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DESIGN AND CHARACTERIZATION OF ORGANIC SOLAR CELLS CONTAINING NANOSTRUCTURED SEMICONDUCTOR THICK FILMS BY COST-EFFECTIVE METHOD

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Abstract. *There is an increasing research interest in the successful designing of low cost, efficient dye sensitized solar cells (DSSC's) as an alternative energy resource for the next generation. However, the construction of low cost, highly efficient and stable DSSC's defines a challenge for practical applications. In this work, we report how DSSC's containing semiconductor oxides, such as* TiO_2 *(Titanium Dioxide),* Nb_2O_5 *(Niobium Pentoxide) and ZnO (Zinc Oxide), and conducting graphite thick films were prepared with many different techniques. Organic dyes extracted from different fruits and vegetables were used as sensitizers in the DSSC's. After the device's assembly, an annealing process was performed, and the resulting films were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Atomic Force Microscopy (AFM) measurements. Also, the influence of the dye molecules on metal oxides was analyzed. The effects of the dye on diode characteristics, such as short circuit current (*I_{sc}*) and open circuit voltage (*V_{oc}*), were measured with and without light exposure. The light intensity influence and the decay of the open circuit voltage as a function of time for different kinds of organic dyes were also studied. Moreover, we present the first results of our efforts towards the construction, characterization and integration of the DSSC's, already showing promising results for small scale power systems.*

Keywords: *semiconductor nanostructures, solar energy, organic solar cells*

1. INTRODUCTION

Human activities cause environmental changes, and a significant amount of those impacts originates from the generation, handling and use of energy. Nevertheless, as energy is essential to all living beings and to civilization, the last few years have seen a remarkable growth in the efforts aiming at alternative forms of energy supply, as the search for clean, renewable and non-polluting sources has been strengthened (Tolmasquim and de Oliveira, 2004). Amongst those, the use and application of solar energy becomes a very reasonable option. One of the forms to convert solar energy into electric power is by means of photovoltaic cells (GTES, 2008).

The search for renewable energy sources is considered one of the priorities of today's society and solar energy emerges as one of the main alternatives. Recently, tremendous efforts have been delivered to improving the efficiency of DSSC's (Ye *et al.*, 2015). However, few studies were carried out in optimizing the design of the architecture of DSSC's so as to improve the efficiency of the solar cell and to extend their application for large scale production. In this work, we propose a design for large scale manufacturing photon-to-electron conversion DSSC's using the semiconductor oxides TiO_2, Nb_2O_5, and ZnO and dye extracted from the fruits and vegetables.

Dye sensitized solar cells (DSSC's) have received much attention as an alternative to silicon-based solar cells due to their potential low cost, easy fabrication and better conversion efficiency. A Typical DSSC consists of the following main components: a dye-sensitized semiconductor photo-anode, an electrolyte with a redox couple (tri-iodide/iodide), a conductive counter electrode and two glass substrates covered by a conductive and transparent layer (TCO Film -

Transparent Conductive Oxide). The DSSC's are categorized as hybrid solar cells, once they are composed by organic and inorganic materials.

These cells were created by Michael Grätzel e Brian O'Regan in the École Polytechnique Féderale of Lausanne in 1991, and are know as Grätzel Solar Cells (O'Regan and Grätzel, 1991). The cells developed by Grätzel's group used nanocrystalline TiO_2 (anatase) with very high superficial area and showed conversion efficiency of 7,9%, using a solar simulator and 12% with diffuse light, photocurrent of 12 mA/cm^2 and stability of 5 million cycles without decomposition. However, with respect to silicon cells, organic solar cells have low energy efficiency, since recent studies (Yella *et al.*, 2011) indicate how best efficiency achieved for organic solar cells a range of 11-12%. A possible primary reason for the loss of efficiency may be associated to the process of diffusion of electrons through the electrode pores, which presents a better profile in traditional silicon cells.

The working principle in a DSSC is based on the recombination between electron and "holes" on the surface of the wide bandgap nanostructured semiconductor oxide (TiO_2, Nb_2O_5, or ZnO), that adsorbs the sensitizers (dye molecules), as illustatred in Fig. 1. Once photons with high enough energy excites electrons in dye molecules, from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), electrons infused into semi-conducting oxide are transported out of cell, creating "holes". Separation of excited electrons and "holes" creates a voltage, and once an electrical load is connected between the terminals, the current flows into the electrodes. Electrolyte containing I^-/I_3^- redox ions is used in DSSC to regenerate the oxidized dye molecules and hence complete the electric circuit by mediating electrons between the nanostructured electrode and counter electrode, that can be graphite, platinum or silver.

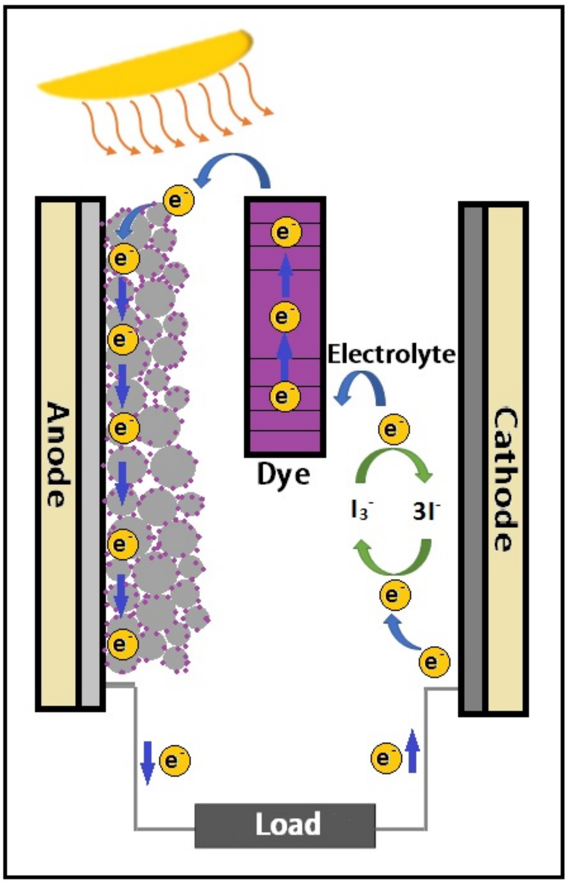

Figure 1. DSSC's working principle

The semiconductor material of the Grätzel cell works as a receiver of the electrons generated by light incidence on the so excited dye, once those electrons, after being generated in the dye, are injected into the conduction band of the semiconductor oxide, resulting in a current flow in the film. Eq. (1) shows the reaction of excitement of the dye, as Eq. (2) shows the sensitization of the semiconductor oxide (represented by TiO_2).

The occupation of the gap which is located in the oxidized dye (S^+), after the electron is injected into the conduction band of the semiconductor oxide, is performed by the reaction with the redox couple (I_3^-/I^-) that exists in the electrolyte, because the iodide (I^-) oxidizes, generating triiodide (I_3^-) and causes the occupation of the gap generated in the dye (S^+), as described in Eq. (3). Following such chemical reactions, the electrolyte suffers a reduction reaction on the counter electrode of the solar cell (Eq. (4)) (Agnaldo, 2006).

$$S + h\nu \rightarrow (S)^* \tag{1}$$

$$(S)^* + TiO_2 \rightarrow e^-(TiO_2) + (S)^+ \tag{2}$$

$$(S)^+ + \frac{3}{2}I^- \rightarrow S + \frac{1}{2}I_3^- \tag{3}$$

$$\frac{1}{2}I_3^- + e^-(counterelectrode) \rightarrow \frac{3}{2}I^- \tag{4}$$

Simplifying the redox reactions of negative and positive electrodes (Eq. (5) and Eq. (6)), we have:

$$3I^- \rightarrow I_3^- + 2e^- \tag{5}$$

$$2e^- + I_3^- \rightarrow 3I^- \tag{6}$$

These reactions are observed when the light hits the surface of a nanoporous DSSC, being absorbed by the dye, which will sensitize the anode. The energy absorbed as a function of wavelength may be calculated through Eq. (7):

$$E = h\nu = h\frac{c}{\lambda} \tag{7}$$

where h is Planck's constant $(6,626.10^{-34}J.s)$, c is the speed of light $(2,998.10^8m.s^{-1})$ and λ is the wavelength used.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation and assembly of DSSC's

Once the main characteristics of DSSC's had been established, the proper semiconductor films and the dyes chosen to integrate the process were assembled. The components used for the synthesis of the organic solar cells are: dyes; nanocrystalline semiconductor; electrolyte (iodine solution); two glass electrodes with a conductive and transparent layer (ITO film) and a catalyst (graphite).

First of all, a indium-doped SnO_2 conducting glass (ITO film) was cleaned with double distilled water and Triton X-100 detergent. An ultrasound device was used for an additional 20 minutes-run cleaning, and the glasses were dried with hot air. Then, the conducting surface was identified by means of a multimeter.

The TiO_2, Nb_2O_5, and ZnO thin films on ITO glass (photoanode) were prepared with 0.5g of TiO_2, 5 mL of Triton X-100 and 1 mL of HNO_3. Conducting glass coated with a mixture of graphite powder, Triton X-100 and 1 mL of HNO_3 was used as a counter electrode. The deposition of the paste can be performed by many different techniques, such as painting, printing or spin coating.

The films coated on ITO glass were annealed at 450 ^{o}C for 60 minutes in a muffle oven. After cooling the thin film at room temperature, the TiO_2 film was sumerged in dye solutions for 24 h at room temperature for the dye to adsorb properly on the surface and to avoid the rehydration of TiO_2 film. The dye was prepared with many different available fruits and vegetables - such as carrots, beets, jaboticaba, strawberry and collard greens - filtered and preserved for further applications with acethone, or ethanol, in fridge.

The prepared photo-anode was placed on top of the counter electrode and they got tightly clipped together. A liquid electrolyte (iodine solution) was then injected into the space between two electrodes, activating the solar cell. Then, the electrical parameters and I x V curves were measured using the characterization system (as seen below). Surface morphology of the deposited TiO_2 film was also studied by Fourier Transform Infrared Spectroscopy (FTIR) and Atomic Force Microscopy (AFM). In Fig. 2, details of the process of preparation and assembly of the DSSC's are shown.

2.2 DSSC's characterization system

The characterization system was designed to be a low-cost assembly to determine the eletric parameters and real modeling of the assembled DSSC's and has been developed to simulate incident solar radiation over a DSSC, while the sample is kept cooled to room temperature, a setup that prevents temperature gradients that could affect the outcomes of current and voltage. The system is basically composed by a chamber, where the sample is conditioned. A 55 W CC lamp is used to simulate the solar irradiance over the cells and a gauged voltage power source is employed. In Fig. 3, the system is pictured. The cooling of the samples is performed using copper pipes that allows cold water to circulate inside of the chamber. The pipes are located below the ceramic base where the cells are placed for characterization.

The output terminals of the DSSC's can be connected to several measuring instruments, such as multimeters or oscilloscopes, for acquiring the expected results. In this experiment, two differet methods were applied: i) current and voltage measured with a variable resitor in the multimeter output; ii) National Instruments® data aquisition system (cDAQ-9188) was used to generate the curves, using the modules NI-9201 and NI-9203 to measure voltage and current, respectively. The interface between software and hardware was implemented via ETHERNET.

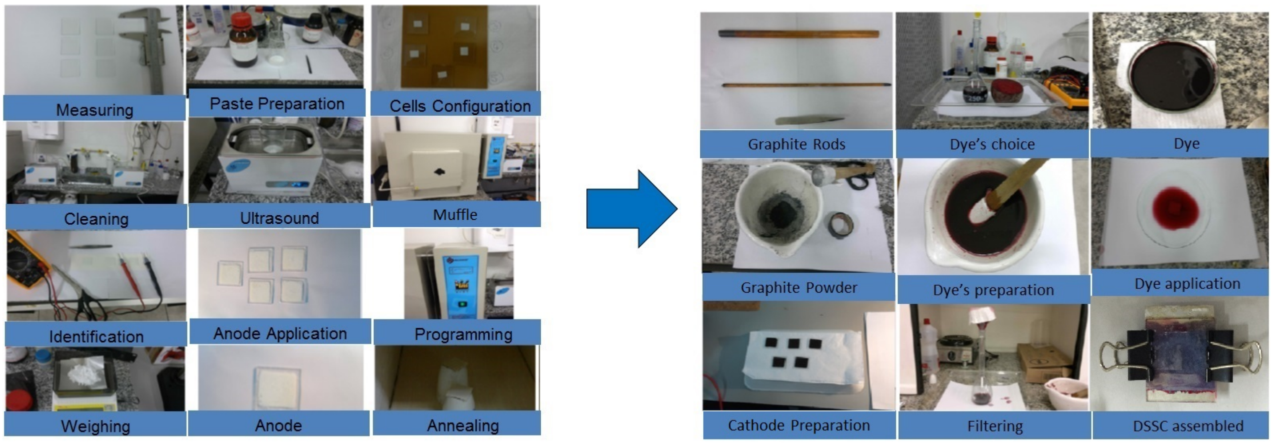

Figure 2. Steps of preparation and assembly of DSSC's

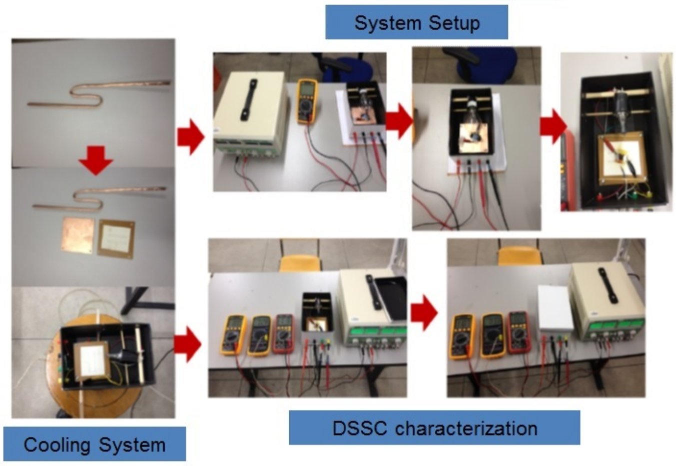

Figure 3. Assembling and application of the photovoltaic cells characterization system

3. RESULTS

Initally we use several different dyes, shown at Table 1, in order to verify wich one could be the best for the solar cells. In the most of the samples, TiO_2 was used as a fotoanode, since it has a wide bandgap and improved stability. The I x V curves were experimentally acquired, by varying the electrical load applied on the cell. Table 1 shows the characteristics of each sample.

Table 1. Samples' data.

Sample	Anode	Cathode	Electrolyte	Dye	V_{oc} (mV)		I_{sc} (mA)	
-	-	-	-	-	Dark	Light	Dark	Light
1	TiO_2	Graphite	Iodine	Carrot	86	108	0,040	0,045
2	TiO_2	Graphite	Iodine	Beet	223	295	0,054	0,430
3	TiO_2	Graphite	Iodine	Mango	82	90	0,030	0,030
4	TiO_2	Graphite	Iodine	Collar Greens	128	248	0,010	0,014
5	TiO_2	Graphite	Iodine	Strawberry	262	403	0,016	0,25
6	TiO_2	Graphite	Iodine	Jaboticaba	540	660	0,007	0, 014
7	Nb_2O_5	Graphite	Iodine	Jaboticaba	326	358	0,061	0,092
8	ZnO	Graphite	Iodine	Jaboticaba	342	356	0,23	0,25

In Fig. 4, the I x V curves that caracterize the solar cells are shown. From these results, we can determine: open circuit voltage, short circuit current, fill factor and efficiency. The open circuit voltage (V_{oc}) is the maximum voltage generated by the photovoltaic device, and can be experimentally obtained by measuring the voltage at the terminals of a cell without load under certain conditions of temperature and incident radiation. The short circuit current (I_{sc}) is the maximum current that can provided by the solar cell, and can be obtained after short-circuiting the terminals of the cell and measuring the current flowing through the device.

Figure 4a shows the I x V curve for sample number 6, using TiO2 as anode and jaboticaba juice as dye. From the plot, we can observe in this sample a high value of Voc along with a low Isc. Figure 4b represents sample number 1, using carrot juice as dye. That sample shows low values for both V_{oc} and I_{sc}, revealing that this is not a proper dye to be used for the DSSC's. Figure 4c (sample number 7) is an example of use of Nb_2O_5 as anode with jaboticaba as dye, showing promising results. Finally, Fig. 4d (sample number 4) shows the use of collard greens (chlorophyll) as dye, with an apparently big difference between the values of V_{oc} in lighted and dark conditions, giving us a clear example on how the photoeletric effect works on the DSSC's.

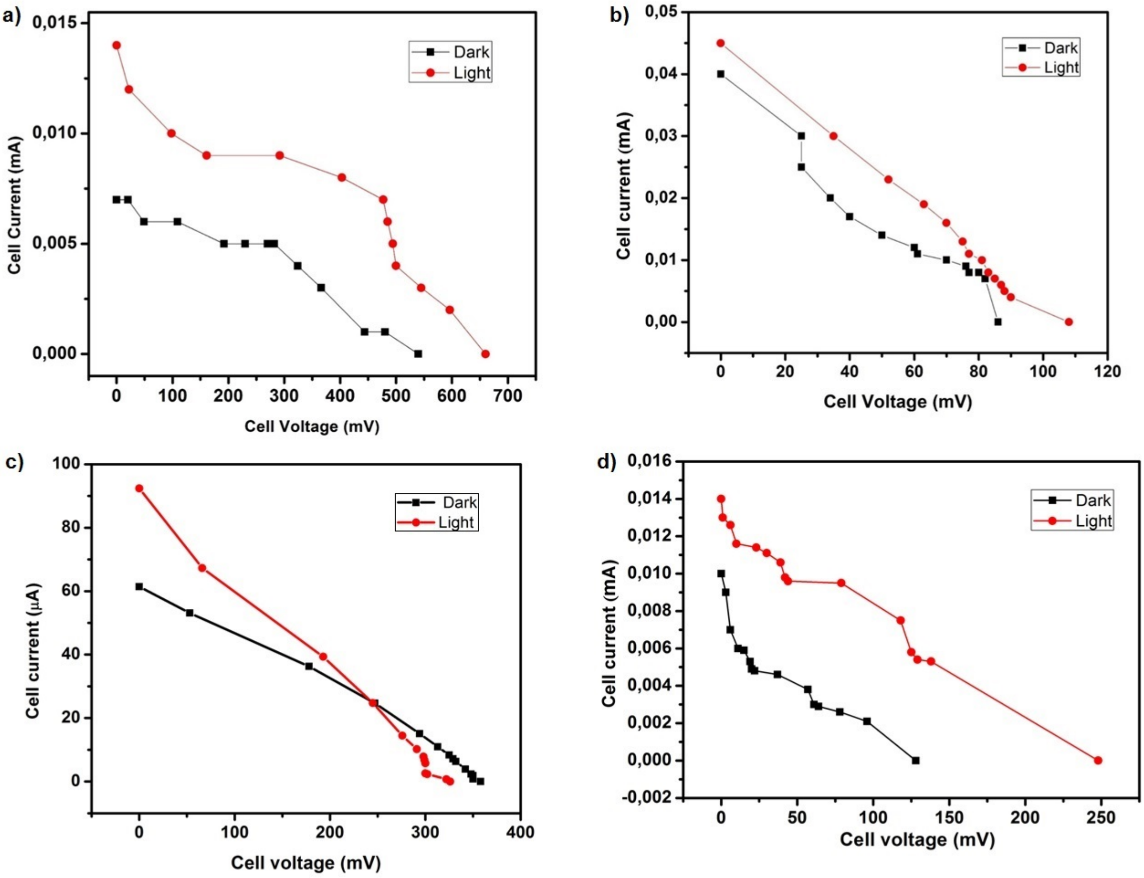

Figure 4. I x V curves for samples using different organic dyes (in dark and lighted conditions)

Details of the thin films structure could be verified with the use of 3D AFM images (Giessibl, 2003), as shown in Figs. 5a and b. This analysis is crucial for the characterization of thin films, characterizing their surface roughness and functional performance of many devices, such as semiconductor films, chemical compounds and biological materials. In Fig. 5a, the AFM image for a 21nm nanopowder TiO_2 thin film is exhibited. The AFM image shown in Fig. 5a indicated that the surface of the TiO_2 thin film was smooth, with estimated root mean square (RMS) roughness of 36 nm and 19 nm for the average size of the thin film's nanoparticles. Figure 5b depicts the AFM image of graphite thin film, even smoother than the previous analyzed film. This films shows RMS roughness of 5 nm and graphite nanopowder particles with the average size of 3,8 nm.

The FTIR spectrum of the DSSC composed by ZnO photoanode and jaboticaba juice as sensitizer is shown in Fig. 6. Fourier transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption, emission and photoconductivity of a particular sample. An FTIR spectrometer collects high resolution data over a wide spectral range and can be used to identify the characteristics of the the composition of the DSSC under analysis (Luo *et al.*, 2009) and (Lohrasbi *et al.*, 2013).

Figure 6 displays the FTIR spectrum of jaboticaba juice as the dye of a sensitized anode and shows most of the characteristic peaks of the anthocyanin. One is led to the conclusion that jaboticaba works as an efficient sensitizer of the DSSC's, as the anthocyanin molecule can be identified in the spectrum of combined dye and photoanode, yielding a better photon conversion. The two peaks at 1235 and 1550 cm^{-1} correspond to phenolic O-H and O-H deformation stretch, respectively. The spectrum also contains a peak at 1060 cm^{-1} corresponding to characteristic C-O stretching vibration of anthocyanins. The strong band at 1397 cm^{-1} corresponds to CH_3 scissoring mode, and exhibits most of the characteristic peaks of β-carotene.

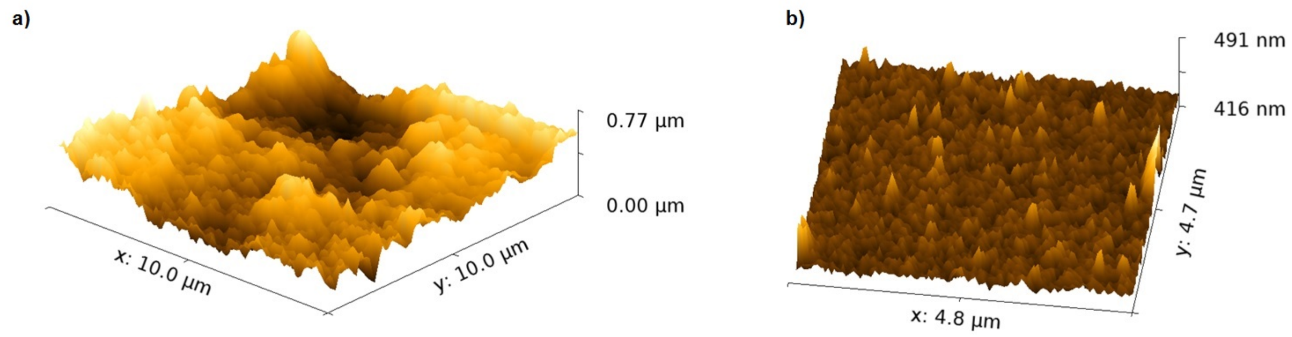

Figure 5. Three dimensional AFM images of thin films

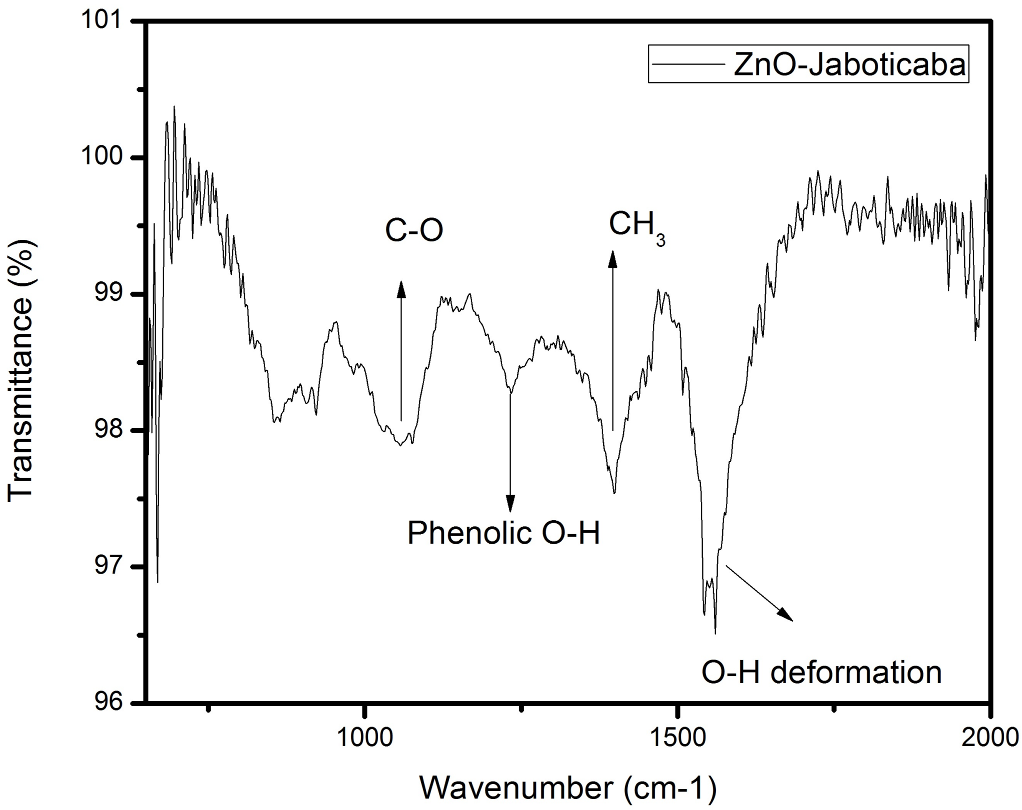

Figure 6. FTIR spectrum for ZnO anode and jaboticaba juice sample

4. CONCLUSIONS

As an outcome of our initial measurements, one observes that some fruits containing high concentration of anthocyanidin molecules - detected in the FTIR analysis - exhibit better efficiency as a dye, and should be targeted for the best thin film preparation technique. Amongst the tested dyes, jaboticaba juice presented the highest values of conversion with V_{oc} of 660 mV maximum. Also, the use of nanostructured semiconductors, such as TiO_2, Nb_2O_5, and ZnO, results in high chemical stability of the cell due to its resistance to photo-corrosion. The samples with TiO_2 and jaboticaba juice as dye presented long stability, as the decay of voltage in time was minimum. Three months-old assembled DSSC's have been tested, yielding the same results once had observed for original recently assembled sample tests.

Therefore, DSSC's are presented as a source of clean, low cost and easy to assemble solar cell production, as they can be constructed using more lightweight and flexible materials, turning their implementation into an easier task. Moreover, the use of natural dyes provides a non-toxic and inexpensive source to sensitize the cells and so provide a high level of UV, visible and near IR absorbance.

For the future works, we intend to improve the use of the electrolyte, once the liquid electrolyte presents loss over time. The use of gel electrolyte would be a good alternative, as proposed in recent works (Sukmawati Arsyad *et al.*, 2013). Also, hybrid dye senstized solar cells will be prepared using a mixture of TiO_2 with other metal oxides (1 to 5%) and perovskites (such as $BaTiO_3$, and their nanocomposites). Among all photo-anode materials, organic-inorganic hybrid perovskites - such as $CH_3NH_3PbX_3$ (X = Cl, Br, I) - have attracted much attention as light-harvesting materials for mesoscopic solar cells (Burschka *et al.*, 2013), resulting in an impressive power conversion efficiency (PCE) of 13.7%.

These DSSC's will be analysed using a solar simulator for the best performance of photo-to-electron conversion efficiency. The parameters obtained can be compared with the characterization system and data acquisition system outcomes. Also, a pyranometer will be used for measuring and control of the irradiance level, providing tools to calculate the efficiency of the DSSC's with minimum error. For the dyes' characterization we intend to obtain the absorption spectra of the different dyes and the semiconductor oxides interaction with ultraviolet-visible spectroscopy, using a UV-Vi spectrophotometer, in order to identify the wavelenghts of absorption peaks that can be correlated with the types of bonds in a given molecule, comparing both spectra of the dye and the adsorbed dye onto the semiconductor oxide thin film surface.

Therefore, the project we follow herewith meets the expectation of developing and characterizing low-cost solar cells, that may turn out to be economically viable. Future assembling in panels or small power modules, providing highly-stable and efficient DSSC's are challenges to be cope with as requirements for large scale power production.

5. ACKNOWLEDGEMENTS

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