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Khaya senegalensis and *Solanum melongena Linn.* as natural sensitizers for dye-sensitized solar cells

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ABSTRACT

Reddish-brown anthocyanins from Solanum melongena Linn. (purple eggplant) and Khaya senegalensis (red-leave Mahogany) were extracted in a mixture of ethanol and water (ratio 4:1 by volume). Solar cells sensitized by the eggplant extracts achieved up to Jsc 3.40 mAcm^{-2} *, Voc 0.350V, ff 0.40 and* η *0.48%, while for the red leave Mahogany dye -sensitized cells the values determined were Jsc 1.38mAcm*$^{-2}$*, Voc 0.325V ff 0.57 and* η *0.36%. Long period stability in energy conversion efficiency of the cells investigated revealed a slight degradation in the of cells efficiencies. Eventhough the results obtained in this work is far below the industrial requirements , the use of natural products as the Sensitizer in dye-sensitized solar cell which enable a faster and simpler production of cheaper and environmentally friendly solar cells has been demonstrated.*

Keywords: Anthocyanins, *Solanum melongena Linn. Khaya senegalensis,* Dye-sensitized solar cell, natural products.

INTRODUCTION

The Silicon Solar cells were first developed over 50 years ago by Bell Labs and are used today to provide reliable electricity in remote locations and to power satellite in space. These Solar cells in use consist of a solid state junction which is capable of separating regions of electron and hole conduction within the thin silicon wafer . The electrons and holes created by the absorption of light in the silicon diffuse at different rate within the regions of the wafer and are eventually collected at the P-N junction.

New technologies which use thin film of inorganic semiconductor materials such as amorpous Silicon, polycrystalline Silicon are been developed and are finding applications in the world markets such as the manufacturing of integrated circuits, computer chips and third world village power source[1].

However , over 100 million watts of convectional solar cells are currently produced yearly for these applications , no solar cell technology had produced an efficient , reliable and cost effective solar module that can be widely used to replace fossil fuel energy sources (which impact harmful effects on the delicate balance of nature on our planet) [2]. Therefore, the conversion of sunlight into electricity in a clean energy system infrastructure is a fundamental issue for worldwide environmental and economy improvements.

The dye sensitized solar cell (DSSC) has become an attractive and cheap device for the conversion of solar light into electrical energy since Graetzel and O' Regan first reported the prototype of this solar cell in 1991[3]. Like photosynthesis this solar cell is a molecular machine that is, one of the first device to go beyond microelectronics technology into the realm of nanotechnology . it is a third generation photovoltaic device that holds significant promise for the inexpensive conversion of solar energy to electrical energy based on the sensitization of wide band gap semiconductor [4]. its relatively simple fabrication process is also an added advantage over other solar cells in operation.

However ,the performances of the solar cell mainly depends on the dye used as sensitizer. The absorption spectrum of the dye and the anchorage of the dye to the surface of TiO_2 are important parameters determining the efficiency of the cell. So far , several organic metal complexes dyes have been adopted in sensitizing the wide band gap TiO_2 . one of the most effective and efficient sensitizer is the transition metal coordination compound (Ruthenium polypyridyl complex). This is because it exhibits lifetime and high efficient metal-to-ligand charge transfer [5]. Moreover, Ruthenium polypyridyl complexes contain a heavy metal which is undesirable from point of view of the environmental aspect, in addition, the process to synthesize the complex is costly and complicated .

In nature , various parts of the shoot and root systems of plants exhibits various colours from red to purple , this is usually ascribed to the present of anthocyanins in them [6]. The Hydroxyl and Crabonxyl present in the anthocyanin molecule can be bound to the surface of porous TiO_2 film which in turn allow for electron transfer from the anthocyanin molecule to the TiO_2 conduction band [7, 8, 9]. In this contribution , the efficiency and stability of DSSC sensitized using natural dyes from *Solanum melongena Linn*. and *Khaya senegalensis* are discussed (Fig .I).

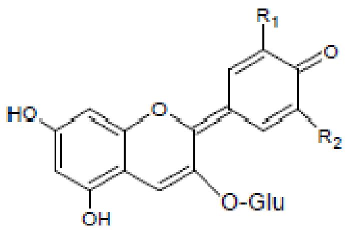


Fig I (a) Delphiniddin 3-[4-(p-coumaroyl)-1-rhamnosyl (1-6)-glucopyranoside] 5- glucopyranoside from *Solanum melongena Linn* . { English; purple eggplant}

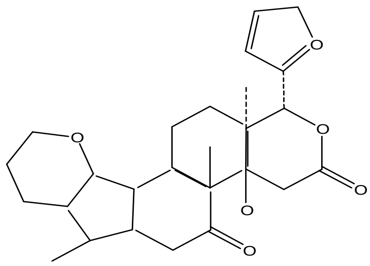


Fig I(b) Triterpenoid from *Khaya senegalensis* { English; red- leave Mahogany}

MATERIALS AND METHODS

2.1 Preparations of natural dye sensitizers

Red Leaves of *Khaya senegalensis* and peels of *Solanum melongena Linn* harvested during sunshine were dried in an open but dark place in the laboratory for several days until their weight becomes invariant. They were then crushed into tiny bits and extracted into a mixture of ethanol- fluka, 96% (v/v) and water (4:1 by volume) keeping them overnight. Both extract remain stable for many months at room temperature in ethanol/water solution.

The residual part were removed by filtration and filtrate was washed with hexane severally to remove oil droplets and chlorophyll that may be present . it is then hydrolysed with few drops of HCl so that the extracts becomes deeper in colour as the natural pH of 3.5 (eggplant) and 3.2 (Mahogany) were adjusted to 1.2. The resulting extracts were centrifuged to further remove any solid residue and were used directly as prepared for the construction of the DSSCs at room temperature.

2.2 Preparation of DSSCs

TiO_2 paste purchased from solaronix (nanoxide –T, colloidal anatase particles size ~ 13nm, ~ 120m^2/g (SA) was coated by screen printing method on pre-cleaned fluorine doped Tin-Oxide (FTO) conducting glasses (Nippon glass sheet 10-12 Ω m^{-2}). Finally, the glass sheet was sintered at 450^{o}C for 30 minutes and furnace-step cooled to room temperature to melt together the TiO_2 nanocrystals and to ensure its good mechanical cohesion on the glass surface.

The TiO_2 electrodes thickness was determined by Dekar profiliometer to be 8.15mm . The impregnation of the electrode was achieved by the immersion of the electrode (face-up) in the natural dye extract for 4-6 hours, this turned the TiO_2 thick- film from white to fairly reddish colour. The impurities/excess dye was washed away with anhydrous ethanol , dried in moisture free air and stored in a dark anhydrous conditions.

DSSCs of 1cm^2 active area were assembled by sandwiching a 60μm thick (before melting) Surlyn polymer foil as spacer between the photoanode and the Patinium counter electrode (prepared by spraying method). Sealing was done by keeping the structure in a hot-press at 80^0 C for 10-14 seconds. The cell was impreginated by introducing a liquid electrolyte (0.5M KI + 0.05M I_2 in solvent of ethylene glycol + acetonitrite with a volume ratio of 4:1) into the cell gap via a pre-drilled hole on the counter-electrode. The hole was later covered to prevent the electrode from leaking.

2.3 Characterization and measurements

UV-visible absorption measurements of the extracts were carried out With Avante UV-VIS spectrophotometer.

Current-voltage (I-V) characteristics of the DSSCs were examined under a standard solar radiation of $1000Wm^{-2}$ using overhead Veeco-viewpoint solar simulator, a four point Keithley multimeter coupled with a Lab-tracer software was used for data acquisition at room temperature.

Based on the I-V curve , power conversion efficiency (η) was calculated according to the equation:

$$\eta = FF \times J_{sc} \times V_{oc}/I \quad (1)$$

where; J_{sc} is the short-circuit voltage (volts), I is the intensity of the incident light (W/m^2), V_{oc} is the open circuit coltage (volts) , FF is the fill factor defined as;

$$FF = J_m V_m / J_{sc} V_{oc} \quad (2)$$

Where ; J_m and V_m are the optimum photocurrent and voltage that can be extracted from the maximum power point of the I-V characteristics (2,3,4, 5,7).

RESULTS AND DISCUSSION

Figure II shows the UV – VIS absorption spectral of *Solanum melongena Linn* and. *Khaya senegalensis* extracts in a mixture of ethanol and water (4:1 by volume). The dye extracts were soluble in ethanol /water solvent and resulted in deep coloured solutions. It can be seen that the extract **A** exhibits a maximum at 542nm while **B** at 525nm shows an absorption maximum. The bands were also broadened with a shoulder at 500nm and 500nm respectively. The different in the absorption characteristics is due to the different type of anthocyanins and colour of the extracts. However ,the combination of *Solanum melongena Linn.* and *Khaya senegalensis* did not affect the absorption peaks, only two peaks which corresponds to the absorbing nature of both extracts were observed.

Generally, anthocyanins and their derivates show a broad absorption band in the range of visible light , this is ascribed to charge transfer transition from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) (13). Absorption spectra of anthocyanidins (anthocyanins without the glycoside group) are mainly dependent on the substitute groups, R1 and R2. (12) as shown in fig. III.

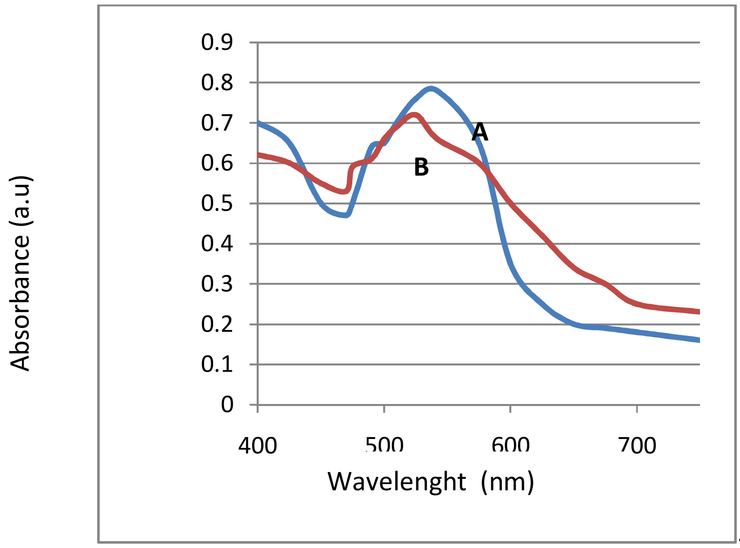
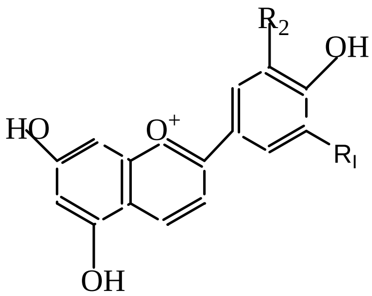


Fig .II Absorption spectral of *Solanum melongena Linn* and *Khaya senegalensis* extracts



	R1	R2
pelargonodin	H	H
cyanidin	OH	H
penindin	OCH_3	H
delphindin	OH	OH
petunidin	OCH_3	OH
malvidin	OCH_3	OCH_3

Fig. III Anthocyanidins structure and the substitute groups R_1 and R_2.[10]

Table I shows the photocurrent – voltage characteristics of solar cells sensitized with extracts *Solanum melongena Linn* and *Khaya senegalensis* and their mixture (50:50)%. The energy conversion efficiency of DSSC prepared using extract obtained from *Solanum melongena Linn* is higher than that of *Khaya senegalensis* , the efficiencies are put at 0.48% and 0.26% respectively. The differences found in the photocurrent of DSSCs investigated could be justified by distinct electron injection efficiencies of anthocyanins for each type of extract and can be influence by the presence of other compounds present [11].

The DSSC sensitized by a mixed extract had an energy conversion efficiency of around the average value of those sensitized with *Solanum melongena Linn* and *Khaya senegalensis.*

Table I, Photoelectrochemical parameters of the DSSCs sensitized by different natural dyes under irradiation with simulated sunlight at 1000wm² intensity (AM 1.5) at the working area of 1.0 cm^2

	J_{SC} (mAcm^{-2})	V_{oc} (V)	FF	η%
Peels of Eggplant	3.40	0.350	0.40	0.48
Red-leave mahogany	1.38	0.325	0.57	0.26
Mixed eggplant-mahogany	2.30	0.335	0.48	0.37

The long period stability of these cells were investigated systematically with perfect sealing to avoid contact with moisture .Unfortunately, cell sensitized with both extract showed poor stability. After been exposed to simulated sunlight for 5 hours .The efficiency of the cells were observed to diminished slightly to 0.44% and 0.23% for *Solanum melongena Linn* and *Khaya senegalensis* DSSCs respectively .

It was reported that this effect could be due to photocatalytic decomposition of anthocyanin by TiO_2 in the presence of ethanol (10), this is observed in the colour of the photoanode which become pale after the long time explosure to simulated sunlight. Hence, the DSSCs prepared using the extracts were unable to function properly just after a short time of operation.

CONCLUSION

We have shown that DSSC of reasonably high efficiency can be developed using *Solanum melongena Linn* and *Khaya senegalensis* extracts obtained by simple extracting process. The results for *Solanum melongena Linn* was slightly better than that of *Khaya senegalensis* sensitiser extract, this is due to the better charge transfer between the *Solanum melongena Linn* dye molecule and the TiO_2 surface which is related to a dye structure [13].

However, efficiency obtained under long – time irradiation period confirmed a reduction in value of energy conversion efficiency for DSSCs prepared. Therefore in terms of long period stability in efficiency of DSSC the sensitizers could be considered not suitable.

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