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STUDYING OF NATURAL DYES PROPERTIES AS PHOTO-SENSITIZER FOR DYE SENSITIZED SOLAR CELLS (DSSC)

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ABSTRACT

Optical and structural properties of pigments plants to be used as photo-sensitizer in Dye Sensitized Solar Cell DSSC have been studied. Several types of natural dyes belonging to Anthocyanin (Raspberries, Shami-berries, Grapes, Hibiscus, Chlorophyll, and a combination of dyes) have been performed.

Dye sensitized solar cells have been made using SOL-GEL technique in preparing thin film components FTO/TiO_2 / Natural Dye / Electrolyte / Pt / FTO. The performances for different types of natural dyes. have been tested.

The DSSC prepared using a combination of natural dyes (Raspberries, Hibiscus, Chlorophyll) by the ratio (1:1:1) as photo-sensitizer, showed the better photovoltaic performance compared with other single dyes.

The efficiency of DSSC prepared was η = 3.04%, the fill factor FF = 60% for cell area a = 4cm^2, short circuit current J_{SC} = 0.6 mAcm^{-2} and open circuit voltage Voc = 0.42 V.

Keywords: Dye-sensitized solar cells; Natural dyes; TiO_2; Anthocyanin; Photo-sensitizer.

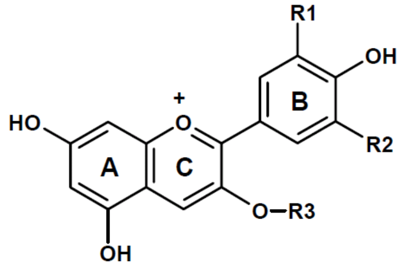
1. INTRODUCTION

A dye-sensitized solar cell (DSSC) is a device for the conversion of visible light power into electricity, based on the sensitization of wide band gap semiconductors [1]. The performance of the cell mainly depends on a dye used as photo-sensitizer. The absorption spectrum of the dye and the anchorage of the dye to the surface of TiO_2 are important parameters determining the efficiency of the cell [2]. Generally, transition metal coordination compounds (ruthenium polypyridyl complexes) are used as the effective sensitizers, due to their intense charge-transfer absorption in the whole visible range. However, ruthenium polypyridyl complexes contain a heavy metal, which is undesirable from point of view of the environmental aspects [3]. Moreover, the process to synthesize the complexes is complicated and costly. [4]. Alternatively, natural dyes can be used for the same purpose with an acceptable efficiency [5–7]. The advantages of natural dyes include their availability and low cost [3]. The sensitization of wide band gap semiconductors using natural pigments is usually ascribed to anthocyanins [1, 2].

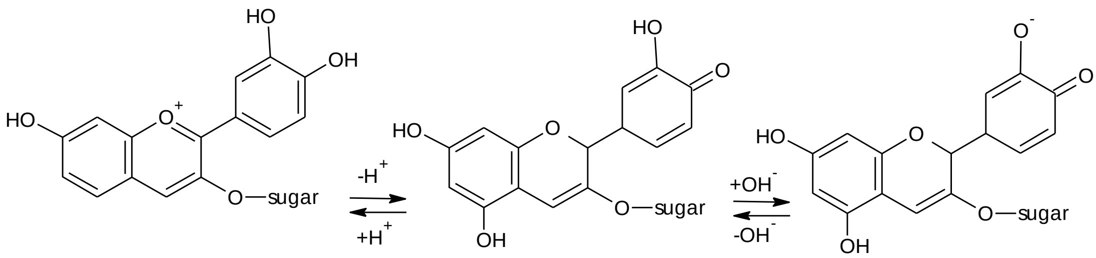
The anthocyanins belong to the group of natural dyes responsible for several colors in the red–blue range, found in fruits, flowers and leafs of plants. Carbonyl and hydroxyl groups present in the anthocyanin molecule can be bound to the surface of a porous TiO_2 film. This makes electron transfer from the anthocyanin molecule to the conduction band of TiO_2 [7]. As reported [1-7], anthocyanins from various plants gave different sensitizing performances. In this paper, home made DSSCs were prepared using natural dyes extracted from Raspberries, Shami-berries, Grapes, Hibiscus, Chlorophyll, as photo-sensitizers, these fruits, flowers and leafs are abundant in Syrian countries, and rich in anthocyanins. The efficiency of the solar cells related to dye structures is discussed. This would be an useful information for selecting anthocyanins and also leads to the synthesis of dyes for DSSCs. The performance of DSSCs using a combination of dyes was also investigated.

II. NATURAL DYES OF ANTHOCYANINS

Anthocyanins are the largest group of water-soluble pigments widespread in the plant kingdom. They are responsible for the colors displayed by many flowers, fruits and leafs of angiosperms.[6] Chemically, these flavonoids are most commonly based on six anthocyanidins: pelargonidin, cyanidin, peonidin, delphinidin, petunidin and malvidin. according to the following general type:



These compounds differ in the methoxyl and hydroxyl substitution pattern of ring (B) as shown in Table.1 and the average amount of Anthocyanins differs in the plant as shown in Table.2. The more widespread anthocyanins in fruits are (3-*O*-glycosides).
The important characteristic of these dyes is that the colors are influenced by the pH of aqueous solutions according to the following general representation:



pH<3 (red) pH=7-8 (violet) pH>1 1(blue)

Table 1: Structures of the major anthocyanin-3-O-glucoside presents in fruits and the respective wavelength at the maximum of absorption in the visible region [6]

Anthocyanin	R1	R2	λ_{max} (nm)	
			R3=H	R3=gluc
Delphinidin	OH	OH	546	541
Petunidin	OH	OCH3	543	540
Malvidin	OCH3	OCH3	542	538
Cyanidin	OH	H	535	530
Peonidin	OCH3	H	532	528
Pelargonidin	H	H	520	516

Table 2: Average amount of Anthocyanins in some foodstuffs [6]

	Anthocyanin source	concentration mg.kg^{-1}
2	Blueberry	825–4200
3	Cherry	20–4500
4	Chokeberry	5060–10000
5	Cranberry	600–2000
6	Currant (black)	1300–4000
8	Red grapes	300–7500
9	Blood orange	2000
10	Plum	20–250
12	Strawberry	150–350
13	Raspberry(black)	1700–4277

III. STRUCTURE OF DYE-SENSITIZED SOLAR CELLS

A dye-sensitized solar cell consists of [7] two conducting glass electrodes in a sandwich arrangement. Each layer has a specific function in the cell. The glass electrodes are transparent which allows the light to pass through the cell. The F:SnO_2 (FTO) coating is a transparent, conductive layer. The titanium dioxide serves as a holding place for the dye. The dye molecules collect light and produce excited electrons which cause a current in the cell. The iodide electrolyte layer acts as a source for electron replacement. The bottom conductive layer is coated with platinum or graphite so that light does not pass through the bottom layer.

Dye-sensitized solar cells produce electricity through electron transfer. Sunlight passes through the conductive glass electrode. The dye absorbs the photons of light and one of the electrons in the dye goes from a ground state to an excited state. The excited electron jumps to the titanium dioxide layer and diffuses across the film. The electron then reaches the conductive electrode, travels through the wire, and reaches the counter electrode. The dye molecule, having lost an electron to the titanium dioxide, is oxidized. The dye obtains electron from the iodine electrolyte and the dye goes back to ground state. This causes the iodine to become oxidized. When the original lost electron reaches the counter electrode, it gives the electron back to the electrolyte as shown in figure 1

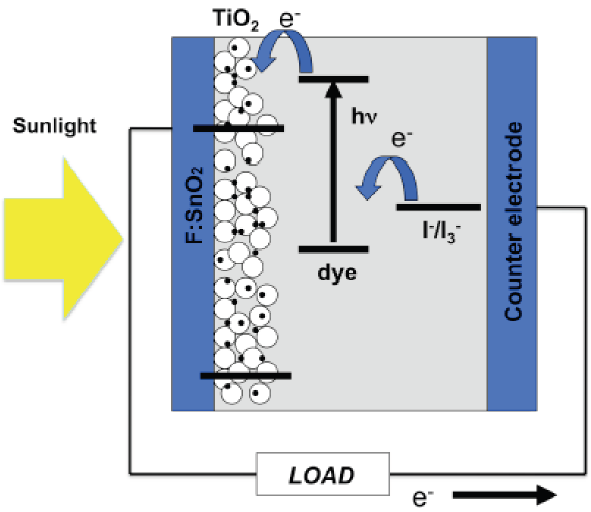


Figure 1: Dye sensitized solar cell DSSC diagram

Dye sensitizers serve as the solar energy absorbers in DSSC, whose properties will have important effect on the light harvesting efficiency and the overall photoelectric conversion efficiency. The ideal sensitizer for DSSC should absorb all light below a threshold wavelength of about 920 nm [7]. In addition, it should be firmly grafted to the semiconductor oxide surface and injected electrons to the conduction band with a quantum yield of unity. Its redox potential should be sufficiently high that it can be regenerated rapidly via electron donation from the electrolyte or a hole conductor. Finally, it should be stable enough to sustain at least 10^8 redox turnovers under illumination corresponding to about 20 years of exposure to natural light .

The sensitizers used in DSSC were divided into two types: inorganic dye (includes metal complex, such as polypyridyl complexes of ruthenium and osmium) and organic dye (includes natural organic dye and synthetical organic dye) according to the structure.

A requirement for the organic dye structure is that it contains several =O or –OH groups capable of chelating to the Ti^{IV} sites on the titanium dioxide surface [2] as shown in Fig. 2. So some natural pigments are not suitable for the DSSC work like strawberries [4].

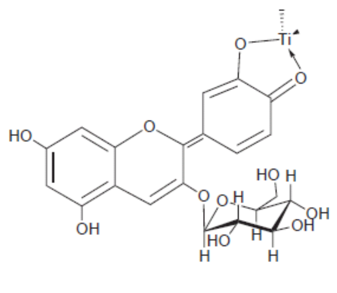


Figure 2: Cyanin-Ti^{IV} complex formed via the adsorption of the dye from solution onto the titanium dioxide surface. [4]

IV. EXPERIMENTAL SECTION

4.1 Natural dyes preparation

The anthocyanins pigments was isolated from natural plants (Raspberries, Shami-berries, Grapes, Hibiscus, green leafs) according to the following procedure [5]:
100 g of natural fruits were crushed in 50 ml solution of methanol/acetic acid/water (25:4:21), and filtered with (whatman filter paper 541-110 mmØ). the filtered extract was passed through a Sephadex LH 20 (Pharmacia) column in the same solvent.
Chlorophyll were extracted from green leafs according to the following procedure [4]: 50 gr of fresh young green Lemon leafs are ground in a mortar with 50 ml of acetone. The dark-green acetone solution obtained from this procedure is filtered according to the same procedure previously, and stored into a dark bottle, at 10 ^{o}C for the subsequent optical studies.

4.2 Optical measurements of dyes solutions

The optical measurements was made using UV-VIS spectroscopy for dyes prepared (Raspberries, Shami-berries, Grapes, Hibiscus, Chlorophyll , and a combination of dyes according to the mixing ratios (1:1:1)). The absorption spectra showed the presence of distinct absorption peaks in the visible region for each type of dye.

Rasperry pigment: optical absorbance spectrum for Raspberry pigment shows a maximum absorption peak in the visible region at the 540 nm wavelength according to absorbance value 55%, as shown in Figure (3).

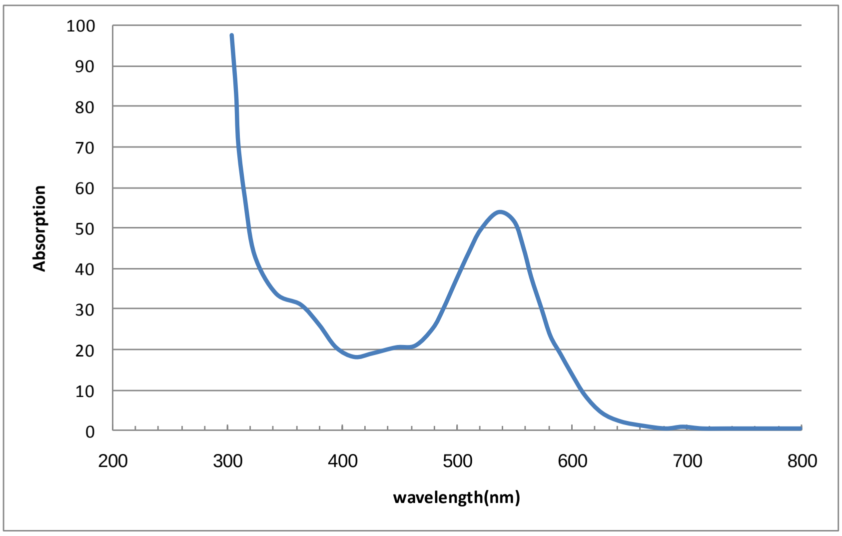


Figure 3: absorption spectrum of Raspberries dye solution

Shami-berries pigment: optical absorbance spectrum for Shami-berries pigment shows a maximum absorption peak in the visible region at the 534 nm wavelength according to absorbance value 46%, as shown in Figure (4).

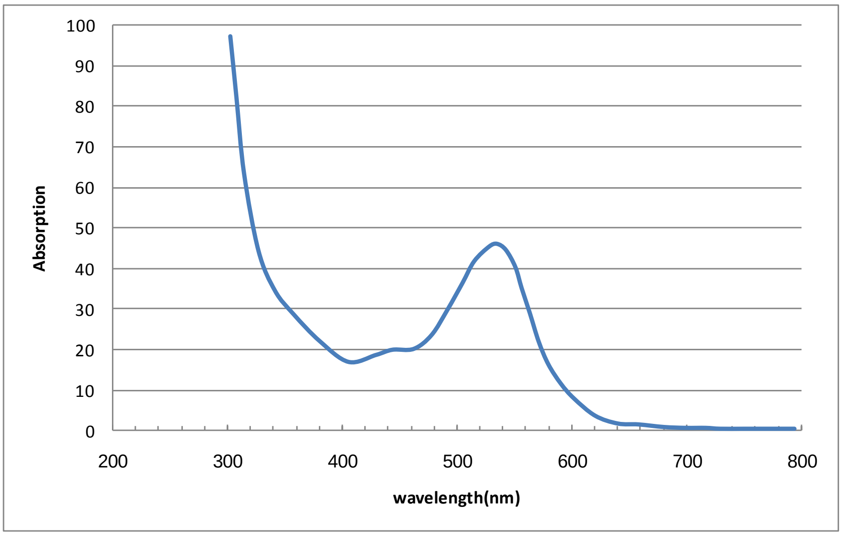


Figure 4:: absorption spectrum of Shami-berries dye solution

Grapes pigment: optical absorbance spectrum for Grapes pigment shows a maximum absorption peak in the visible region at the 560 nm wavelength according to absorbance value 22%, as shown in Figure (5).

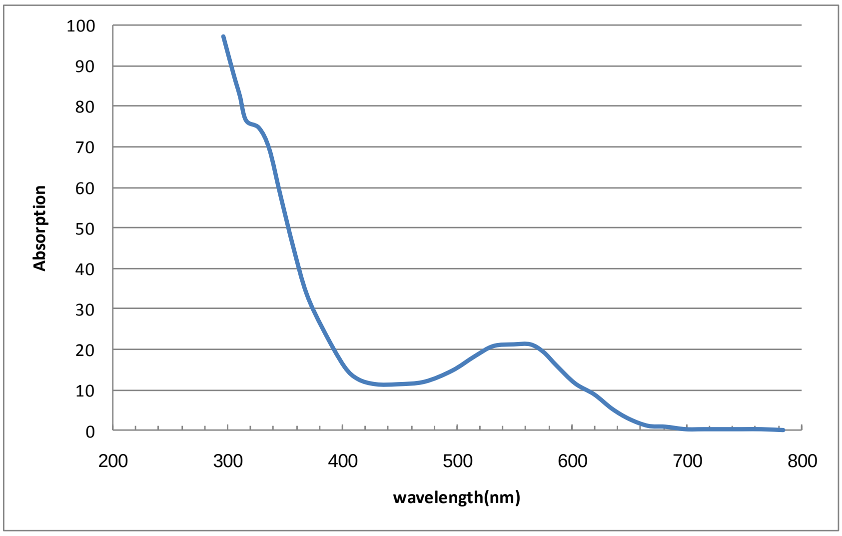


Figure 5:: absorption spectrum of Grapes dye solution

Hibiscus pigment: optical absorbance spectrum for Hibiscus pigment shows a absorption peaks in the UV and visible region at the 283 nm and 542 nm wavelength according to absorbance value 59% and 17% respectively, as shown in Figure (6).

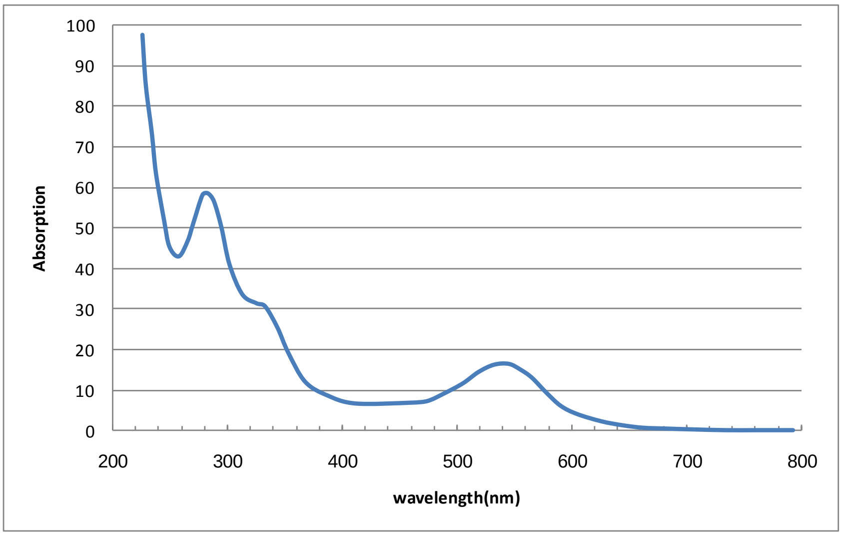


Figure 6: absorption spectrum of Hibiscus dye solution

Chlorophyll: optical absorbance spectrum for Chlorophyll shows a two absorption peaks in the visible region at the wavelength 405 nm (blue) and 627 nm (red) according to absorbance value 22% and 86% respectively, as shown in Figure (7).

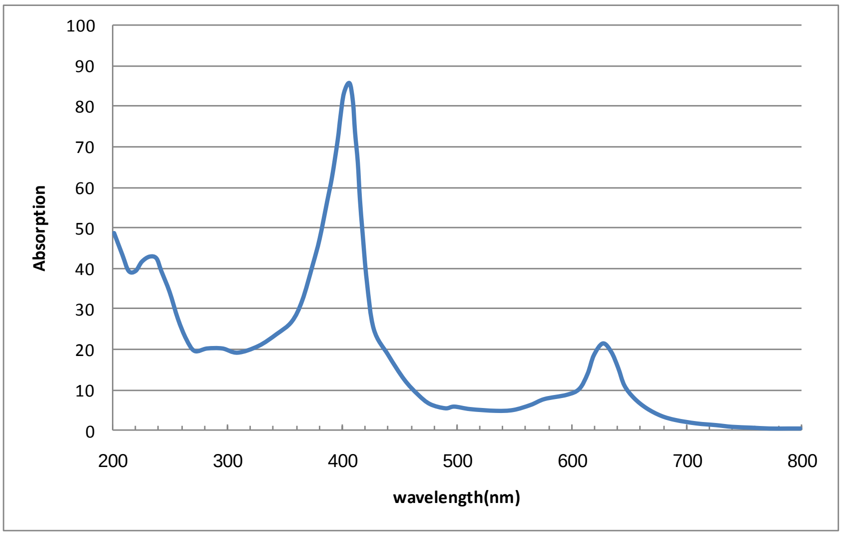


Figure 7: absorption spectrum of Chlorophyll dye solution

a combination of dyes: optical absorbance spectrum for a combination of dyes (Raspberry, hibiscus, chlorophyll) with mixing ratios (1:1:1) shows three absorption peaks in the visible region at the wavelength 542 nm (anthocyanine) and 403 nm, 623 nm (chlorophyll) according to absorbance value 70%, 32% and 19%. respectively, as shown in Figure (8). Consequently, we find this combination of anthocyanine and chlorophyll gives a good absorption range for each of the red, green and blue wavelength.

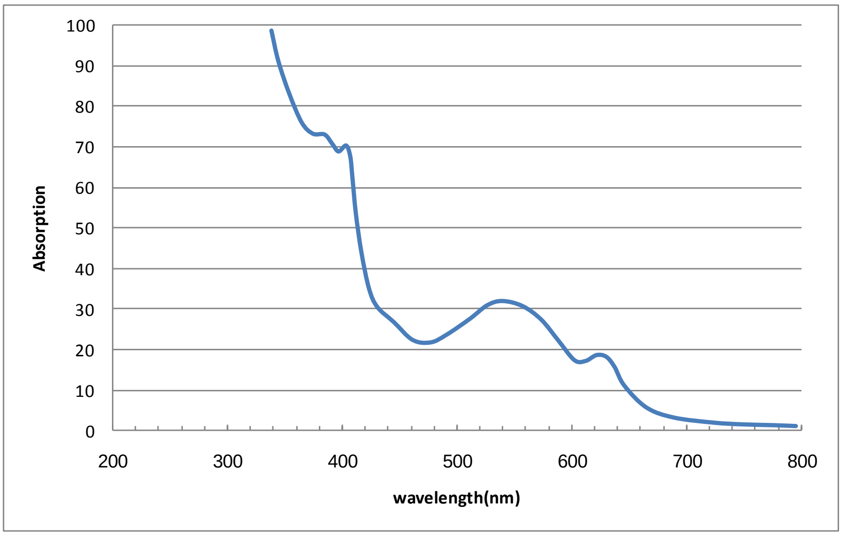


Figure 8: absorption spectrum of a combination of natural dyes solution (Raspberries, Hibiscus, chlorophyll) by the ratio (1:1:1)

IV.3 Preparing FTO transparent conductive oxide using SOL-GEL technique

Fluorine tin oxide thin films SnO_2: F (FTO) using SOL-GEL technique dip coating method for window materials in DSSC solar cells have been prepared as follows [8]: 0.3 mol/100 ml of $SnCl_4.5H_2O$ ethanol and distilled water and stir using magnetic stirrer for one hour, NH_4F as doping material then add slowly with doping ratio F/Sn of 6% by weight with stirring for 24 hours.

Soda lime glass substrate surface pretreatment, to ensure uniform wetting, was carried out by cleaning with detergent, followed by alcohol and distilled water rinses.

Coating process were applied to glass substrates by dip coating 4 mm/s withdraw speed . then the film treated in the furnace at 600 °C for one hour, then at 200 °C for 15 minutes to obtained the crystalline form of the FTO film. Figure (9) shows transmittance spectrum of prepared FTO films (F/Sn of 6% by weight). We note the increasing transmittance values with increasing wavelength values, reaching to the highest values in the near infrared. Table.3 summarizes optical and electrical properties of FTO prepared films.

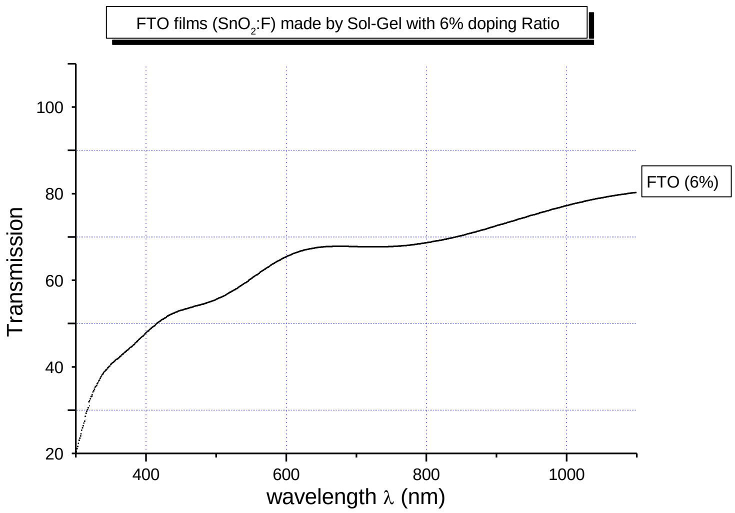


Figure 9: Transmission spectrum of FTO thin films (SnO_2:F) 6% doping Ratio at (600) ^{0}C

made by Sol-Gel with (4mm/sec) dipping speed

Table 3: average transmission values ,sheet resistance and resistivity of FTO thin films SnO_2:F of 6% doping Ratio at (600) ^0C made by Sol-Gel with (4mm/s) dipping speed

SnO2:F thin films FTO (F/Sn = 6%)						
resistivity	sheet resistance	Film thickness	total Spectrum	NIR	Vis	UV
Ω.cm	Ω / □	nm	1100−300 nm	800-1100 nm	400-800 nm	300-400 nm
1.5E-03	50	290	58%	75%	62%	38%

IV.4 Preparation of the titanium oxide TiO_2 electrode

The TiO_2 solution is prepared by addition of 20 mL of nitric acid solution (pH 3–4, in distilled water) to 12 g of colloidal TiO_2 powder (Degussa P25) in a mortar while grinding with a pestle. Each 1 ml addition of the dilute acidic solution proceeds only after the previous mixing and grinding has produced a uniform lump-free paste. Using tape we determine the active area 2×2 cm^2 of the FTO glass plate, and 20 μl of the TiO_2 solution are distributed uniformly on the active area by spray method and then sliding a glass rod over the plate. The film is then allowed to dry in air. After one minute, the tape is carefully removed and the film is annealed at 450 °C for 30 minutes. The TiO_2-coated conductive glass is allowed to slowly cool to room temperature, and stored for later use.

IV.5 Photo-sensitizer dye deposition:

The deposition of natural dye on TiO_2 layer have been performed according to the following procedure [7-10]:

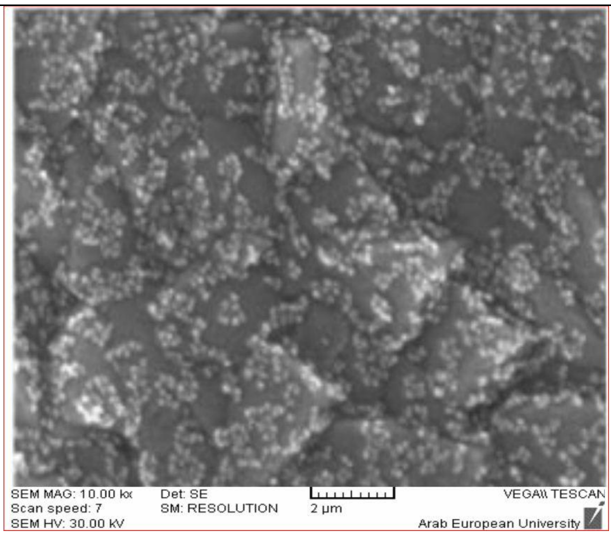
TiO_2 electrode heated to 70° C using hot air gun for 10 minutes to insure full dryness, then the electrode was immersed in a solution of natural sensitized dye for 24 hours. for adsorption of cyanin to the surface of TiO_2 , complexation to Ti^{IV} sites.

Then the stained electrode is washed in water and ethanol, and gently blotted dry. If the electrode is not used immediately, cyanin-stained electrode (dark-purple color) should be stored in acidified distilled water (pH of 3–4, acetic acid) in a closed dark-colored bottle. While chlorophyll stained electrode (light green–yellow color) should be stored in the acetone and chlorophyll solution until the electrode is ready to be assembled into DSSC.

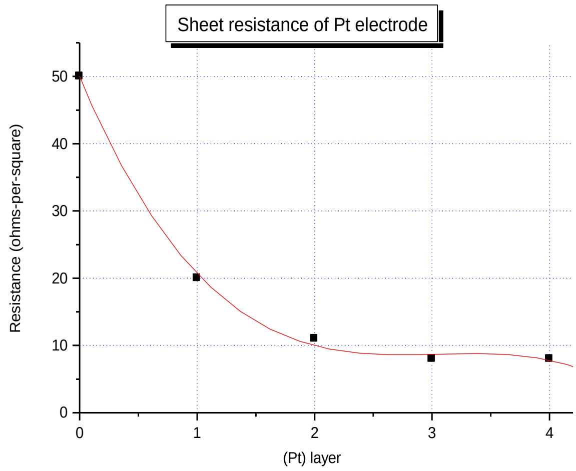
IV.6 Counter electrode preparation

Platinum counter electrode have been prepared according to the following procedure [11, 12]: 0.05 mol/100 ml of H_2PtCl_6, iso-propanol and stir using magnetic stirrer for half an hour, coating process were applied to FTO glass substrates by dip coating 4 mm/s withdraw speed. then the film treated in the furnace at 400 °C for half an hour, then at 200 °C for 15 mn to obtain the metal reflective mirror layer of platinum.

The sheet resistance decreases significantly with increasing the number of Pt layers deposited and we found the lowest value for the third Pt layer deposited as shown in Figure (10 - a). Figure (10 - b) shows the (SEM) of nanostructure platinum layer resulting .



(10−B)



(10−A)

Figure 10: A-sheet resistance with number of Pt layers deposited of the counter electrode ,
B- SEM of the Pt counter electrode

IV.7.Preparation of electrolyte solution

Iodide electrolyte solution was prepared according to the following procedure [7,12]: Add 6.7g of lithium iodide (LiI) to 100 ml of acetonitrile acetonitrile as solvent, with stirring for a quarter of an hour. Then add 1.3 g of iodine (I_2). Stir and store in a dark container. So we get rich solution of pair (oxidation - reduction) I^- / I^-_3 and upon which the cell depends on its work according to the following reaction .

$$I_2 + I^- \leftrightarrow I^-_3$$

V. ASSEMBLE DEVICE AND DETERMINE OUTPUT CHARACTERISTICS

The cyanin-stained TiO_2 electrode is carefully removed from the dark storage bottle of the dyeing solution and rinsed with distilled water then rinsed with ethanol. And full drying the stained electrode should be made to remove the humidity from the porous TiO_2 film before the iodide electrolyte is applied to the film .The dried electrode is placed face up, and the conductive side of the Pt counter electrode faces the TiO_2 film. So all of the TiO_2 is covered by the Pt counter electrode, then two drops of the iodide/iodine electrolyte solution placed at the edges of the plates. The liquid is drawn into the space between the electrodes by capillary action. The two exposed sides of the device will be the contact points for the negative and positive electrodes so that electricity can be extracted to test the cell as shown in Figure (11). Two binder clips are used to hold the plates together loosely at the other edges.

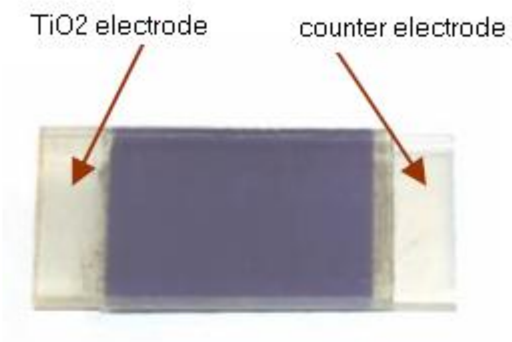


Figure 11: Assembled DSSC solar cell showing offset glass plates, and electrical contact points.

V.1 Studying the prepared DSSC performances

Cell performances were studied as effective area of the DSSC was the area of the TiO_2 dyed with photosensetizer. We calculated the dimensions of the effective area ($2 \times 2\ cm^2$) and the output current was divided by this area.

V.2 (I-V) curves

The cell was illuminated by a 50 W (GE 12V or equivalent) tungsten halogen lamp equipped with integral parabolic reflector and UV and IR blocking filter, and calibration of the light sources could be made by adjusting the light intensity or distance from the cell to the light source. Light sources were adjusted to 1.5 AM (100 mW/cm^2) to the surface of the cell (DSSC) studied. Figure (12) shows the equivalent circuit used to measure (I-V) curves of the resulting DSSC. The full current-voltage (I–V) curves were then measured using a 500-Ω potentiometer as a variable load as shown in Figure (13).

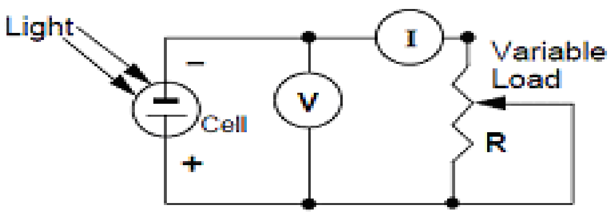


Figure 12: experimental setup for measuring the current-voltage characteristics of DSSC [4].

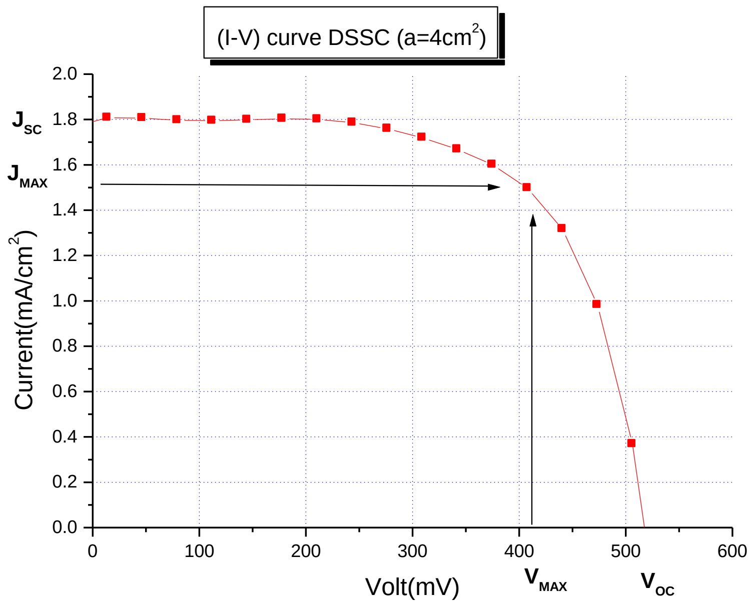


Figure 13: current–voltage (I-V) curve of DSSC solar cell 4 cm^2 illuminated at 1.5AM stained with cyanin dye.

V.3 Solar conversion efficiency measurement

The solar conversion efficiency (η) of a DSSC can be estimated using the conversion efficiency formula [7-13]:

$$\eta = \frac{P_{\max}}{P_{in}}$$

where P_{max}, and P_{in} denote the maximum output power and the input power, respectively. The fill factor (FF) of a DSSC can be estimated using the formula:

$$FF = \frac{P_{\max}}{J_{SC} \times V_{OC}}$$

where V_{oc} is the open-circuit voltage and J_{sc} is the short-circuit current. The solar conversion efficiency of a DSSC can be calculated by:

$$\eta = \frac{J_{SC} \times V_{OC} \times FF}{P_{in}}$$

Table 4 summarizes specification of prepared DSSC, where different types of photo-electrode have been made using different types of natural dyes. And then DSSC solar cells have been assembled and (V_{OC} , J_{SC} , FF , η) tested. We note that the DSSC cell using chlorophyll gave less value for solar conversion efficiency, and DSSC cell using Raspberry gave higher value for solar conversion efficiency because it contain a higher concentration of anthocyanine. While DSSC cell using mixture of dyes (raspberry, hibiscus, chlorophyll) has shown the highest value for the solar conversion efficiency compared with the rest of the prepared solar cells.

Table 4: The open circuit voltage , short circuit current, fill factor, and efficiency of the DSSC prepared with different types of natural dyes

	DSSC FTO/TiO2/Natural Dye/Electrolyte/Pt/FTO	V_{OC} (volts)	J_{SC} (mA/cm^2)	FF %	η %
1	Raspberries	0.429	0.269	64.8	1.50
2	Shami-berries	0.419	0.195	58.6	0.96
3	Grapes	0.340	0.091	61.1	0.38
4	Hibiscus	0.388	0.161	60.0	0.75
5	Chlorophyll	0.225	0.017	54.1	0.04
6	combination of dyes	0.420	0.600	60.2	3.04

VI. CONCLUSION

Optical properties of the natural anthocyanins dyes that exist in plants, have been studied, with different ratios and compositions. Transmission spectrum of the dye solutions (Raspberries, Shami-berries, Grapes, Hibiscus, Chlorophyll , and combination of dyes) was studied and showed good transmittance in the green region (520nm , 570 nm) of the spectrum. The study showed the possibility of using natural plant dyes that contain a high concentration of anthocyanins (such as Raspberries) as good organic dye instead of Ruthenium dyes N3 Dye used for Gratzl cells. While black grapes is not useful to increase the efficiency of DSSC cells. Dye sensitized solar cell DSSC, has been made using SOL-GEL technique in preparing thin film components, in the order (FTO/TiO_2/Natural Dye / Electrolyte / Pt / FTO) and testing performances for different types of natural dyes .

The DSSC prepared using a combination of natural dyes (Raspberries, Hibiscus, chlorophyll) by the ratio (1:1:1) as photo-sensitizer showed the better photovoltaic performances compared with other single dyes because of the increased sensitivity of the solar cell with total optical absorption for all different types of these dyes. The efficiency of the DSSC prepared was η=3.04% and fill factor FF=60% for cell area, short circuit current and open circuit voltage: a= 4 cm^2, Jsc = 0.6 mAcm^{-2}, Voc = 0.42 V) respectively.

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