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Safety assessment of *Cola nitida* extract as sensitizer in dye sensitized solar cell

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ABSTRACT

Extracts from red kola nut (cola nitida) 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 3.42 mAm^{-2} and 422 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 enviromentlly friendly dye cells.

Keywords: *kola nitida*, band-gap, photoelectrochemical solar cell, natural dye, semiconductor.

INTRODUCTION

The world energy demand is still increasing . At the moment , fossil fuels and nuclear energy are the main energy sources . This classical energy sources cannot provide us with the enough energy for the future any more. One problem is that the resources are limited. The stock of carbon based fuels might be exploited in roughly fifty years time. Another big problem is that carbon dioxide, the final product of burned fossil fuel, is known to influence earth climate significantly. Nuclear has always been subject of intensive public discussion due to the security and health risks of nuclear power stations and the following problem of radioactive waste.

To find a lasting solution to these problems, efforts have been in top gear to develop new, alternative energy sources over the last decades. One of these alternatives energy sources is the solar energy; the sun is reliable, clean, for free and can be used all over the world. Therefore, the conversion of sunlight into electricity by photovoltaic cells is widely used in the meantime.

Photovoltaic (PV) effect was first observed in 1839 by the French scientist Edmund Becquerel, it was not fully comprehensible until the development of quantum theory of light and solid state physics in early to middle 1900s. Since its first commercial use in powering orbital satellites of the US space programs in the 1950s, PV has made significant progress with total U.S. photovoltaic module and cell shipments reaching $131 million dollars in 1996. While most PV cells in use today are silicon-based, cells made of other semiconductor materials are expected to surpass silicon PV cells in performance and cost , and become viable competitors in the PV marketplace.

Dye-sensitized solar cells (DSSCs) have become one of the most promising alternatives for the photovoltaic conversion of solar energy as compared to the conventional solid p-n junction photovoltaic devices and are currently undergoing rapid development in an effort to obtain robust, efficient, and cheap devices that are suitable for practical use. At the heart of a DSSC system is a mesoporous oxide layer composed of nanometer-sized particles anchored by a monolayer of the charge-transfer dye, especially Ru-polypyridyl- complex (sensitizer).

However, much attention has been paid to survey the effective sensitizer dyes. It is necessary for sensitizer dyes to have enough energy levels to transfer electrons and anchor group(s) to have affinity for semiconductors. One of the most efficient sensitizers are synthetic dyes, such as ruthenium(II) polypyridyl complexes with carboxylated ligands, since these compounds present intense and wide-range absorption of visible light as well as suitable ground- and excited-state energy levels with respect to TiO_2 conduction band energy and to the redox potential of electron donor [1,2,3]. On the other hand, many studies have also concentrated on exploration into natural dyes, such as cyanin [4], anthocyanin [5,6], tannin [7], chlorophyll [8,9] and so on for sensitizers. Although these natural dyes often work poorly in DSCCs, these are expected as low cost and prepared easily comparing to ruthenium(II) polypyridyl complexes.

In this paper, the natural dyes were extracted from red kola nut (*cola nitida*) ,the interaction between the dye molecule (the core molecular groups of natural dyes) and TiO_2 porous film was investigated.

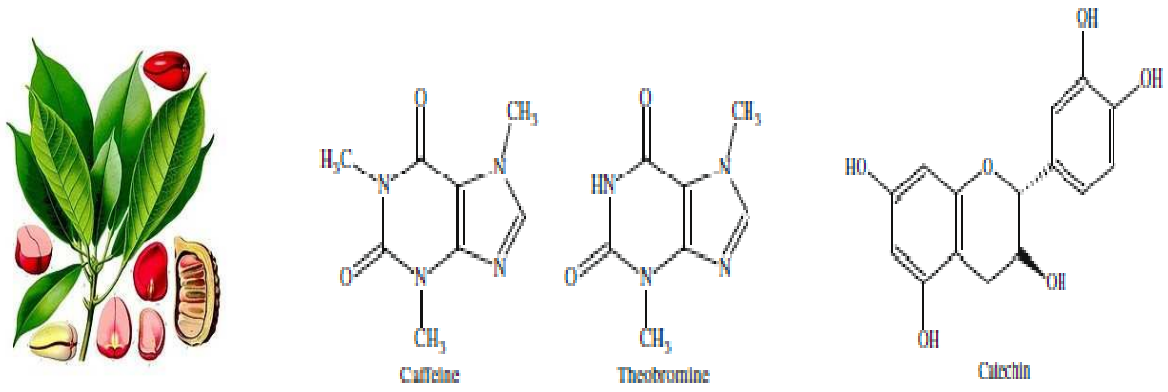

Fig. I; (a) *Cola nitida* plant and nut (English ; kola nut) , (b) Structures of representative kola nut constituents[20].

1.1 Economic uses of kola nut.

Kola nut extract is used in the food industry as a natural flavoring agent [10]. The extract also finds use as a natural herbal preparation for the treatment of mental and physical fatigue [11] . The nut itself is also exported worldwide for extraction and is used in the manufacture of methylxanthine-based pharmaceuticals [12]. In 1886, the druggist, John S. Pemberton, from Atlanta, Georgia, invented the popular soft drink, Coca-Cola, by combining coca and kola extracts for use as a headache and hangover remedy [13] .Up –to-date, chewing of fresh kola nut remains a 'social lubricant', with strong cultural significance for many indigenous West African people, particularly those of Islamic faith who are forbidden to consume alcohol [14], beside dye extracted from the fruit is been used for the coloration of textile fabrics in northern Nigeria.

MATERIALS AND METHODS

2.1 **Materials**

Transparent conductive Oxide coated glass (TCO 10-12 ohm/m^2, 1.00x1.00 cm^2), Ti-Nanoxide D and Surlyn polymer foil were purchased from Solaronix. Dinitroamine Platinum (II) was procured from Johnson Matthey Catalysts for Counter anode preparation, Acetonitrile, sodium carbonate and sodium acetate combined in making electrolyte were purchased from Aldrich. Dye extract was obtained from the natural product (kola nut).

2.2 **Preparations of natural dye sensitizers**

Red kolanut (*cola nitida*) 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 3.7 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.

2.3 Preparation of electrolyte

The electrolyte solution for natural DSSCs was prepared by dissolving 2.075 g of KI and 0.19 g of I_2 in 25ml of ethylene glycol/acetonitrile mixture (4:1 by volume).

2.4 **Preparation of DSSCs**

TiO_2 paste purchased from solaronix (nanoxide –T, colloidal anatase particles size ~ 13nm, ~ 120m^2/g was coated by screen printing method on pre-cleaned fluorine doped Tin-Oxide (FTO) conducting glasses . Finally, the glass sheet was sintered at 450°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 TCO.

The TiO_2 electrodes thickness was determined by Dekar profiliometer to be 8.10mm . The impregnation of the electrode was achieved by the immersion of the electrode (face-up) in the natural dye extracts for 3-5 hours, this turned the TiO_2 thick- film from pale-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 Platinium counter electrode (prepared by spraying method). Sealing was done by keeping the structure in a hot-press at 80^0 C for 11-15 seconds. The cell was impregnated with the liquid electrolyte via a pre-drilled hole on the counter-electrode. The hole was later covered to prevent the electrode from leaking.

3.0 measurements of photoelectrochemical characteristics

UV-visible absorption measurements of the extracts was carried out With Avante UV-VIS spectrophotometer. Photoelectrochemical measurements of DSSCs were performed under a standard solar radiation of $1000W/m^{-2}$ using overhead Veeco-viewpoint solar simulator (equipped with AM 1.5 filter) and a four point Keithley multimeter coupled with a Lab-tracer software was used for data acquisition at room temperature. The active/working cell area was $1.00cm^{2.}$. Based on the I-V curve, power conversion efficiency (η) was calculated according to the equation:

$$\eta = FF \text{ x } J_{sc} \text{ x } V_{oc} / I \qquad (1)$$

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 voltage (volts) , FF is the fill factor defined as;

$$FF= J_mV_m / J_{sc} V_{oc} \qquad (2)$$

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 [15].

RESULTS AND DISCUSSION

Figure I 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 610nm and 440nm while **B** at 610nm shows an absorption maximum. The **B**- band is broadened with a shoulder at 560nm. The difference in the absorption characteristics is due to the different composition of chlorophyll (610nm) and Catechin (440nm) in the solutions which in turn gives different colours to the extracts.

Table I 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 610nm and 440nm respectively (as depicted in figure I) . 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).

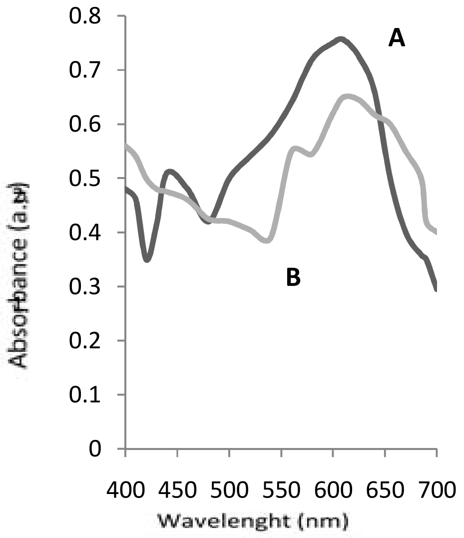

Fig.II Absorption spectra of ; (A) Catechin and chlorophyll (B)Catechin from kola nut.

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

DSSC sensitizers	J_{SC} (mAcm^{-2})	V_{oc} (mV)	FF	η%
Extract A	3.42	422	0.37	0.53
Extract B	2.86	376	0.41	0.39

However ,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 4–5 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.

The energy conversion efficiency obtained using kola ectract (A) in DSSC (0.53%) compared favourable with the results obtained using Rosella (0.37%) [16], Achiote seeds (0.37%) [17] , *lawsonia inermis* (0.66%) [18] and Mulberry(0.52%), Blueberry(0.61%), Jabotical's skin(0.56%)[19] .

CONCLUSION

In this approach, natural dyes were extracted from *Cola nitida* 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 low-cost, efficient photochemical solar cells became possible.

Among the different dyes investigated , the dye containing mixture of chlorophyll and Catechin 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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