

Dye-sensitized solar cell using natural anthocyanin dyes extracted from *Sorghum Spp* (Poaceae) sheaths

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Abstract

Dye-sensitized solar cells (DSSC) have been extensively investigated due to their environmental friendliness and low production cost. However, the toxicity and the cost of synthesis pigments limit the use of said prototypes. The aim of this study is to develop and characterize bio-photovoltaic cells based on anthocyanin dyes extracted from sorghum spp sheaths. Thus, the photo-electrode is made by depositing a thin layer of titanium dioxide and the counter electrode conductivity has been improved with a platinum film. The photoelectrochemical properties of pigments are evaluated by UV-Vis spectrophotometry and cyclic voltammetry. Four fractions (F1, F2, F3 and F4) of flavonoid and anthocyanin pigments are separately detected in crude extract. The highest conversion efficiency of 0.42% was exhibited by acidified F4 fraction and would be linked to the intense absorption of visible light in acidic medium but also the capacity of the F4 fraction to efficiently inject electrons into the TiO₂ conduction band. Moreover, acidification improves significantly the conversion efficiency of the crude extract and F4 fraction respectively from 0.18 % to 0.33% and 0.20% to 0.42%. Pigment separation reveals some masking effect when all the pigments are in mixture. The anthocyanin dyes of sorghum Spp sheaths constitute potential photosensitizers that can be valued in the development of cheap bio-photovoltaic cells.

Key words: anthocyanins, sorghum spp, bio-photovoltaic cells, electricity, Niger.

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I. Introduction

Renewable energies such as biomass, wind, geothermal, hydro and solar are increasingly in demand because of growing energy needs, the depletion of fossil fuel reserves, the risk of accidents, waste nuclear energy, air pollution, global warming and climatic hazards [1]. Solar energy is one of the most important and clean resources. It finds essentially his application through photovoltaic cells. The first produced cell was made in 1956 at Bell Labs USA and has a conversion power of 6% [2]. The optimization of the technology allowed to reach conversion rates of more than 20% for the first generation of monocrystalline silicon cells. However, the basic material used (pure monocrystalline silicon) is relatively expensive for large scale operation. Subsequently, more efficient and accessible second and third generation photovoltaic cells based on less expensive materials have been developed. However, the production cost is still high. Therefore, the major challenge remains the development of low cost solar cell, efficient and easy to manufacture. In this context, Michael Grätzel and Brian O'Regan, suggested in 1991 (Nature), a credible revolutionary alternative simulating the solar radiations energy transformation mechanism by chlorophyll of plants (photosynthesis) [3]. Thus, for more than twenty (20) years, the photosensitive pigment cells known as "dye-sensitized solar cells (DSSCs)" are considered as the future device for solar energy harvest and conversion in electricity. Their advantages are mainly low cost production, low energy payback time, flexibility, performance also at diffuse light and multicolor options. It is based on the sensitization of wide band gap n-type semiconductor through a dye used as sensitizer. Some parameters such as the absorption spectrum of the dye, the anchorage of the dye to the surface of semiconductor are important for the efficiency of the cell [4]. The pigments generally used are organometallic complexes of ruthenium, cobalt such as N719, N3, black dye [5]. The conversion yield obtained with these pigments is of the order of 10 to 11% [2]. However, the rarity of certain transition metals such as the element (Ru), the potential latent risks due to the use of heavy metals and the relatively high cost of pigment synthesis further limit the increased development of this prototype [2]. For this reason, beyond synthetic organic pigments and organometallic pigments, natural pigments are a first choice alternative and their use is part of a sustainable development approach. Indeed, natural pigments are free of metals, they are non-toxic, non-carcinogenic, widely accessible, available at very low cost and biodegradable naturally without any other form

of pollution [6;8]. In addition, natural dyes found in flowers, leaves and fruits can be extracted by a simple procedure [9;10]. All these properties make them good candidates for dye sensitized solar cells (DSSC). Numerous studies on cells sensitized with natural pigments have been carried out and appreciable conversion yields have been obtained. Calogero et al. [11] showed that cells sensitized with natural anthocyanins and betalaines provided a conversion efficiency of the order of 2.06%. In addition, a maximum conversion of about 2.87% was obtained with Kenaf Hibiscus pigment [12]. Several other pigments from leaves, flowers, stems, roots, seeds and fruits have been used in DSSCs [13;14;15]. In Niger, *sorghum spp* is a dyeing plant widely used in textiles because of the anthocyanins present in these sheaths. This plant finds most of its use in the artisanal field especially in basketry to decorate in red, blue, pink or orange colors the mats in the regions of Tillabéry, Agadez, Maradi and Zinder (Niger) [21]. There are lack of studies on the use of natural dyes in solar energy in the region. The present study seems to be the first initiative of *sorghum spp* valorization as a dye plant in Niger in solar energy. Its uses for energy production does not pose any environmental problem, besides this plant is available and can be cultivated in Niger in large quantities at an affordable cost.

II. Material And methods

2.1. Chemicals and instrumentation

Chemicals used in this research are Ti-nanoxide paste–anatase (Solaronix), plastisol T (Solaronix), Indium Transparent Oxide (ITO) conducting glass slides (50x50x1,1mm<6 ohm/sq), tetra butyl ammonium iodine (TBAI), iodide (I₂), Acetonitrile (Sigma Aldrich), Absolut ethanol (VWR) and detergent. All these chemicals were used without further modification or purification. Instrumentation applied for research are hotplate, glassware, hydrophilic cotton, wattman papers N^o1, Rotavapor (Rotavapor R-III – Buchi), aluminum foil, blinder clips, scotch tape 3M, spectrophotometer Evolution-300 UV-VIS, Bipotentiostat/Galvanostat (μ STAT 400, DropSens), SVC-3 Voltammetry cell, RE-1B Ag/AgCl Ref Electrode, GCE Glassy carbon electrode OD:6mm ID:3mm, Pt counter electrode for VC-3 cell, PK-3 Electrode Polishing kit (CH Instruments, Inc.), Digital multimeters (UNI-T30B and ALDA DT-830D) and a decade resistance box (DR06).

2.2. Plant materials and Natural dye extraction

Natural dye was extracted from dried *sorghum spp* sheaths that have been freshly harvested and identified in the Department of Biology of the Faculty of Sciences and Technologies of Abdou Moumouni University of Niamey. These plant samples were first washed, dried under in an oven at 50 °C and grinded as a powder which was used to perform the dye extraction. The dye extractions were followed by a sequence of maceration, filtration and decantation to remove any precipitate present in the crude extract. In fact, twenty grams (20 g) of sheaths powder are macerated with 100 mL of 70% ethanol for 24 hours and this process was repeated 3 times to extract the maximum of dye compounds. Subsequently, the collected extracts were filtrated and dried by concentrating and evaporating solvents. Colorful dark-red powder was obtained as crude extracts. The crude pigments separation was done by column chromatography, whereby the glass column was filled with 60 g of silica gel (60-120 mesh) and chloroform and acetone in 4:1 ratio was used as the developing solvent. The separated dye components were collected, recovered and concentrated in vacuum in a rotary evaporator below 60°C. Then crude extract and its recovered components were taken back in ethanol solution and used as sensitizers.

2.3. Fabrication of electrodes and assembling of dye-sensitized solar cells

The photo-electrode fabrication was done by using Ti-nanoxide-D pastes (Solaronix) as TiO₂ nanoparticles source. This paste was allowed to perform TiO₂ thin layer deposition on the surface of Indium Transparent Oxide (ITO) glass with Doctor Blade technic. The Indium doped conducting Tin Oxide (ITO) glasses should be firstly washed with detergent solution, rinsed with ethanol and then dried. Before TiO₂ paste deposition on cleaned ITO glass, the conductive part should be found by using a digital multimeter. At the conductive part, a scotch tape (3M) was used in order to make a square pattern by leaving a 1 cm x 1 cm room. TiO₂ paste is distributed evenly with a glass rod and then dried. The Scotch tape is opened and the TiO₂ film glasses were preheated at 200 °C for 10 min and then sintered at 500 °C for 30 min [15]. Cooling is performed by decreasing gradually the temperature by jumping of 100 °C from 500 °C to room temperature. The TiO₂ electrodes were immersed in ethanolic dye solution and the container was covered with aluminum foil and was left for 24 h. The TiO₂ plate was removed and rinsed with ethanol to clean the edge of the layer and remove the unabsorbed dyes. The counter electrodes were fabricated by depositing a thin layer of platinum using Plastisol T (Solaronix, Co. Ltd.) as a platinum precursor and then sintered at 450 °C for 30 min. So, the dye-sensitized TiO₂ electrode and the Pt counter electrode were assembled with paperclip (binder clips) to form a solar cell by sandwiching a redox (I⁻/I₃⁻) electrolyte solution. The electrolyte solution was composed of tetrabutylammonium iodide (TBAI, 0.5 M) and iodine (I₂, 0.05 M) in acetonitrile. Fig. 1. shows different process of DSSCs fabrication.

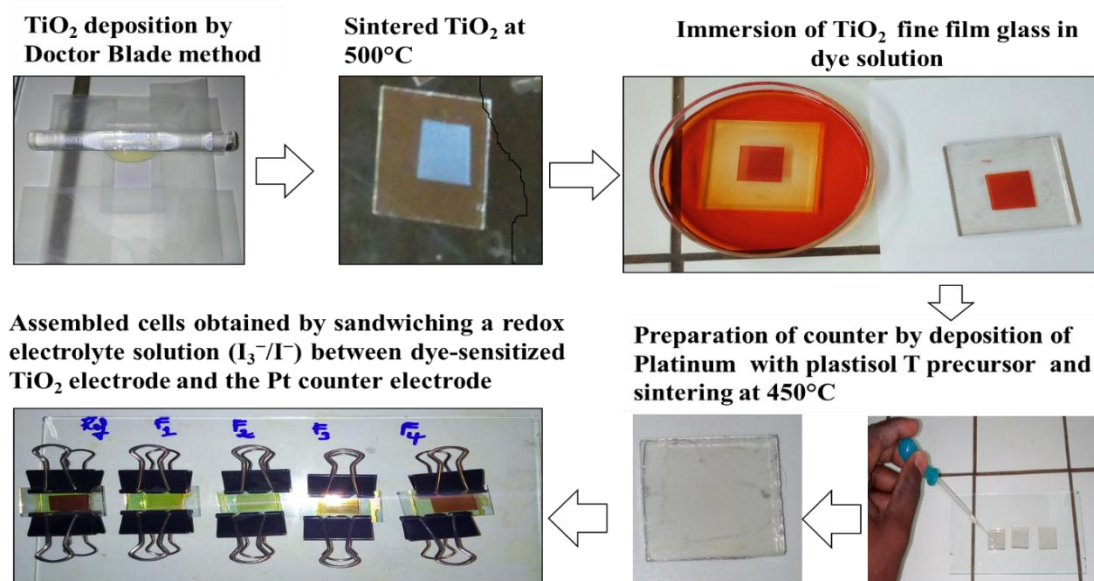


Fig. 1. Different process of DSSCs fabrication

2.4. UV-Vis spectrophotometric characterization and power conversion efficiency measurements

The crude extract ethanolic solution and its recovered components were characterized by *UV-Visible* spectrophotometry in the wavelength range 200-800 nm with a spectrophotometer *evolution 300* Uv-Visibe. The photovoltaic parameters of the DSSCs such as the fill factor (FF) and the overall conversion efficiency (η) were measured under incident light of 1000 Wm^{-2} (AM 1.5) [15] using a Led projector of 50 W (Ip66). Then the fill factor (FF) and the power conversion efficiency (η) of solar cells were calculated using the following equations [6], [9], [10], [11], [15] :

$$FF = \frac{V_m \times J_m}{V_{oc} \times J_{sc}}$$

$$(1) \quad \eta = \frac{FF \times V_{oc} \times J_{sc}}{P_{in}} \times 100$$

(2)

where J_{sc} is the short-circuit photocurrent density (mAcm^{-2}); V_{oc} is the open-circuit voltage (V), J_m and V_m are the optimum photocurrent and voltage that can be extracted from the maximum power calculated from the J–V data, P_{in} is the intensity of the incident light (1000 Wm^2). The cell active area was about 1 cm^2 . The current and voltage values were measured using two digital multimeters (UNI-T30B and ALDA DT-830D) and a decade resistances box. These different materials and the schematic equivalent circuit was shown in fig. 2. All measurement values were made gradually in interval of 10s, allowing for each reading stabilization. The comparison of the performance of DSSCs based on natural extracts was done with standard DSSC prepared with ruthenium dye (N719), a reference dye which show in this paper a solar energy conversion efficiency of 2.39 %.

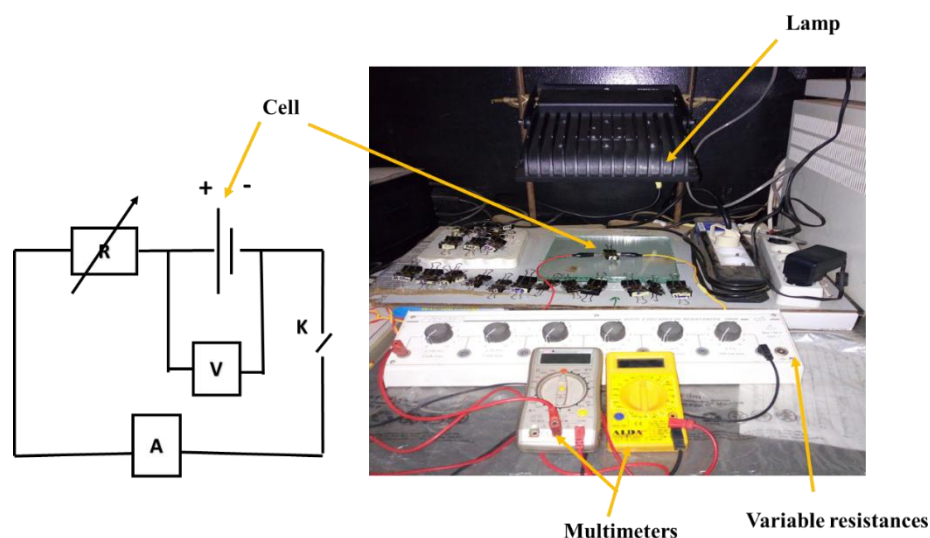


Fig. 2. Schematic equivalent circuit for the I-V measurements

2.5. HOMO–LUMO and band gap calculations

Studies of the electrochemical behavior of the dyes were carried out using cyclic voltammetry with a Bipotentiostat/Galvanostat DropSens (μSTAT 400) connected on an electrochemical cell equipped with 3 electrodes configuration and piloted with Drop View 8400 software. The analysis was done in these specifications: scan rate: 50 mV.s⁻¹, range of 1000 mV to +1000 mV. The initial direction is positive and number of cycles is 3. The supporting electrolyte used was 0,1 M KNO₃ solution. The energy band gaps of the extracted pigments were estimated using UV–Vis spectrum and the Tauc relation [10] :

$$\alpha \cdot h\nu = A (h\nu - E_g)^{1/2} \text{ or modestly } (A \cdot h\nu)^2 = f(h\nu). \quad (3)$$

Then, both energy band gaps and reduction onset potential obtain from cyclic voltammetry data were used to calculate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the investigated pigments using the following relationship:

$$E_{\text{LUMO}} - E_{\text{HOMO}} = G_{\text{ap}} \quad (4)$$

With the A/AgCl couple used as a reference, the energies of the HOMO and LUMO levels are calculated by considering the potentials at the thresholds of the electrochemical phenomenon produced and the characteristic value of the potential of the Ferrocene couple (from 4.4 eV) which allows to calibrate the reference electrode [23], [24]. Thus, in a simple way, the energy levels of HOMO and LUMO were calculated using the following empirical equations [24]:

$$E(\text{HOMO}) = -e [E_{\text{ox}}^{\text{seuil}} + 4.4] \quad (5)$$

$$E(\text{LUMO}) = -e [E_{\text{red}}^{\text{seuil}} + 4.4] \quad (6)$$

III. Result

3.1. UV-visible Absorption of natural dyes

The crude extract of *sorghum spp* show a broad and intense absorption in the visible range between 400 and 550 nm as it can be seen from fig. 3. An absorption peak around 270-280 nm and another peak between 450-550 nm were observed. A not very remarkable absorption band between 320-360 nm was observed legally. After addition of concentrated hydrochloric acid (HCl 1M) to the crude extract, the appearance of *sorghum spp* crude extract (orange-dark color) turned into orange coloration (color of the acidified extract) resulting in an equilibrium shift of anthocyanin towards their flavylium cation (AH⁺). Fig. 3 compares the absorption spectra of non-acidified and acidified anthocyanin extract of the *sorghum spp* sheaths dye. Acidified crude extract shows an intense peak at 485 nm wavelength showing a hyper chromic effect of the dye absorption signal. The obtained hyper chromic effect will facilitate the produced dye-sensitized solar cell to absorb visible light spectrum more effectively at low energy solar radiation; thus resulting in an improved overall photovoltaic performance.

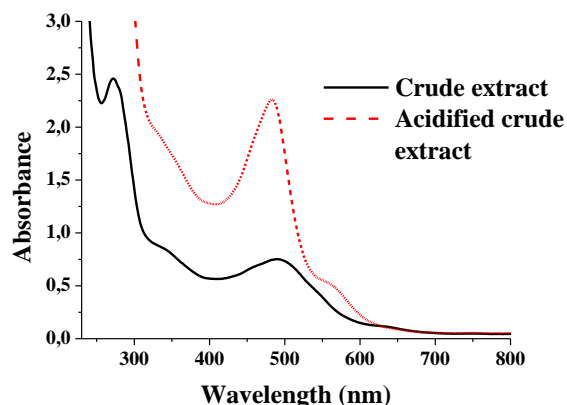


Fig. 3. UV–vis absorption spectra of sorghum spp dye

The column chromatographic separation showed four different colored fractions: yellow (F1), followed by yellow-orange (F2), then orange (F3) and lastly red-dark (F4) as can see in following Fig. 4.

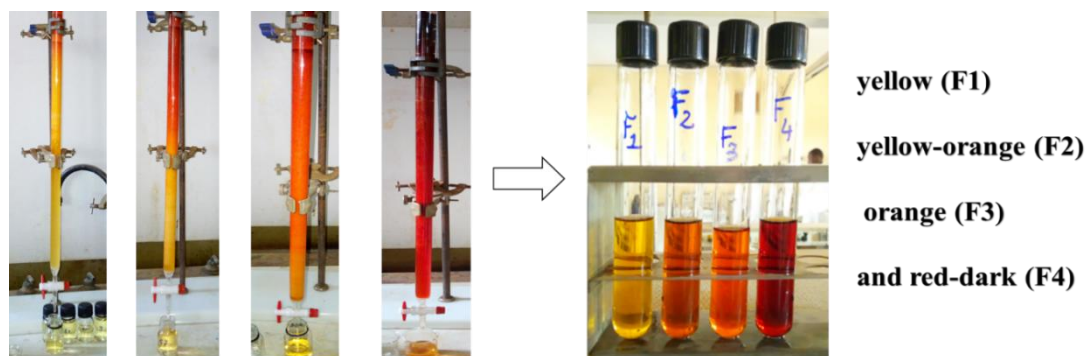


Fig. 4. Different colored fractions obtained from column chromatographic separation.

The separated compounds showed different absorption characteristics to that of flavonoids and anthocyanins with peaks below 500 nm in visible region as can be seen in Fig. 5.

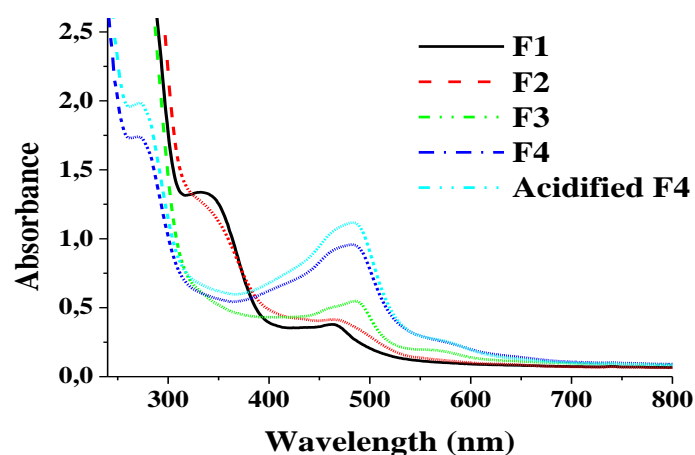


Fig 5. UV-visible absorption of fractions obtained from column chromatographic separation.

3.2. Photoelectrochemical properties of DSSCs sensitized by sorghum spp dyes

Photovoltaic tests of DSSCs using extracted dyes from *sorghum spp* as sensitizers were performed by measuring the current density–voltage (J–V) curves under irradiation with white light from a led of 50W in AM 1.5 condition (1000Wm^{-2}). The performance of different dyes from *sorghum spp* as sensitizers in DSSCs was evaluated by short circuit current density (J_{sc}), open circuit voltage (V_{oc}), maximum power (P_{max}), fill factor (FF), and energy conversion efficiency (η). The photoelectrochemical parameters of the DSSCs sensitized with crude extract, acidified crude extract, F1, F2, F3, F4 and acidified F4 dyes were shown in Table 1. Results of N719 (ruthenium-based dye) are also shown for comparison.

Table 1. Current density –voltage (J–V) characteristics and power conversion efficiencies (η) of DSSCs from crude extract and recovered dyes.

Extracts	V_{oc} (V)	J_{sc} (mAcm ²)	P_{max} (mW cm ²)	FF	η (%)
Crude extract dyes					
Crude extract	0.391	1.31	180	0.35	0.180
Acidified crude extract	0.352	2.86	325	0.32	0.33
Components separated by silica gel column chromatography					
F1	0.041	0.014	0.1577	0.27	0.00016
F2	0.225	0.35	26	0.33	0.026
F3	0.270	0.60	61	0.37	0.061
F4	0.397	1.31	200,97	0,39	0,20
Acidified F4	0.329	3.17	420	0.41	0.42
Reference ruthenium-based dye (N719)					
N719	0.791	8.10	2386.3	0.37	2.39

The I-V curves of the DSCs using the crude extract and acidified crude extract of *sorghum spp* sheaths are shown in fig. 6. As displayed in Table 1 and Fig. 6a, The Voc of these DSSCs are 0.391 and 0.352 V, and the Jsc of 1.31 and 2.86 mAcm⁻² have been measured respectively for the crude extract and acidified crude extract. The fill factors of these DSSCs are 35% and 32%, which led to the efficiencies of 0.18 and 0.33% respectively. It has been observed that higher efficiency and Jsc are obtained from the DSSC sensitized by acidified crude extract.

In order to improve the photoelectric conversion efficiency, the pigments contained in the crude extract are partially separated by silica gel column chromatography. Four types of pigments including F1, F2, F3, and F4 (Fig.4) were obtained and their photovoltaic parameters were determined as shown in the Fig. 6 and the Table 1.

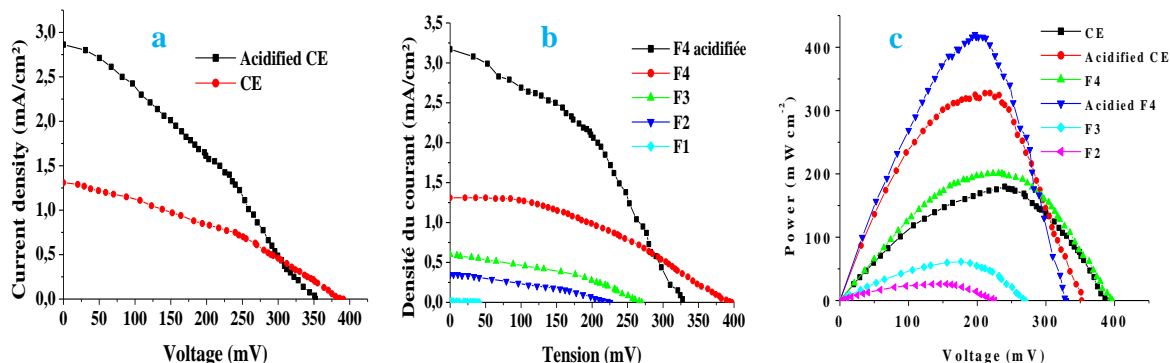


Fig. 6: The current density-voltage curves of DSSCs sensitized by crude extract (CE) and acidified CE (a); F1, F2, F3, F4 and acidified F4 compounds (b) and their power- voltage curves (c).

The J-V (current density-voltage) curves of DSSCs sensitized by F1, F2, F3, F4 and acidified F4 compounds were shown in Fig 6b. The Jsc of F1, F2, F3, F4 and acidified F4 obtained were 0.014, 0.35, 0.60, 1.33 and 3.17 mAcm⁻² and their power conversion efficiencies of 0.00016, 0.026, 0.061, 0.20, 0.42 % were obtained respectively for F1, F2, F3, F4 and acidified F4 (table 1).

The electrochemical properties of each pigment were investigated by using cyclic voltammetry to determine the energy levels of LUMO and HOMO. Fig. 7 shows the cyclic voltammograms of different dyes sensitizers. In this figure the onset reduction potential of each pigment has been determined.

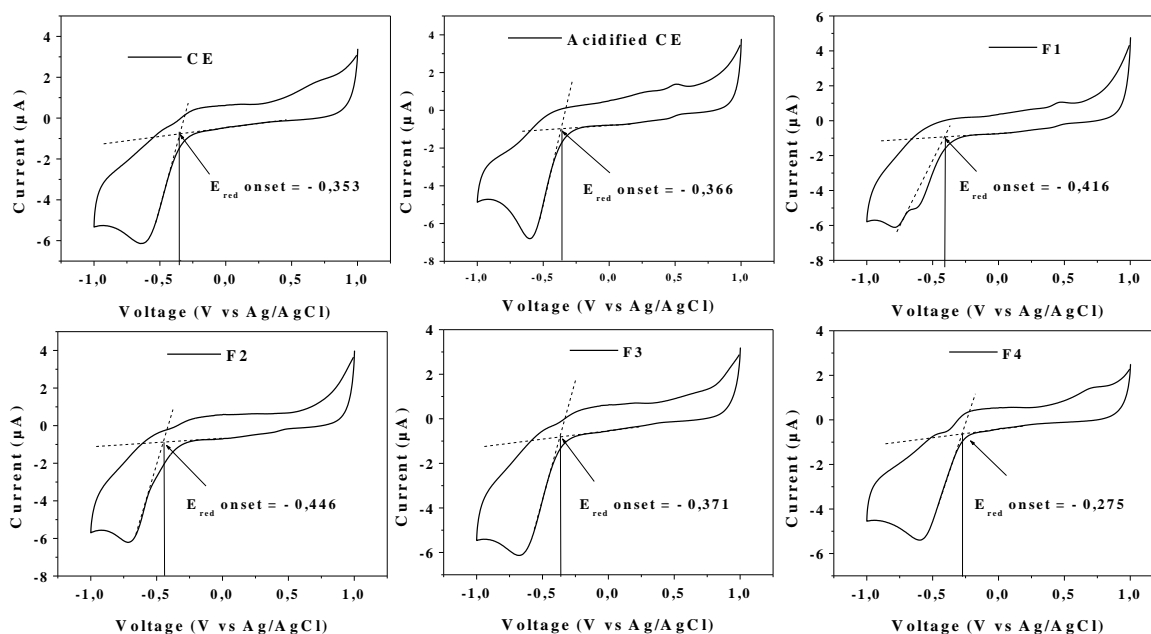


Fig. 7. Cyclic voltammograms of different dyes sensitizers.

The onset reduction potential and the gap energy of each pigment allowed the calculation of the energy levels of the LUMO and HOMO as can be seen in the table 2.

Table. 2: Calculated HOMO–LUMO energy levels and band gap energies of *Sorghum spp* extracts.

Extraits	$E_{\text{red}}^{\text{onset}}$ (V)	Gap energy (eV)	HOMO (eV)	LUMO (eV)
CE	-0.35	2.15	-6.20	-4.05
ACE	-0.36	2.02	-6.06	-4.04
F1	-0.41	2.45	-6.43	-3.98
F2	-0.44	2.30	-6.25	-3.95
F3	-0.37	2.38	-6.41	-4.03
F4	-0.27	2.25	-6.56	-4.31
F4A	-0.33	2.27	-6.34	-4.07

The position of HOMO and LUMO energy levels for different dyes sensitizers was shown in the Fig. 8.

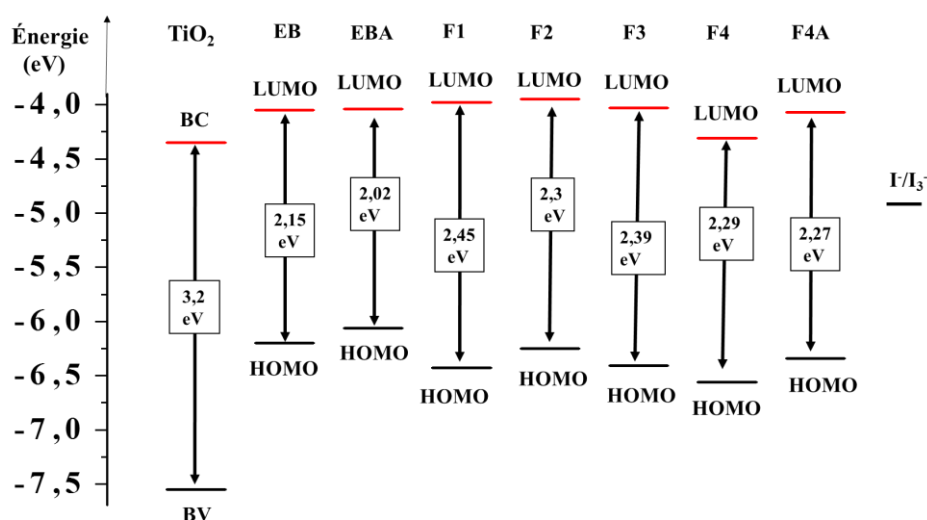


Fig. 8: Illustration of the position of HOMO and LUMO energy levels for different dyes sensitizers.

IV. Discussion

For UV-visible absorption of natural extracted dyes, the absorption around 270-280 nm could be attributed to the phenolic group and that between 450-550 nm would be related to the pyrylium nucleus and the conjugation of the two benzene rings of anthocyanin compounds [10;16]. The band between 320-360 nm would indicate the presence of aromatic acid residue in these anthocyanin compounds [16;17]. The anthocyanins are sensitive to pH changes due to a reversible structural change that occurs in the C ring of the molecules [15]. This property was investigated by using concentrated solution of hydrochloric acid (HCl, 1M). After addition of concentrated hydrochloric acid (HCl), the obtained hyper chromic effect will enhance the absorption of visible light spectrum more effectively at low energy solar radiation and would improve overall photovoltaic performance. Similar effect had been reported by Lim et al. [15]. This indicates that light absorption properties of the pigment can influence the DSSC performances.

The obtained column chromatographic compounds belong mainly to group of flavonoids [16]. Characterization of these separated flavonoid compounds was carried out by comparing UV–Vis spectrum and then compared to some specific dye standards from reports [17].

All separated dyes presented absorption peaks in visible region at around 450-530 nm that signified the presence of anthocyanins and flavonoids. However, F4 compound shows the important absorption in visible region. The comparison of F4 absorption peak which is around 484 nm with UV–Vis spectral data of specific dye standards reported by Harborne [17], indicate the presence of anthocyanins dye, probably apigeninidin derivatives [16; 17; 20 ; 22]. Otherwise, Pale et al., 1997 [20] isolated a new anthocyanidin from the sheaths of *Sorghum caudatum* and identified as 7-0-methylapigeninidin on the basis of spectral data. This pigment was found in low concentration both in grains and in leaf sheaths [20]. In an other hand, a stable 3-deoxyanthocyanidin, apigeninidin chloride, has been isolated with a high yield (10% in dried material) as the major pigment in the sheaths of *Sorghum caudatum* [22]. Our findings are well in accordance with the use of *Sorghum spp* as a source of red dye [21]. The F1 fraction that exhibited absorption peaks at 463 nm, 342 nm and around 275 nm may indicate the presence of some flavonoid in the mixture. The peaks observed for the F3, F4 and acidified F4 dyes are more intense compared to those of F1 and F2 which are lower. This explains the best photovoltaic performance of F3, F4 and acidified F4 pigments. Moreover, all these pigments have intense

absorptions in the ultraviolet around 275-284 nm. However, peaks around 320 nm are also observed for F1 and F2 pigments, thus marking the potential presence of aromatic acid residues in these pigments [16 ;17].

For DSSCs characterization, an enhancement of the efficiency of the DSSCs from 0.18 to 0.33% by simple acidification of the extract was observed. It means that the pH significantly influences the photovoltaic performance of pigments extracted from *sorghum spp* sheaths. This performance is mainly due to the better collection of light radiation from the acidified extract compared to the non-acidified extract. Moreover, the acidification of this crude extract would have allowed the hydrolysis of the osidic functions linked to the anthocyanidin pigments and thus the release of the anthocyanin pigment more efficient in the photovoltaic conversion. Such properties have been reported in several earlier works [15, 16]. In an other hand, a reason for the better efficiency, is that, at pH below 2, anthocyanin existed as flavylium ion, which is the stable form of anthocyanin [18]. Additionally, anthocyanin molecules are known to contain hydroxyl groups [5, 18]. The presence of hydroxyl groups in anthocyanin molecules helps in the binding of dye molecules to TiO₂ nanoparticles surface [5, 6], thus contributing to improve the photoelectric conversion efficiency [5].

To boost photoelectric conversion efficiency, column separation of crude extract was done. We note that these parameters increase when we go from the DSSC sensitized with F1 pigment to that sensitized with the acidified F4 pigment. These parameters show that DSSC performance depend on the type and polarity of the molecules. So, of these four separate pigments, F4 shows the best photoelectric conversion efficiency, mostly when it was acidified. Thus, acidification of F4 dye has shown improvement in the photocurrent conversion efficiency of DSSC (Fig 6b), with a conversion efficiency (η) of 0.42%, open circuit voltage (V_{oc}) of 329 mV, short circuit current density (J_{sc}) of 3.17 mAcm⁻², and fill factor (FF) of 0.41, under irradiance of white light compared to F4 without acidification that exhibits conversion efficiency of 0.20%. This aspect also shows the highest observed maximum power for DSSC sensitized to F4 pigment as shown in Fig. 6c. This performance is comparably better than many anthocyanin extracts reported from other sources [6]. The photocurrent current density and conversion efficiency of DSSC sensitized with crude extract dye are lower when compared to that of the acidified recovered fraction (F4) of anthocyanins. This may probably indicate a possible masking effect when all components are present in mixture [10;15]. Otherwise, as reported in [10], DSSC sensitized by the first compound obtained with column chromatography did not perform well, so DSSC sensitized by F1 and F2, did not perform well in this investigation also. This could suggest that F1 and F2 extract did not adsorbed efficiently onto TiO₂ nanoparticles, or oxidized dye could not be regenerated or the excited electrons were not efficiently transferred to the electrode from these pigments because of recombination process [2;5;10].

The electrochemical properties of each pigment would explain performance of the DSSCs. For good performance of the DSSCs, electron transfer and mobility must be favorable. Thus, the energy level of the lowest unoccupied molecular orbital (LUMO) of the excited pigment should be close to the conduction band of the semiconductor in order to facilitate the injection of electrons before any further deactivation process and / or recombination. The results show that the energy levels of the LUMO of the crude extract (EB), of the acidified crude extract (EBA) of the fractions F1, F2, F3, F4 and acidified F4 are much higher and above the level of the TiO₂ conduction band.

All these extracts can then inject electrons into the TiO₂ conduction band. However, it is observed that the energy levels of the LUMO obtained from the acidified fraction F4 and F4 (respectively - 4.31 and - 4.07 eV) are the lowest and closest to the conduction band of TiO₂ (Table 2). This means that the injection of electrons into the TiO₂ conduction band would be more favorable with the F4 fraction as a sensitizer compared to the other fractions. On the other hand, it could also mean that the processes of recombination and deactivation are weak or reduced, even inhibited, with these pigments (F4 and F4 acidified) compared to the fractions F1, F2 and F3 which are more distant from the conduction band of TiO₂. This electrochemical property partly explains the highest overall conversion yields obtained with the DSSCs sensitized with the acidified F4 (F4A) and F4 fraction compared to the other fractions (Table 2).

In addition, the acidified CE and acidified F4 presented more absorptions which are broad and intense emerging at around 485 nm upon the addition of concentrated hydrochloric acid to the CE and F4 extracts. This action would give rise to a new energy level of HOMO which are more favorable for dye regeneration. This HOMO level can facilitate efficient electrons injection to the semi-conductor conduction band. In other hand, a long life time of oxidized dye at LUMO causes inefficient dye regeneration that leads to a decay of V_{oc} . As reported by Lim et al. [10], for efficient regeneration of dye to take place, the HOMO level of the dye has at least 100-200 mV more positive than the potential redox of the mediator. Our electrochemical results reveal that the HOMO levels of the acidified extracts (acidified CE and acidified F4) are closer to the redox potential compared to that of non-acidified extracts. This explains the reduction of the V_{oc} of the DSSC sensitized with acidified extracts.

V. Conclusion

In this study, dye-sensitized solar cells fabrication using natural dye extract mainly flavonoid groups from the sheaths of *sorghum spp* as photosensitizer is reported. The performance of the crude extract and its separated constituents in solar energy conversion are investigated. The results show that among these extract constituents, acidified F4 fraction which mainly constituted of anthocyanins present higher overall energy conversion efficiency of 0.42%. This is due to the better charge transfer between the F4 dye molecules and the TiO₂ surface which is related to a dye structure (anthocyanins). The acidification of pigment using concentrated hydrochloric acid has demonstrated an improved overall conversion efficiency as likely caused by improvement of both absorption and adsorption properties of the pigments.

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