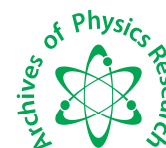




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Effect of natural dye extracting temperature on the performances of dye sensitized solar cells using *Petrocarpus Erinaceus*

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ABSTRACT

Natural pigments containing anthocyanins extracted at different temperatures from *petrocarpus erinaceus* (African rosewood) were studied as possible sensitizers for TiO₂ by assembling dye-sensitized solar cells . Photocurrent densities ranging from 1.11 to 2.15 mA cm⁻² were obtained with photovoltages ranging from 390 to 431 mV. The overall efficiency and fill factor of these cells varied from 0.23 to 0.51 and 0.50 to 0.57 respectively. Among the different extracts studied, the extract obtained at 323K gave the best photosensitized effect, which can be used as an environment-friendly, low-cost alternative system, especially for educational purposes.

Keywords: Dyes, natural pigments, solar cells, *petrocarpus erinaceus*

INTRODUCTION

The world energy demand is still increasing. At the moment fossil fuel and nuclear fuel are the main energy sources. One problem is that the resources are limited and exhaustible ; nuclear energy has always been subjected of intensive public discussions due to the security and health risks of nuclear power station and the attendant problems of radioactive waste, carbon dioxide the final product of burned fossil fuel is known to impact harmful affects on the delicate balance of nature on our planet (1). According to recent predictions the inevitable permanent decline in the global oil production rate is expected to start within the next 10 to 20 years- worldwide oil prices will then rise considerably favoring the introduction of various renewable energy sources such as the direct conversion of solar energy, hydroelectric power and wind power(2).

Although, these fore-mentioned renewable energy sources neither run out nor have any significant harmful effect on the environment but the amount of power they can supply often depends on geographical and weather conditions. Among the renewable energy sources the field

of photovoltaic is of major importance as solar energy is largely abundant surpassing our present global annual energy needs by a factor of 10,000.

Photovoltaic offers many advantages over other methods of converting solar energy into electrical energy these include ; simplicity, profitability and environmental compatibility in addition it produce no gaseous or thermal pollution. Therefore the harnessing of this enormous potential of free solar energy represents an exciting challenge to scientists, politicians as well as the global economy.

Drastic improvements in photovoltaic device manufacture led to a remarkable increase in energy conversion efficiencies and significant price cuts. However due to some fundamental concepts of classical inorganic pn-junction solar cells, such devices will always demand the use of extremely pure starting materials and somewhat sophisticated production procedures. A very promising alternative to classical, inorganic pn-junction solar cells is the concept of nanoporous, dye-sensitized photoelectrochemical solar cells, introduced by O'Regan and Grätzel in 1991 (3).

Those cells whose working mechanism is based on photoelectrochemical mechanism resembling the photosynthesis in green part of plant exhibit impressive white light energy efficiencies of up to 12% while they are based on cheap starting materials and simple printing or doctor blade techniques (3,4). They thereby represent the only known alternative conceptual approach rivaling conventional solid-state solar cells.

The sensitization of wide band gap semiconductors using natural dyes/pigments is usually ascribed to anthocyanins (4,5,7). The anthocyanins belong to the group of natural dyes responsible for several colors in the red-blue range, found in roots, stem, fruits, leaves and flowers and plants. Carbonyl and hydroxyl groups present in the anthocyanin molecules can be bound to the surface of a nanoporous TiO_2 . This makes the electron transfer from the anthocyanin molecules to the conduction band of TiO_2 (8) . It has been emphasized by many researches to obtain useful dyes as photosensitizers in dye sensitized solar cell (DSSC) from natural products, some natural dyes used as sensitizers of DSSCs have been reported (4-13).

In this study, DSSCs were prepared using natural dye extracted from African rosewood (*Petrocarpus erinaceus*) as sensititizer as this plant is abundant in tropical countries and rich in anthocyanin (10), the effects of extracting temperatures of the dye solution on the stability and efficiency of DSSCs sensitized with the dyes were also investigated.

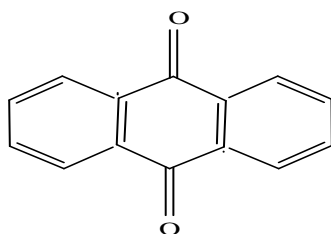


Fig .I. Anthraquinone from *Petrocarpus erinaceus* (African rosewood)

MATERIALS AND METHODS

2.1 Preparation of Dye sensitizer solutions

Dry stem of *Petrocarpus erinaceus* chosen was cut into tiny pieces and extracted into a mixture of Ethanol (Fluka 96%(v/v) and water (75:25 by volume) at different temperature of 300k (room temperature), 308k, 323k, 338, and 353k respectively. The residual parts were removed by filtration and filtrate were washed severally with hexane to remove any oil and chlorophyll that may be presenting in the extract. The extracts were then hydrolyzed with few oil drops of HCl so that the extract became deep reddish-brown in colour. The resulting extracts were centrifuged to further remove any solid residue and used as such in DSSCs fabrication.

2.2 Preparation of Electrodes

The conductive glass plates (Fluorine-doped tin oxide glass sheet, with sheet resistance 15ohm/cm²) and Titanium-nanoOxide paste were purchased respectively from Solaronix SA and Aldrich and used as received.

The FTO substrate (cut into 1.2x1.2cm² dimension) was ultrasonically cleaned in water-isopropanol and heated at 723K for 30 minutes prior this deposition to provide a blocking underlayer. It is then pre-treated by immersion in 40mM TiCl₄ solution (placed in distilled water) at 343k for 20 minutes. Thin film on the substrate was later sintered at 723K for 25minutes. Then mesoporous TiO₂ thick film were deposited by screen-printing method on the substrate and sintered at 773k for 30minutes ; to melt together the Titanium particles , to allow for adhesion of the film onto the substrate and to allow for good electrical contact. As a final step, the photo anode was re-treated in 40mM TiCl₄ solution at 343K for 20min and heated to 773K for 20 minutes. The final thickness as determined by a Dekar profilometer was 8.2um. Platinum coated counter electrodes were prepared according to published procedures (6).

2.3 DSSC Assembly

The photoanodes were immersed (face-up) in the natural dye sensitizer solution for to chemo-adsorbed the dye onto theTiO₂ porous thick-film and this turn the fairly whitish photoanode to fairly reddish-brown colour. Other impurities/excess dye were washed away with anhydrous ethanol and dried in moisture free air. It was noticed that upon increasing the immersion time the photoanode- colouration became weaker therefore, the best cells were prepared using 4 hours immersion time. This may be attributed to dye aggregation and a weak interaction between the dye and the metal oxide surface indicating the surface chemistry requires optimization.

DSSCs of 1cm² active were assembled by sandwiching a 60µm thick (before melting) Surlyn polymer foil as spacer between the photoanode and the Patinium counter electrode. Sealing was done by keeping the structure in a hot-press at 80⁰ C for 12-15 seconds. The liquid electrode (0.5Mkl + 0.0MI₂ in solvent of ethylene glycol + acetonitrile with a volume ratio of 4:1) was introduced into the cell gap via a pre-drilled hole on the counter-electrode. The hole was later covered to prevent the electrode from leaking.

2.4 Measurements

The UV-visible absorption spectra of the dye solutions were recorded with Avante spectrophotometer. The current voltage (I-V) characteristics of the DSSCs were examined under

a standard solar radiation of 100mW/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 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 current (A/m²), 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;

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

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 (4, 6,10).

RESULTS AND DISCUSSION

The dyes extracted from *Petrocarpus erinaceus* at different temperatures were soluble in mixture of ethanol and water (75:25) and resulted in deep reddish-brown solution with the deepest colour in extract done at 323k.

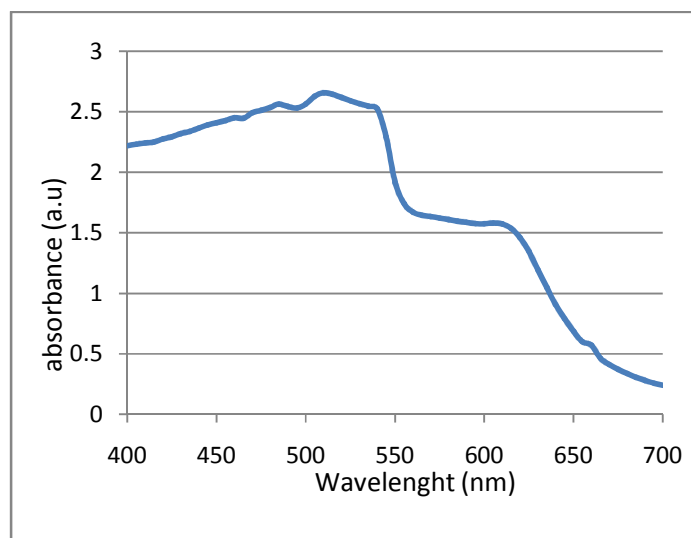


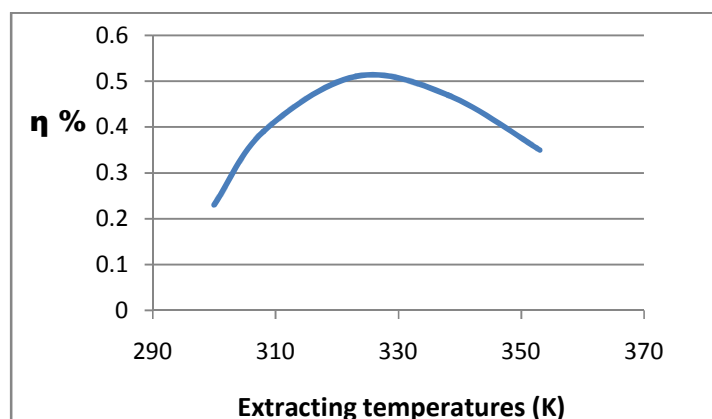
Fig. II. Optical absorption spectrum of *Petrocarpus erinaceus* dye (extracted at 300k).

Fig.II shows the optical absorption spectrum of the dye extract at room temperature (300k) displayed an intense absorption in the 400-500nm region with a broad shoulder at 605nm. Further studies on the photoanodes impregnated with dye depict a visible absorption band shifts to higher energy showing a broad maximum around 445nm

Table I. Photovoltaic parameters of DSSCs prepared using *Petrocarpus erinaceus* sensitizer extracted at different temperatures

J_{sc} (mA/cm ²)	V_{oc} (mV)	Ff	η %	Extracting temperature(K)
1.11	390	0.53	0.23	300
1.72	450	0.56	0.39	308
2.08	431	0.57	0.51	323
2.15	422	0.52	0.47	338
1.68	416	0.50	0.35	353

Table I summarized the overall results of the photovoltaic performances of the DSSCs developed using dye solutions extracted at different temperatures, under irradiation with stimulated sunlight at 100mWcm⁻² intensity (AM 1.5) at room temperature. The highest efficiency of 0.51% was obtained from the device sensitized with dye solution extracted at 323k with an open-current voltage of 431Mv and fill factor of 0.57. One of the reasons for this could be due to the highest amount of dye absorbed onto the TiO₂ film compared with other dyes obtained at different temperatures ,

**Fig.III. Variation of efficiency of DSSCs with dye extracting temperatures**

However, the efficiency as well as the fill-factor gradually decreased as the extracting temperature of the dye increases (Fig.III) this fall could be due to a decrease in the stability of anthocyanin at elevated temperatures, the thermal degradation of anthocyanin could be due to a loss of glycosyl moieties and α -diketone formation . The long-term stability test on the cells was carried out with perfect sealing to avoid contact with moisture for a period of 4 hours under simulated irradiation of 100mW/m².

Even though these cells showed a declining , both the open-circuit voltage and short-circuit current density as depicted in table 1 showed a reasonably good stability.

CONCLUSION

Natural dyes are environmentally friendly and inexpensive sources of sensitizer for DSSCs and have now proven to be commercially feasible. Anthraquinone extracted at different temperature

capable to sensitize TiO₂ photoanode and their respective cells exhibited comparable photovoltaic parameters. In particular cell sensitized with dye extracted at 323k presented the best performance of 0.51% i.e, the optimum extracting temperature of dye for DSSC's operation was found at 323k which lies between the room temp and the boiling point of water. The cost performance (defined as conversion efficiency/cost of dye) of DSSCs sensitized with dye solution extracted at a temperature of 323k is larger than that of DSSC using Ruthenium complex. This evidence is expanding the interest in both photochemistry and Anthraquinone chemistry, it will promote it to a potential new sensitizer by and large providing us with alternatives for powering our society.

Acknowledgements

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