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FULL PAPER

Influence of Deposition Methodology and Heating Treatment on Dye Sensitized Solar Cell with Natural Extract

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Abstract:

In this study, it was investigated the photovoltaic parameters of Dye Sensitized Solar Cells (DSSC) and the thin coating morphology of TiO_2 by Doctor Blading and Spin Coating methods, sintered at 450 ºC and 450 ºC with a heating rate of 0.4 ºC s^{-1}, using a natural dye extract from Hibiscus. These properties were studied by scanning electron microscopy (SEM), photochronoamperometry and curves j-V. It was demonstrated that all solar cells produced are photosensitive with an excellent charge injection. The cell with a better energy conversion (jsc = 0.53 mA cm^{-2}; Voc= 0.471 V and FF= 0.518), uniform and flawless morphology was obtained to cell coated by Doctor Blading method, with a heat treatment of 450 ºC/0.4 ºC s^{-1}.

Keywords: anthocyanins; gratzel cells; hibiscus; PV cells

1. Introduction

Dye sensitized solar cell (DSSC) is a low cost solar cell, belonging to the 3rd generation group of PV (photovoltaic) devices [1]. These systems are based on dye sensitization of semiconductor films, as: TiO_2, ZnO, Nb_2O_5, and others [2].

Figure 1 shows a schematic representation of the DSSC assembly and the typical operation of these systems.

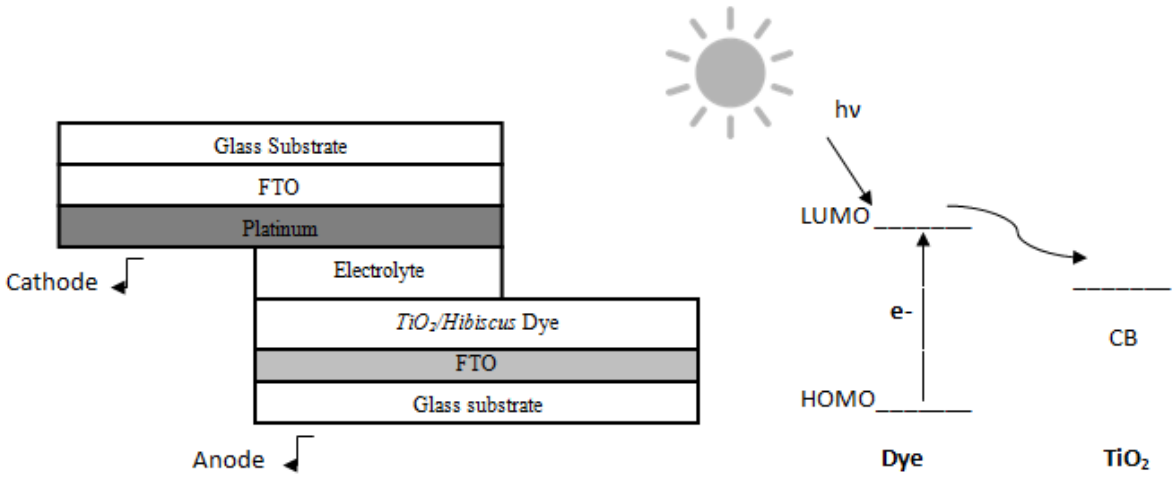

Figure 1.Schematic structure of the DSSC with dye extract from *Hibiscus.*

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DSSC are assembled in a sandwich format and its principle of operation occurs when the dye is irradiated by light and excites to a LUMO state. This state is energetically higher than conduction band edge of the semiconductor (TiO_2) which causes the electron to flow to this band (CB) and consequently to the external circuit, until it reaches the counter electrode (cathode) [3]. In addition, the electrolyte performs in the charge intermediation, regenerating the dye and allowing the flow of current [4, 5]

Dyes have an important role in the development of these systems. The light performance to energy cell transformation, depends on the absorption spectrum and the dye anchorage on the semiconductor surface [3]. Usually, coordination transition metals compounds (commercial dyes) are used as effective sensitizers, but they have a high cost, which leads to the study of new low-cost dyes, such as those extracted from natural products [4]. Natural dyes containing anthocyanins have shown different solar energy efficiencies, such as 0.09%, 0.24%, 1% and others [8]. Auxochromes groups (COOH and OH) present in the structure of these pigments causes them to absorb light within the visible energy range from sunlight, in a less efficient way, when compared to commercial dyes, but presenting a lower cost and adequate deposition technique, making their use viable.

The semiconductor oxide film is deposited on the conductive side of the glass through different techniques, such as Dip Coating, Doctor Blading, Spin Coating, Sputtering and others [10]. Doctor Blading and Spin Coating are simple techniques for the production of films, since they are able to generate films with appropriate porosity and high surface area [11, 12]. Figure 2A-B shows the schematic representation of (2A) Doctor Blading and (2B) Spin coating.

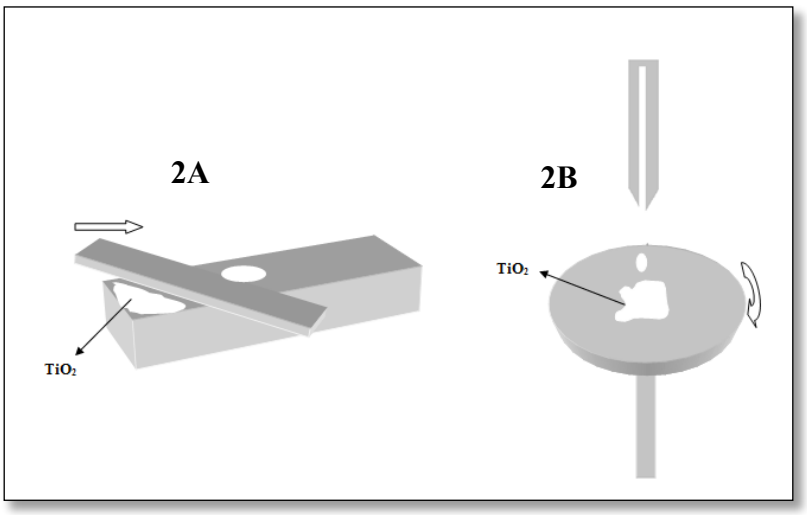

Figure 2. Representation of Doctor Blading (A) and Spin Coating (B) methods.

In the Doctor Blading method, the layer is formed with a few drops of the precursor (TiO_2) when dripped into the substrate, which is spread with an apparatus [7, 13]. In the Spin Coating method, a few drops of precursor are deposited on substrate, at a high speed to spread the coating material to form a layer [14].

These two techniques of deposition, combined with the heating treatment used, generate films, which in all of the photovoltaic system, present different light absorption capacities, due to the different uniformities, porosity and morphology of the films [11, 15]. Therefore, this work have the objective of evaluating the uniformity of the deposited TiO_2 film through these two deposition methodologies, combined with a heat treatment of 450 ºC and 450 ºC with a heating rate of 0.4 ºC s^{-1} (450 ºC/0.4ºC s^{-1}) to verify which of them generates solar cells with better characteristics of film morphology and harvesting light, using an extracted dye from the *Hibiscus* solution.

2. Material and Methods

For the extraction, 6.25 g of Hibiscus flower

was extract in 65 mL with acidified (citric acid; pH=3) ethanol solution (70%) at 5 ºC for 12 h and used as dye [16,17].

2.1 Dye Sensitized Solar Cell Preparation

TiO_2 electrode film (photo anode) was prepared with commercial TiO_2 anatase, by the methodology proposed by Paurussulo [18]. The TiO_2 emulsion was coated by the Doctor Blading and Spin Coating method (540 rpm for 10 s) in a monolayer on FTO (Figure 3A). Then, the coated plate was sintered at 450 ºC and 450 ºC/0.4 ºC s^{-1} for 30 minutes. The *Hibiscus* dye was attached to the TiO_2 surface (Figure 3B), by immersing the coated electrode in the dye solution for 24 h. The platinum counter electrode (Figure 3C) was prepared by cyclic voltammetry using three electrodes, which are the FTO (working electrode), Ag/AgCl (reference electrode) and platinum (counter electrode) at a scan rate of 10 mV s^{-1} with a supporting electrolyte prepared by K_2PtCl_6 $1x10^{-4}$ mol L^{-1} dissolved in 0.1 mol L^{-1} of HCl [19]. It was used 4 cycles with a potential range of V=-0,5V to V=0,5V [19]. The solar cell was assembled in a sandwich format with an electrolyte prepared with 0.5 mol L^{-1} of *tert*-butyl-pyridine, 0.6 mol L^{-1} of tetra-butyl-ammonium iodide, 0.1 mol L^{-1} of lithium iodide and 0.1 mol L^{-1} of resublimated iodine, solubilized in methoxypropionitrile (Figure 3D).

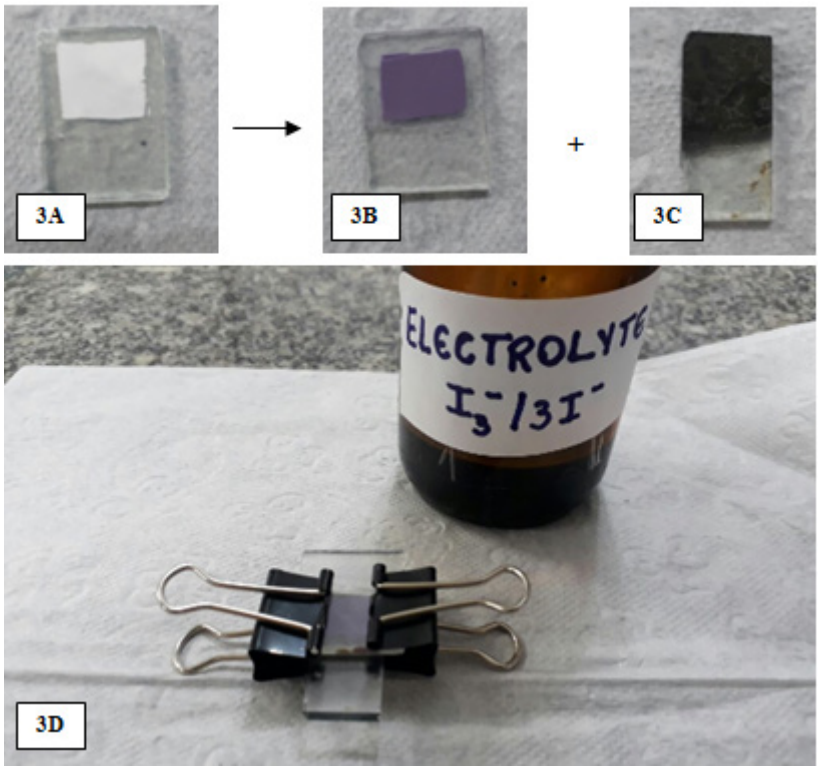

Figure 3. DSSC schematic preparation with (A) FTO/ TiO_2, (B) FTO/TiO_2/Dye working electrode, (C) FTO/Platinum counter electrode and (D) DSSC in sandwich format of photo anode and counter electrode with $I_3^-/3I^-$ electrolyte.

2.2 Characterization Techniques

The anthocyanin present on the TiO_2 film was confirmed by the increase in the color intensity of the film, to a brighter red coloration, when concentrated hydrochloric acid was added, as described by Narayan [20] and Lim et al., [21]. The films morphology and thickness were evaluated by Scanning Electron Microscope (SEM) images (Model Tescan® Vega 3) with a magnification of 1000x. The electrochemistry measurements were obtained under illumination with an AM 1.5G using an intensity of 100 mW cm^{-2} (Model Zhenium Zhaner® with a solar simulator LOT ORIEL LS0106) in an area of 0.2 cm^2 at 25 ºC. The solar energy efficiency (η) was calculated as follows [8]:

$$\eta = \frac{\mathbf{j_{sc}V_{oc}FF}}{\mathbf{Pin}}.\mathbf{100}\%$$

where $\mathbf{j_{sc}}$ is the short circuit current, $\mathbf{P_{in}}$ power of the incident light, $\mathbf{V_{oc}}$ the open circuit potential and **FF** the fill factor of the cell, defined as the radio of the maximum power output from a DSSC to produce the J_{sc} and V_{oc} [8].

3. Results and Discussion

In Figure 4 are shown the SEM images of the TiO_2 film coated by Doctor Blading and Spin Coating methods, sintered with 450 ºC and 450 ºC/0.4 ºC s^{-1}.

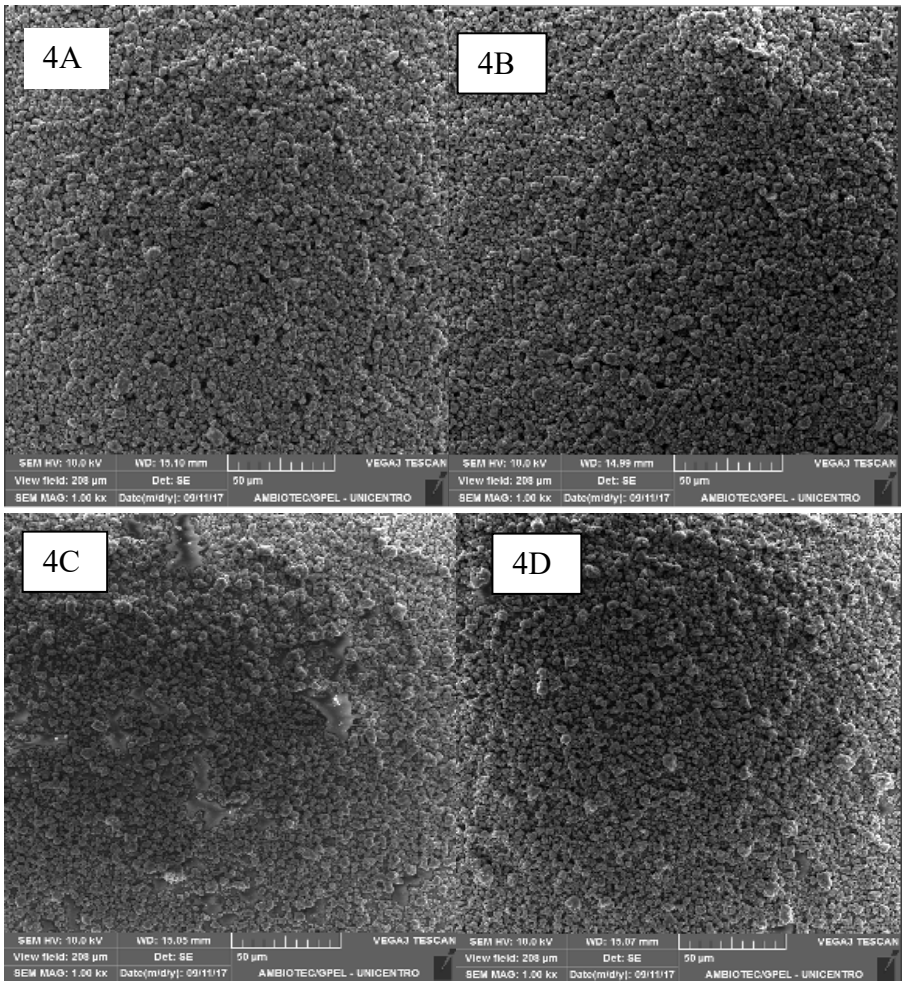

Figure 4. SEM images of the film FTO/TiO_2, coated and sintered by (A) Doctor Blading at 450 ºC/0.4 ºC s^{-1} and (B) at 450 ºC (C) Spin Coating at 450 ºC /0.4 ºC s^{-1} and (D) at 450 ºC.

The TiO_2 films coated by the Doctor Blading method produced better morphological results, because of their homogeneity, without cracks and flaws when compared to the thin coated of the Spin Coating method, being necessary more layers, to form more uniform films, consequently having a higher cost. About the sintering process, there were no differentiations in the morphology, confirming that the sintering is more related with the porosity of the films, that cannot be analyzed with this technique, being necessary other methods to verify this parameter [22]. In Figure 5 and Table 1 are shown the thickness of the film, obtained by the SEM images.

Table 1. Thickeness of the films coated by Doctor Blading and Spin coating method sintered at different treatment.

Deposition	Sintering	Thickness /µm
Doctor Blading	450 ºC	40.14
Spin Coating	450 ºC	6.53
Doctor Blading	450 ºC/0.4 ºC s^{-1}	29.21
Spin Coating	450 ºC/0.4 ºC s^{-1}	4.39

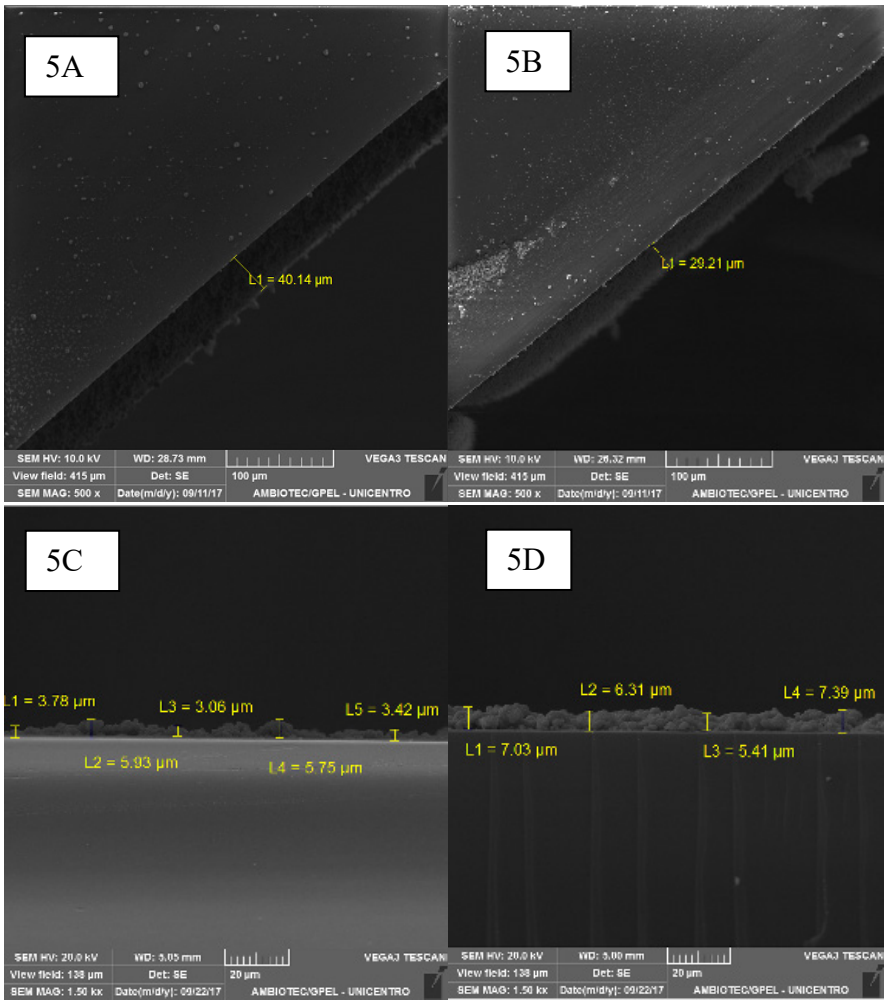

Figure 5. SEM images and thickness of the TiO_2 film coated and sintered by (A) Doctor blade at 450 ºC/0.4 ºC $s^{-1}$and (B) at 450 ºC (C) Spin Coating at 450 ºC /0.4 ºC s^{-1} and (D) at 450 ºC.

The results of Figure 5A-D and Table 1 indicate that the films deposited by Doctor Blading present higher thickness when compared to those deposited by Spin Coating. Both quantities of the semiconductor material are added under the FTO to deposition, but this vast variation in thickness is due to the great waste when using the Spin Coating, due to high rotation, much of the material is lost, generating less thick films. Doctor Blading method generate films with better morphology, but their thickness is variable, depending on the strength used to spread the oxide on substrate, obtaining films with different thicknesses, as evidenced in SEM images of Figure 5A-D. Photocronoamperometry measurements are shown in Figure 6 to cells analyzed.

All solar cells produced are photosensitive, because when there was incidence light on them, the cells showed an instantaneous increase of the current as depicted in Figure 6. This capability of instantaneous injection of loads is an important parameter for solar devices, since a good loading/unloading time proves that the systems present rapid interfacial reactions [23].

Films sintered at 450 ºC/0.4 ºC s^{-1} using a Doctor Blading method, produced a cell with highest current density, close to j = 0.48 mA cm^{-2}. This deposition methodology generates thicker films and with higher amounts of TiO_2 than Spin Coating method, facilitating the adsorption of the dye on the surface of the oxide. Sintering with heating rate also influences the density of the current that the cell generates, improving the light absorption [23]. The cells produced with heating rate of 0.4º C/s^{-1} by Spin Coating method presented low values of photocurrent when compared to Doctor Blading method, but the thermal treatment, potentiated in 0.07 mA cm^{-2} the photocronoamperometry measurement. In Figure 7 are shown the j-V characteristics of the cells analyzed, and in Table 2 the photovoltaic parameters.

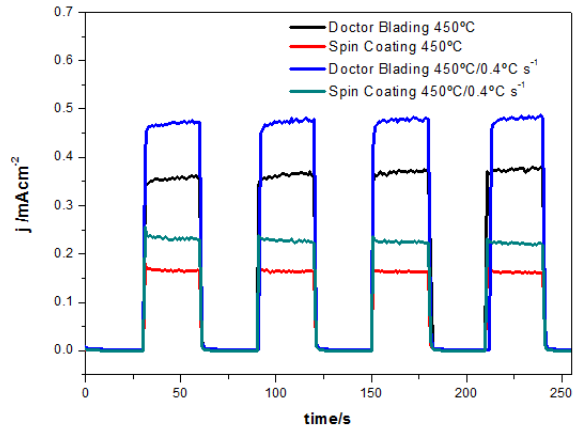

Figure 6. Photocronoamperometry to cells with TiO_2 film coated by Doctor Blading and Spin Coating methods, with FTO/TiO_2 film sintered at 450 ºC and 450 ºC/0.4 ºC s^{-1} under solar illumination of 100 mW cm^{-2}.

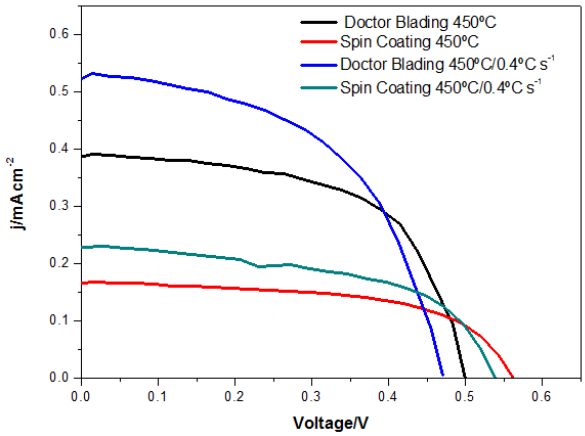

Figure7. Photocurrent density voltage curves to DSSC coated by Doctor Blading and Spin Coating methods with FTO/TiO_2 film sintered at 450 ºC and 450 ºC/0.4 ºC s^{-1} under solar illumination of 100 mW cm^{-2}.

The parameters extracted from the j-V curves, verified that the sintering at 450 ºC /0.4 ºC s^{-1} potentiated the photoelectrochemical results of current generated by the cell. The best J_{SC} result obtained, equivalent to 0.39 mA cm^{-2}, was the cell with heating treatment deposited via Doctor Blading. This high value in comparison to the others, was fundamental for the energy conversion efficiency of the cell, which reached 0.13%, being 0.02% higher when compared to the sintered cell at 450 ºC via the same deposition methodology.

In spite of the higher values of current density and energy conversion efficiency of the cells produced with the sintering treatment of 450 ºC/0.4 ºC s^{-1}, the V_{OC} had a slight decrease of 0.03V for the films deposited by Doctor Blading and 0.02V for Spin Coating methods. The open circuit potential is related to the processes of charge recombination (process in which photoinjected electrons are transferred across the TiO_2-electrolyte interface to oxidized species of the redox couple [2],) as described by Viomar et al., [19], Frank et al., [2] and Guimaraes et al., [24]. For both samples sintered with heating ramp, they presented lower values of V_{OC}, proving that the charge recombination processes were maximized, which is not productive for the cell, since the electron that is in the semiconductor recombines with the electrolyte, before running through an external circuit, which results in an increase in the temperature of the cell, generating energy losses due to heat [19, 23,25]. This fact is also evidenced by the FF, since smaller results were found when the thermal treatment of 450/0.4 ºC s^{-1} is used, proving that these are more distant of ideality [23, 25].

Table 2. Photovoltaic parameters extracted from current vs potential curves

Deposition-Sintering	j_{sc} /mA cm^{-2}	V_{oc} /V	FF	η /%
Doctor Blading-450 ºC	0.39	0.500	0.588	0.11
Spin Coating-450 ºC	0.17	0.562	0.581	0.06
Doctor Blading-450/0.4 ºC s^{-1}	0.53	0.471	0.518	0.13
Spin Coating-450ºC/0.4 ºC s^{-1}	0.23	0.539	0.536	0.07

4. Conclusions

The Doctor Blading Method can generate films with higher thickness and with a better homogeneity compared to the Spin Coating method. The films sintered at 450 ºC with heating rate of 0.4 ºC s^{-1} have better current density, but the recombination process with this treatment is maximized, causing a decrease of Voc, observed for both methodologies of deposition. These results obtained, show that Doctor Blading method is more suitable than Spin Coating method, to produce films, used in DSSC devices, to reduction of raw materials and for the

improvement of the cells parameters.

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