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Preparation and Study of the Natural Photosensitizers Extracted from *Black Grapes* and *Beetroot* for Dye-Sensitized Solar Cells

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Abstract

The efficiency of DSSCs depends on the material that absorbs the light and converts it into energy. In this work, two natural dyes were extracted from Black Grapes and Beetroot and used as photosensitizers for DSSCs and compared to solar cells using synthetic dyes as photosensitizers. The experimental results showed that the efficiency of the solar cells that used Black Grapes (DSSC2) as a photosensitizer was 2.246%, which is higher than the solar cells that used Beetroot (DSSC1) as a photosensitizer, which got a value of 2.012%.

Keywords: DSSCs, Natural dye, Anthocyanin, and PCE.

تحضير ودراسة المحسّسات الضوئية الطبيعية المستخلصة من العنب الأسود والشمندر للخلايا الشمسية الصبغية

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الخلاصة

تعتمد كفاءة **DSSCs** على المادة التي تمتص الضوء وتحوله إلى طاقة. في هذا العمل ، تم استخلاص صبغتين طبيعيتين من العنب الأسود والشمندر واستخدامهما كمحسّسات ضوئية لـ **DSSCs** ومقارنتها بالخلايا الشمسية باستخدام الأصباغ الصناعية كمحسّسات ضوئية. أظهرت النتائج التجريبية أن كفاءة الخلايا الشمسية التي تستخدم العنب الأسود **(DSSC2)** كمحسس ضوئي بلغت 2.246٪ وهي نسبة أعلى من الخلايا الشمسية التي استخدمت الشمندر **(DSSC1)** كمحسس ضوئي والتي بلغت قيمتها 2.012٪.

1. Introduction

To convert sunlight into electrical energy, numerous types of solar cells have been created and manufactured over the years. Polycrystalline, amorphous, and crystalline solar cells have been used in a wide variety of household and industrial uses in various forms[1,2]. Dye-Sensitized Solar Cells (DSSCs), which are based on semiconductor's with a wide band gap and can convert visible sunlight into electrical energy, are one example[3]. DSSCs are attractive and promising for solar cell applications that have been used extensively in all countries of the world, and their PV mechanism is well understood[4].

The performance of the solar cell also depends mainly on the dye used as the photosensitizer, because the spectrum of absorption and anchoring of the dye on the surface of a semiconductor is very important to determine how efficiently the solar cell by the four steps of electron

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injection, charge recombination, dye regeneration, and electron collection at the counter electrode[5,6]. Charge separation occurs initially in the dye electrons used as a photosensitizers and proceeds to the interface between the dye and semiconductor[7]. The DSSC consists of a counter electrode (CE), a redox electrolyte, and an electrode consists semiconductors sensitized with a suitable dye, such as ZnO or TiO_2. When photons strike the photoanode electrode, the dye attached to ZnO or TiO_2 absorbs the incident photons. A photoelectron is then released from the utilized dye's exciter level and transferred to the semiconductor's conduction band, where it proceeds to the outer circuit. Through the reduction of the tri-iodide ion at the counter electrode and subsequent oxidation of the iodide ion at the dye, the electrolyte facilitates the electron transport and the sensitizer's regeneration[4].

The surface shape of the photoanode electrode and the dye employed are significant elements that affect the electron transport and efficiency of the DSSC[8]. Ruthenium is the preferred material used in DSSC as a dye sensitive to visible light[9]. However, ruthenium-based synthetic dyes are toxic, relatively expensive as well as complex synthetic procedures, and difficult to synthesize[10,11]. Moreover, ruthenium polypyridyl complexes contain a heavy metal, which is not environmentally desirable, and health risks due to their toxic nature[12,13].

Synthetic dyes have greater efficiency and durability; however, synthesizing these dyes is more complicated, costly, and requires toxic materials. As a result, the manufacture of such dyes can endanger not only humans but also the environment, as an alternative to ruthenium or industrial dyes, researchers are currently focusing on dyes extracted from natural sources as a natural dye to convert light into electrical energy. Because natural dyes are non-toxic, abundant, environmentally friendly, low cost, high photons-harvesting efficiency, and easy preparation[14,15]. These natural photosensitizers are extracted from leaves, roots, commonly available fruits, and flowers which are capable to be able to absorb visible light having wavelengths in the visible region of the solar spectrum[16].

The overall DSSC process is outlined as follows in Figure.1: Initially, dye photoexcitation may pass an electron into the semiconductor's conduction band ($TiO_{2\ film}$). Finally, when the electrolyte catalyst regenerates, the electron will travel through the circuit's external load and once more reach the counter electrode ($Pt_{\ film}$). The electrolyte redox couple electrons will initially regenerate from the oxidized dye molecules.

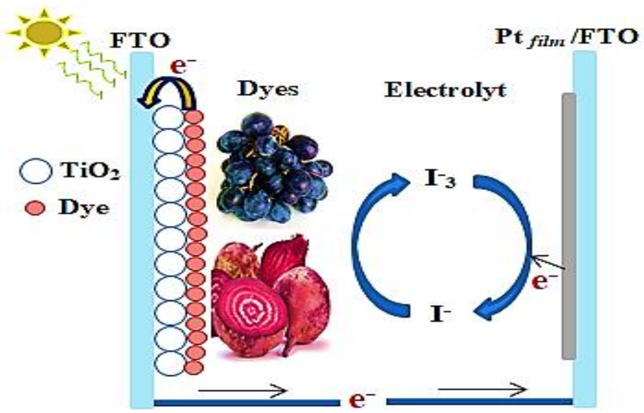


Figure -1 Shows a schematic of a DSSCs with the dyes extracted

We used a new and unique method that is relatively easy and less expensive to extract the natural dye (a rich source of anthocyanin) from cultivated and widely available *Black grapes* and *Beetroot* on farms in Iraq and use it as a photosensitizer in DSSCs in this research.

2. Experimental Methods

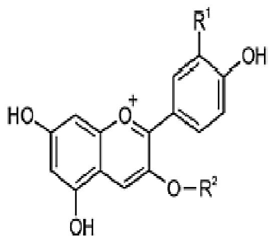
2.1. Materials

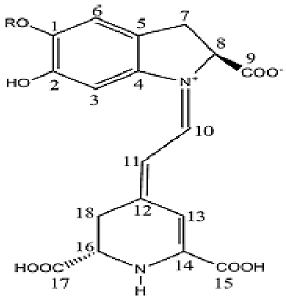
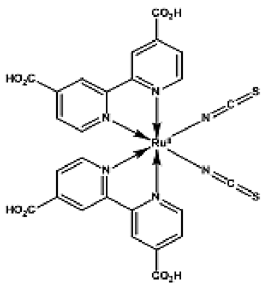
Fresh *Black Grapes* and fresh *Beetroot* were procured from a nearby farm in the Iraqi province of Thi-Qar Al-Fajr. The translucent TiO2 paste (20–25 nm), FTO conductive glass (3.75 Ω), platinum wire (pt), Ru (N719), and redox (I^-/I^{-3}) electrolyte solution were all supplied by the Solarsharif firm. Additionally, ethanol (99.9%) was bought from Merck Chemical.

2.2. Natural Sensitizers Preparation

The following procedures were performed to prepare natural dye extracts: Fresh plants were washed in distilled water to remove dust and dirt before being cut into small pieces of 1 mm^2. 5 g of samples is dissolved in 50 ml of ethanol (0.5:5) and stirred for 10 hours at room temperature and to give enough contact time for the solvent to extract the dye. The extracts were then extracted for 5 min at 2500 rpm in a centrifuge (Sigma, Model: 2-16P). Filter sheets were used to separate the solid fibers from the solution, leaving a clear, pure natural dye. These natural dye extracts were then put in a beaker lined with aluminium foil to shield the sample from light exposure and used to make the DSSCs. This was done for two weeks at room temperature to thoroughly extract the natural dye from the solution.

Table 1- Types of material, symbols, and chemical structure of natural dyes extracted from *Black grapes* and *Beetroot.*

Scientific name	*Symbol*	*chemical structure[17,2,3]*	*Dyes extracted in this work*
Black grapes 	*D1*		

Beetroot 	*D2*		
Ruthenium(II) 	*N719*		

2.3. Preparation of Dye-Sensitized Solar Cells

The photoanode, counter electrode, and device fabrication were done as per our earlier papers[20,21,22]. As illustrated in Figure 2, the nanostructured TiO_2 paste was applied to the FTO glass substrate using the doctor blade approach to create a TiO_2 film with an active region of 1 cm^2 and a thickness of 12 µm. The thin film thickness reduces light loss by reducing scattering and refraction. When the film is thinner, light is less likely to scatter and refract as it passes through the solar cell, which increases the chance that it will be absorbed and converted into electrical energy. Overall, a thin-film thickness of about 12 µm provides a good balance between increasing solar cell efficiency, improving its stability, and reducing costs. The electrode ($TiO_{2\ film}$) was gradually heated for 10 min at 100 C°, 10 min at 200 C°, 10 min at 300 C°, 15 min at 400 C°, and 30 min at 450 C°. The working electrode was chilled to 60 C° before being submerged in a sensitizer dye solution for 24 h at room temperature without exposure to light. The $TiO_{2\ film}$ was separated from the solution at the end of the adsorption and dried for 15 min. Parallel to this, a $Pt_{\ film}$ was deposited on the FTO glass using the thermal evaporation in vacuum (TEV) method with a 1 cm^2 active region. A sandwich cell was created by combining the working and counter electrodes. The electrolyte solution was iodide/triiodide, and a drop of electrolyte solution containing I^-/I^-_3 was injected into the cell, and the counter electrode hole was sealed with a sealing spacer.

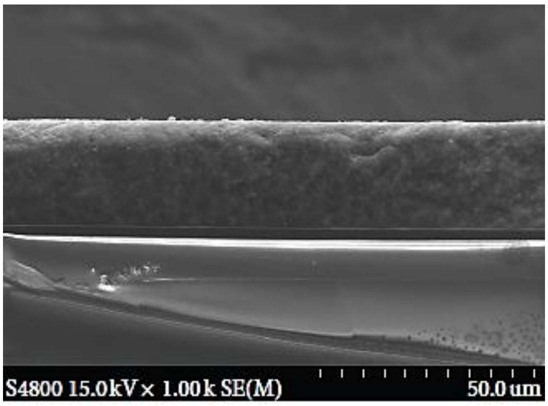


Figure -2 The cross-section of TiO_{2film} with a thickness of about 12 μm.

2.4. Measurements and characterization

UV-Vis (Perkin Elmer, Lambda 35) absorption spectroscopy was used to investigate the efficiency and optical properties of extracted dyes spectra from *Black grapes* and *Beetroot*. The DSSCs current-voltage curves were obtained by applying an external bias to the cell and measuring the induced photocurrent with a Keithley digital source meter under white light irradiation (Keithley 2601, USA). The incident light was 100 mW cm^{-2} in strength, and the instrument was fitted with a 300W solar simulator (Solar Light Co., Inc., USA) as the light source, the fill factor (FF) can be calculated with the following formula:

$$FF = \frac{Imax\ x\ Vmax}{Isc\ x\ Voc}$$

where I_{sc} is the short-circuit photocurrent and V_{oc} is the open-circuit photovoltage for P_{max} (maximum power output), and Imax and V_{max} are the photocurrent and photovoltage for P_{max} (maximum power output). A DSSCs overall power conversion efficiency (PCE) is defined as follows:

$$\text{PCE} = \frac{Isc\ x\ Voc\ x\ FF}{Pin}\ x\ 100\%$$

where P_{in} is the input power.

3. Results and Discussion

3.1. Surface morphology of TiO_2 film

After applying the paste on the FTO conductive glass using the doctor blade method, a thin film layer was created through thermal treatment. According to the FE-SEM picture, which is depicted in Figure 3, the diameter of the TiO_2 particle is around 25 nm. There, the particles are seen to be evenly distributed.

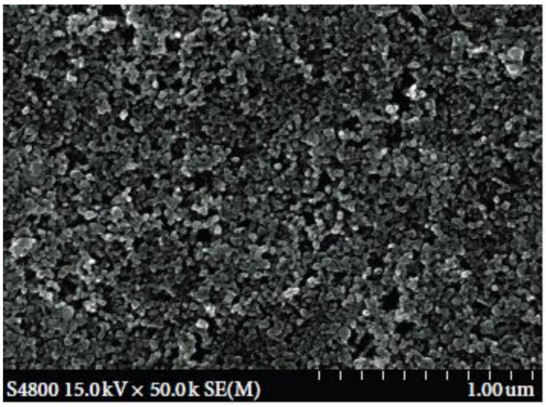


Figure -3 The FE-SEM image of the morphology of the TiO_2 thin films.

3.2. X-ray diffraction studies

XRD patterns of the $TiO_{2\ film}$ are shown in Figure. 4 to observe the crystalline structure. The film has an anatase phase of TiO_2 crystal structure that matches the JCPDS card no. 21–1272 standard data. All of the observed peaks are visible in the $TiO_{2\ film}$ deposited on FTO glass at 2Ө = 25.240°, 37.870°, 47.660°, and 62.720° for the (101), (004), and (204) planes, respectively. The existence of the stable $TiO_{2\ film}$ is indicated by the anatase phase. The enhanced crystallinity of annealed $TiO_{2\ film}$ with crystallite size 25 nm can be due to a high-intensity peak (101). The broadening of XRD peaks indicates the formation of nanocrystalline material, which is ideal for DSSCs.

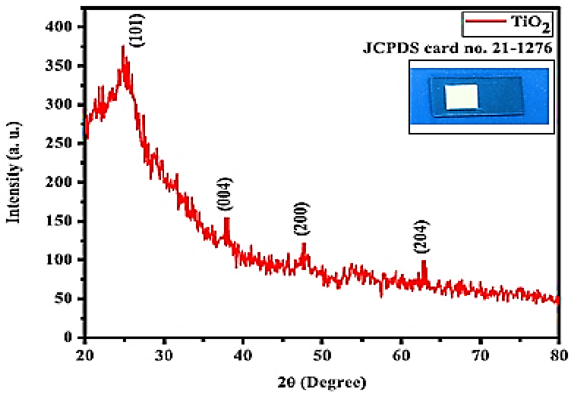


Figure -4 The XRD spectrum of TiO_2 film

3.3. Performance of DSSCs with the extracted natural dyes

Figure 5 shows the J-V characteristic curves of the dye-sensitized solar cells based on Beetroot, Black grapes, and N719 are DSSC1, DSSC2, and DSSC3, respectively.

The photoelectrochemical parameters of the DSSCs are listed in Table 2. Different dyes show different photoelectric conversion efficiency; that is, 2.012% and 2.246% are DSSC1 and DSSC2, respectively.

Table 2- Photoelectrical parameters of DSSCs sensitized by Black Grapes and Beetroot dye

Sensitizer	***J_{sc} (mA cm^{-2})***	***V_{oc} (V)***	***FF (%)***	***PCE (%)***
DSSC1	**7.75**	**0.53**	**0.47**	**2.012**
DSSC2	**8.64**	**0.52**	**0.5**	**2.246**
DSSC3	**16.36**	**0.58**	**0.65**	**6.167**
Sensitizer	***J_{sc} (mA cm^{-2})***	***V_{oc} (V)***	***FF (%)***	***PCE (%)***

According to Table 2's photovoltaic results, it was discovered that DSSCs sensitized with dyes extracted from black grapes(DSSC 1) have greater Voc, Isc, and PCE than DSSCs sensitized with dyes extracted from beetroot (DSSC 2). Look at Figure 5.

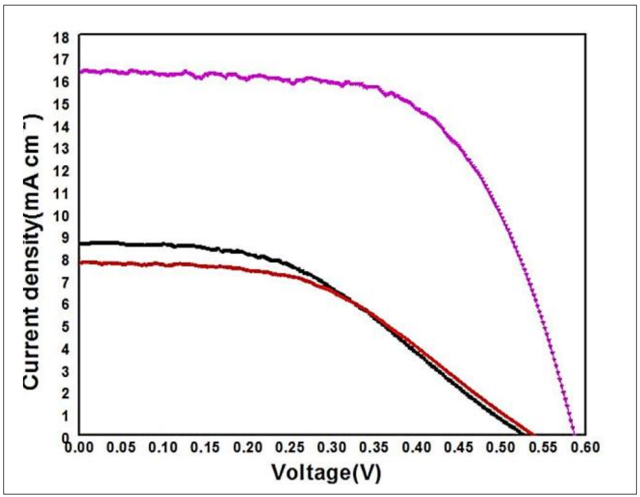


Figure -5 Current–Voltage characteristics curves for different dyes

The ability of plants to absorb light varies based on their chemical composition and the cellular structure of their leaves and roots. For example, black grapes have a pigment called Anthocyanin, a substance that acts as a natural pigment that absorbs the full spectrum of light. Thus, black grapes absorb more light due to the presence of this strong pigment. Further treatment of the TiO_2-coated FTO glass provides more sites for dye absorption resulting in higher pigment concentrations that ensure greater absorption of sunlight. As for Beetroot, it does not contain a strong pigment like Anthocyanin, but it does contain another pigment called Betalain, which helps absorb light in a limited way. Thus, black grapes have a greater ability to absorb light than Beetroot.

4. Conclusion

Natural dyes can be obtained easily from natural sources such as plants, fruits, and vegetables. They are considered more environmentally safe as well as effective in absorbing light, especially anthocyanin, and chlorophyll. They are characterized by their ability to absorb the full spectrum of light, which increases the efficiency of the solar cell, while industrial dyes require a production process. complex, high cost, and can cause environmental pollution. In general, the use of natural dyes in dye-based solar cells is a preferred option for many people due to the benefits mentioned above, and it is expected that interest in them will increase in the future.

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