cola nitida*. Phenol content of the two most popular kola specie of nuts is in same range 0.27%, flavonoids were in the range of 0.12-0.14%. The flavonoids from *C. acuminata* tree is composed of $C_4H_{10}N_40_2$ (Fig. 1).

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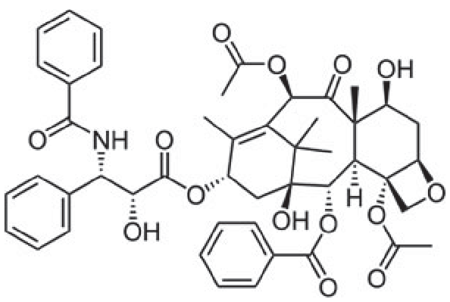

Fig. 1 Chemical Structure of *Camptothecins* (CPT) [8]

C. acuminata's chemical structure is shown in Fig. 1, spectroscopy table [12] reveals weak to medium presence of chloroalkanes in *C. acuminata*.

B. spectabilis [11] is a widespread woody hollow indented plant that grows as a shrub or thorny woody vine reaching to a height of 12cm in tropical and sub-tropical forests; it is a native of India. It contains many phytochemicals (Fig. 2) such as flavonoids, saponins, quinones, triterpenoids, phenols, sterols, glycosides, tannins, furanoids and little sugar.

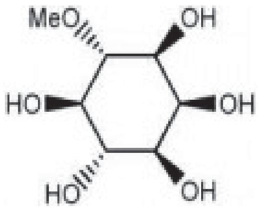

Fig. 2 Bonding of alkene with *B. spectabilis* [11]

B. spectabilis (Fig. 2) has strong cis-disubstituted alkenes presence of the vinyl C-H bond.

II. EXPERIMENTAL DETAILS

300 g of fresh *C. acuminata*, 450 g of fresh *L. arboreus* leaves and 300 g of fresh *B. spectabilis* leaves were crushed separately using a milling machine. The milled samples were soaked in methanol in three separate TLC tanks; methanol level was 3 cm above crushed leaves inside the tanks, which were covered to prevent evaporation of methanol. Mixture in each tank was filtered using a funnel and cotton wool. This was preferred to filter paper because of its organic origin; pure dye solution was separated from the chaff and stored in large reagent bottles and covered. A Liebig rotary evaporator was used to recover dye extracts from mother liquor.

A. Preparation of DSSC

The TiO_2 film was prepared by blending 12 g of commercial variety of TiO_2 powder (Assay, 98% min), in 20ml of concentrated HNO_3. The mixture was properly mixed and the paste was spread over Fluorine doped Tin Oxide (FTO) conducting glass (735140-5EA ALDRICH) of dimension: 50mm × 50mm × 22mm and surface resistivity 7Ω / m^2. The TiO_2 nanoparticles had an average particle size of 20 nm, they were deposited using screen printing procedure (masking paper mesh) on the FTO conducting glass in order to obtain a thickness of 20 μm, the active DSSC area was 0.54 cm^2 (0.6 cm X 0.9 cm). The TiO_2 was sintered for 1h to improve the compactness of the thin film and consolidate it to enhance its absorption and increase the internal voids of film organization. Then the sintered TiO_2 thin film was soaked in the dye until the natural dye molecules was adsorbed on the TiO_2 surface. Methanol was used to clean the FTO surface of any dye smear. After cleaning, the DSSCs were coupled and ready for testing.

Glass Insulation spacers were stuck on all edges of the base of conductive glass while assembling DSSC to create space between photoelectrode and counter electrode, thus enabling ease of injection of electrolyte.

B. Current- Voltage Characterization

Photoelectric parameters were determined using a digital multimeter Model 2400 under solar irradiation of AM 1.5 (100 mW/cm^2). The absorption spectra of dyes were determined with Genesys spectrophotometer, model ID- 2L7J355002. The results obtained were plotted in an I-V curve from data of open circuit voltage V_{oc} (V) and short circuit current J_{sc} (mA), fill factor (FF) and conversion efficiency η% were further determined.

III. RESULTS AND DISCUSSION

Fig. 3 shows the absorption spectra wavelength and absorbance of the three dye extracts. The absorption value of *C. acuminata* for wavelength ranging from 500 nm to 800 nm peaked at 660 nm, while that of *L. arboreus* for the same wavelength range from 500 nm to 800 nm peaked at 670 nm. The absorption range of *B. spectabilis* for wavelength range between 500 nm and 800 nm peaked at 660 nm. From past researches, chlorophyll absorption value is highest in the blue and red regions of absorption spectra. *C. acuminata* at the wavelength of 660 nm had chlorophyll absorption value of 2.32%, *L. arboreus* at wavelength of 670 nm recorded an absorption value of 0.70% and *B. spectabilis* at 660 nm recorded an absorption value of 0.52%. Although their absorption spectra wavelengths are close as revealed in Fig. 3, they have wider measure of chlorophyll absorption values. Kola is highest with a value of 2.32% while *B. spectabilis* is least with a value of 0.52%. Absorption spectra offers necessary details on absorption transition between the ground and excited states of the dye. Only photons absorbed by dye really produce current, this depends on absorption spectrum sensitizing the TiO_2.

Fig. 4 shows the Scanning Electron Microscope (SEM) image of TiO_2 nanoparticles produced through screen printing procedure. The particle size of TiO_2 nanoparticle is 20 nm and properly sintered to ensure adsorption of organic dye molecules.

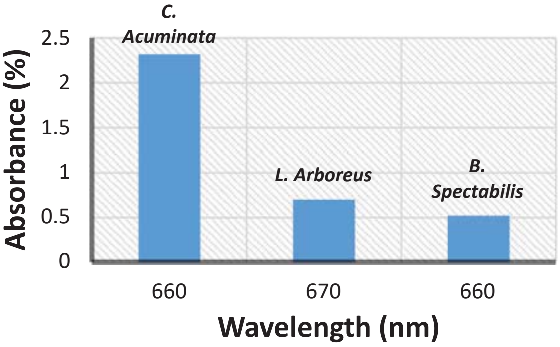

Fig. 3 Comparison of Absorbance against Wavelength for *C. acuminata, L. arboreus and B. spectabilis*

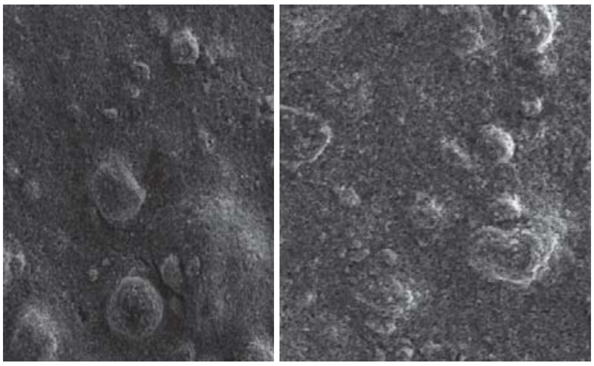

Fig. 4 SEM micrographs of fabricated TiO_2

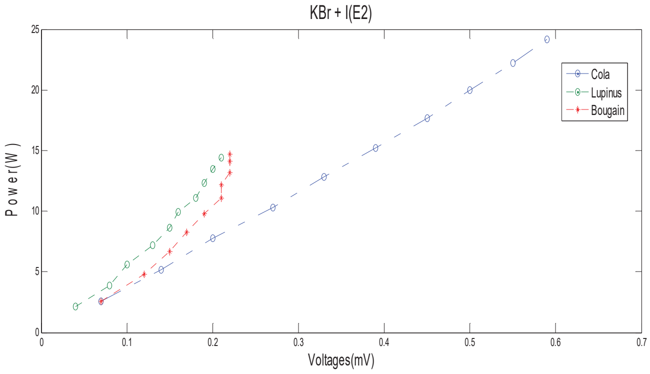

Fig. 5 I-V characteristics of DSSCs with *C. acuminata, L. arboreus* and *B. spectabilis* with electrolyte KBr + I

IV. DSSC POWER OUTPUT AND VOLTAGE

Figs. 5-7 show the record of the power output versus voltage for the DSSCs as observed for the various dye extracts. *C. acuminata* power output versus voltage was (0.24W, 0.7V), the graph showed that *L. arboreus* and *B. spectabilis* followed similar trends with value of (0.15W, 0.23V), using KBr + I electrolyte. Fig. 6 shows *L. arboreus* with higher values of power output and voltage; *C. acuminata* (0.55W, 0.4) and *L. arboreus* (0.7W, 28V). Fig. 7 reveals the interaction of dye cocktail of the three dye extracts, using KCl+I electrolyte, *C. acuminata* recorded highest power output, *B. spectabilis* has very low marginal power output. Tables I A and B show values of photoelectric parameters obtained from the DSSCs.

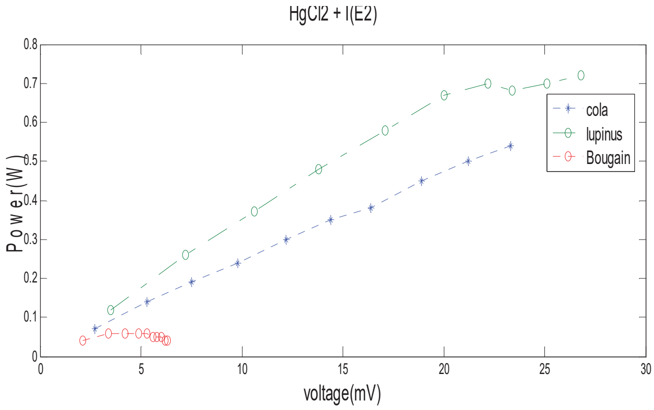

Fig. 6 I-V characteristics of DSSCs with *C. acuminata*, *L. arboreus* and *B. spectabilis* with electrolyte $HgCl_2$+ I

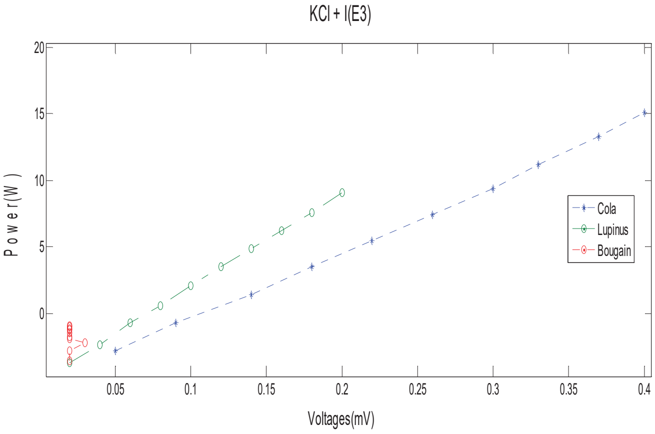

Fig. 7 I-V characteristics of DSSCs with *C. acuminata, L. arboreus* and *B. spectabilis* with electrolyte KCl + I

TABLE I A
PHOTOELECTRIC PARAMETERS OF DSSCS WITH NATURAL DYE EXTRACTS

Dye	I_{sc} (mA /cm^2)	V_{oc} (mV)	FF	P_{max}	η%
C. acuminata	E1 = 0.027	28	0.140	0.019	0.069
	E2 = 0.026	25			0.096
	E3 = 0.022	20			0.075
L. arboreus	E1 = 0.034	28	0.320	0.149	0.089
	E2 = 0.021	14.2			0.056
	E3 = 0.013	15			0.050
B. spectabilis	E1 = 0.023	6.2	0.114	1.723	0.006
	E2 = 0.026	14.3			0.00063
	E3 = 0.015	4.0			0.000001

E1: Mercury Chloride and Iodine; E2: Potassium Bromide and Iodine; E3: Potassium Chloride and Iodine

TABLE I B
PHOTOELECTRIC PARAMETERS OF DSSCS WITH DYE MIXTURES USING POTASSIUM BROMIDE AND IODINE AS ELECTROLYTE

Dye Mixtures	FF	P_{max}	η%
C. acuminata and *B. spectabilis*	0.666	0.200	2.139
C. acuminata and *L. arboreus*	0.363	0.190	0.019
B. spectabilis and *L. arboreus*	0.293	0.252	2.529
C. acuminata, *L. arboreus* and *B. spectabilis*	0.0671	0.008	0.078

The conversion efficiencies of the DSSCs prepared from the dye extracted from *C. acuminata* were (0.056%, 0.096% and 0.075%) for ($HgCl_2$ +I), (KBr +I) and (KCl + I) electrolyte sensitizers respectively, with open-circuit voltage V_{oc} of (24 mV, 25 mV and 20 mV) respectively. *B. spectabilis* recorded V_{oc} (6.2 mV, 14.3 mV and 4.0 mV) at internal conversion efficiencies of (0.063 %, 0.06 % and 0.00001 %) respectively with the three electrolyte combinations. *L. arboreus* had conversion efficiencies of (0.089%, 0.056% and 0.050%) respectively, with the three electrolyte sensitizers and V_{oc} of (28 mV, 14.2 mV and 15 mV) respectively. The short circuit current; J_{sc} were (0.027 mA, 0.026 mA, 0.018 mA), (0.034 mA, 0.021 mA, 0.0131 mA) and (0.023 mA, 0.026 mA 0.015 mA) respectively for *C. acuminata*, *L. arboreus* and *B. spectabilis* DSSCs.

The conversion efficiency of 0.019 % was recorded for the dyes cocktail mixture, fill factor was 0.36; an improvement over using a single dye extract; dyes have [13], [14] high incident photon to current efficiencies (IPCE) in IR. The power efficiency (η) of the solar cells was calculated from:

$$\eta = \frac{FF \times Jsc \times Voc}{Pin} \times 100\%$$

P_{in} is the power density of incident light [15].

From the result in Tables I A and B, the DSSC of the combined electrolyte sensitizers improved photoelectric conversion efficiency; this could be due to synergetic dye sensitization leading to increased efficiency [16]. V_{oc} of natural dye was lower than that of ruthenium dye which could be due to the molecular structure of organic dye which has mostly O and OH ligands and not the –COOH ligands possessed by ruthenium dye which would combine with hydroxyl of the TiO_2 particles producing ester and the coupling effect on TiO_2 conduction band resulting in faster electron rate of transport [17].

V.CONCLUSIONS

Organic dye cocktails of extracts from *C. acuminata* and *L. arboreus* used for the fabrication of DSSC gave promising values in terms of current generation. Higher maximum power output was recorded than that obtained for the individual DSSCs. The internal conversion of the dye cocktail however had lower value than the single dye. This could be as a result of unfavorable interactions [13], [14] between dye molecules. The efficiency of the combination of *C. acuminata*, *L. arboreus and B. spectabilis* dyes showed promising value between 0.1- 0.3% thus indicating a rapidly emerging source of alternative energy supply that would be a very good replacement for the most commonly used silicon solar cells since it is cheaper to produce. However, more work needs to be done on the DSSC to improve on its efficiency and commercialization.

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