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Extract from *cynodon dactylon:* A viable alternative to ruthenium based complexes for dye sensitized solar cells

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ABSTRACT

Dye sensitized solar cells (DSSCs) are devices that convert visible light into electricity based on the photosensitization of wide band-gap semiconductors, such as TiO_2, SnO or ZnO. Most of the efficient DSSCs are sensitized with the dyes having ruthenium based complexes. We have compared the performance of a dye sensitized solar cell based on *chlorin* dye with that of a ruthenium based DSSC and a plain cell. *Chlorin* dye was extracted from *cynodon dactylon* which is popularly called bahama grass and titanium (iv) oxide was our wide band-gap semiconductor. The absorption spectrum revealed that the ruthenium dye peaked at 264nm, while the *chlorin* dye peaked at 355nm and 505nm. Meanwhile, both dyes showed appreciable absorbance beyond the ultraviolet region. The conversion efficiency for the cells were 1.7%, 1.008% and 0.03% for the ruthenium, *chlorin* and plain cells respectively. A diurnal study of their electrical characteristics showed that the local dye from *cynodon dactylon* is a viable sensitizer for TiO_2. Avaspec 2.1 spectrophotometer was used to obtain the optical absorption spectrum, while an Oriel class A solar simulator was used for current-voltage characterization.

Keywords: *Ruthenium, bahama grass, photovoltaic performance, dye sensitized cell*

1. INTRODUCTION

Dye sensitized solar cells (DSSCs) are devices that convert visible light into electricity based on the photosensitization of wide band-gap metal oxide semiconductor such as TiO_2, SnO2 or ZnO [1,2]. DSSCs have attracted a lot of interest towards development and improvement of new families of dyes and metal complexes [3]. DSSCs are photoelectrochemical in nature and have gained considerable academic and industrial interest because of high energy conversion efficiency, high-stability semiconductor and sensitizer, simple assembly technology and low manufacturing cost [4]. Most of the efficient DSSCs are sensitized with the dyes having ruthenium based complexes that have been shown to operate with power conversions up to 10% using nanoporous TiO_2 electrodes [5-8]. DSSC is composed of the dye-adsorbed wide band-gap semiconductor (example TiO_2) film formed on a transparent conductive oxide (TCO) substrate, the I_3 / I redox electrolyte and the Pt counter electrode [9,10]. F-doped SnO_2 (FTO) is usually used as the TCO material. In order to induce good contact between TiO_2 and electrolyte, TiO_2 film should have a mesoporous structure. TiO_2 acts as electrolyte acceptor and electron transport layer, while electrolyte acts as hole transport layer. The adsorbed dye molecules become excited under the irradiation of visible light and inject electrons into the conduction band of the semiconductor within pico- to femto-second [4]. The photo-injected electrons are collected at FTO via the porous TiO_2 network by diffusion process with rate of about micro- to mili-second. The oxidized dyes are regenerated by oxidation of iodide with nano-second time scale. Photovoltage is generally determined by the energy difference between the Fermi level of TiO_2 and redox potential of electrolyte [11]. In DSSC, the dye-adsorbed TiO_2 film plays an important role because it serves as a pathway for photo-injected electrons.

Preparation and development of synthetic dyes as a sensitizer of DSSC normally requires multistep procedures, which involves a variety of solvents and time consuming purification processes, making synthetic dye production very expensive [1,12]. Several studies have found the possibilities of using natural dyes as sensitizers for DSSC's [1,13,14]. The use of natural dyes as sensitizers for DSSCs have several advantages over rare metal complexes and other synthetic dyes, in that they can easily be extracted from fruits, vegetables, and flowers with minimal chemical procedures, thus attracting a lot of interest in producing a low cost and yet easy to fabricate DSSCs as alternative to silicon photovoltaics [15]. Natural pigments containing anthocyanins and carotenoids have shown overall solar energy efficiencies up to 1% [1,16]. Anthocyanins consist of a large family of widespread flavonoids in plantsand they are responsible for many fruits and flora colours.

In this research work, the blade method was used to deposit sol-gel derived nanocrystalline TiO_2 (n-TiO_2) onto an FTO glass substrate. The titanium (iv) oxide film was subjected to annealing treatment to enable it serve as a photo-electrode for DSSC [5,17] and thence doped with *chlorin* local dye. The local dye was extracted from *cynodon dactylon* commonly called bahama grass. A second electrode was sensitized with ruthenium based dye while a third unstained electrode was fabricated. Three solar cells were prepared for comparative analysis. Optical studies and the current-voltage characteristics of the cells were carried out. Figures 1 and 2 are the optical absorption spectra of un-doped TiO_2 showing that the semiconductor is active only under ultraviolet light because of its wide band-gap [8,18].

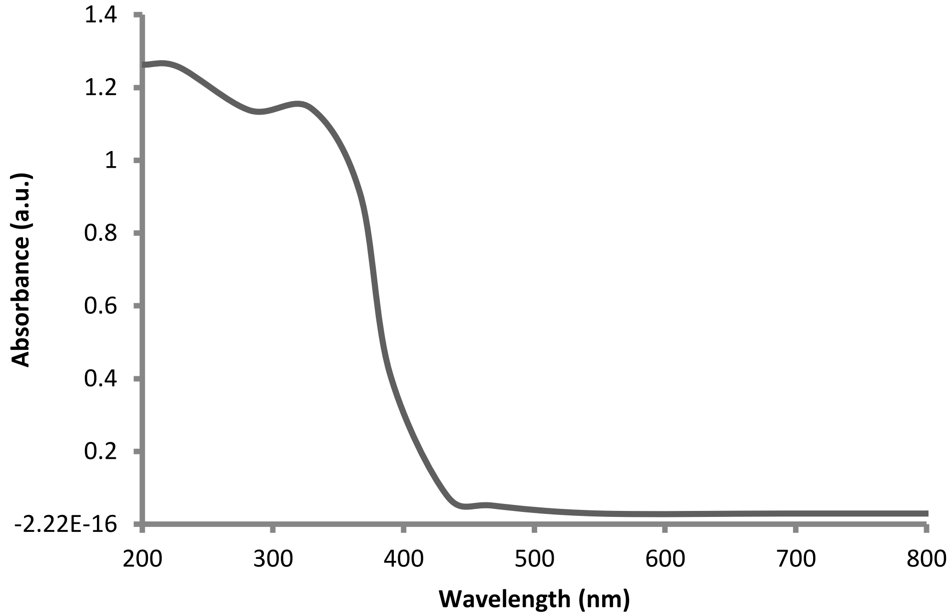

Figure 1. UV-vis spectra of nanoporous titanium dioxide[8]

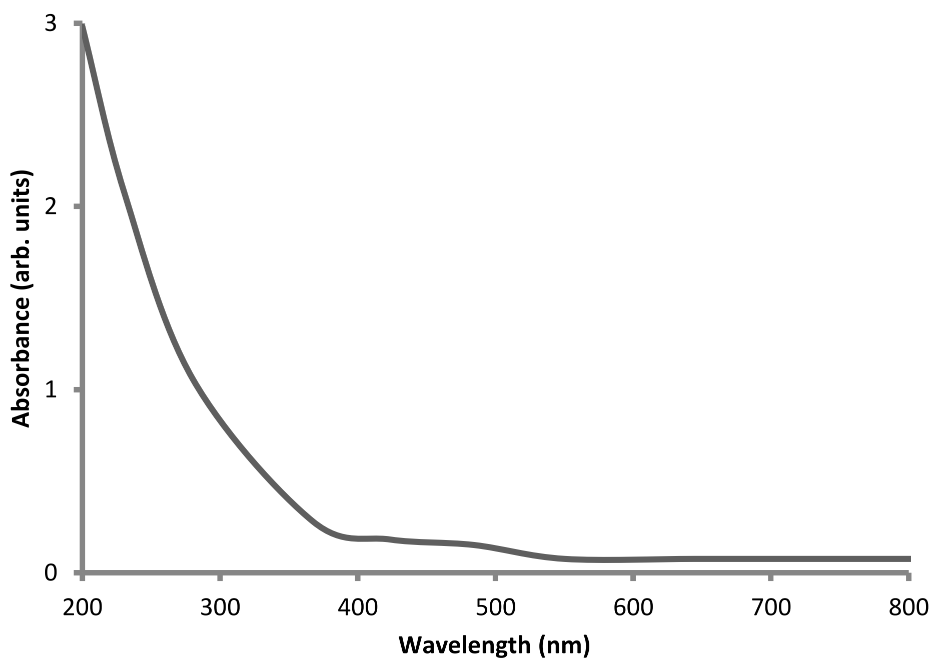

Figure 2. Optical absorption spectra of a finite segment of titanium dioxide nanowire[18]

2. EXPERIMENTAL DETAILS

2.1 Preparation of the local dye

The *chlorin* local dye was extracted from *cynodon dactylon* commonly called bahama grass. The grass was blended and the green pigment extracted with 90% ethanol. The extract was purified by column chromatography and some copper ions were introduced into the extract.

2.2 Electrode Deposition

A sol-gel derived nanocrystalline titanium (iv) oxide (Ti-nanoxide T/sp, Solaronix SA, Rue de e' duriette 128) was deposited onto an FTO glass substrate through the blade method. The active area of a 2.5cm x 2.5cm FTO was identified and covered on each of the two parallel edges with a double layer of masking tape to control the thickness of the TiO_2 film. Before deposition, the glass substrate was cleaned with acetone, then methanol and etched through plasma treatment for 1minute. The nc-TiO_2 was applied at one of the edges of the conducting glass and distributed with a squeegee sliding over the tape-covered edges.

2.3 Thermal Treatment

The nc-TiO_2 electrode was allowed to dry naturally for about 15 minutes before removing the adhesive tapes. The edges were cleaned with ethanol. Using an electric hot plate, the film was subjected to thermal annealing at 200^0C for 10 minutes. Immediately after annealing, the electrode was sintered for about 30 minutes at 400 ^{o}C using carbolite 201 tubular furnace.

2.4 Sensitizer Impregnation

The thermally treated electrode was immersed overnight into a solution of the *chlorin* dye. Another thermally treated working electrode was immersed into a solution of rythenium complex (ruthenium 620, 1H3 TBA, Solaronix) with a concentration of $3x10^{-4}$ mol/L in dry ethanol and allowed to stay overnight. The electrode was preheated at 80 ^{o}C for 15 minutes before it was dipped into the dye solution. This process helps in the prevention of rehydration of the TiO_2 surface or capillary condensation of water vapours from ambient air inside the nanopores of the film. The presence of water in the pores decreases the injection efficiency of the dye. After dye sensitization, the dye-coated film was rinsed in ethanol, then dried using hot-air blower and kept in dark in an air tight case till solar cell assembly.

2.5 Optical Measurement

Avaspec 2.1 spectrophotometer was used to obtain the optical absorption spectrum for the dyed working electrode. This measurement was carried out at room temperature before storing the dyed nc-TiO_2 electrode. The result was displayed as graph of optical absorbance (arbitrary units) versus wavelength (nm).

2.6 Solar Cell Characterisation

The current-voltage (I-V) characterization was achieved using an Oriel class A solar simulator while data acquisition was computerised. Measurements were done at a solar intensity of 100mW/cm^2. Outdoor electrical power measurement was carried out for three days within a space of three weeks using a thermocouple and Mastech MY64 digital multi-meter. The outdoor diurnal power measurement was done on top of a zinc roof measuring 6.5m from ground.

3. RESULTS AND DISCUSSION

The optical absorption spectra (Figure 3) shows that the dyed electrode noticeably absorbed light in the visible region. The ruthenium-dyed electrode peaked at 350nm while the *chlorin*-dyed film had two peaks 355nm and 505nm. Figure 3 shows clearly the natural dye greatly improved the absorbance of the wide band-gap titanium (iv) oxide and could compete favourably with the ruthenium complex.

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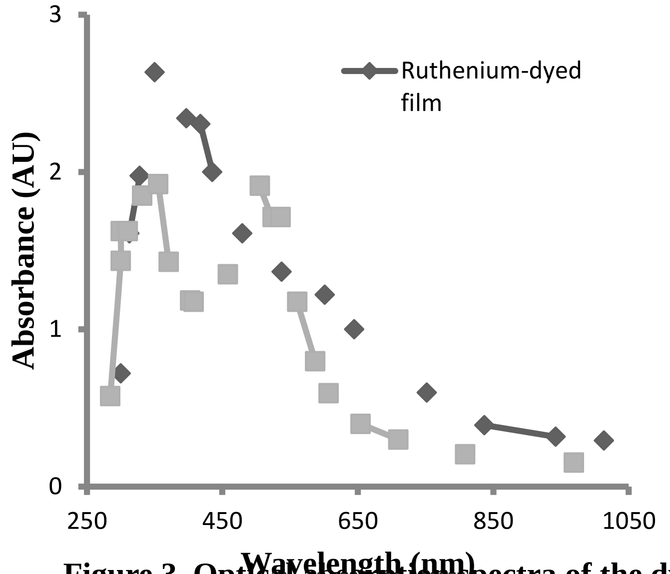

Figure 3. Optical absorption spectra of the dyed nc-TiO_2 films

Figure 4 illustrates the current-voltage characteristics for the three cells while the photovoltaic parameters are shown in Table 1. The ruthenium-dyed cell exhibited the best photovoltaic performance, followed by the *chlorin*-dyed cell. The un-dyed cell showed a very poor performance indicating that the dyes actually improved the efficiency of the DSSCs.

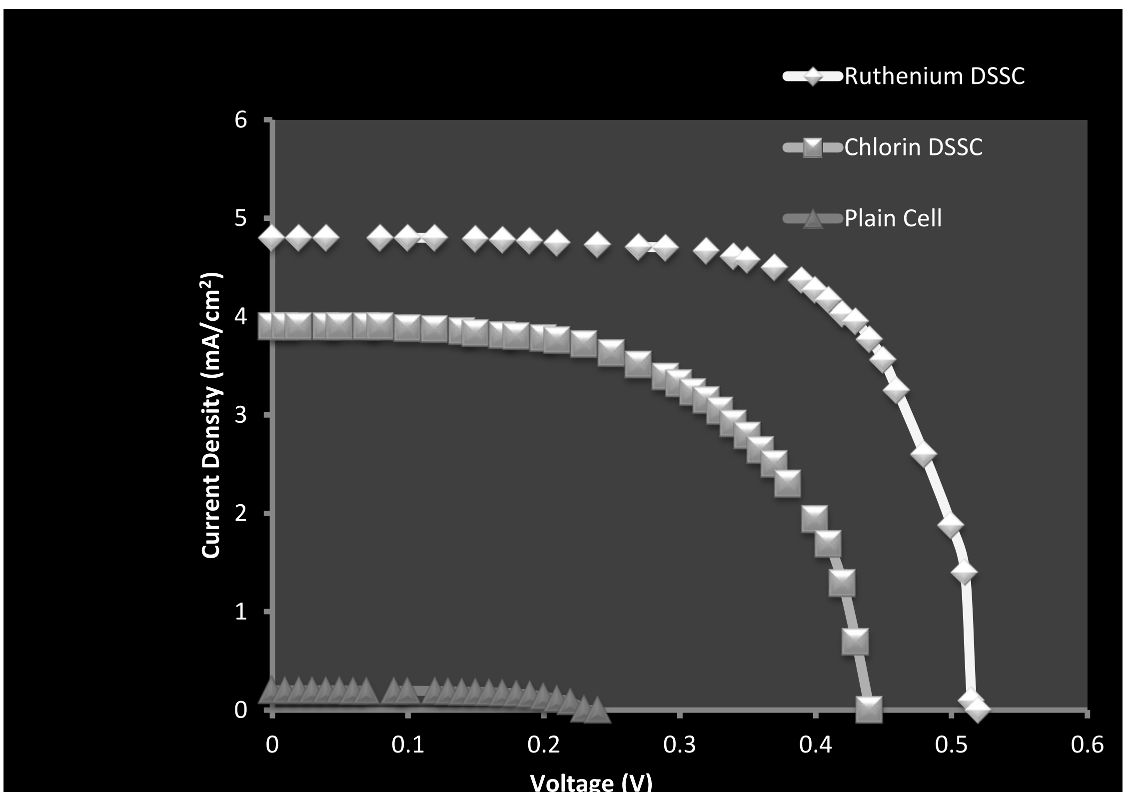

Figure 4. The current-voltage curves

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Table 1. Photovoltaic parameters for the various solar cells

Sample cell	Open Circuit Voltage (V)	Short Circuit Current (mA/cm^2)	Fill Factor	Efficiency (%)
Ruthenium-dyed	0.52	4.80	0.69	1.71
Chlorin-dyed	0.44	3.90	0.59	1.01
Plain	0.24	0.20	0.63	0.03

The diurnal power variation studies for days one, two and three are shown in Figures 5, 6 and 7 respectively while the cells performances were summarized in Tables 2 and 3. *Chlorin*-dyed DSSC exhibited the best performance on the first day but could not maintain the lead on the second day. Figure 7 revealed that the cell stained with the local dye behaved as poor as the plain cell on the third day. Meanwhile, the ruthenium-dyed cell maintained an almost stable performance all through.

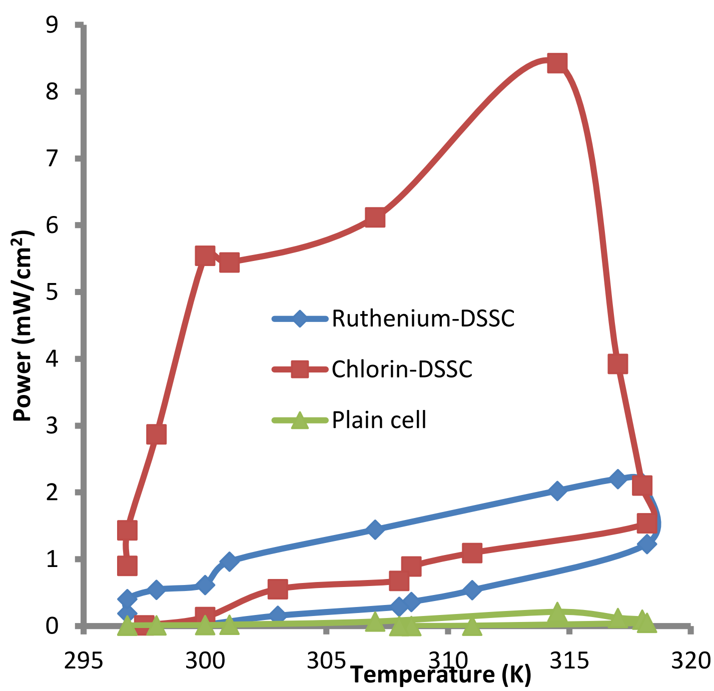

Figure 5. Power-Temperature curves for the cells (Day 1)

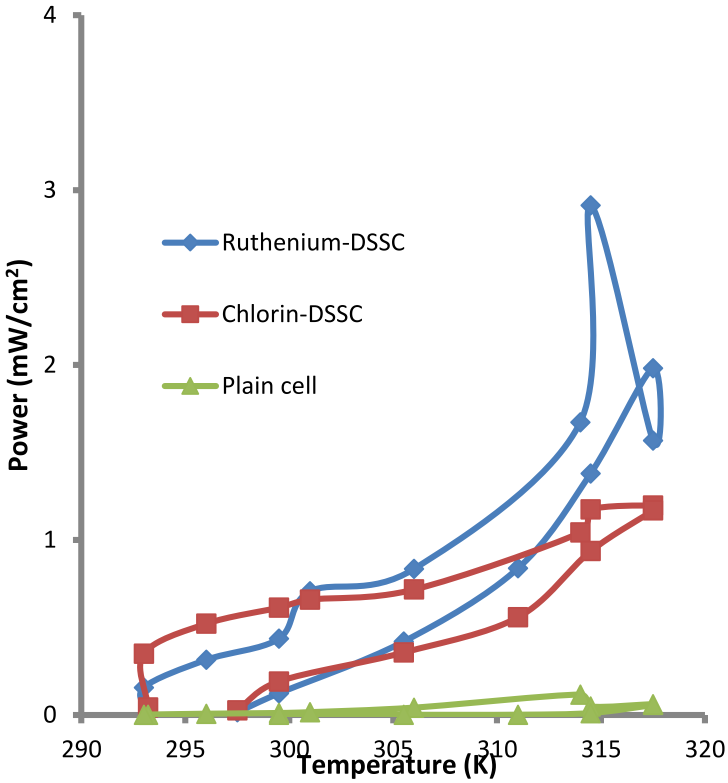

Figure 6. Power-Temperature curves for the cells (Day 2)

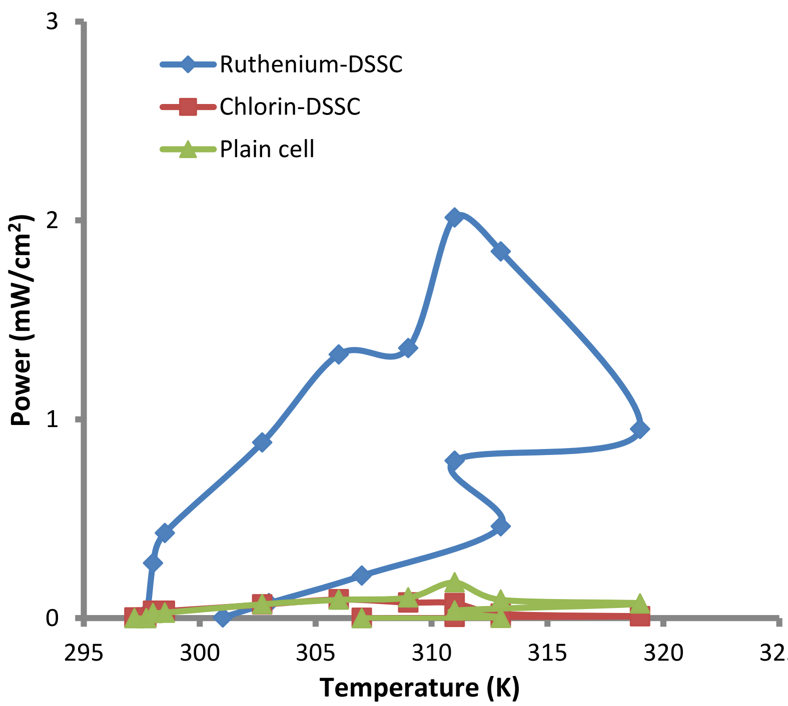

Figure 7. Power-Temperature curves for the cells (Day 3)

Table 2. Peak power obtained from outdoor measurements

Sample Cell	Maximum Power: Day 1 (mW/cm^2)	Maximum Power: Day 2 (mW/cm^2)	Maximum Power: Day 3 (mW/cm^2)
Ruthenium-dyed	2.20	2.91	2.01
Chlorin-dyed	8.43	1.20	0.09
Plain	0.21	0.12	0.18

Table 3. Average power obtained from outdoor measurements

Sample Cell	Average Power: Day 1 (mW/cm^2)	Average Power: Day 2 (mW/cm^2)	Average Power: Day 3 (mW/cm^2)
Ruthenium-dyed	0.87	0.89	0.71
Chlorin-dyed	2.60	0.64	0.03
Plain	0.05	0.03	0.05

4. CONCLUSION

Two dye sensitized solar cells were fabricated using nanocrystalline TiO_2 films sensitized with ruthenium based dye and *chlorin* local dye. A third cell which served as control was fabricated using an unstained TiO_2 electrode. *Chlorin* dye was an extract from *cynodon dactylon.* which is popularly called bahama grass. Optical characterization using Avaspec 2.1 spectrophotometer showed that the sensitized titanium dioxide electrode could absorb incident solar radiation beyond the ultraviolet region. Hence, our local dye was a good sensitizer for TiO_2 which alone cannot absorb light in the visible region. Best overall energy conversion efficiency of 1.71% was obtained from the ruthenium-based DSSC, but the *chlorin* dye gave a commendable efficiency of 1.01%. A very poor energy conversion efficiency of 0.03% was obtained from the plain cell which was a clear indication that the sensitization process greatly improved the photovoltaic performance of the other two DSSCs. The outdoor diurnal measurements proved the ruthenium dye to be a good and stable sensitizer for TiO_2 electrode. The outdoor measurements also clearly indicated that the local dye can even perform better than the ruthenium dye if adequately treated.

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