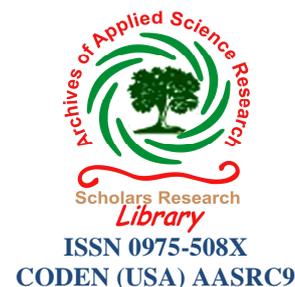




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Utilization of Natural *Morinda lucida* as photosensitizers for dye-sensitized solar cell

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ABSTRACT

Extracts from *Morinda lucida* were used as natural sensitizers of a wide band-gap semiconductor (TiO_2) in photoelectrochemical solar cells. The natural dye, adsorbed onto the semiconductor surface, absorbs visible light and promotes electron transfer across the dye/semiconductor interface. Photogenerated current density and voltage as high as 2.56 mA m^{-2} and 440 mV respectively were obtained and effective energy conversion efficiency of 0.53% was achieved. This simple and cheap techniques of cell preparation therefore open up a perspective of commercial feasibility for inexpensive and environmentally friendly dye cells.

Keywords: *Morinda lucida*, band-gap, photoelectrochemical solar cell, natural dye, semiconductor.

INTRODUCTION

This twenty-first century is gradually forming into the perfect energy storm. Rising energy prices, diminishing energy availability and security, and growing environmental concerns are quickly changing the global energy panorama. Energy and water are the keys to modern life and provide the basis necessary for sustained economic development. Industrialized societies have become increasingly dependent on fossil fuels for myriad uses.

Modern conveniences, mechanized agriculture, and global population growth have only been made possible through the exploitation of inexpensive fossil fuels. Securing sustainable and future energy supplies will be the greatest challenge faced by all societies in this century(1).

In 1998, the global annual energy was about 12.7TW, the expected global annual energy in 2050 is estimated to be 26.4 – 32.9TW, in 2100 this number may increase to 46.3 – 58.7TW (2). Definitely, additional energy greater than the total of all the energy currently produced is

needed . Therefore, the requirement to develop inexpensive renewable energy sources has stimulated new approaches for the production of efficient, low-cost solar cells (3).

Generally, photovoltaic devices are based on the concept of charge separation at an interface of two materials of different conduction mechanism. To date this field has been dominated by solid-state junction devices, usually made of silicon, and profiting from the experience and material availability resulting from the semiconductor industry. The dominance of the photovoltaic field by inorganic solid-state junction devices is now being challenged by the emergence of a third generation of cells, based, e.g. on nanocrystalline oxide and conducting polymers films. These offer the prospective of very low cost fabrication and present attractive features that facilitate market entry. It is now possible to depart completely from the classical solid-state cells which are replaced by devices based on interpenetrating network junctions.

The dye sensitization of nanoporous semiconductors that mimic natural photosynthesis in the conversion and storage of solar energy has been intensively investigated (4) ,a highly efficient solar cell based on dye-sensitized nanoporous TiO₂ thin film electrode, and power conversion efficiency as high as 10% was obtained.

However,effort has been intensified towards dyes used as sensitizers. Since it plays a key role in the harvesting of sunlight and transferring of solar energy into electric energy.

The best – studied example is that of Ru –bipyridyl dye bound via carboxylate bonds to anatase (TiO₂) crystallites. This complex is found to have intense charge – transfer absorption in the whole visible range, long excited lifetime, highly efficient metal – to – ligand charge transfer (MLCT) and with a power conversion efficiency of about 11% - 12% (5) . On the contrary, for the weak binding energy with TiO₂ film and the low charge – transfer absorption in the whole visible range, natural dyes sensitizers perform poorly in Dye sensitized solar cell (DSSC) (6).

Naturally, various parts of the shoot and root – system of plants shows various color from red to purple and contain various natural dyes which can be extracted by simple procedures. In this study, DSSCs were prepared using Natural yellowish -dye extracted from the stem- back of *Morinda lucida* and used as sensitizer, as this fruit is relatively abundant from Senegal to Sudan and southward to Angola and Zambia; it is sometimes planted around villages like in Benin Nigeria .The extract from the plant is rich in anthraquinone as shown in figure Ia (7). The interaction between the dye molecule (the core molecular groups of natural dyes) and TiO₂ porous film was investigated.

Economic importance of Morinda lucida

Tests with animals confirmed the attributed activity of several traditional medicinal applications of *Morinda lucida*. Extracts showed anti-inflammatory, antifever and pain-reducing activity in tests with rats and promoted gastric emptying and intestinal motility. Leaf extracts showed in vitro antimalarial activity against *Plasmodium falciparum* while in several other tests antidiabetic properties were confirmed. Inhibiting effects on cancer tumours in mice have also been reported. (8,9).

The wood of *Morinda lucida* yields yellow to red dyes. In Nigeria and Gabon the root bark (figure Ib) is used to dye textiles into scarlet red. On occasions of national grief or the death of a

chief, the Ashanti people of Ghana dye cotton cloths red with the root bark of *Morinda lucida*. These cloths, called 'kobene', are worn as mourning dress by official people and by the family of the deceased. The root is the most important traditional source of yellow dye for textiles in the Kasai Province of DR Congo. The bitter-tasting roots are used as flavouring for food and alcoholic beverages and in Nigeria they are popular as chewing sticks. The wood is yellow (hence the name brimstone tree), darkening to yellow-brown in the sapwood and to dark brown in the heartwood. It is medium-weight and hard; it works and finishes well, and it is durable, being resistant to fungi, termites and other insects. It is excellent for making charcoal, but is also used for construction, mining props, furniture, canoes, poles and fuelwood (10). The wood is yellow (hence the name brimstone tree), darkening to yellow-brown in the sapwood and to dark brown in the heartwood. It is medium-weight and hard; it works and finishes well, and it is durable, being resistant to fungi, termites and other insects.

In West Africa *Morinda lucida* is an important plant in traditional medicine. Decoctions and infusions or plasters of root, bark and leaves are recognized remedies against different types of fever, including yellow fever, malaria, trypanosomiasis and feverish condition during childbirth (11). The plant is also employed in cases of diabetes, hypertension, cerebral congestion, dysentery, stomach-ache, ulcers, leprosy and gonorrhoea. In Nigeria *Morinda lucida* is one of the four most used traditional medicines against fever (12). In Côte d'Ivoire a bark or leaf decoction is applied against jaundice and in Congo it is combined with a dressing of powdered root bark against itch and ringworm (13).

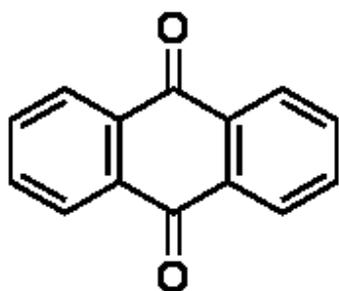


Fig 1 (a) Anthraquinone Structure from *Morinda lucida*. Colour; reddish brown (b) bark peels from *Morinda lucida*

2.1 Preparations of natural dye sensitizers

Bark of *Morinda lucida* were cut into slices and dried in an airy 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.

The residual part were removed by filtration and filtrate was; (A) used as prepared, (B) washed with hexane severally to remove oil droplets and chlorophyll that may be present. Both (A) and (B) were then hydrolysed with few drops of HCl so that the extracts becomes deep redish in

colour as the natural pH of 4.2 was adjusted to 1.2. Both resulting extracts were centrifuged to further remove any solid residue and used directly as prepared for the construction of the DSSCs at room temperature. In this condition, both extracts remained stable for many weeks at room temperature in ethanol/water solvent.

2.2 Preparation of DSSCs

TiO₂ paste purchased from Solaronix (nanoxide -T, colloidal anatase particles size ~ 13nm, ~ 120m²/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°C for 30 minutes and furnace-step cooled to room temperature to melt together the TiO₂ nanocrystals and to ensure its good mechanical cohesion on the glass surface.

The TiO₂ electrodes thickness was determined by Dekar profilometer to be 8.15mm .

The impregnation of the electrode was achieved by the immersion of the electrode (face-up) in the natural dye extracts A and B for 4-6 hours, this turned the TiO₂ thick- film from fairly 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 1cm² 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 80⁰ C for 10-14 seconds. The cell was impregnated by introducing a liquid electrolyte (0.5M KI + 0.05M I₂ in solvent of ethylene glycol + acetonitrile with a volume ratio of 4:1) into the cell gap via a pre-drilled hole centered on the counter-electrode. The hole was later covered to prevent the electrode from leaking.

2.3 Characterization and measurements

The crystalline phases of the TiO₂ film was identified by x-ray diffraction (science RAD-2R) using graphite monochromatized CuK_α radiation (λ =0.154nm).

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

Current-voltage (I-V) characteristics of DSSCs were examined under a standard solar radiation of 1000W/m⁻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 DSSC 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 extractable from the maximum power point of the I-V characteristics curve (4, 8, 9).

RESULTS AND DISCUSSION

Generally, anthocyanins and their derivates show a broad absorption band in the range of visible light 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, R_1 and R_2 , (14), i.e.,

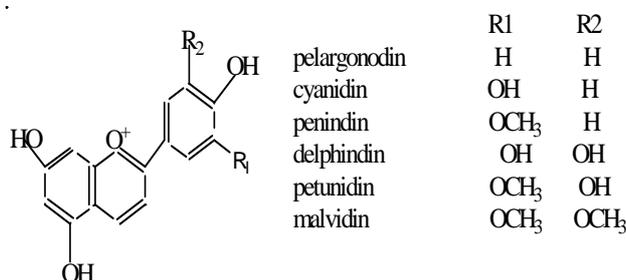


Figure II. Anthocyanidins structure and the substitute groups R_1 and R_2 .

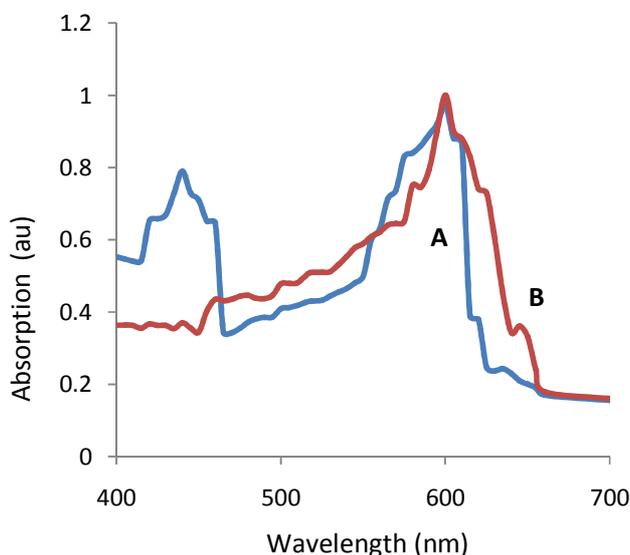


Fig III Absorption spectra of ; (A) anthraquinone and chlorophyll (B) anthraquinone from *Morinda lucida*

Figure III shows the UV – VIS absorption spectral of extracts A and B. Both 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 600nm and 440nm while **B** broadened- band at 600nm shows an absorption maximum. The difference in the absorption characteristics is due to the different composition of chlorophyll (440nm) and Anthraquinone (600nm) in the solutions which in turn gives different colours to the extracts. As shown ,both dye extracts strongly and equally absorbed light at $\lambda = 600\text{nm}$.

Table I. Photoelectrochemical parameters of the DSSCs sensitized by natural dyes A and B under irradiation with simulated sunlight at 1000Wm^2 intensity (AM 1.5) at the working area of 1.0 cm^2

DSSC sensitizers	$\lambda_{\text{max}}(\text{nm})$	$J_{\text{sc}} (\text{mA cm}^{-2})$	$V_{\text{oc}} (\text{mV})$	FF	$\eta\%$
Extract A	600 and 440	2.56	440	0.47	0.53
Extract B	440	1.15	350	0.63	0.25

Table 1 shows the maximum reproducible values of the energy conversion efficiency, the open-circuit voltage and the short-circuit photocurrent of the cells sensitized with extracts (**A**) and (**B**). The energy conversion efficiency of the cell sensitized with extract **A** is significantly higher than the **B** cell , this could be attributed to the fact that cell made from extract **A** enjoys sensitization at peaks 600nm and 440nm respectively also, the low cell B efficiency could be related to low injection efficiencies indicating that the overlap of the dye excited states and the metal oxide state conduction band, the dye regenerative kinematics , and the dye excited state life time are not optimal (as depicted in figure III) . However no deviation from this trend was observed when attempts were made to enhance the absorption of the individual dyes (i.e; by varying the duration of immersion). Moreover ,both cells show no invariance in the efficiency under 3 hours Continuous stimulated sunlight illumination but on exposure to direct sunlight noticeable decay was seen in about 5–6 hours in both cells. This effect could be attributed to the UV in sunlight which seems to degrade the pigments as observed in the fairly fading away of the photoanode colour.

CONCLUSION

In this approach, natural dyes were extracted from *Morinda lucida* using different cheap techniques for possible application as sensitizers in DSSCs .The attached dyes, rather than the semiconductor itself, are the absorbing species. They inject electrons into the semiconductor conduction band upon excitation. These electrons are then collected at a conducting surface, generating photocurrent. As a result of this advancement, the development of environmental friendly, inexpensive and efficient photochemical solar cells became commercially feasible.

Among the different dyes investigated , the dye containing mixture of chlorophyll and Anthraquinone extracts gave a significantly higher photocurrent, voltage and reasonable efficiency, this could be due to better interaction between the surface of TiO_2 and the dye molecules. However, studies on the long-term stability of the cell developed revealed a decay in the efficiency over time.

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