The Construction and Comparison of Dye-Sensitized Solar Cells with Blackberry and N719 Dyes

Maryam Shirkavand[1], Mohammad Bavir[*,2], Ali Fattah[3], Hamid Reza Alaei[4], Mohammad Hossein Tayarani Najaran[5]

[1] Physics Dept, Khayyam University, Mashhad, Iran

[2] Electrical and Computer Engineering Dept, Shahab Danesh University, Qom, Iran

[3] Faculty of Electrical Engineering and Robotic, Shahrood University of Technology, Shahrood, Iran

[4] Faculty of Physics, IAU Varamin-pishva Branch, Tehran, Iran

[5] Faculty of Physics, Ferdowsi University of Mashhad, Mashhad, Iran

Abstract: In a dye-sensitized solar cell (DSSC), the amount of light absorption depends on the design of the pigments, which determines the strength of light absorption and the optical range of the cell. In this paper, we have constructed and studied two fairly similar pattern of DSSCs in structure. The thickness of TiO_2 used for both cells is taken to be 2 μm. We have used an industrial N719 dye for one of the cells and a natural blackberry dye for the other. The N719 dye is the most common dye used in DSSCs. The results obtained from the I-V curve indicate a 700 mV open-circuit voltage (V_{oc}), an 8.57 mA short-circuit current (I_{sc}), a 70% fill factor (FF) and a 4.2% efficiency for the N719 sample. Blackberry is a natural dye which has no toxic effects in comparison with the industrial samples. The results obtained from the blackberry cell experiment indicate a 770 mV V_{oc}, a 2.08 mA I_{sc}, a 70% FF and a 1.13% efficiency.

1. INTRODUCTION

DSSCs are considered as proper economic substitutions for P-N junction semiconductor photovoltaic cells [1]. In contrast to the silicon cells in which the matter is responsible for both the light absorption and charge transfer, these two processes are completely separated in the electrochemical structure of DSSCs. The light is absorbed by a kind of molecule named "dye" which is sensitive to the

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* Corresponding author. E-mail: **m.bavir@shahabdanesh.ac.ir**

visible spectrum. These molecules are scattered on the surface of a semiconductor substrate with a wide band gap. The charges on the surface are separated by injecting the charges into the conduction band that have undergone optical excitation in the dye [2-3].

The charges are transferred from the semiconductor's conduction band to the charge collector. Various nanostructures of oxide semiconductors are available for use in the optical electrode of DSSCs which have their own pros and cons. The nanostructures are constructed in the shapes of nanoparticles, nanowires, nanotubes and nano-belts with three-dimensional structures like as flowers, stars, oxide bulks, etc. [4-5]. These nanostructures have larger internal contact surfaces in comparison with the surfaces of solid structure materials. The nano-scale dimension of these structures can also be effective in the movement and transfer of charges. The nano-scale dimensions limit the mean free path of the electric charges and thus demonstrate different electrical properties. This property of the nanostructures is known as the quantum confinement effect. These nanostructures can also play an important role in the field of optical effects by creating photonic band gaps and optical scattering [6].

The main absorbent parts of light in DSSCs are the pigments, which only responds to specific wavelengths of the solar spectrum based on the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels. Photons in these wavelengths create the photoelectrons in the dye and thus a photocurrent in the solar cell. Dyes are sensitive to light form a thin cover on the cell's photo-electrode. The special characteristic of dyes is their HOMO and LUMO levels, which release electrons and transfer them to TiO_2. The most effective dyes in DSSCs are Ruthenium (Ru) complexes which are made by the Gratzel group. These complexes are coupled to the surface of TiO_2 through the carboxyl group (coo-). Ru complexes have important absorption properties. In most studies conducted on DSSCs, poly-pyridine Ru complexes are chosen as the light-sensitive dyes. They are selected regarding their optical and oxidation-reduction properties and also the facility of changing the coupling surface of poly-pyridine ligands and introducing proper groups around the ligands to improve their oxidation-reduction and spectral properties [7].

The revival process of oxidized dyes: In order to revive the dye by the redox pair, the rate of this process should overcome the recombination rate of the injected electrons with the dye cations.

2. TYPES OF DYE

The various types of dye can be divided into two main categories as follows:
- Red dye: which absorbs light in 400-800 nm wavelength range.
- Black dye: which absorbs IR light up to 900 nm.

Polypyridine complexes of Ru have been the first selection of dyes in most of the research due to the wide knowledge accumulated throughout the years in regards to their photophysics and photoredox chemistry. The N719, N3, Z907 and black dye (N749) are the most effective sensitizers of titanium dioxide which are used worldwide as the control dyes in DSSCs due to their high energy efficiency. Fig. 1 shows the molecular structure and energy conversion efficiency for these dyes.
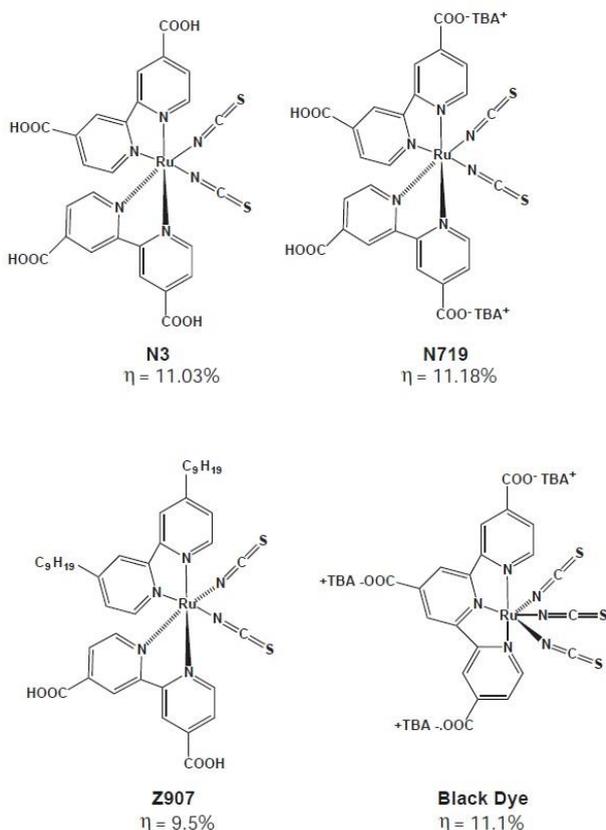
Fig. 1. Molecular structure and energy conversion efficiency of the main light-sensitive dyes [8]

Absorption in the visible and near-infrared spectrum in these dyes helps the charges for transfer from metal to ligand in the complex. N719, N3 and Z907 dyes can absorb a wide range of the visible spectrum from 400 to 800 nm, while the N749 dye absorbs the near-infrared spectrum up to 900 nm. N719 dye has the similar structure as N3 dye [8-10]. An ideal dye in a photovoltaic cell plays the part of a semiconductor with a 1.4 eV energy gap [11].

In other words, photons absorption with a wavelength smaller than 900 nm, creates the created electron-hole pair and implants it into the semiconductor. As a critical part in DSSCs, the sensitizer should have the following conditions:

- High absorption of light in the visible spectrum.
- A strong interfacial bond with the semiconductor (existence of =O and –OH groups).
- Ability to inject electrons in to the semiconductor's conduction band.

Also, the ability of quick reduction by the redox pair in the electrolyte and stability in the base and oxidized forms are some of the properties needed for a good dye. Efforts for finding dyes with high stability and proper light absorption led to the presentation of dyes based on black dye, N719 and N3 poly-pyridyl Ru complexes by the Gratzel group. These dyes have high stability and light absorption efficiency due to the existence of metal ligands for faster transmission of carriers. The injection process happens really fast in the Ru complex, resulting in a decrease in the recombination of electrons and oxide dyes [12]. Fig. 2 illustrates the components and principle in a typical DSSCs.

The molecules HOMO is centered on Ru-d orbitals wheras LUMO is a π^* orbital centered mainly on the ligand. The isothiocyanate ligand reduces the LUMO surface which leads to a red shift in the absorption spectrum of the complex and also easier reception of electrons from the iodide ions in the electrolyte. Carboxyl groups exist in Ru complexes for tighter coupling with the surface of the titanium dioxide. This tight coupling leads to large electronic interactions between the ligand and the conduction band of the titanium dioxide and more effective injection of electrons from the Ru complex to the titanium dioxide [14].

The Ru complex is deposited on the surface of the titanium dioxide through the bidentate coordination of carboxylate or ester bonds [15]. In addition to the mentioned dyes, some other dyes are also used in the structure of DSSCs which have lower efficiency in comparison with the poly-pyridine dyes; such as porphyrin, phthalocyanine, perylene, and their derivatives (Fig. 3).
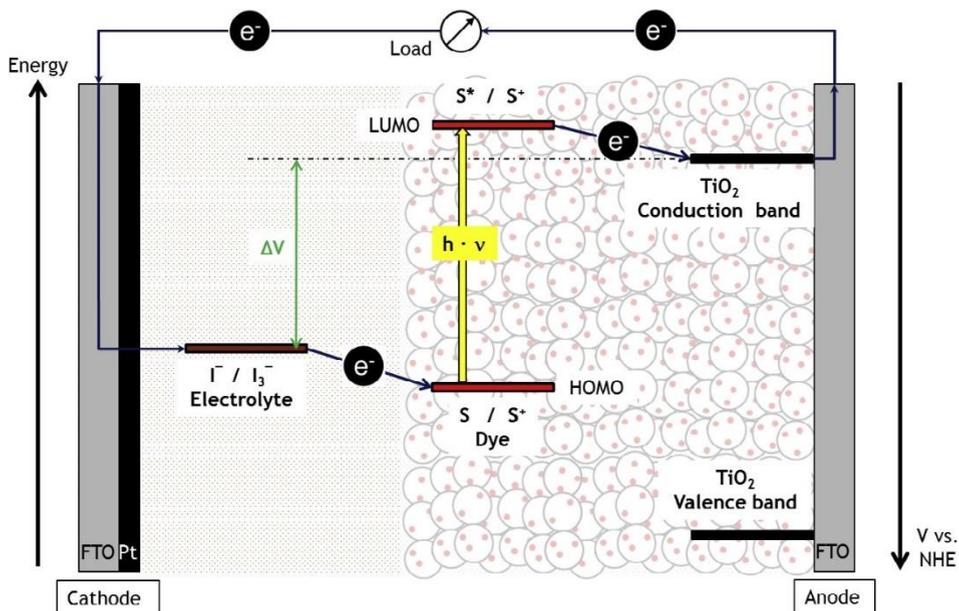
Fig. 2. Schematic of the dye layer [13]

| porphyrin | phthalocyanine | perylene |
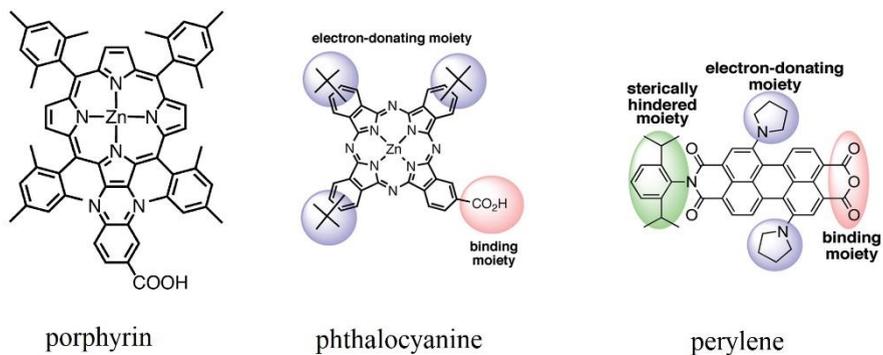
Fig. 3. The porphyrin, phthalocyanine and perylene dyes used in the structure of DSSCs [16].

3. RESULTS AND DISCUSSION

At first, we cut a 1×1 cm piece from the insulator side of the Fluorine-doped Tin Oxide (FTO). The active area of TiO2 was 0.25 cm^2. After washing, we placed the substrates in an aqueous solution of TiCL$_4$ with a density of 40 milli-molars, at 70 °C for 30 minutes. After the treatment stage, the substrate is washed with deionized water and ethanol. Then, we completed the doctor blade deposition process using scotch tape and a Pasteur pipette; and dried the substrate for 6 minutes at 125 °C. In the first sintering process, we heated the substrate up to 500 °C and cut it after complete cool down. After that, the post-treatment stage was carried out. In the second sintering stage, the substrate was heated again in 500 °C for 30 minutes and then cooled down to 80 °C. In this temperature, we kept the substrate soaked in Dye-N7190.5 solution for 22 hours.

After cutting a piece the size of the anode from the FTO and piercing it for pouring the electrolyte, and after washing procedures similar to the ones carried out for the anode, we heated the cathode at 460 °C for 15 minutes. Then, we slowly brought the temperature down so that the cathode doesn't crack. When it's completely cooled down, we added a drop of platinum on its surface. When the surface is entirely covered with the platinum, we heated the cathode at 460 °C for 15 minutes.

Sealing the solar cell: A 30 µm spacer smaller than the FTO is used for sealing the cell. We took the anode out of the dye and soak it in ethanol for a while so that the remaining dye is washed off. We heated and dried the cathode and stack the parts respectively. We placed the cathode and anode on a heater at 120-150 °C for 10 seconds, in a way that they don't slip and the cathode is placed on the heater first. We put pressure on different parts of the spacer with a metal holder until it melts by the heat and the anode and cathode are connected. After cool down of the cell, we put one or two drops of electrolyte in the hole and used vacuum to take it into the cell. Then, we blocked the hole on the cathode with a hot slide using a piece of spacer. At the end, we made sure of the surface homogeneity and lack of cracks, and inspected the thickness of the substrate by cutting it in half and measuring the cross sectional area by a Cambridge-S360 scanning electron microscope (SEM). The surface thickness was 2 µm (Figs. 4 and 5).

It is observed that the thickness of the micro-metric substrate is an important parameter in the amount of dye absorption by the surface.
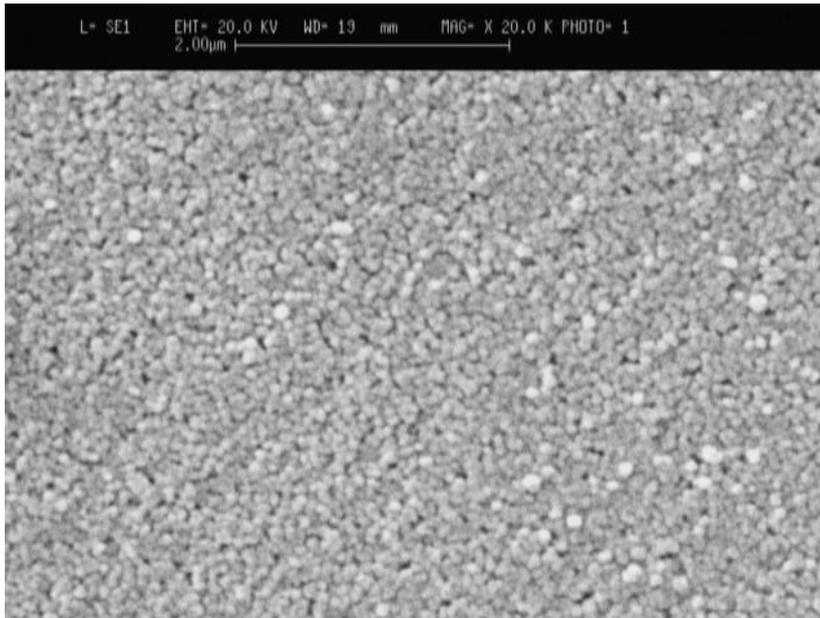
Fig. 4. A SEM image of the surface of TiO_2 micro metric coverage.
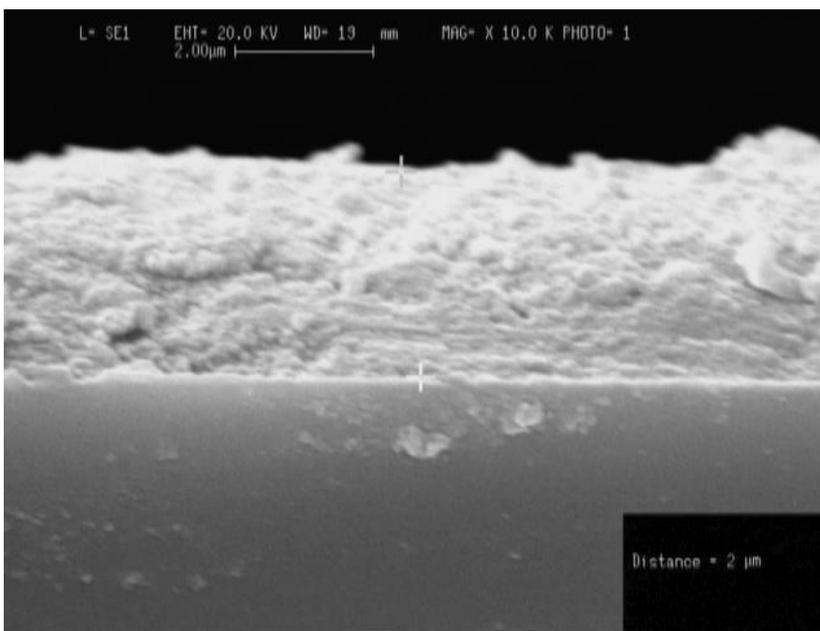
Fig. 5. A SEM image of the cross sectional area of TiO_2 micro metric coverage.

A. Characterization of the DSSCS

The main parameters of a solar cell are determined by I_{sc} and V_{oc} obtained under standard illumination conditions (AM 1.5). The FF is one of the main parameter to determine the overall capabilities of a cell. It characterizes the quality and idealness of a solar cell. The FF is the ratio of maximum generated power P_{max} to theoretical power maximum P_{theo} of a solar cell. The general formula for FF is [17]:

$$FF = \frac{P_{max}}{P_{theo}} = \frac{J_{max} \cdot V_{max}}{J_{sc} \cdot V_{oc}} \qquad (1)$$

V_{max} and I_{max} are the voltage and current of the I-V curve where the generated power is at the maximum. The efficiency η is the ratio between maximum generated power P_{max} to electrical input power P_{in} due to the irradiant light. The efficiency under standard illumination conditions is given by [17]:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{FF \cdot I_{sc} \cdot V_{oc}}{W_{in}} \qquad (2)$$

B. Results of the N917 Dye

In order to produce a 0.5 milli-molar N719 dye solution, we have used ethanol or acetonitrile/tert-butane solvents.
The test of UV-VIS was carried out for the N719 dye in the range of 300-800 nm as shown in Fig. 6. The absorption peaks were observed at specific wavelengths of 386,487 and 620 nm. The highest peak was correspondent to the 620 nm wavelength. It states the suitable wavelength range of pigment solution to be absorbed which is between 350-650 nm.
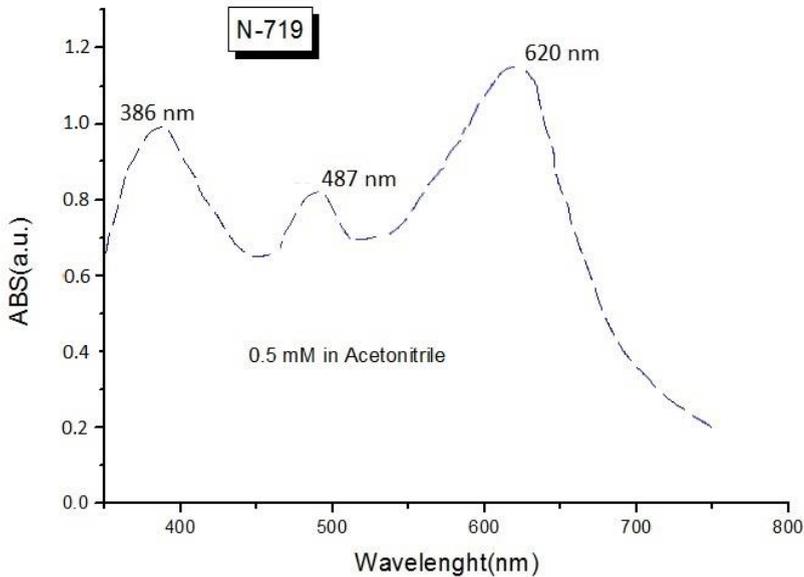
Fig. 6. The UV-VIS spectrum of a 0.5 molar dye solution (solvent of ethanol) in 300 to 800 nm wavelengths range with N719 dye

The current-voltage characteristic or I-V curve shows (Fig. 7) the relationship between the current and voltage of the cell in different charges exerted on its ends from zero to infinite resistance (which correspond to open and short circuits, respectively). The cell efficiency and FF can be calculated based on the shape of this curve.

The I-V curve of the constructed cell is plotted using autolab PGSTAT302N and AM1.5 solar simulators.

Finally, a cell is constructed with a thickness of 2 μm, a V_{oc} of 770 mV, an I_{sc} of 8.57 mA, a FF of 70% and efficiency of 4.2% using the anode which was made by the doctor blade method.

The photo-electrochemical parameters of the solar cell are summarized in Table. 1.

Table. 1

Thickness (μm)	V_{OC} (mV)	I_{SC} (mA)	FF (%)	η (%)
2	700	8.57	70	4.2

The resulted values for N719 dye
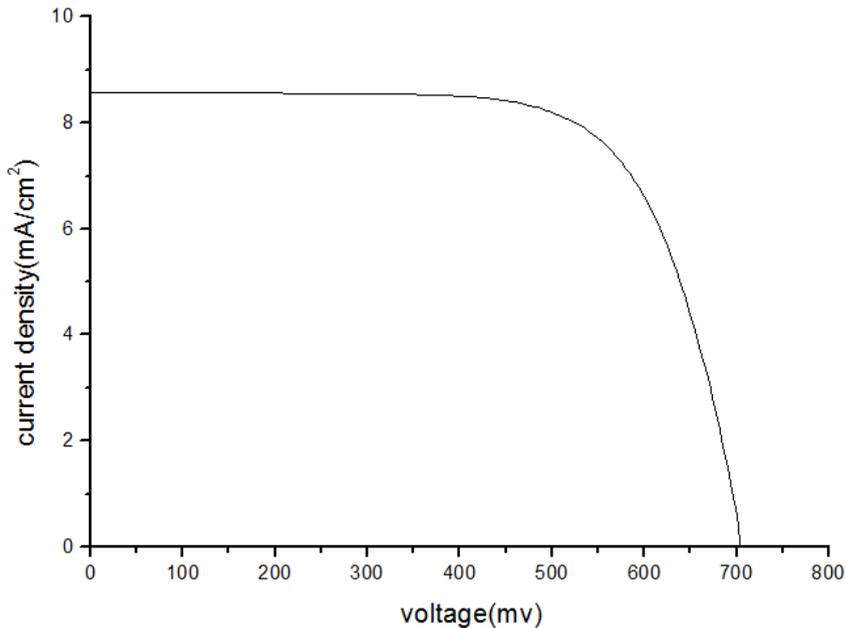
Fig. 7. The I-V curve of N719 dye

C. Results of the Natural Blackberry Dye

Using natural dyes instead of dangerous chemical reducers does no harm to the environment or the researchers. Continuing our experimental research, we make an effort to construct a nanostructured solar cell using a natural blackberry dye. In respect to antioxidant activities, blackberry contains strong photo-chemicals such as anthocyanins. Anthocyanin is the dye because of which the blackberry dye is black.

The wavelength range from 500 to 800 nm is analyzed using the UV-VIS test (Fig. 8). The absorption peaks are observed in 522, 589 and 644 nm wavelengths. The highest peak corresponds to 644 nm which implies an adequate absorption range (window) between 500 and 650 nm for the dye solution.

Finally, a cell is constructed with a porous film thickness of 2 μm, a V_{oc} of 770 mV, an I_{sc} of 2.08 mA, a FF of 70% and efficiency of 1.13% (Fig. 9).

The parameters of this experiment presented in Table 2.

Table. 2
The resulted values for blackberry dye

Thickness (μm)	V_{OC} (mV)	I_{SC} (mA)	FF (%)	η (%)
2	770	2.08	70	1.13
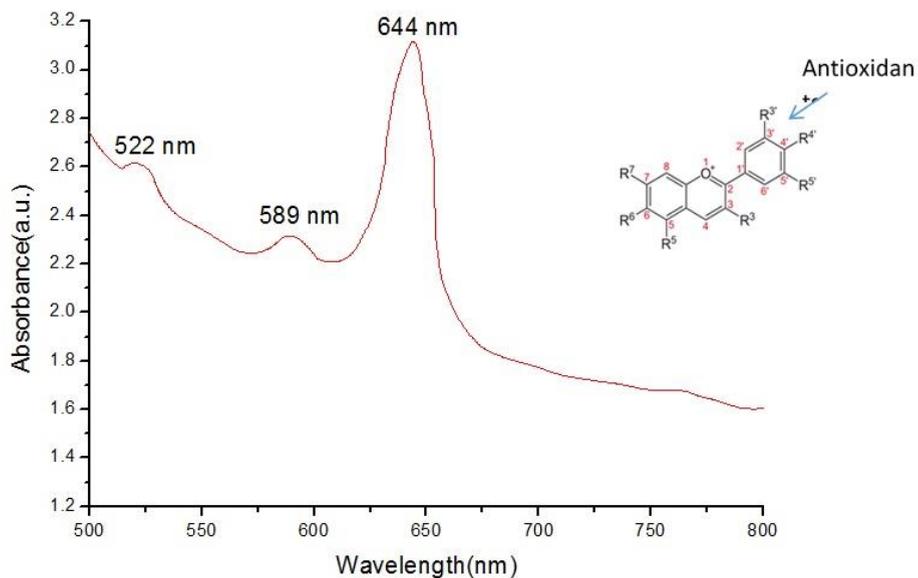
Fig. 8. The UV-VIS spectrum of a 0.5 molar dye solution (solvent of ethanol) in 500 to 800 nm wavelengths range with blackberry dye
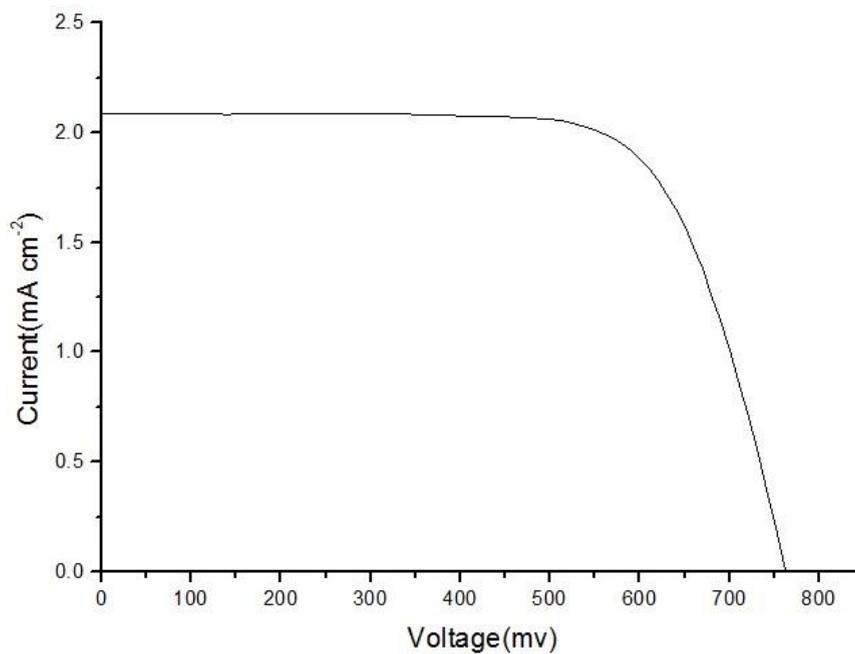
Fig. 9. The I-V curve of blackberry dye

4. CONCLUSION

The recombination process depends heavily on the electron density in the TiO_2 electrode, and thus on the intensity of light and the voltage of the cell. The revival process depends on the iodine density, electron viscosity and the structure of the dye. The results obtained from the I-V curve indicate a 700 mV V_{oc}, an 8.57 mA I_{sc}, a 70% FF and a 4.2% efficiency for the N719 sample. The results obtained from the blackberry cell experiment indicate a 770 mV V_{oc}, a 2.08 mA I_{sc}, a 70% FF and a 1.13% efficiency. By comparing the two constructed solar cell samples with equal thickness for the industrial N719 dye and the natural blackberry dye, it can be concluded that the N719 dye used in DSSCs yields higher efficiency in comparison with the natural blackberry dye, in spite of toxicity.

The main reason of I_{sc} being higher in N719 dye compared with blackberry dye is related to photon absorption range which is higher for the former pigment, which depends on their structures. It can be confirmed by paying attention to Fig. 6 and Fig. 8.

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