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Effect of TiO_2 Photoanode Films on the Performance of Dye Sensitized Solar Cell with *Rauvolfia Vomitoria* Fruit Extract

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Abstract Dye sensitized solar cells (DSSC) were investigated using *Rauvolfia vomitoria* fruit extract as natural sensitized of TiO_2 thin film. The cells were evaluated for various thicknesses of photoanode. The optical properties were analysed 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 results showed that the optimum thickness is 10 µm which achieved a short-circuit current density (J_{sc}) of 0.1 mA/cm² and an open voltage (V_{oc}) of 0.65 V while the conversion efficiency (η) is 0.055%.

Keywords: *DSSC, natural dye, photoanode thickness, energy conversion, efficiency*

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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 from transparent conductive oxide (TCO). 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 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 were extracted from leaves, barks, flowers, fruits, and used as molecular sensitizers. The dyes contain anthocyanins, betacyanins, carotenoid, 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%. However, DSSC efficiencies were stilled lower, compared to the other generation PV cells [9]. Researchers tried continually to overcome the issue of low efficiency in DSSC.

Senguta et al. reviewed several parameters to improve the photoanode performance in order to get high power conversion efficiency [10]. The photoanode film thickness and metal-TO_2 nanocomposites were found to be the ways to improve the efficiency. In DSSC, anode film thickness played an important role in the high generation of charge collection and reduction of the charge recombination rate [11]. Kumari et al. [12], studied the photovoltaic properties at different photoanode thicknesses and reported that 12 µm thickness was enough to enhance the photovoltaic activity.

In this paper, we explored a relatively simple and less expensive method to develop DSSC cells using a fraction extracted from *Rauvolfia vomitoria* fruit, a local plant Moreover, we studied the performance of DSSC obtained. Titanium dioxide (TiO_2), which provided a wide band gap, served as an electron transport to produce DSSC cells. We reported the I-V characteristic performances by varying

the film thicknesses. 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. The morphology of the TiO_2 surface was observed using a scanning electron microscope (SEM). The optoelectronic parameters of DSSC were obtained through exposure to the illumination of a halogen lamp of 78 mW / cm².

2. Experimental Details

2.1. Materials

Titanium dioxide TiO_2 (Ti-nanoxide, T / SP), and platinum (platisol, T / SP) were used to make electrodes. 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.

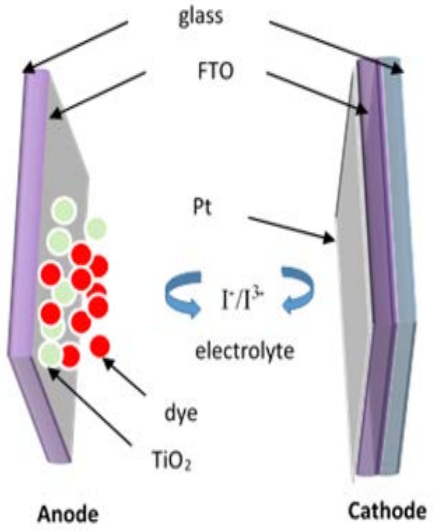

Figure 1. Diagram of dye sensitized solar cell components

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 the reference electrode, and a platinum wire as counter-electrode.

The acquisition of 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 spectrum was recorded with PERKIN ELMER (Spectrum 65, UK) spectrometer. The surface morphology of TiO_2 and the thickness were carried out with a scanning electron microscope (SEM, HIROX, model SH 4000 M, France).

2.3. Dye Extraction

The dyes were extracted from the fruits of *Rauvolfia vomitoria*, a local plant. The ripe fruits were washed with water to remove dust particles and then grounded with a super blender to obtain a paste. Then, 100g of the resulting paste was extracted three times by maceration with 1000 mL of acetone (1:10, m/V) at 25°C. The obtained sample was filtered with filter paper (Whatman), then concentrated to dryness under vacuum at 40°C using a rotary evaporator. The resulting concentrated was dissolved in water and successively with hexane and ethyl acetate. After evaporation, the fraction of hexane was used as a dye.

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). 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, TiO_2-coated plate was heated at 80 ° C for 5 minutes, then gradually at 450° C for 40 minutes with a hot plate. Next, TiO_2 electrode was removed from the hot plate and cooled down. 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, 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

In order to investigate the dye on TiO_2 thin film electrode performance, sandwich type cells with 1 mm of hole were made on 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 and 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 was 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. Samples were made with various thicknesses of photoanode. DSSC cell was placed in the dark before any measurement.

3. Results and Discussion

3.1. Surface Morphology of TiO_2 Electrode

Figure 2 shows a porous structure of TiO_2 with various holes. The dye fill the different holes. This connection

permits the transfer of the electron from the dye to the TiO_2 semiconductor. However, the morphologies are directly related to the thickness film. The smoothest surfaces were observed on the titanium electrode without crack for low thicknesses. As the thickness increases, cracks and roughness appear [11,12,13].

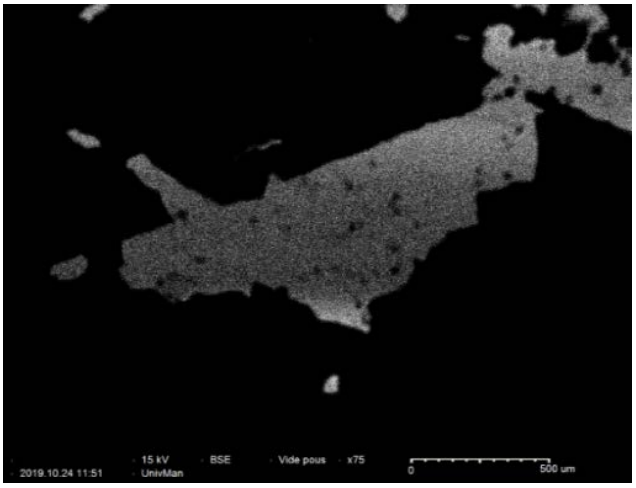

Figure 2. Rauvolfia v. dye adsorbed on TiO_2

3.2. Dye Absorption Spectrum

The absorbance of the dye extracted from *Rauvolfia v.*, observed in Figure 3 indicates a high absorption between 400 nm and 500 nm, in the visible range. An examination of Figure 3 reveals that a peak appears at 459.25 nm and 486.33 nm. Similarly, the absorption band corresponds to carotenoid pigments, as reported [14,15]. Due to their absorbance, carotenoids are candidates for DSSC sensitization [16,17]. The presence of carbonyl and hydroxyl groups in their structure allows them to adhere easily to titanium dioxide and facilitate photovoltaic conversion [18].

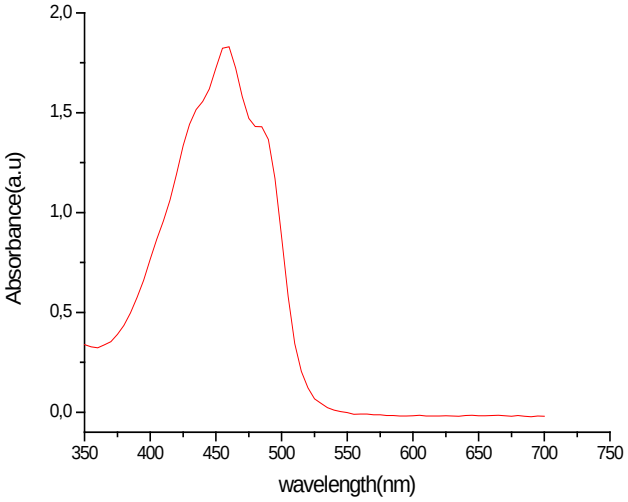

Figure 3. Absorption spectrum of Rauvolfia v. dye

3.3. Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectroscopic analysis in Figure 4, revealed the presence of three bands, one weak and two strong bands between 3000.4 and 2851.9 cm^{-1}, attributed to aliphatic C-H stretching vibration of CH_2 and CH_3 groups. The bands observed at 1464.34 and 1377.60 cm^{-1} confirmed the presence of CH_2 and CH_3 groups, respectively. The spectrum also indicated the presence of a strong absorption band at 1742.1 cm^{-1} corresponding to carbonyl moiety of ester function and was confirmed by the presence of a band characteristic of aliphatic C-O bond at 1118.5 cm^{-1}.

The presence of the bands at 1118.5 cm^{-1} on the one hand and 1161.59 cm^{-1} on the other can be assigned to the presence of the aromatic bond. The fraction of *Rauvolfia* dye has the following characteristic groups of ester, carbonyl (C = O) and will be adsorbed to TiO_2 thin layer.

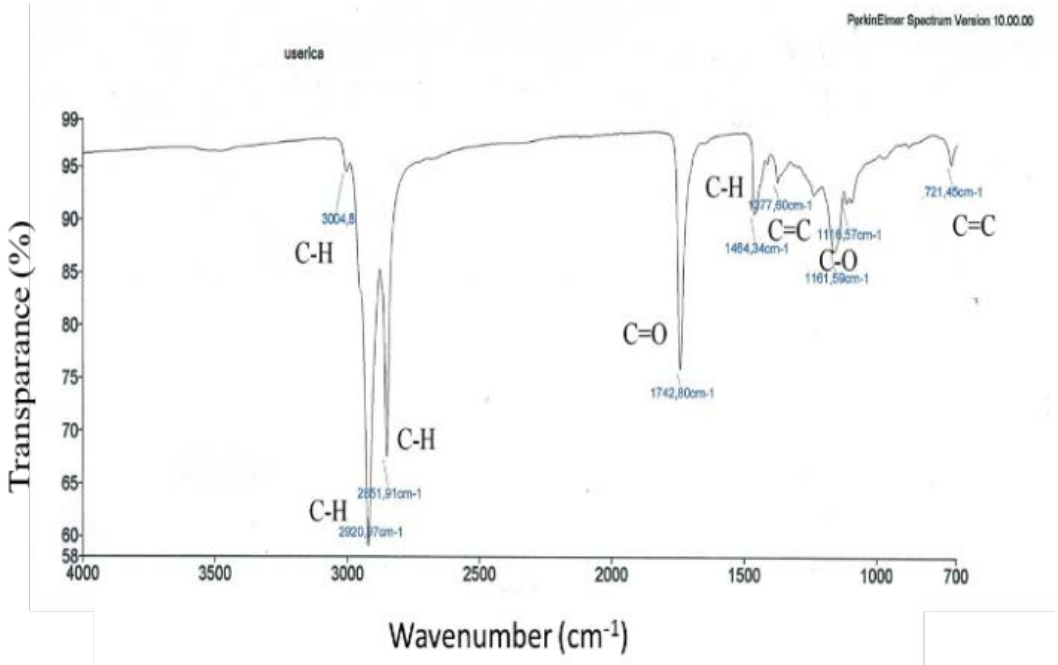

Figure 4. FTIR spectrum of Rauvolfia v. dye

3.4. Electrochemical Study of the Dye

HOMO and LUMO energy levels of the dye fraction were evaluated in the cyclic voltammetry method. In this context, the working electrode is a platinum disc of 3mm of diameter with Ag / AgCl as the reference electrode and a platinum wire counter electrode. Tetrabutylammonium tetrafluoroborate (TBATFB) at 0.1 M was 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):

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

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

Where: E_{ox} and E_{red} are respectively the oxidation and reduction potentials of the extract taken from the voltammograms (Figure 5) which show reversible cycles.

Following the oxidation and reduction potentials, the calculated HOMO and LUMO levels are 4.98 eV and 2.56 eV respectively. LUMO level of the dyes is above the potential 4.4 eV of I^-/ I^{3-} redox couple electrolyte and indicates that, there is a driving force for the dye generation

Besides, HOMO energy level of the dye is higher compared to the TiO_2 extraction work (3.2 eV). These different HOMO and TiO_2 energy positions indicate that electron transfer from the dye to TiO_2 is possible.

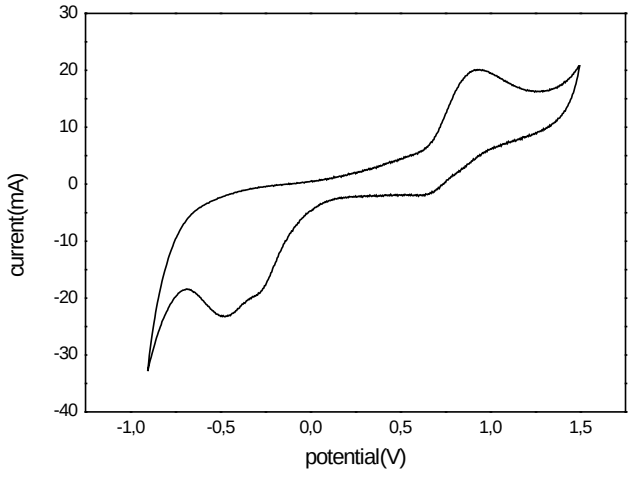

Figure 5. Cyclic voltammogram of *Rauvolfia v.* dye in acetonitrile solution containing 0.1 M TBATFB supporting electrolyte at 50 mV/s rate

3.4. Effect of the Photoanode Thicknesses on the Performance of the Dye Solar Cell

The performances of the dye solar cells (DSSC) were evaluated with the photovoltaic parameters. In the dark, we observed negligible open-circuit voltage (V_{oc}) and current density. The conversion efficiency (η) and the fill factor (FF) were calculated according to the following relations:

$$FF = \frac{J_{\max} * V_{\max}}{J_{sc} * V_{oc}} \quad (3)$$

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

where, J_{sc} is the short-circuit current density, (J_{max}) is the maximum current density, V_{max} is the maximum voltage, V_{oc} is the open-circuit voltage were determined from the (J-V) curve in Figure 6 and the incident light intensity (P_{in}). The photoelectric parameters of the cells from different photoanode films are listed in Table 1.

As seen from Figure 6 and Table 1, the short-circuit current density (Jsc) increases abruptly with increasing thickness from 5µm to 10µm, and then gradually decreases afterward. Variations in J_{sc} can be explained by the generation of photons. An increase in electrode thickness will directly increase the internal pore surface area and absorption capacity of the dye. Therefore, a thicker electrode can absorb more photons, leading to a higher Jsc. However, if the electrode thickness is greater than the depth of light penetration, the number of photons useful for electron generation will reach a limit and, therefore, J_{sc} cannot be increased beyond the penetration depth, resulting in more recombination centres and electron losses [13,14,15,16,17,18,19]. Besides, V_{oc} decrease by increasing thickness, related to the back transfer of the electron between I_3^- ions and the conduction band electrons in TiO_2 electrode [20]. Thus, the optimum thickness was, 10 µm to achieve a higher photocurrent and power conversion efficiency of 0.055%. Dye extracted from saffron (0.06%) [21], lycopene(0.057%) [22], gave a similar efficiency matched to our dye. However, the power conversion of DSSC made with natural dye remained low compared to the stable complexed ruthenium [23].

Table 1. Photovoltaic parameters of DSSC for TiO_2 films

Thickness (µm)	Jsc(A/cm²)	Voc(V)	FF	η(%)
5	9.47E-5	0.72	0.60	0.053
7	9.94E-5	0.69	0.61	0.052
10	**1.009E-4**	**0.65**	**0.65**	**0.055**
14	1.003E-4	0.62	0.57	0.045
15	1.001E-4	0.61	0.56	0.044
18	9.946E-5	0.59	0.56	0.042

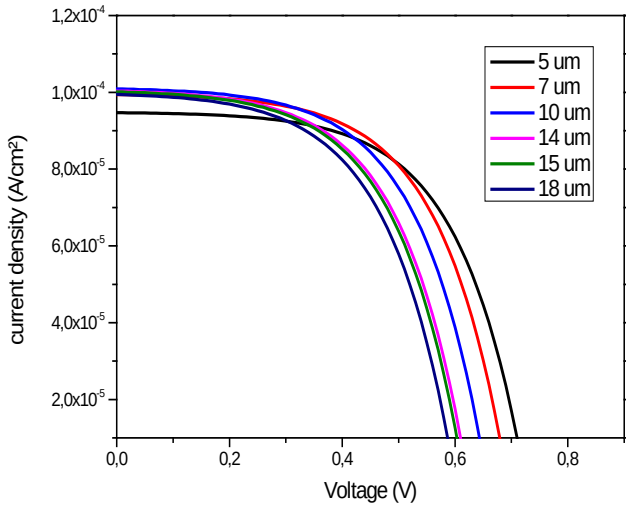

Figure 6. I-V characteristic of different TiO_2 films

4. Conclusion

The study showed the effect of various photoanode thicknesses on the photovoltaic response of dye solar cells (DSSC) using *Rauvolfia Vomitoria* fruit extract as a natural sensitizer. The obtained DSSC with 10 µm of TiO_2 thin film exhibited good photovoltaic properties. The highest photocurrent and power conversion efficiency achieved, were respectively 0.1 mA/cm² and 0.055%. Despite their fair efficiency, the natural dyes used in DSSC cells are promising. These dyes are easy to elaborate, and environmentally friendly.

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