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**MICROSTRUCTURAL, MORPHOLOGICAL AND ELECTROCHEMICAL
ANALYSIS OF SEMICONDUCTOR SPIN-COATED THIN FILMS
ELECTRODES FOR DYE-SENSITIZED SOLAR CELLS WITH NATURAL
DYES AS SENSITIZERS**

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Abstract. *Dye-sensitized solar cells (DSSC's) have been considered as an important energy resource in recent years due to its low-cost fabrication compared to silicon-based and thin film solar cells. A typical DSSC consists of three main components: a dye-sensitized semiconductor photo-anode, an electrolyte with a redox couple and a conductive counter electrode. The natural dyes containing anthocyanins, were extracted from flowers and vegetables by simple extraction techniques and used as photosensitizers in the dye-sensitized solar cells. Photo-anodes films with different nanostructured semiconductors were prepared and characterized by Fourier Transform Infrared Spectroscopy, Atomic Force Microscopy and Scanning Electron Microscopy. The Fourier Transform Infrared spectrum was obtained after the dye coating on the TiO₂ layer, to identify the light absorbance behavior according to the functional groups present in the dye molecules. The photovoltaic performance was carried out to understand the effect of the different photo-anode and the interaction with the dyes on the cell's efficiency. A new work has been designed with the results of our efforts towards the construction, characterization and integration of the DSSC's. The increasing of short-circuit current and chemical stability of the device reveal the promising characteristics to extend the natural dye-based DSSCs fabrication for large scale production.*

Keywords: *solar cells, natural dyes, thin films.*

1. INTRODUCTION

There is an increasing demand of alternative sources of energy, which leads to the development of a technologically advanced society, committed to its environmental sustainability. Among them, solar power becomes an interesting choice for clean, renewable and non-polluting sources, as photovoltaic cells are employed to convert solar energy into electric power. Among the variety of solar cells, dye-sensitized solar cells (DSSC) are considered to be a promising alternative to silicon based solar cells because of their low fabrication cost and reasonably high-power conversion efficiency (Jasim, 2011). Recently, natural organic dyes are being used as sensitizers in the solar cells are attracted by several researchers due to their longer stability, environment friendly and easy availability of dye molecules (Luo, *et al.*, 2009).

The basic operation of the dye-sensitized solar cells (DSSC's) is based on the interaction of a semiconductor material (anode) and a dye, that works as a sensitizer, with an electrolyte and a conductive counter electrode, which

works like a cathode, as illustrated in the Fig. 1. The semiconductors films were used as anodes, because of their high-energy bandgap and it can absorb radiation only in the ultraviolet region, and therefore it is not responsible for the release of electrons when struck by sunlight. Its main role is only to transport the charges (Ye, *et al.*, 2015).

In general, the dye can absorb the range of the visible light, when it obtains the necessary energy passes from the highest occupied molecular orbital (HOMO) to the lower unoccupied molecular orbital (LUMO). If the energy of the LUMO level is greater than that of the oxide conduction band, the electrons will be injected from the dye into the semiconductor, making the transport by diffusion through the cells' contacts - the location which the cell interacts with the external circuit. From the external circuit closed, the electrons return to the device, reaching the photo-cathode. Natural dyes are promising alternative sensitizers for DSSC's because of their easy production, wide availability, low cost, and eco-friendly behavior. In fact, several natural pigments such as anthocyanin, chlorophyll, tannin and carotene have been successfully used as sensitizers in DSSC's (Kim, *et al.*, 2013).

The electrolyte is the intermediate between the two electrodes, closing the internal circuit of the cell. When the electrons are injected into the oxide, the dye becomes oxidized, and the regeneration of the species is due to the electrolyte, being regenerated by the counter electrode. Due to all these internal reactions, it is essential that the chemical composition of the elements is maintained unchanged to ensure cycle stability and current generation. In such case of these electrolytes, iodide liquid electrolytes are strongly corrosive and easily evaporable, which inhibits the stability of DSSC. So, it is necessary to find out the alternative method for stable electrolytes to enhance the stability of DSSC. Therefore, a significant effort has been made to produce polymer-gel electrolyte to apply for DSSC's (Wang and Yen, 2011).

The present work deals with a polymer-gel electrolyte based on polyvinylpyrrolidone (PVP) and iodine applied for natural organic dye-sensitized solar cell devices (Sampaio, *et al.*, 2016). The influence of the photo-anode film on the performance of photo electrochemical DSSC's is crucial, as the photoelectrode should possess important features including: nanoparticles of large surface area, which is suitable for chemisorption of dye molecules; continuity of semiconductor anode nanoparticles without any cracks, which is required for efficient electron flow and highly porous microstructure for interaction of electrolytes with dye molecules during the photosensitization process.

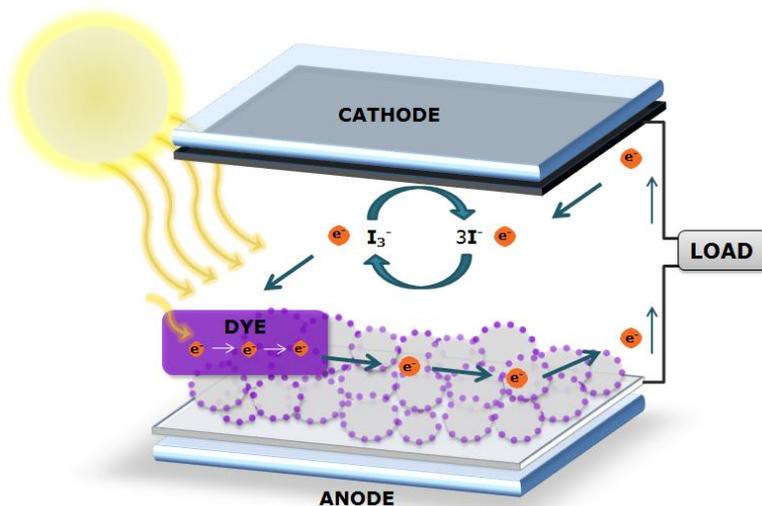


Figure 1. DSSC's working principle.

2. EXPERIMENTAL PROCEDURE

The experimental procedure to build DSSC's consists of the preparation of the thin films which are used as anode and cathode, annealing, the application of dye, injection of the electrolyte and final assembly of the DSSC's.

Initially, an 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. The TiO_2 , Nb_2O_5 , and ZnO anode thin films were deposited over a ITO glass (photoanode) which was prepared with 0.5 g of the semiconductor anode nano-powder, 5 mL of Triton X-100 and 1 mL of HNO_3 . A conducting glass coated with a mixture of graphite powder as a counter-electrode was prepared using 5 mL of Triton X-100 and 1 mL of HNO_3 was prepared. The deposition of the prepared paste was performed by spin coating.

The films coated on ITO glass were annealed at 450 °C for 60 minutes in a muffle oven. After cooling down to room temperature, the anode thin film was submerged into the dye solution for 24 h at room temperature, to avoid the rehydration of anode film and also to adsorb properly on the surface of the film. In the present work, three different

dyes were used: *purple cabbage* and the extract of the flowers *Ixora coccinea* and *Thunbergia erecta*. The prepared photo-anode was placed on top of the counter electrode and tightly clipped together, as can be seen in the Fig. 2. A liquid/polymer-gel electrolyte (iodine + polyvinylpyrrolidone solution) was then injected into the space between the two electrodes to activate the solar cell.



Figure 2. Assembled DSSC.

3. RESULTS AND DISCUSSION

The thin films structure and morphology of 3D Atomic Force Microscopy (AFM) Microscopy (SEM) images are represented in Fig. 3. The surface roughness and functional performance of the semiconductor thin film analyses are essential for the characterization of thin films, and the establishing values of the parameters were analyzed using AFM, which measure forces less than $1 \mu N$ between the surface of the tip that sweeps a small area along the surface of the sample. A topographic image is then generated from the interaction of the forces of attraction and repulsion between the tip and the surface of the sample. The most frequent use for the topographic analysis of the anode in case of the photovoltaic cells was this AFM can also map some mechanical and physicochemical properties (Giessibl, 2003).

The greatest advantage of this technique is to obtain the details of the surface of the sample, even if only a small area is analyzed. The ideal result yields a low-roughness surface, with the generated images perfectly uniform, because a homogeneous film hinders the chances of recombination (Subramanian, *et al.*, 2013). However, many factors are determinant for such results, such as the deposition method itself (spin coating allows greater thickness control and is less prone to non-uniformity when compared to the Doctor Blade method (mostly used in many literatures), homogeneity (often some grains resist ultrasound and cause deformations on the surface), and contamination of the sample during handling and others.

The surface morphological behavior of the thin films was analyzed using Scanning Electron Microscopy (SEM) and the images are shown in Fig. 4. The surfaces of the electrodes are characterized, in order to analyze the efficiency of the deposition method of the nanocrystalline oxide film. This analysis is of great importance since it allows the detailed visualization of the anode structure after annealing and before being sensitized, thus making it possible to identify possible grains, impurities or cracks that impair the uniformity of the film and thus facilitate the occurrence of recombination. In the case of impurities, the EDS (X-ray Dispersive Energy Spectrometry) analysis can also be used to identify its composition, as well as allows us to verify the mesoporous structure, essential for the dye to be well adsorbed (Vernon-Parry, 2000).

The AFM image for TiO_2 nanostructured thin film exhibited a smooth surface (Fig. 3a), similar to Fig. 3c, which shows the surface of ZnO anode. Fig. 3b shows that the Nb_2O_5 exhibited a higher roughness film with less uniform surface. This can be also confirmed by SEM images (Fig. 4), where the void spaces in the Nb_2O_5 anode (Fig. 4b) as clearly identified in the film, instead a mesoporous structure was seen in the case of TiO_2 and ZnO anodes (Fig. 4a and Fig. 4c).

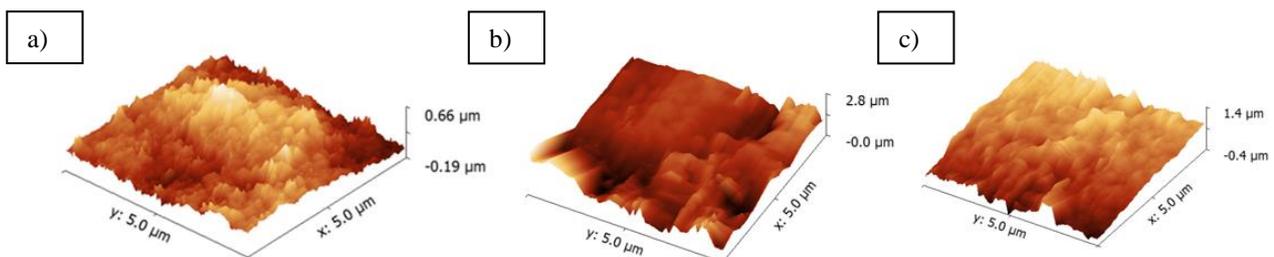


Figure 3. AFM images of the anode films. (a) TiO_2 ; (b) Nb_2O_5 ; (c) ZnO.

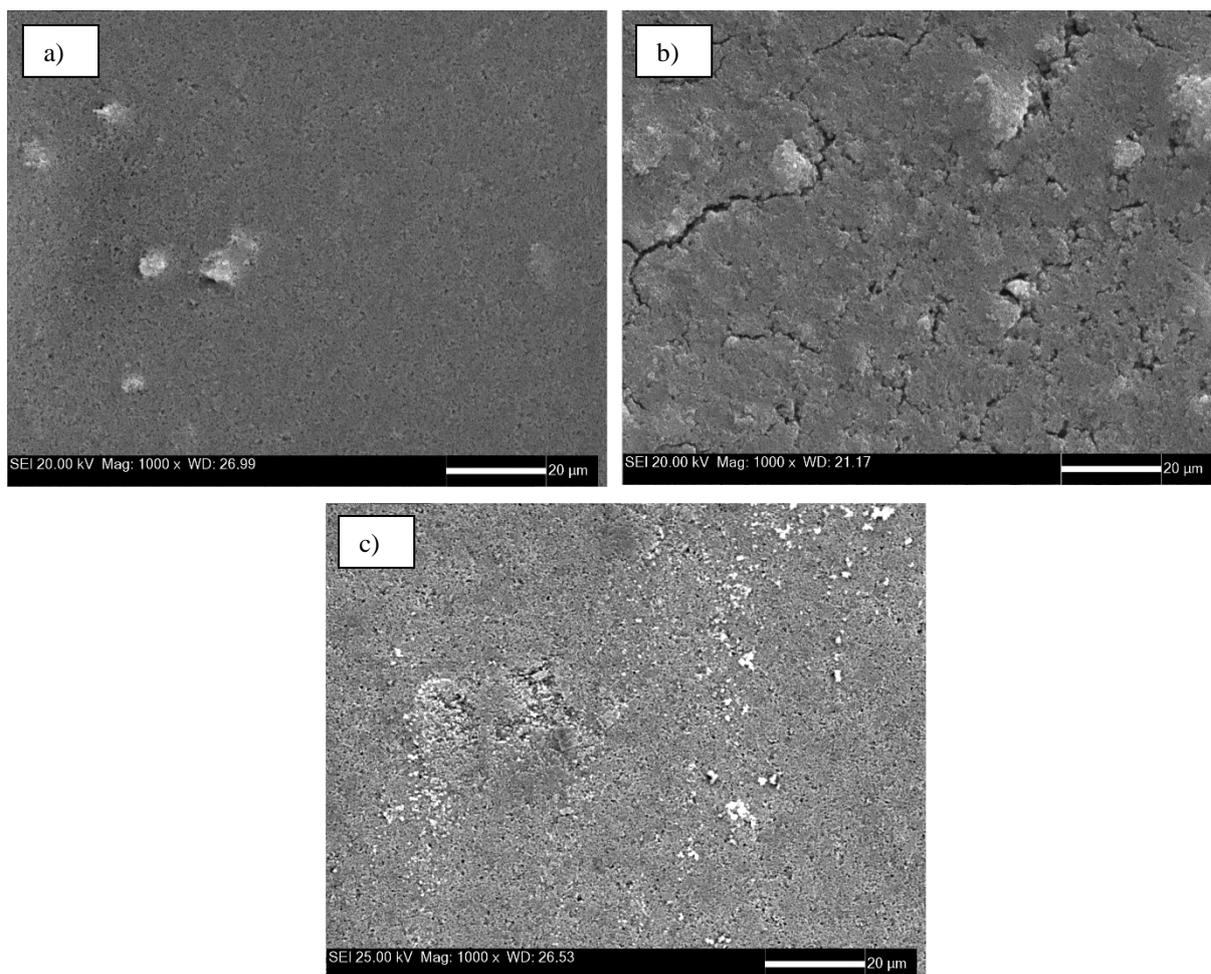


Figure 4. SEM images of the anode films. (a) TiO_2 ; (b) Nb_2O_5 ; (c) ZnO .

The infrared spectroscopy of the Fourier transform (FTIR) was used to obtain an infrared spectrum of absorption, emission and photoconductivity of the DSSC's, showing the compounds characteristics and functional groups present in the dye molecules. The FTIR spectroscopy is an efficient technique for making measurements of the substance's ability to transmit, reflect, or absorb infrared radiation, making it possible to characterize physically traces of the present elements structure, composition and modes of vibration of the samples.

Figure 5 displays the FTIR spectrum of TiO_2 anodes with *Ixora coccinea*, *Thunbergia erecta* and purple cabbage dyes, and shows most of the characteristic peaks of the anthocyanin present in the samples. As can be seen, the spectral region between 1600 and 1700 cm^{-1} admits infrared absorption of $\text{C}=\text{C}$ and can be related to the stretching vibrational mode of the aromatic $\text{C}=\text{C}$ in the anthocyanin molecule. Also, the peak at 1630 cm^{-1} corresponds to the double bond ($\text{C}=\text{C}$) stretching vibration. The broad band in the range of $2100 - 2130\text{ cm}^{-1}$ indicates the presence of $\text{C}-\text{O}-\text{C}$ stretching vibrational mode. Contaminants can also be identified, as can be seen by the strong band of $\text{H}-\text{O}-\text{H}$ (water) present, which affects the capacity of the dye to absorb energy and consequently, affects the overall device's performance.

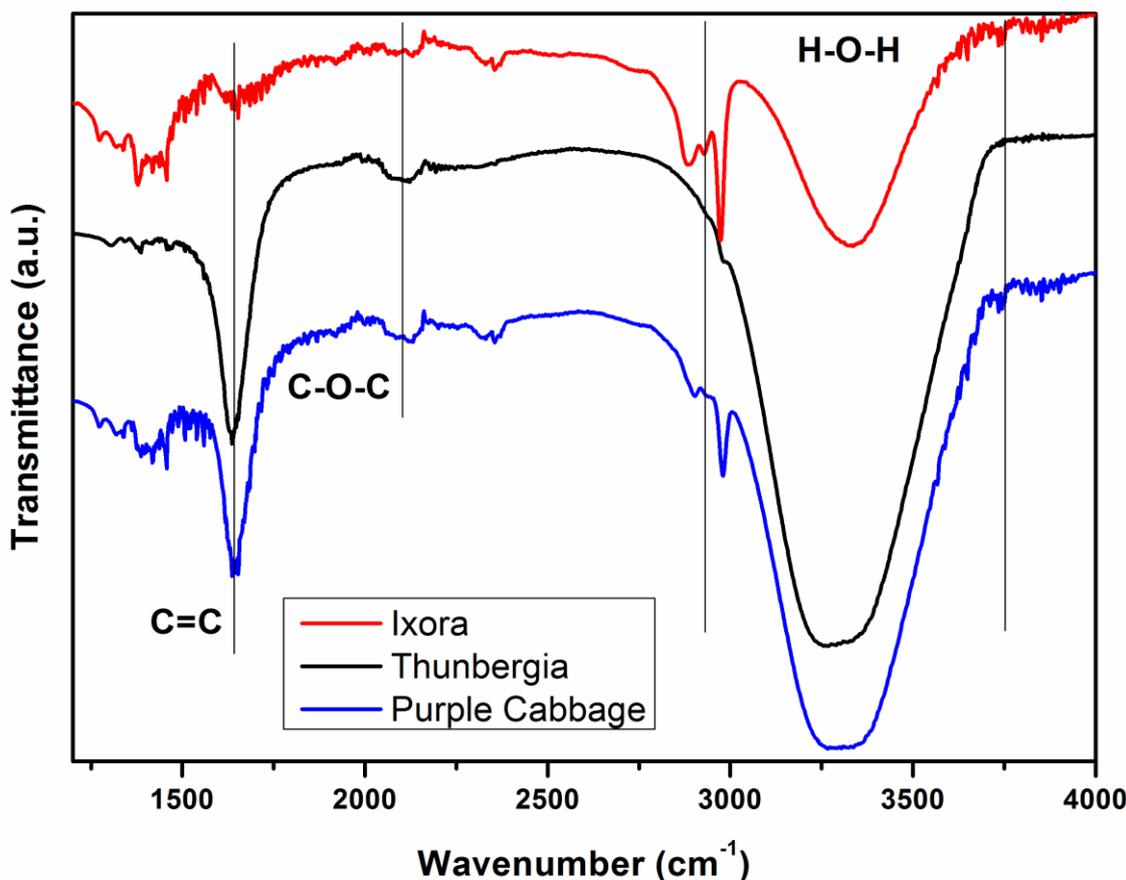


Figure 5. FTIR spectra for the photo-anodes sensitized with different dyes obtained from *Ixora coccinea*, *Thunbergia erecta* and purple cabbage.

A photovoltaic cell produces a potential difference at its terminals due to the sensitization action of the photons over the excitation of a dye. When an electrical load is connected to this cell, a photocurrent will be generated. Thus, an equivalent circuit to the current source in parallel with a diode, associated with the series (R_s) and parallel or shunt (R_{sh}) resistances, can be designed (Liyuan et al., 2006).

One of the main parameters to be observed in the characterization of a photovoltaic cell is its current *versus* voltage curve (Fig. 5a), which can be obtained experimentally by varying the applied load on the cell or can also be estimated mathematically. Once the $I \times V$ curve is drawn, the solar cell performance can be characterized and it is possible to determine its main parameters, such as: 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 obtained experimentally by measuring the voltage at the terminals of an uncharged cell under certain incident temperature and radiation conditions. The short-circuit current (I_{sc}) is the maximum current that the solar cell can supply, and can be obtained short-circuiting the terminals of the cell and measuring the current flowing through the device. The Fill Factor (FF) is given by the relation between the Maximum Power Point (P_{max}) and the product $V_{oc} \times I_{sc}$.

With the coupling of an electrical load to a photovoltaic device, the load resistance increases, the output power will also increase, on comparison to the $I \times V$ curve, between their intersection points. This point is known as the Maximum Power Point (P_{max}), which can be defined as the highest energy point of a solar cell and must be searched by power control systems associated with photovoltaic power generation devices. The values of voltage and current at the point of maximum power are denoted by V_{mp} and I_{mp} , respectively, as can be seen in Figure 5b.

The photovoltaic performance for three different sensitizers and a TiO_2 anode with graphite cathode is depicted by Fig. 6. The Current (I) versus Voltage (V) curves efficiently the promotion of the electrons transfer across the dye/semiconductor interface. The photo-current of the sample using *Ixora coccinea* dye (Fig. 6a) linearly decreased with the potential, which can be attributed to more charge recombination and electron scattering effects at the photo-anode films. The purple cabbage sample has shown the highest open circuit voltage (V_{oc}) and short-circuit current (I_{sc}) values, but also presents a linear decrease. Fig. 6c shows the higher fill factor, that it is related to a better electronic distribution along the semiconductor film, which gives a higher efficiency. The obtained results for the three cells: *Ixora coccinea*, *purple cabbage* and *Thunbergia erecta* are summarized in Table 1.

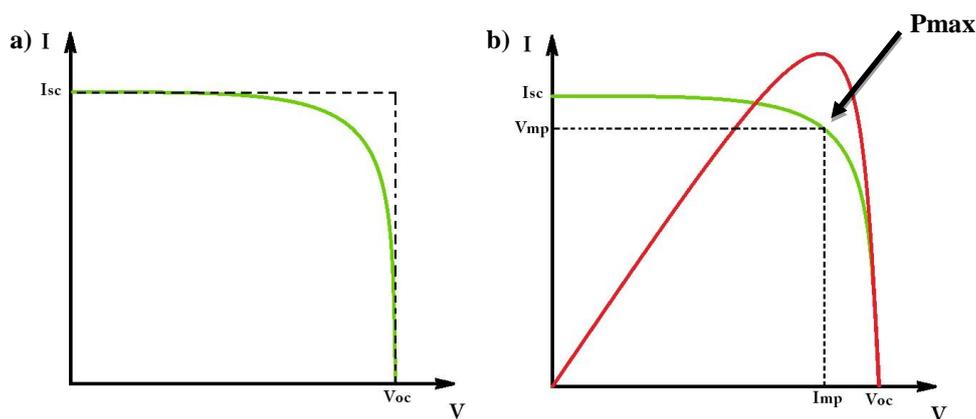


Figure 5. Typical performance curves. (a) Current versus voltage; (b) Current and power versus voltage.

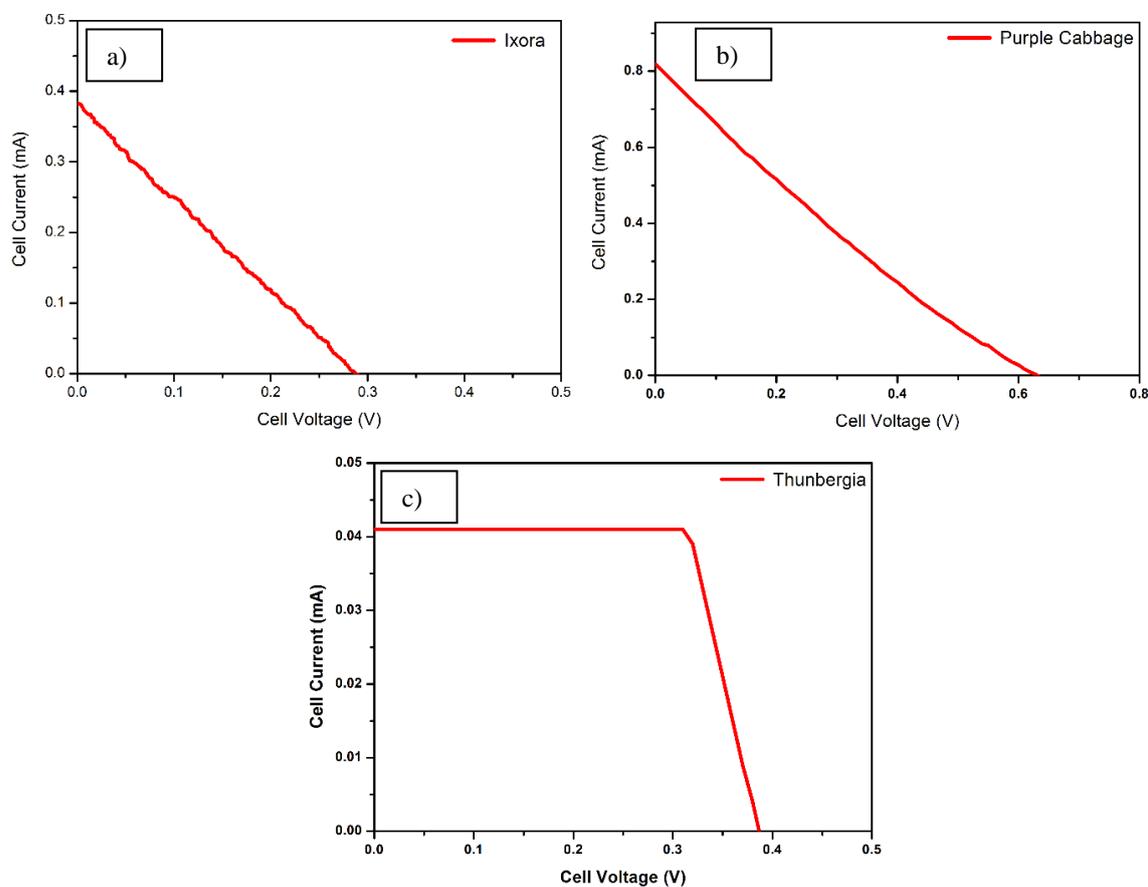


Figure 5. Current vs. voltage curves for different sensitizers. (a) *Ixora*; (b) *Purple cabbage*; (c) *Thunbergia erecta*.

Table 1. Voltage vs. current values of the samples with different sensitizers.

Dye	V_{oc} (mV)	I_{sc} (mA)
<i>Ixora</i>	284	0,387
<i>Purple Cabbage</i>	630	0,819
<i>Thunbergia Erecta</i>	376	0,041

4. CONCLUSIONS

The microstructural, morphological and electrochemical behavior of different spin-coated photo-anodes thin films, sensitized by natural dyes extracted from flowers and vegetables was studied in this research work. The spin coating method was successfully applied for the photo-anodes, resulting in homogenous thin films, for ZnO and TiO₂ substrates. For the Nb₂O₅ paste the results were not satisfactory, since the granulometry of the Nb₂O₅ powder is higher than the ZnO and TiO₂. These analyses were confirmed by SEM and AFM studies. FTIR showed that some fruits containing high concentration of anthocyanin molecules exhibit better efficiency as a dye. This pigment is remarkable for its fast absorption in semiconductor oxides. The photovoltaic performances of the DSSC's results showed that the purple cabbage dye has exhibited the highest values of V_{oc} and I_{sc} , whereas *Thunbergia erecta* showed higher fill factor, which contributes directly to the cell's efficiency. Therefore, this present research work 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, resulting in highly-stable and efficient DSSC's are the challenges to be achieved as requirements for large scale power supply provided by this kind of solar cells.

5. ACKNOWLEDGEMENT

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