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Dye sensitized solar cell using extracts from *Carapa procera* bark as natural sensitizer

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Abstract

Dye sensitized solar cells (DSSC) were investigated using the extracts of the bark from *Carapa procera* as natural sensitizers of TiO_2 thin film. The optical properties were analyzed with UV-Vis spectroscopy and Fourier Transform Infrared spectroscopy (FT-IR).The morphology of the TiO_2 surface was observed with a scanning electron microscope (SEM). Energy levels were estimated by cyclic voltammetry, in the presence of tetrabutalamonium tetrafluoroborate (TBATFB), in anhydrous acetonitrile solution (ACN). The DSSC prepared by the dyes, achieved the open-circuit voltage (V_{oc}) which varied from 0.32 V to 0.48V, while short-circuit current density (J_{sc}) ranged from 0.45 to 0.75 mA / cm². The best efficiency of 0.16% was established with the parity of mixture.

1. Introduction

Dye sensitized solar cells belong to a new generation of photovoltaic conversion materials. These cells were developed by Grätzel and O'Regan [1]. The cells include two electrodes, a photoanode and a photocathode made of transparent conductive oxide (TCO). The TiO_2, a porous semiconductor, was coated on the photoanode, which allowed to fix the dye or sensitizer. The sensitizer absorbed the sunlight. A platinum thin-film was coated on the photocathode, and acted as a catalyst. An electrolyte was injected between both electrodes. Ruthenium complexes were used as sensitizers. These synthetic dyes have a good efficiency ranging from 11 to 12% and a good thermal stability [2]. However, the production of this rare metal is costly and harmful to the environment. Therefore, the use of natural dyes is a new alternative. These dyes are abundant in nature, easy to extract, non-toxic and environmentally friendly. The dyes are extracted from leaves, barks, flowers, fruits, and used as molecular sensitizers. The dyes contain anthocyanins, betacyanins, carotenoids, tannins [3-4]. Several studies reported that natural dye sensitizers have been used successfully. Zhou et al., [5] studied natural dyes extracted from fruits and different parts of a plant. The extraction of mangosteen pulp with ethanol gave an efficiency of 1.17%. Moreover, Roy et al. [6] showed a short current density Jsc of 3.22 mA / cm^2, an open voltage V_{oc} of 0.89 V and an efficiency of 2.09% using the Rose Bengal. Marco and Calogero [7] reported a conversion of 0.66%, using blood orange juice as a sensitizer. Wang et al. [8] realized the modification of coumarin structure to obtain derivatives that served as sensitizers. These sensitizers gave a conversion efficiency of 7.6%. The optimization of the dyes by modifying their structure appears promising.

In this paper, we explored a relatively simple and less expensive method to develop DSSC cells using two fractions extracted from *Carapa procera*, a local plant. Moreover, we studied the performance of DSSCs obtained from the combination of these two extracts. As far as, we know, the dyes from this plant were used for the first time as sensitizers in DSSC cells. Titanium dioxide (TiO_2), which provided a wide band gap, served as electron transport to produce DSSC cells. The optical properties of the dye were studied with UV-Vis absorption spectroscopy and Fourier Transform Infrared spectroscopy (FT-IR). Cyclic voltammetry (CV) was used to estimate energy levels and the feasibility of energy transitions. The morphology of the TiO_2 surface was observed using a scanning electron microscope (SEM). The optoelectronic parameters of DSSC were obtained through an exposure to illumination of a halogen lamp of 78 mW / cm².

2. Material and Methods

2.1 Materials.

Titanium dioxide TiO_2 (Ti-nanoxide, T / SP), and platinum (platisol, T / SP) were used to make electrodes. The TC030 glass, has a thickness of 3mm and a resistivity of 15Ω / square. Both electrodes were sealed with a thermoplastic (Meltonix 1170-60 / 60). The electrolyte (AN-50) containing I^-/ I^{3-} was injected into the space between both electrodes. All these materials were obtained from Solaronix Switzerland. Anhydrous acetonitrile, with a purity of 98%, is from Aldrich. It was associated with tetrabutylammonium tetrafluoroborate (TBATFB) obtained from Acros for cyclic voltammetry measurements.

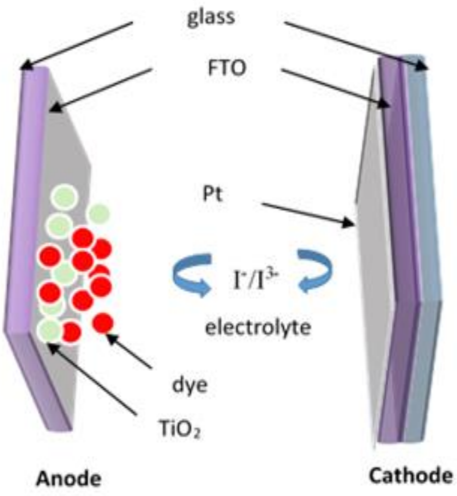

Figure 1 : Diagram of dye sensitized solar cell components

2.2 Apparatus and instruments

Voltammograms of various registered dyes used acetonitrile solution with 0.1M tetrabutylammonium tetrafluoroborate as electrolyte. Measurements were made with a Palmsens potentiostat whose working electrode was a platinum disc with Ag / AgCl as reference electrode, and a platinum wire as counter-electrode.

The acquisition of the current-voltage density (J-V) was done with an Arduino microcontroller coupled with a computer and a halogen illumination lamp of 78 mW / cm². UV-Vis absorption was measured using JENWAY (7315, Germany) spectrometer. FTIR spectra were recorded with SHIMADZU (8400S, Japan) spectrometer. The surface morphology of TiO_2 was carried out with a scanning electron microscope (SEM, HIROX, model SH 4000 M, France).

2.3 Dye extraction

We collected samples from the stem bark of *Carapa procera*. The obtained samples were washed with water in order to remove dust particles and then they were dried at 25 °C in the dark for three weeks in the laboratory. The dried samples without moisture, were crushed with a super mixer to produce a fine powder. This powder (500g) was extracted three times by maceration at room temperature in the mixture ethanol / water (90:20, v/v). The extract was filtered with a filter paper (Whatman), and then concentrated, under a vacuum at 40 ° C, using a rotary evaporator. The resulting concentrated powder (98g) was dissolved in 250 ml of water and successively washed with hexane and ethyl acetate solutions. After evaporation, the ethyl acetate extract (12.6 g) was fractionated on silica gel column chromatography to afford *Carapa dyes* 1 and 2.

2.4 Preparation of TiO_2 photo anode and platinum counter electrode

The fluorine-doped tin oxide (2.5 cm, 2.5 cm, 0.3 cm) conductive glass (TC030) was cleaned with acetone and ethanol for 10 minutes. The nanocrystalline film preparation was carried out with the titanium dioxide paste (Ti-nanoxide T / sp). The TiO_2 paste was then deposited on the conductive FTO glass side according to Doctor Blade’s method. Scotch tape was used to provide non-contact areas for electrical contact. After an air drying, the TiO_2-coated plate was heated at 80 ° C for 5 minutes, then gradually at 450° C for 40 minutes with a hot plate. Then, the TiO_2 electrode was removed from the hot plate and cooled down. The TiO_2 coated glass with an active surface of 1 cm² was immersed into the dye extract for 24 h. At the end of the adsorption, the TiO_2 film was removed from the solution and dried up for 15 min. In parallel, the platinum counter electrode (T / SP) was prepared with the other conductive glass electrode and annealed at a temperature of 400 ° C for one hour.

2.5 DSSC assembling

To investigate the performance of the dye on TiO_2 thin film electrode, sandwich type cells with 1 mm of hole were made on the platinum coated electrode. The first step was to isolate the active layer of TiO_2 by the sealing material (Meltonix 1170-60, 60 microns thickness). The photoanode which contains the dye was brought into contact with the platinum-coated counter-electrode, put on a hot plate. Subsequently, both electrodes were sealed by raising the temperature to 120 ° C in a few seconds. The open hole was used to inject the electrolyte (AN 50). The final step is to close the hole using the thermoplastic and a glass cover. A copper wire was glued to each electrode with the silver glue, to collect charges. DSSC cell was placed in the dark before any measurement.

3. Results and discussion

3.1 Surface morphology of TiO_2 electrode

The Figure 2 shows a porous structure of TiO_2 with various holes of different diameters. The non-compact morphology of TiO_2 and the absence of crack on the surface is appropriate for the application of DSSC because the dye can be easily adsorbed on the TiO_2 surface. This connection allows the transfer of the electron from the dye to TiO_2 semiconductor.

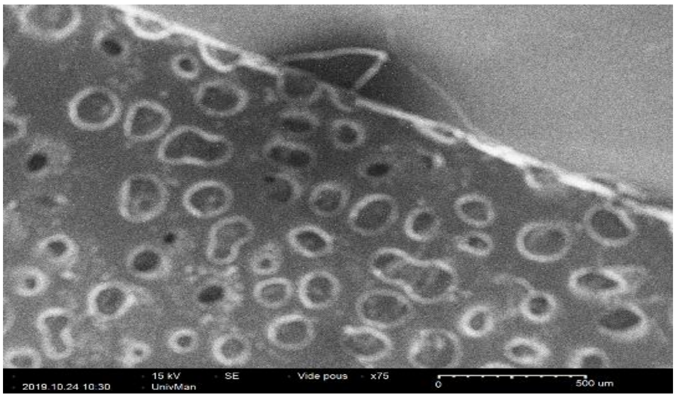

Figure 2 *: Carapa* dye adsorbed on TiO_2 surface

3.2 Dye absorption spectrum

The absorbance of *carapa 1* shown in Figure 3 indicates a high absorbance of 460nm at 587nm where peaks occur at 490nm and 523nm.This absorption range is similar to anthocyanin compounds [9, 10]. Due to their absorbance, anthocyanins are candidates for DSSC sensitization [11, 12, 3]. The presence of carbonyl and hydroxyl groups in their structure allows them to adhere easily to titanium dioxide and facilitate photovoltaic conversion [13, 14] Anthocyanins are abundantly present in all parts of plants, fruits, flowers, leaves and barks. Moreover, these molecules exhibit various colorations such as yellow, blue, red, etc. [15, 16]. The absorbance of *carapa2* extract does not show a peak in the visible region, as indicated in Figure 4 (a).

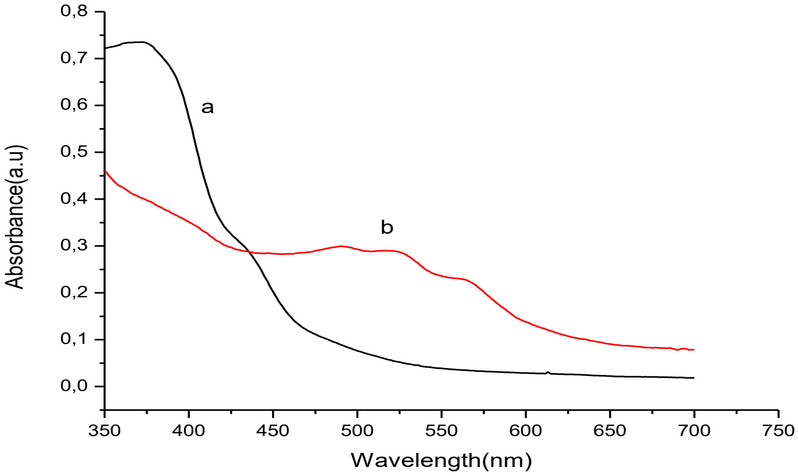

Figure 3 *:* Absorption spectrum of (a) *carapa 2* and (b) *carapa 1* dye.

3.2 Fourier Transform Infrared spectroscopy (FT-IR)

The FTIR spectrum was used to show the presence of different characteristic groups in *carapa* fractions 1 and 2. Figure 4 shows an absorption band range from 4000 to 600 cm $^{-1}$. As shown in Figure 4 (a), *carapa* fraction 1, shows OH stretching vibration at 3364.02 cm-1. The vibrations of CH_3 and $C-H_2$ appear respectively at 2922 cm^{-1} and 2853.2 cm^{-1}. In addition, carbonyl absorption band (C = O) is observed at 1718 cm^{-1}. The vibration at 1558.63 cm^{-1}, corresponds to C = C group. The characteristic groups present in *carapa* fraction 2 are observed in Figure 4 (b). For *carapa* fraction 2, OH vibration is observed at 3240 cm $^{-1}$. CH_3 and $C-H_2$ vibrations also appear at 2919 and 2850 cm^{-1}. The absorption bands at 1558, 1378 and 1063 cm^{-1} respectively correspond to the functional groups C = C, C-N and C-O. Fractions of *carapa* 1 and 2 have the following characteristic groups of hydroxide (OH), ester, carbonyl (C = O) and will be adsorbed to TiO_2 thin layer.

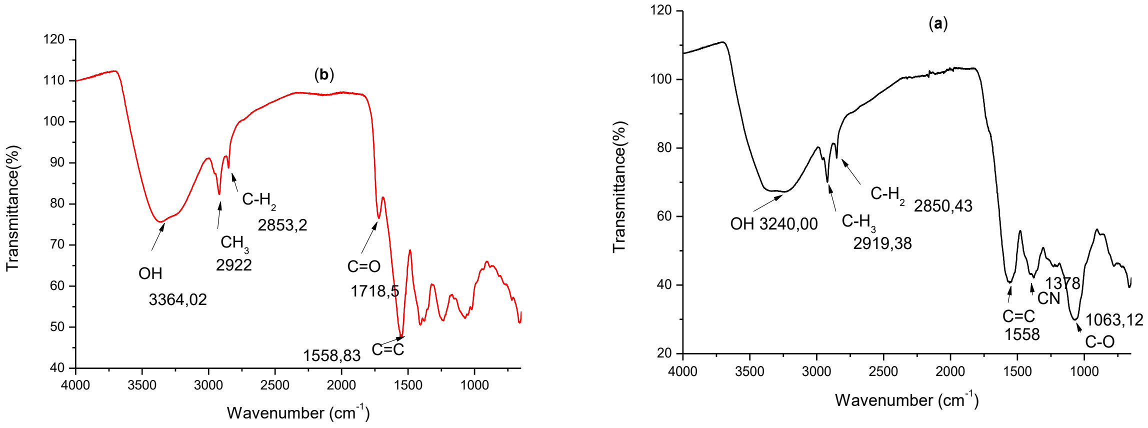

Figure 4 *:* FTIR spectra of (a) *carapa 2* dye and (b) *carapa1* dye

3.3 Electrochemical study of the dye

HOMO and LUMO energy levels of the dye fractions were evaluated in cyclic voltammetry method. In this context, the working electrode is a platinum disc of 3mm of diameter with Ag / AgCl as reference electrode and a platinum wire counter electrode. Tetrabutylammonium tetrafluoroborate (TBATFB) at 0.1 M were used as the supporting electrolyte in acetonitrile solution. Before any measurement, the electrolyte was purged with argon. The scanning speed was 50mV/s and the potential window was -2v to 2v. LUMO and HOMO levels were estimated according to the relations (1) and (2):

$$E_{homo} = -e(E_{ox} - 4.4)\ (\text{eV}) \tag{1}$$

$$E_{lumo} = -e(E_{red} - 4.4)\ (\text{eV}) \tag{2}$$

Where: Eox and Ered are respectively the oxidation and reduction potentials of the extracts taken from the voltammograms (Figure 5) which show reversible cycles. Following the oxidation and reduction potentials, the calculated HOMO levels are 5.6 ev and 5.7ev for the extracts of *Carapa procera* 1 and 2 respectively, while LUMO levels are 3.12ev and 2.9ev. LUMO levels of the dyes are above the potential 4.4ev of I^-/ I^{3-} redox couple electrolyte and indicates that, there is a driving force for the dye generation. Beside this, HOMO energy levels of the dyes are higher compared to the TiO_2 extraction work (3.2ev). These different HOMO and TiO_2 energy positions indicate that electron transfer from the dye to TiO_2 is possible. These different energy positions are shown in Figure 6.

3.4 Conversion efficiency (η) and fill factor (FF)

The performances of the dye fractions used as sensitizers were evaluated with the photovoltaic parameters. The performance results of *carapa 1* and *carapa 2* fractions and their combination are shown in Table 1. In the dark, we observed negligible open-circuit voltage (Voc) and current density. The conversion efficiency (η) and the fill factor (FF) were calculated according to the following relations:

$$FF = \frac{J_{max} * V_{max}}{J_{sc} * V_{oc}} \tag{3}$$

$$\eta = \frac{J_{sc} * FF * V_{oc}}{P_{in}} \tag{4}$$

where the short-circuit current density (Jsc), the maximum current density (Jmax), the maximum voltage (Vmax), the open-circuit voltage (Voc) were determined from the (J-V) curve in Figure 7 and the incident light intensity (P_{in}). The photoelectric parameters of the different cells are listed in Table 1.

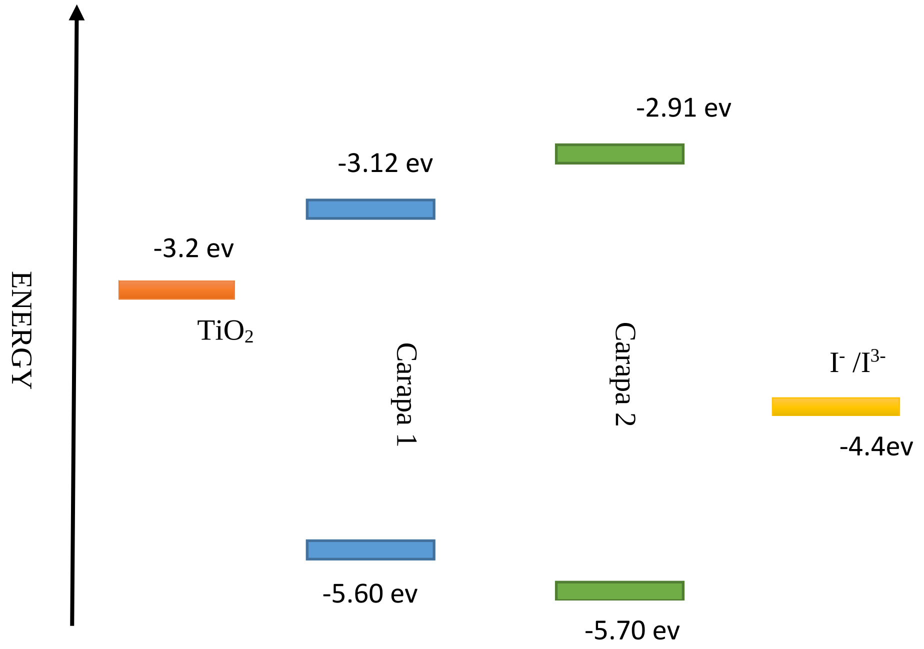

Figure 5 : Diagram of energy levels showing the HOMO and LUMO energy of *Carapa procera* fractions

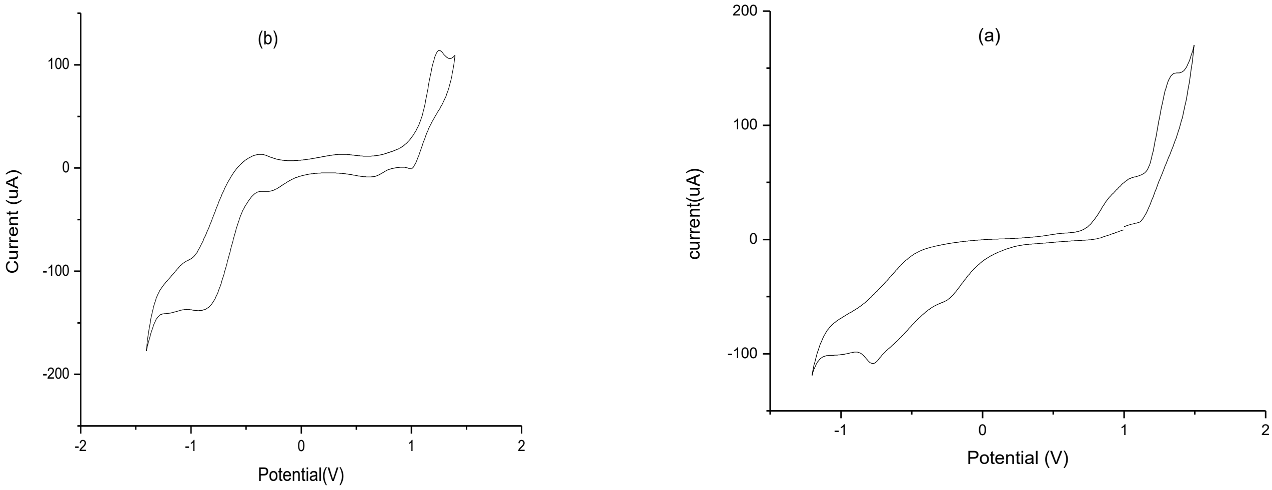

Figure 6 : Cyclic voltammogram of *carapa* 1(a) and 2(b) from methyl acetate fraction in acetonitrile solution containing 0.1 M TBATFB supporting electrolyte at 50 mV/s scan rate.

Table 1 : Photoelectrical parameters of DSSC sensitized by different fractions of *Carapa procera*

dye	**Voc(V)**	**Jsc(mA/cm²)**	**FF(%)**	**n(%)**
carapa 1	0.48	0.45	50.50	0.125
carapa 2	0.32	0.75	54.46	0.11
mixture	0.46	0.53	51.46	0.16

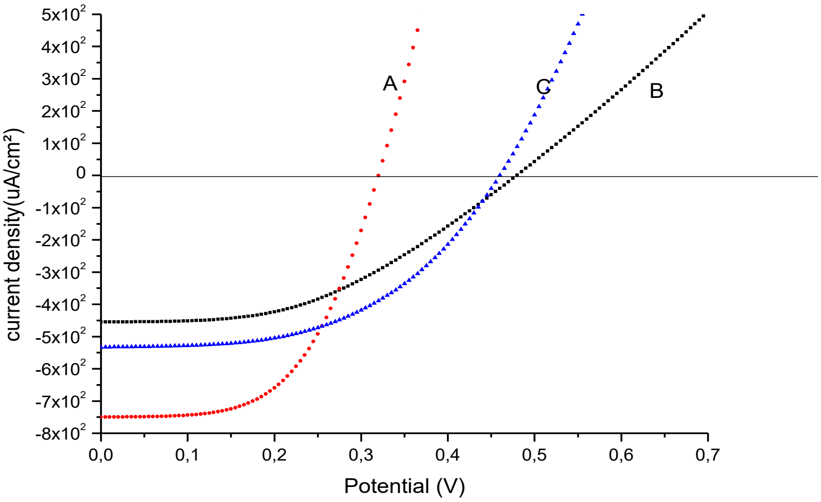

Figure 7 : Current density –voltage (J-V) curves for the DSSCs sensitized by the fractions of Carapa procera fraction 2 (A) , Carapa procera fraction 1(B), mixure of the two fractions (C).

Open circuit voltages (Voc) vary from 0.32 to 0.48 v while short-circuit currents (Jsc) range from 0.45 to 0.750 mA. *Carapa* 1 extract gives a conversion efficiency of η = 0.125%, and is significantly improved by a mixture of *carapa* 2 extract with a power conversion η = 0.11%. The efficiency of the mixture is η = 0.16%, which gives a gain of 28%. The effect of the absorption complementarity of the incident light of both dyes is beneficial and gives a better result. However, this spectral response is due to the presence of several chromophore molecules in various extract dyes. These pigments contain radicals, COOH, OH and CO which attach to TiO_2 semiconductor easily. These different points of contact allow the transfer of electrons from the dye to TiO_2, [15,16]. The variation of these different efficiencies also depends on the concentration of the dyes [17]. However, the power conversion of both extracts remains low compared to the stable complexed ruthenium. The connection between the chromophores of the different extracts and the thin layer of TiO_2 is weak.

Conclusion

The extracts of *Carapa procera* bark were used as sensitizers for DSSC cells. We also studied the effect of the absorption complementarity of the fractions. The different produced cells gave Voc which varied from 0.32 to 0.48 v and Jsc which went from 0.45 to 0.75 mA. The power conversion of 0.125% provided by *carapa 1* extract was improved by a mixture of the extract of *carapa 2*. The mixture exhibited an efficiency of 0.16% and allowed good charge transfer from the dye to TiO_2 semiconductor. Despite their fair efficiency, the natural dyes used in DSSC cells are promising. These dyes are easy to elaborate, less expensive and environment friendly.

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