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Dye-Sensitized Solar Cell Using Saffron Petal Extract as a Novel Natural Sensitizer

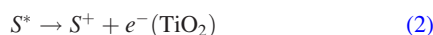
Natural dye extract of the saffron petal, purified by solid-phase extraction (SPE) technique, has been studied as a novel sensitizing dye to fabricate TiO₂ nanoparticles-based dye-sensitized solar cells (DSSC). The extract was characterized using ultraviolet–visible (UV–Vis) and Fourier transform infrared (FTIR) spectroscopies to confirm the presence of anthocyanins in saffron petals. The typical current–voltage and the incident photon to current efficiency (IPCE) curves were also provided for the fabricated cell. The saffron petal extract exhibited an open-circuit voltage (Voc) of 0.397 V, short circuit current density (Jsc) of 2.32 mA/cm², fill factor (FF) of 0.71, and conversion efficiency of 0.66%, which are fairly good in comparison with the other similar natural dye-sensitized solar cells. These are mainly due to the improved charge transfer between the dye extract of saffron petal and the TiO₂ anode surface. Considering these results, it can be concluded that the use of saffron petal dye as a sensitizer in DSSC is a promising method for providing clean energy from performance, environmental friendliness, and cost points of view. [DOI: 10.1115/1.4034908]

Keywords: saffron petal, delphinidin, TiO₂, nanoparticle, dye-sensitized, solar cell

Introduction

Dye-sensitized solar cells (DSSC) are energy devices invented for converting visible light into electricity, based on the sensitization of wide-band gap metal oxide semiconductors such as TiO₂ [1]. Since their appearance in the 1990s [2], DSSCs have drawn much attention from the scientific community, due to the ease of fabrication, low cost, the ability to generate electricity in cloudy conditions, and also under artificial light. In addition, there is no drop in their efficiency at high temperatures and they are also environmentally friendly [3,4]. As shown in Fig. 1, a DSSC consists of a metal oxide semiconductor, sensitizing dyes adsorbed onto the metal oxide semiconductor as anode, an electrolyte, and a counter electrode [5]. The primary processes that occur in a DSSC can be summarized as follows [6]:

- (1) The dye, upon absorption of a photon ($h\nu$), excited from the ground state (S) to the excited state (S^*).
- (2) The excited electrons are injected into the conduction band of the TiO₂ electrode, resulting in the oxidation of the photosensitizer.



- (3) The injected electrons in the conduction band of TiO₂ are subsequently transported between TiO₂ nanoparticles with diffusion toward the back contact (TCO) and consequently

reach the counter electrode through the external load and circuit. The oxidized photosensitizer (S^+) accepts electrons from the I^- ion redox mediator, regenerating the ground state (S), and I^- is oxidized to the oxidized state, I_3^-



- (4) The oxidized redox mediator, I_3^- , diffuses toward the counter electrode and is reduced to I^- ions.

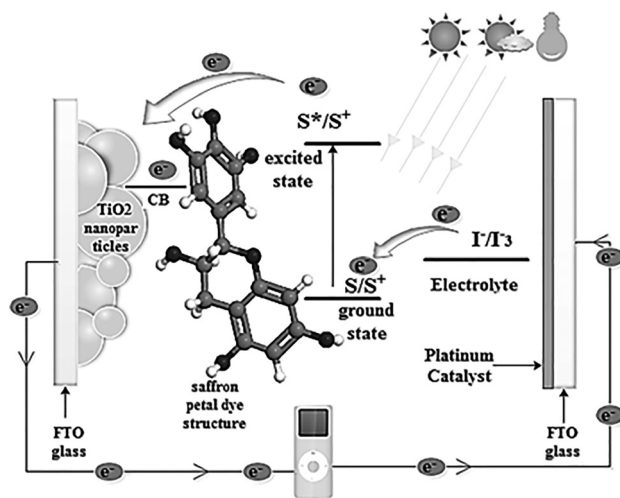


Fig. 1 Schematic performance of a dye-sensitized solar cells reaction

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Basic structure	Anthocyanidins	Visible colour	R _{3'}	R _{4'}	R _{5'}	R ₃	R ₅	R ₆	R ₇
	Pelargonidin	Red	H	OH	H	OH	OH	H	OH
	Cyanidin	Magenta	OH	OH	H	OH	OH	H	OH
	Delphinidin	Purple	OH	OH	OH	OH	OH	H	OH
	Peonidin	Magenta	OCH ₃	OH	H	OH	OH	H	OH
	Petunidin	Purple	OH	OH	OCH ₃	OH	OH	H	OH
	Malvidin	Purple	OCH ₃	OH	OCH ₃	OH	OH	H	OH

Fig. 2 The basic structure of anthocyanins in flavylium cation [21]

Overall, the electric power is generated without permanent chemical transformation.

The performance of a DSSC is largely based on four energy levels of the component: the excited state and the ground state of the photosensitizer, the Fermi level of the TiO₂ electrode, which is located near the conduction-band level, and the redox potential of the mediator (I^-/I_3^-) in the electrolyte. The photocurrent obtained from a DSSC is limited by the energy difference between the ground and excited states of the dye. The smaller the ground and excited states energy gap, the larger the photocurrent is provided, mainly because of the utilization of the long-wavelength region in the solar spectrum [7]. The energy gap between the excited state and the conduction-band level of TiO₂ is also important. The energy of the excited state must be sufficiently negative with respect to the conduction band of TiO₂ for effective injection of electrons. In addition, the substantial electronic coupling between the excited state and the conduction band of TiO₂ leads to an effective electron injection. The ground state of the complex must be sufficiently more positive than the redox potential of the I^-/I_3^- redox mediator for effective acceptance of electrons [6]. Considering the mechanism of solar energy conversion in DSSCs, it is fair to say that one of the most important components of a DSSC is the dye. Ruthenium-based dyes have already been used but, are not suitable for photovoltaic systems from both economic and environmental viewpoints; as the toxicity and rareness limit the application of these dyes. To overcome these limitations, several natural pigments such as anthocyanin, chlorophyll, tannin, and carotene have been examined as sensitizer DSSCs [8–13]. The main reasons that researchers have been interested in natural pigments are their availability, environment friendliness, and affordability. A number of research works indicate the suitability of anthocyanin pigments in DSSCs as a sensitizer [9,10,14–17]. Anthocyanins are responsible for different colors of plant parts, including roots, stems, leaves, flowers, and fruits [18]. As shown in Fig. 2, six anthocyanidins, including cyanidin, delphinidin, malvidin, pelargonidin, peonidin, and petunidin are common in vascular plants [19,20]. Anthocyanins have enough free –OH groups to bind TiO₂ nanocrystallites and can inject electrons into the TiO₂ conduction band at an ultrafast rate when excited with visible light [22]. Also due to the extended π conjugation and the presence of positive charge and free –OH groups on the flavylium cation, the anthocyanins are enabled to absorb light in the visible

spectrum, leading to a large variety of dye colors [23,24]. Among different anthocyanins, delphinidin has a suitable structure for binding with TiO₂. Delphinidin has six –OH groups in its structure and hence could effectively inject electrons to TiO₂ conduction band, compared to the other anthocyanins structures. One of the main sources of delphinidin is saffron petals [25]. Currently, saffron petals are unusable and discarded as agricultural waste. In a global scale, the volume of this waste was about 8762 tons in 2014 [26]. Therefore, it could be an underexploited resource in DSSCs fabrication. Figure 3 depicts some saffron flowers, showing the petals' shape and pattern, and the chemical structure of delphinidin which is extracted from petals.

This research was focused on the extraction of delphinidin pigments from saffron petals to fabricate a nanoparticle titania-based DSSC. To the best of our knowledge, this is the first study that is focused on characterization of the DSSC efficiencies based on saffron petals dye. The photovoltaic performance of the saffron petal-based DSSC was evaluated by measuring current–voltage characteristics and the incident photon to current efficiency (IPCE). Also, the extracted dye was characterized by ultraviolet–visible (UV–Vis) and Fourier transform infrared (FT-IR) spectroscopy.

2 Materials and Methods

2.1 Preparation of the Natural Dye Sensitizer. Fresh saffron flowers were collected from a farm in Torbat-E-Heydariyeh region (Iran), the most important area of saffron production in the world. Iran now accounts for more than 90% of the world production of saffron [26,27]. The petals were separated from other parts of saffron flowers and dried in a dark and naturally ventilated room at the temperature of about 37 °C. This method of drying was chosen to provide the most stable condition for anthocyanins during drying [25]. The dried petals were crushed and sieved (16 meshes) and was protected from exposure to direct sunlight. In order to extract anthocyanins, ultrasonication was carried out using an ultrasonic processor (Sonic VCX 750) at a frequency of 20 kHz. The optimum extraction conditions that maximize the extracted anthocyanins were found to be a ratio of solvents to sample of 20 ml/g, acidic ethanol concentration of 25.02% ($pH = 2$), temperature of 25.8 °C, and extraction time of 15 min [25]. The resulting solution was also protected from exposure to sunlight and stored at about 5 °C. The solid residues were then filtered out from solution, using filter papers, to obtain a pure and clear natural dye solution. Further purification was performed using solid-phase extraction (SPE), according to the protocol reported by Wrolstad [28]. This extract was also stored at 5 °C and used for further characterization as a sensitizer in fabrication of DSSC.

2.2 Fabrication of DSSCs. To prepare the transparent electrodes, a fluorine-doped tin oxide (FTO) conductive glass sheet having the resistance of 15 Ω/\square was purchased from Dyesol Company (Queanbeyan, Australia). The FTO glass was first cleaned in a detergent solution and then washed with water and ethanol. The FTO glass was cut into some pieces and then were

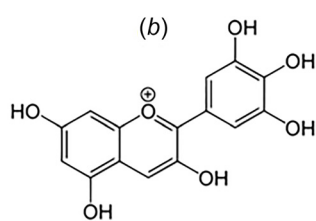


Fig. 3 Saffron petals (a) and chemical structure of delphinidin (b)

immersed in 100 ml of TiCl_4 water solution (40 mM) at 70°C for 30 min, then washed with water and ethanol and dried in an oven at 80°C . A thin film of titanium dioxide (TiO_2) was coated on the FTO glass plates using “doctor-blading” technique. The coated plates were gradually heated at 325°C for 5 min, then they were heated to 375°C , and finally, were sintered at 450°C for 30 min. This procedure increases the compactness of the internal voids of the film’s structure and removes the organic loads. Consequently, the interconnection of the TiO_2 nanoparticles is improved, and hence, the absorption performance of TiO_2 film is enhanced [29]. Subsequently, the TiO_2 film was treated in 40 mM TiCl_4 solution at 70°C for 30 min, then rinsed with water and ethanol, and sintered at 500°C . The films prepared by this method attained a thicknesses of $10\ \mu\text{m}$. The sintered TiO_2 films were cooled down to room temperature and then immersed in the previously prepared solution of natural dye for 24 h for final preparation of the electrodes. The concentration of the dye was $\cong 0.4\ \text{mM}$ as determined by using Beer’s law and the previously reported extinction coefficient of $30,900\ \text{M}^{-1}\text{cm}^{-1}$ at $555\ \text{nm}$ [30]. To prepare the counter-electrodes a 1.5 mm diameter hole was drilled in each FTO-glass plates. The perforated plates (as substrates) were washed and cleaned with water and ethanol in order to remove any residual of glass powder or organic contaminants. The Pt catalyst was deposited on the conductive face of the FTO plates by dropping hexachloroplatinic acid ($\text{H}_2\ \text{PtCl}_6$) solution (5 mM in isopropanol) followed by heating at 500°C for 30 min. They were then sintered in air at $350\text{--}400^\circ\text{C}$ for 1 h in a furnace and finally cooled down to room temperature [31]. The anode and the Pt counter-electrode were assembled into a sandwich type cell and sealed using a thermopress with a hot melt gasket of 25 ml thickness made of the Surlyn ionomer (Solaronix, Aubonne, Switzerland). The aperture of the Surlyn frame was larger than the TiO_2 area. A drop of electrolyte solution was placed on the hole in the back of the cathode. The electrolyte (LiI 0.8 M, I2 0.05 M, in acetonitrile) was introduced into the cell by means of vacuum back-filling. The cell was placed in a small vacuum chamber to remove inside air. Again by exposing the cell to ambient pressure, the electrolyte was driven into the cell. Finally, the hole was sealed and closed by heating another Surlyn film and putting a thin cover glass onto the hole [16].

2.3 The Apparatus and Measurements. The UV–Vis absorption spectrum was recorded by a Perkin Elmer L25 spectrophotometer (range of 200–1100 nm). The Perkin Elmer Spectrum RX I FT-IR instrument was used to identifying the functional groups present in the sample. The current–voltage curves were recorded with an analyzer (potentiostat/galvanostat, PalmSens) under the AM 1.5 ($100\ \text{mW}/\text{cm}^2$) illumination from a solar simulator (Luzchem, Gloucester, ON, Canada). The incident photon to current conversion efficiency (IPCE) was obtained by measuring short-circuit photocurrent under incident monochromatic light

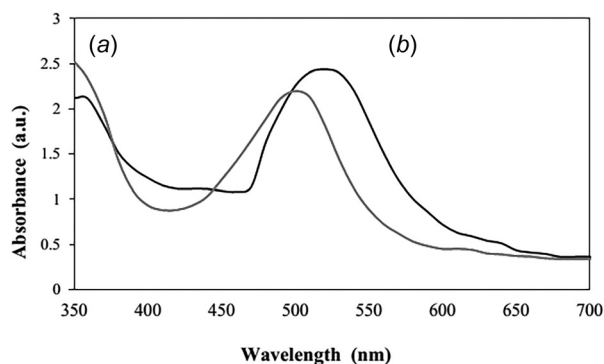


Fig. 4 UV–Vis absorption spectrum of (a) the dye solution obtained from saffron petal and (b) dye after adsorption onto the TiO_2 surface

irradiated by monochromatic incident light of 1×10^{16} photon/ cm^2 under $100\ \text{mW}/\text{cm}^2$ with bias light in DC mode (model Jarrel Ash monochromator), using a 100 W halogen lamp and a Thorlabs calibrated photodiode.

3 Results and Discussion

3.1 UV–Vis Absorption Spectra. In order to understand the visible-light response of the saffron petal dye, the UV–Vis absorption spectrum was recorded which is shown in Fig. 4(a). The saffron petal dye extract shows a maximum absorption peak at around 510 nm. The extended π conjugation, as well as the presence of positive charge and free $-\text{OH}$ groups in delphinidin structure, allows the dye to absorb light in the visible region [23,24]. Figure 4(b) shows the UV–Vis absorption spectrum of dye adsorbed on TiO_2 film. In this case, the maximum absorption peak is at about 530 nm. Furthermore, Fig. 4 also shows that the absorption spectrum of the adsorbed dye onto anode is broader than the absorption spectrum of saffron petal dye extract with a clear shift to the higher wavelengths. The red shifting the peak from 510 nm to 530 nm might be due to the binding of anthocyanins to the TiO_2 . In other words, the binding between dye and TiO_2 through the carbonyl and hydroxyl groups, brings the ground and excited states closer together, and hence, the energy required to effect the electron promotion is, therefore, less and, consequently, the wavelength that provides this energy is higher [32].

3.2 FTIR Spectroscopy and IPCE. The dye structure of saffron petal possesses several $\text{C}=\text{O}$ and $-\text{OH}$ groups which are capable of anchoring to the Ti sites on the TiO_2 surface. FT-IR spectrum reveals the presence of hydroxyl group in the molecular structure of saffron petal extract, which can be bound to the surface of TiO_2 film. The Fourier transform infrared (FTIR) spectra of the saffron petal dye extract is shown in Fig. 5. The peak occurred at $3365\ \text{cm}^{-1}$ is assigned to $-\text{OH}$ stretching vibration of the anthocyanin dye of saffron petal. Moreover, the two peaks at 2862 and $2946\ \text{cm}^{-1}$ and a peak at $1033\ \text{cm}^{-1}$ are assigned to $-\text{CH}$ stretching mode and $-\text{CO}$ vibration, respectively [33]. Therefore, the FT-IR spectrum confirms the presence of hydroxyl group in the molecular structure of anthocyanin dye which can be bound with the surface of TiO_2 porous film. The incident photon to electron conversion efficiency IPCE is a powerful and informative technique for measuring the percentage of photons hitting the device’s photoreactive surface and producing charge carriers. It is the ratio of the photocurrent to the rate of incident photons as a function of wavelength. The IPCE spectra of the DSSC sensitized with saffron petal dye is shown in Fig. 6. As seen, the maximum IPCE of the saffron-petal-dye-based DSSC is about 22%. This occurred at 540 nm and red-shifted by 30 nm relative to the maximum absorption peak wavelength. It shows good absorption properties and a good adsorption of saffron petal dye on TiO_2 surface [34]. The IPCE value at 380 nm is assigned to direct excitation of TiO_2 [17].

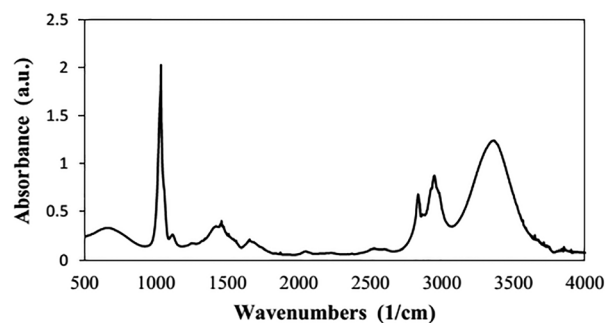


Fig. 5 Fourier-transform infrared spectra for the purified dyes obtained from the saffron petal

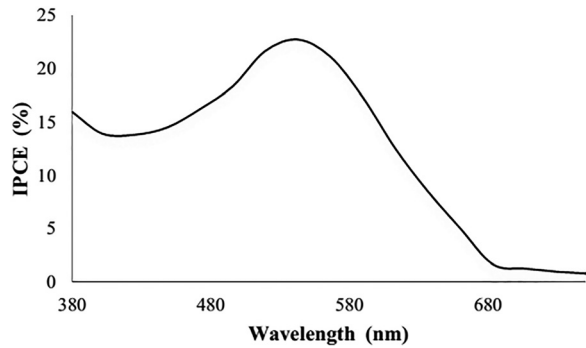


Fig. 6 IPCE curve photoaction spectra on DSSC of the saffron petal

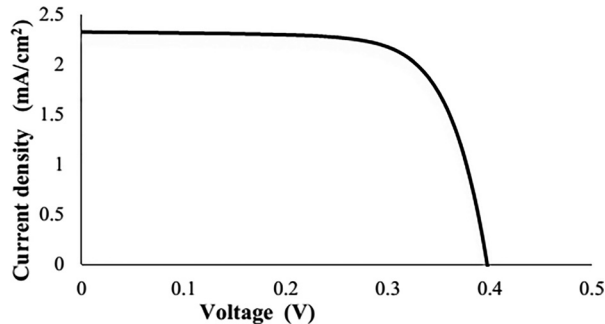


Fig. 7 Photocurrent–voltage (J – V) curve for dye-sensitized solar cell using saffron petal dye

3.3 Photovoltaic Performance of the DSSCs. Figure 7 shows the J – V curve of the TiO_2 -based DSSCs sensitized with the natural dye extract from saffron petal. Photovoltaic performance parameters such as fill factor (FF) and the power conversion efficiency (η) are defined as follow [34]:

$$\text{FF} = \frac{J_{\text{max}} \times V_{\text{max}}}{J_{\text{sc}} \times V_{\text{oc}}} \quad (5)$$

$$\eta(\%) = \frac{J_{\text{sc}} \times V_{\text{oc}} \times \text{FF}}{I_{\text{inc}}} \times 100 \quad (6)$$

Where J_{sc} is the short-circuit current density (mA/cm^2), and V_{oc} is the open-circuit voltage (V). J_{max} (mA/cm^2) and V_{max} (V) are the current density and voltage, respectively, in the J – V curve, at the point of maximum power output. The cell exhibited a short-circuit photocurrent density of $2.32 \text{ mA}/\text{cm}^2$, an open-circuit photovoltage of 0.397 V , and a fill factor of 0.71 , yielding a power conversion efficiency of 0.66% under the standard test conditions (a cell temperature of 25°C , solar irradiance of $1000 \text{ mW}/\text{cm}^2$ and an air mass of 1.5). Considering other similar DSSCs the J_{sc} of $2.3 \text{ mA}/\text{cm}^2$ is high and the fill factor of 0.71 is noticeably high [29,35–40]. The good J_{sc} may be due to the capability of the sensitizer to absorb sunlight over a wider region of the solar spectrum, and the higher power conversion efficiency, which is fairly good in comparison with the other similar studies [29,36,38,41–46]. The high fill factor shows a low equivalent

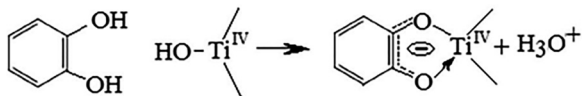


Fig. 8 Schematic illustration of the complex reaction of the hydroxylated TiO_2 surface by catechol [48]

series resistance and high equivalent shunt resistance [47] and it can be related to the good sensitization properties of saffron petal dye extract. This improved performance is mainly due to the chemical structure of saffron petal dye. The Catechol group ($\text{C}_6\text{H}_10(\text{OH})_2$) in B-ring of delphinidin causes the chelation of Ti (IV) that involves the replacement of a surface hydroxyl group by deprotonated ligand in a mononuclear bidentate geometry, which binds strongly the catechol to the TiO_2 nanoparticles [34,48,49] (Fig. 8).

4 Conclusion

The purified natural dye extracted from saffron petal, which is commonly unusable part of saffron flower, was used as a sensitizer in DSSC. This natural sensitizer was introduced for the first time, in this study, for developing new DSSCs and, therefore, it has not been yet studied and reported in the literature. Pigment extraction was performed using ultrasonic procedure, which was carried out also for the first time. The most important pigment of saffron petal dye extract is delphinidin. It was found that due to the presence of six hydroxyl groups in delphinidin, this anthocyanidin has a good ability to bind strongly with TiO_2 surface. The saffron petal-sensitized DSSC exhibited the power conversion efficiency of 0.66% , the short circuit current density (J_{sc}) of $2.32 \text{ mA}/\text{cm}^2$, the open-circuit voltage (V_{oc}) of 0.397 V , and the fill factor (FF) of 0.71 . The results demonstrated that utilizing saffron petal dye extract as a sensitizer in DSSCs was an encouraging option with the advantages such as availability, low-cost and non-toxicity, and reasonable efficiency. It should be emphasized that, despite the low power conversion efficiency of natural dyes, they are promising due to their environmental friendliness, low-cost production, and relatively simple fabrication. Further studies are required to be done on the approaches to increasing the power conversion efficiency of this new dye by, for instance, improving its structure through adding the functional groups like $-\text{OH}$ or $-\text{COOH}$ to binds strongly with the TiO_2 nanoparticles. Also, it would be worthwhile to measure the oxidation potential by cyclic voltammetry.

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