PERFORMANCE of a DYE SOLAR CELL CO-SENSITIZED with *DELONIX REGIA* and *CARICA PAPAYA* EXTRACTS.

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Abstract- **We report an improved performance of a dye solar cell co-sensitized with Delonix regia (DR) flower extract and Carica papaya (CP) Leaf extract. Nano-crystalline TiO_2 film electrodes were sensitized with aqueous extracts of DR flowers, CP Leaf and a 1:1 combination of the two extracts. The resulting photoelectrodes were successfully incorporated in dye-sensitized solar cells (DSSCs) The photovoltaic performance of the DSSCs was evaluated under 100 mW cm^{-2} light intensity (1 sun AM 1.5 light,). The CP sensitized cell gave a current density (J_{sc} = 0.610mA/cm^2) an open circuit voltage (Vo_c = 0.518V) a fill factor (ff = 0.59) and an overall solar energy conversion efficiency of 0.187 %. Also the DR sensitized cell yielded a current density (J_{sc} = 0.680mA/cm^2) an open circuit voltage (Vo_c = 0.532V) a fill factor (ff = 0 .549) and an overall solar energy conversion efficiency of 0.20%. Finally, the cell co-sensitized cell yielded (V_{0c} = 0.518, I_{sc} =0.744, FF: 0.69, efficiency = 0.27%) This represents a 35% improvement in efficiency and 26% improvement in ff over that of DR. The results obtained are consistent with their complementary photo absorption windows and the possible reduction of dye molecule aggregation.**

Keywords: **Dye sensitized solar cell, co-absorbents, co-sensitized, Carica papaya, photoelectrode**

I. INTRODUCTION

The dye-sensitized solar cell (DSSC) promises a cheap photovoltaic energy production by combining the advantages of low cost processing, low cost components and superior performance compared to silicon solar cells under diffuse light conditions. Nevertheless, the technology still suffers from a number of technical challenges that have hindered large-scale deployment, notably, difficulty in scale-up, low efficiencies and stability. Recent improvements in materials and technology have led to efficiencies exceeding 11% for single junction DSC [1]. Much of this progress is related to advancement in the synthesis of new dyes and electrolyte additives. However, state of the art dyes incorporate ruthenium [2,3] an expensive and rare metal. Recent effort has been directed at developing cheaper non-ruthenium metalated and pure organic dyes. In this regard, plant extracts have attracted a lot of attention as potential sensitizers but the efficiencies attained have been low. Effort to improve efficiency includes co-sensitization to broaden the absorption spectra of the dye. It should however be noted that co-sensitization in some cases lead to reduced overall efficiency. *Delonix regia* (DR) phylogenetically belongs to the *Fabaceae* family. The red colour of the "flamboyant" flowers is a consequence of their anthocyanin contents: cyanidin 3-*O*-glucoside, cyanidin 3-*O*-rutinoside, and pelargonidin 3-*O*-rutinoside. [4,5] Thus, it is a potential sensitizer for mesoporous semiconductors in a dye solar cell [6]. Carica papaya [CP] is a tree-like herbaceous plant, a member of the *Caricaceae* family. The leaf extract of CP contains an appreciable concentration of phenolic acids with caffeic acid being the most abundant [7], the crude extract of the leaf also contains abundance of carothenoids [6]. In this work, we report synergistic co-sensitization of mesoporous TiO_2 with aqueous extracts of DR flowers and CP leafs.

II. EXPERIMENTAL PROCEDURE

A. Preparation of Electrodes

Transparent conductive fluorine-doped SnO_2 glass (FTO) of sheet resistance 14ohm/sq and nanocrystalline TiO_2 paste (Ti-Nanoxide D/SP) containing 15-20 nm anatase particles and 100 nm diffusing particles were purchased from Solaronix. All reagents were of analytical grade. The photoanode was prepared by first spin coating a blocking layer on the FTO glass followed by the nanocrystalline TiO_2. The blocking layer was deposited from a 2.5wt% titanium citrate precursor. Four layers were deposited; each layer was followed by a heat treatment at 250ºC for 10mins. After the final layer, the film was sintered at 450ºC in a furnace for 30 min. Subsequently, the nanocrystalline TiO_2 paste was deposited by screen-printing giving a final film thickness of 9µm as confirmed by a surface profiler (Dektak 150). Subsequently, the film was sintered in air for 30mins at 400°C. The counter electrode was prepared by screen printing a platinum catalyst gel coating (Pt-Catalyst T/SP, Solaronix) onto the FTO glass, dried at 100 °C and fired at 400 °C for 30 min in a furnace.

B. Preparation of Dye Sensitizer Solution and electrode sensitization

DR flowers and CP leafs were harvested fresh and used immediately. The ethanolic extract was prepared by crushing the fresh sample in a mortar with ethanol; the resulting extract was filtered and used immediately without further purification. The warm sintered photo anode (70ºC) was slowly immersed in the sensitizer solution, and kept at room temperature overnight to complete the sensitizer uptake. It was subsequently rinsed with ethanol and dried. For the co-sensitization, the photoanode was immersed in a 1:1 mixture of the ethanolic extract of *DR* and CP.

C. DSSC Assembling

The sensitized photoanode was pressed against the platinum-coated counter electrode slightly offset to each other to enable electrical connection to the conductive side of the electrode (Fig. 1). A 50 µm space was retained between the electrodes, using two layers of a 25 microns thick thermoplast hot-melt sealing foil (Meltonix 1170-25 , Solaronix) Sealing was done by keeping the structure in a hot-press at 100 °C for 1min . The liquid electrolyte (Iodolyte AN-50, Solaronix) was introduced by capillary action into the cell gap through a channel previously fabricated at opposite sides of the hot melt adhesive; the channel was then sealed with an epoxy based resin.

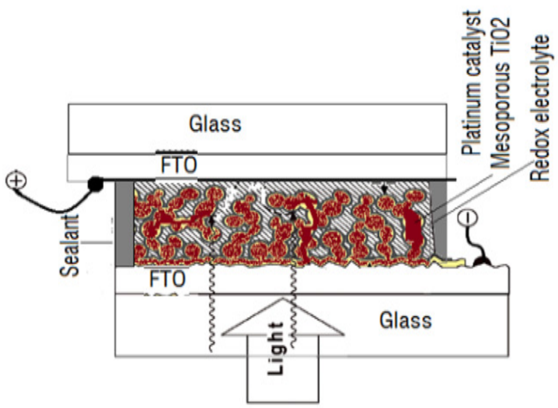

Figure 1. Schematic of a dye-sensitized photovoltaic cell.

D. Characterization

The current–voltage (I–V) measurement was obtained using a Keithley 2400 source meter under AM 1.5 illuminations using a 'Newport' class A solar simulator. Scanning electron images of the nanocrystalline TiO_2 films were taken with Carl Zeis Evo MA-10 SEM. The absorption spectrum of the dye was recorded on Ava-Spec–2048 spectrophotometer. The cell active area was 0.5 cm^2. Thickness measurements were obtained with a Dektak 150 surface profiler. X-ray microanalysis was carried out with Oxford INCA EDX analyzer. Sheet resistance was measured with a Signatone four point probe resistivity system.

III. RESULTS AND DISCUSSION

Fig. 2 and 3 show the SEM image and X-ray microanalysis of the mesoporous TiO_2 after annealing at 500ºC for 30 min respectively. The mesoporous nature of the film is clearly evident. The X-ray microanalysis reveals the presence of Ti, O and N; the presence of nitrogen might indicate doping of the TiO_2 by Nitrogen during sintering.

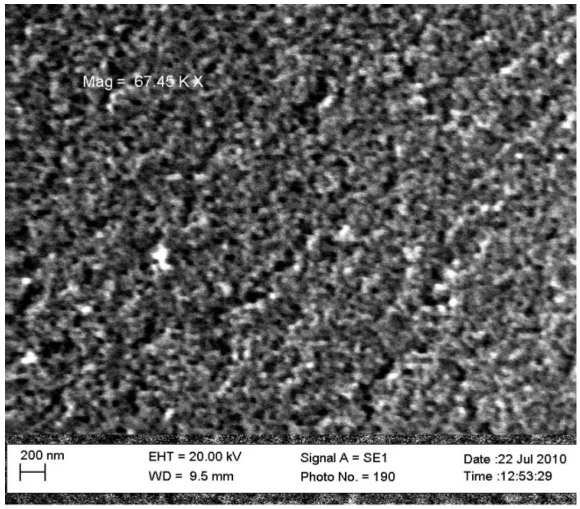

Fig. 2. Scanning electron microscope images of TiO_2 layer the sample was annealed at 500ºC for 30mins.

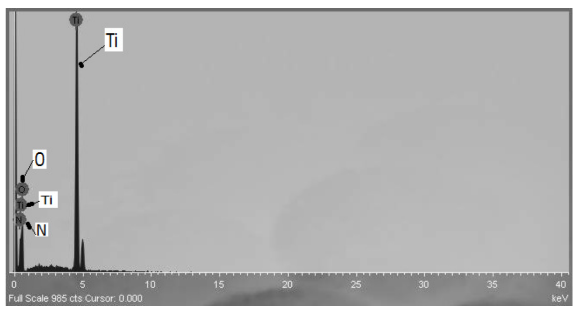

Fig. 3. X-ray microanalysis of the TiO_2 layer showing the presence of Ti, O and N.

Fig. 4 shows the I-V characteristic curves of the prepared dye-sensitized solar cells sensitized with CP extract, the DR and mixtures of the two. The CP sensitized cell gave a current density (J_{sc}) of 0.610mA/cm^2, an open circuit voltage (Vo_c) of 0.518V, a fill factor (ff) of 0.59 and an overall solar energy conversion efficiency of 0.187 %. The DR sensitized cell yielded J_{sc} = 0.680mA/cm^2, Vo_c = 0.532V, ff = 0.549 and an overall solar energy conversion efficiency of 0.20%. Finally, the co-sensitized cell yielded V_{0c} = 0.518, I_{sc} = 0.744, ff = 0.69, efficiency = 0.27%.

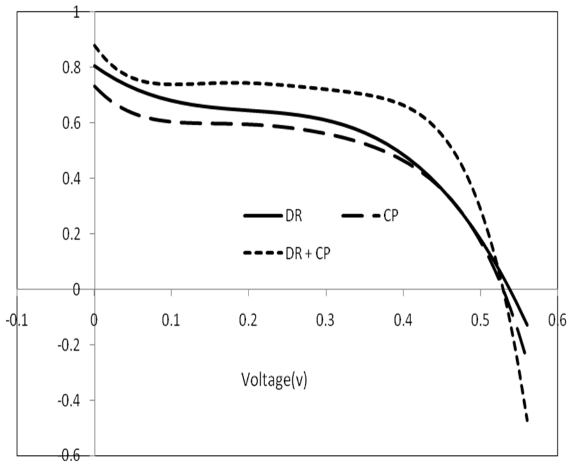

Figure 4: I-V- characteristics of the different cells at AM 1.5 illuminations.

The increased short circuit current of the co-sensitized cell is most likely due to increased light absorption and photocurrent generation because of broadened photo absorption from the two dyes. Fig. 4, shows the absorption spectra of the *Carica papaya* extract, the absorption band at 380nm-490nm with a peak at 400 nm is too narrow for the generation of high photocurrent. For efficient light harvesting, the spectral overlap with the solar spectrum should be maximized so that as much of the sun's energy as possible is utilized in exciting the dye, and promoting a high density of electrons into the excited state.

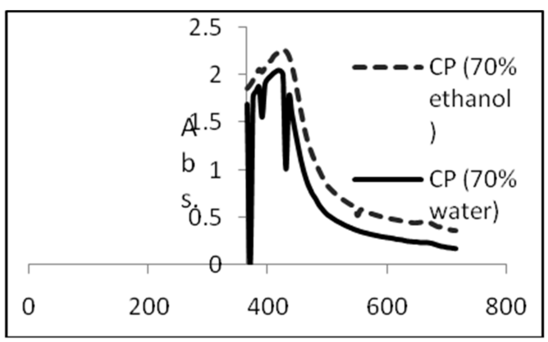

Figure 5: Absorption spectra of crude extract of the CP leaf in various solvents.

Table 1 shows the relative increase in V_{oc}, I_{sc}, and fill factor `of the DR+CP cell relative to DR cell.

TABLE 1

cell	Voc(V)	Isc (mA/cm^2)	Fill factor	eff. (%)
DR	0.532	0.680	0 .549	0.200
CP+DR	0.518	0.744	0.690	0.270
% increase	2.7	9.4	26	35

This represents a 35% improvement in efficiency and 26% improvement in fill factor over that of DR. The results obtained may be explained in terms of a possible reduction of dye molecule aggregation at the semiconductor/electrolyte interface leading to a more efficient coverage of the oxide surface and better insulation of the underlying conductive oxide from the oxidized electrolyte. It should be noted that the leaf extract of CP contains an appreciable concentration of phenolic acids with caffeic acid being the most abundant; the presence of carboxylic acid functional group in this compounds would enable efficient anchorage to the semiconductor surface and act as spacers to prevent dye aggregation.

IV. CONCLUSION

Efficient co-sensitization of a dye solar cell with extracts of *Delonix regia* and *Carica papaya* has been demonstrated. We observe a 35% improvement in efficiency and 26% improvement in fill factor over that of *Delonix regia* sensitized cell. The results suggest a more efficient dye molecule packing at the semiconductor/ electrolyte interface, due to a reduction in dye molecule aggregation. We posit that the abundance of phenolic acids in the Carica *papaya* may act as spacers in a manner similar to better known co–adsorbents.

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