# **RESEARCH PAPER**

# Energy Production Using Dye-sensitized Solar Cells by TiO<sub>2</sub> Nanoparticles Fabricated with Several Natural Dyes

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## ABSTRACT

The present work displays the use of natural dyes extracted from native plants as sensitizer for fabrication of dye-sensitized solar cells (DSSCs). The native plants named as comellia sinensis, punica granatum L. var sativa k.maly, morus nigra, rubia tinctorum and brassica oleracea were collected from Kashan area, Iran. The extracted dyes were characterized with the aid of UV-Vis and Fourier transform infrared (FT-IR) spectroscopies. The FT-IR results revealed the presence of hydroxyl groups in the chemical structures of the natural dyes, improving the interaction of between photosensitizer and TiO<sub>2</sub> surface in solar cell devices. In addition, photoelectrochemical performance of the DSSCs based on the natural dyes illustrated short-circuit photocurrent (Jsc) and open-circuit voltages  $(V_{\sim})$  ranging from 0.5 to 2.36 mA/cm<sup>2</sup> and 0.38 to 0.62 V, respectively. Since cyanidin- glucoside compounds were the main pigment of brassica oleracea, interaction between plenty of hydroxyl groups of these compounds and TiO, surface was very efficient, this sensitizer owned the best photovoltaic performance among all the natural dyes.

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## INTRODUCTION

Dye-sensitized solar cells (DSSC) developed by Grätzel *et al.* have attracted more attention in converting solar energy due to their environmental friendliness and low cost of production [1]. A DSSC is commonly constructed from a nanocrystalline porous semiconductor electrode-absorbed dye, a counter electrode, and an electrolyte containing iodide and triiodide ions. The dye molecules can easily absorb visible light, and inject electrons from the excited state into the conduction band of metal oxide. The injected electrons transfer from the nanostructured film to the current collector and the dye is renewed by an electron donor in the electrolyte solution. The DSSC is fully regenerated using electron transfer to the electron acceptor at the counter electrode [2].

So far, various synthetic transition metal complexes such as Ru complexes have used as sensitizers [3, 4]. Since the preparation approaches of the metal complexes need toxic solvents, complicated procedures and chromatographic purification steps which are very time-consuming and have low yields, natural dyesensitizers extracted from some leaves, fruits, flowers, and vegetables have been considered as suitable alternative dyes for DSSC devices [5-8]. Natural pigments including anthocyanins [9], flavonoids [10], chlorophyll [11,

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Fig. 1. The chemical structure of current anthocyanins in the plants.

12], tannins [13, 14] and carotenoids [15, 16] have been successfully applied as sensitizers in DSSCs due to their non-toxicity, cost, efficiency, and complete biodegradation [6-8]. Flavonoids and their related compounds, a great group of natural phytochemicals, have been found in many plant tissues, where they are inside the cells or on the surfaces of different plant organs. These natural compounds have been divided based on their chemical structures as follows: flavonols, flavones, flavanones, isoflavones, catechins, anthocyanin, and chalcones. Moreover, flavonols are divided into three classes: flavonoids (2-phenylbenzopyrans), isoflavonoids (3-benzopyrans), and neoflavanoids (4-bezopyrans).[10]

The anthocyanins contain an original flavonoid group that is responsible for cyanic colors ranging from pink salmon through red and violet to dark blue of most flowers, fruits, leaves and stems. The most common anthocyanins in flowers are pelagonidin (orange), delpinidin (blue-red), petunidin (blue-red) and malvidin (blue-red). The chemical structures of common anthocyanidins are shown in Fig. 1 .[9]

The performance of natural dye sensitizer in DSSC has been estimated by open circuit voltage (*Voc*), short circuit current (*Jsc*), fill factor (*FF*), and energy conversion efficiency ( $\eta$ ) [17]. In 2008, Sicilian orange juice dye was employed as photosensitizer in DSSC by Calogero and Marco [18]. Also, Roy *et al.*, investigated that by using Rose Bengal dye as sensitizer, the *Jsc* and *Voc* of their DSC reached to 3.22 mAcm<sup>-2</sup> and 0.89 V, respectively, resulting in 2.09% conversion

efficiency [19]. Furthermore, Wang *et al.*, studied application of natural coumarin dyes as sensitizers in their DSC, which provided an efficiency of 7.6% [20-22]. Zhou *et al.*, considered several natural dyes from the herbal sources including leaves, flowers, fruits, and used them as sensitizers to make DSSC. Among them, the ethanol extract of the mangosteen pericarp showed the highest efficiency of 1.17% [23]. In this study, the extracted dyes from several native plants were used as natural sensitizer for fabrication of DSSCs. The photovoltaic studies showed the conversion efficiency of DSSCs depends on the intensity and range of absorption light as well as chemical structure of the natural dyes applied as sensitizers.

## MATERIALS AND METHODS

## Chemicals

The solvents and chemicals such as tetra-nbutyl-titanate (Aldrich), 4-tert-butyl pyridine(4tBP) (Aldrich), acetonitrile (Fluka), valeronitrile (Fluka),  $H_2PtCl_6$  (Fluka), iodine (I2) (99.99%, Superpur1, Merck), lithium iodide(Lil) (Merck), acetylacetone (acac) (Merck), acetone (Merck), ethanol (Merck), FTO glass (TEC-15, Dyesol) and Cis-bis (isothiocyanato)-bis(2,20-bipyridyl-4,4dicarboxylato)-Ru(II) (N719) (Dyesol), HCI (37%, Merck) were purchased from Merch and Aldrich.  $H_2O$  was purified by distillation and filtration (Milli-Q).

## Preparation of TiO, nanoparticles

Nano-titanium oxide was prepared via sol-gel method using tetra-n-butyl-titanate and deionized

water under ultrasound irradiation [24]. In a typical procedure, 2.0 mmol of tetra-n-butyl-titanate was added into deionized water and sonicated for 10 minutes under power of 70 W. Then 1.0 ml of HCl solution (2.0 M) was added dropwise into the solution within 15 minutes. The obtained gel was dried at 90°C for 24 h. Finally, the yellowish solid was calcinated at 600°C for 2h.

## Extraction of natural dyes

The methanol extracts of natural dyes were prepared by the following steps. At first, the fresh parts of the plants collected from Kashan area, Iran, were washed with water several times and vacuum dried at 40 °C. After crushing the plants into a fine powder using a mortar, the powders were immersed in methanol at ultrasound bath for 2 h. Then the extracts were filtrated out, concentrated at 40°C, dried and kept in dark at 4°C to characterize.

## Preparation of DSSC devices

The electrodes of fluorinated tin oxide (FTO) glass were cut to the size of  $2.4 \times 2.4$  cm<sup>2</sup>, and cleaned sequentially using isopropanol, deionized water and acetone. TiO, nanoparticles was deposited onto the FTO electrode with the aid of electrophoretic deposition (EPD) technique at a constant voltage of 10 V. Electrical contact was made with crocodile clips along the top edges of the electrodes. The electrodes deposited with TiO, were sintered at 450 °C for 30 minutes, and then immersed in the ethanol solutions of the extracted dyes or 0.3 mM of N719 dye (for comparison) for one day. The counter electrode was platinized by coating with a drop of H<sub>2</sub>PtCl<sub>6</sub> solution (0.003) M in ethanol) on the FTO glass. The coated FTO was then sintered at 400 °C and maintained the electrode at this temperature for at least 15 minutes. Finally, the counter electrode was placed on the top of the dye-sensitized TiO, film so that the conductive side of the counter electrode faces the TiO<sub>2</sub> film. The gap between two electrodes was sealed by a thermal adhesive film (Surlyn, Dupont). The internal space of the cell was filled with a liquid electrolyte (0.5 M Lil, 50 mM I,, 0.1 M 4-tertbutylpyridine in 80:20 acetonitrilevaleronitrile) [25]. In order to estimate shortcircuit current  $(J_{sc})$ , open-circuited voltage  $(V_{oc})$ and fill factor (FF), photocurrent-voltage (I-V) curves of the cells were investigated.

#### Spectroscopy analysis

TiO, nanoparticles were characterized using a Philips Xpert X-ray powder diffraction (XRD) diffractometer (CuK $\alpha$ ,  $\lambda$  = 0.154056 nm), at a scanning speed of 2 <sup>o</sup>/min from 10<sup>o</sup> to 80<sup>o</sup> (2θ). Scanning electron micrographs (SEM) of TiO, were recorded on a 3-TESCAN MIRA. UV-Vis absorption spectra of the extracted natural dyes were obtained with a Perkin Elemer UV-Vis spectrophotometer. The photo current-voltage characteristics of the solar cells were measured with an electrochemical analyser (CHI630A, Chenhua Instruments Co., Shanghai) under solar simulator illumination (CMH-250, Aodite Photo Electronic Technology Ltd, Beijing) at room temperature. I-V curves were obtained by using an external bias to the cell and measuring the generated photo-current with a Keithley model 2400 digital source meter. The voltage step and delay time of photocurrent were 10 mV and 40 ms, respectively. Based on I-V curve, the fill factor (FF) and efficiency for energy conversion ( $\eta$ ) were calculated as follows [26, 27]:

# $FF = P_{max} / (J_{sc} V_{oc})$

The fill factor can assume values between 0 and less than 1 and is defined as the ratio of the maximum power ( $P_{max}$ ) from the solar cell to the product of  $V_{oc}$  and  $I_{sc}$  pursuant to:

$$\eta = J_{c}V_{c}FF/I_{c}$$

# **RESULTS AND DISCUSSION**

Fig. 2 shows XRD pattern of TiO<sub>2</sub> nanoparticles. The reflection peaks in this pattern can be attributed to anatase phase of TiO2 (JCPDS no. 04-0477). The crystallite size (D) of the nanoparticle has been calculated by the Debye–Scherrer equation (D =K $\lambda/\beta$  cos  $\theta$ ), where  $\beta$  (full-width at half-maximum or half width) is in radian and  $\theta$  is the position of the maximum of the diffraction peak, K is the so-called shape factor, which usually takes a value of about 0.9, and  $\lambda$  is the X-ray wavelength (1.5406Å for CuK $\alpha$ ) [28]. According to the Debye–Scherrer equation, the average particle size of the as synthesized nanoparticles is about 12 nm.

In order to investigation of morphology and particle size of  $TiO_2$ , SEM image of  $TiO_2$  was taken and shown in Fig. 3. The SEM image presents spherical particles with diameters about 100 nm composed of very fine particles.

Fig. 4. shows UV–Vis absorption spectra of the

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Fig. 2. XRD pattern of TiO<sub>2</sub> nanoparticles.



Fig. 3. SEM image of TiO<sub>2</sub> nanoparticles.

dyes extracted with methanol from roots, leaves and fruits of the native plants. It was found that the absorption peaks of natural dyes related to *comellia sinensis, punica granatum* L. var sativa k. maly, *morus nigra, rubia tinctorum* and *brassica oleracea* are in the visible region. An obvious difference in the absorption characteristics is among the extracts that obtained from the natural dyes. The absorption peak of extract from *comellia sinensis* leaves is in a wide range from 400 to 700 nm with absorption maximum at 403 nm. The UV– Vis absorption spectrum of the extract of *punica granatum* fruit skin as shown in Fig. 3 reveals that the maximum absorption wavelength is between 400-425 nm. The extracts of *morus nigra* fruits and brassica oleracea leaves show broad absorption peaks between 400-700 nm with maximum absorption of 400 nm. Additionally, the UV–Vis peak related to the root extract of *rubia tinctorum* appears at 400-650 nm with maximum absorption



Wavelength (nm)

Fig. 4. UV–Vis absorption spectra of the natural dyes extracted from (a) *comellia sinensis*, (b) *punica granatum* L. var sativa k. maly, (c) *morus nigra*, (d) *rubia tinctorum* and (e) *brassica oleracea*.

Table 1. Photovoltaic performance of DSSCs based on natural dyes and N719 under AM 1.5 (100 mW cm<sup>-2</sup>).

Plants	λ <sub>max</sub> (nm)	Voc(V)	J <sub>sc</sub> (mA/cm²)	FF	n (%)
Camellia sinensis	403	0.42	0.52	0.64	0.14
Punica granatum	436	0.55	1.14	0.62	0.39
Morus nigra	400	0.55	1.51	0.60	0.51
Rubia tinctorum	403	0.38	0.50	0.618	0.11
Brassica oleracea	400	0.62	2.36	0.60	0.88
N719	532	0.70	11.9	0.50	4.08



Fig. 5. J–V characteristics of DSSCs with natural dyes.

of 403 nm.

Then total performance of natural dyes as semiconductor sensitizers in dye-sensitized solar cells was evaluated in terms of maximum wavelength,  $\lambda_{max}$ , short circuit current,  $J_{sc'}$  open circuit voltage,  $V_{oc}$ , fill factor, *FF*, and conversion efficiency ( $\eta$ ) were measured and inserted in Table 1. I–V curve of the N719 and the natural dyes extracts are shown in Fig. 4. As shown in Fig. 4. and Table 1, the conversion efficiency of the DSSCs

sensitized with *brassica oleracea* extract is 0.88%, with open circuit voltage ( $V_{oc}$ ) of 0.62 V, shortcircuit current density ( $J_{sc}$ ) of 2.36 mA/cm<sup>2</sup>, and fill factor (*FF*) of 0.60.

The conversion efficiency of the DSSCs sensitized with *morus nigra* extract is 0.51%, with open-circuit voltage ( $V_{oc}$ ) of 0.55 V, short-circuits current density ( $J_{sc}$ ) of 1.5 mA/cm<sup>2</sup>, and fill factor (*FF*) of 0.618. The conversion efficiency of the DSSCs sensitized with *punica granatum* extract



Fig. 6. FT-IR spectra of the natural dyes obtained from (a) *comellia sinensis*, (b) *punica granatum* L. var sativa k. maly, (c) *morus nigra*, (d) *rubia tinctorum* and (e) *brassica oleracea*.



Fig. 7. Chemical structure of (-)-epigallocatechin gallate as the most flavonoid in camellia sinensis leaves.

is 0.39%, with open-circuit voltage ( $V_{oc}$ ) of 0.55 V, short-circuit current density ( $J_{sc}$ ) of 1.14 mA/ cm<sup>2</sup>, and fill factor (*FF*) of 0.62. The conversion efficiency of the DSSCs sensitized with *camellia sinensis* extract is 0.14%, with open-circuit voltage ( $V_{oc}$ ) of 0.42 V and short-circuit current density ( $J_{sc}$ ) of 0.52 mA/cm<sup>2</sup>, and fill factor (*FF*) of 0.64. The conversion efficiency of the DSSCs sensitized with *rubia tinctorum* extract is 0.11%, with opencircuit voltage ( $V_{oc}$ ) of 0.38 V, short-circuit current density ( $J_{sc}$ ) of 0.5 mA/cm<sup>2</sup>, and fill factor (*FF*) of 0.58. For comparison, a N719 standard DSSC with  $J_{sc}$ =11.9 mAcm<sup>-2</sup>,  $V_{oc}$  = 0.7 V, FF= 49%, and  $\eta$ = 4.08 was achieved.

FT-IR spectra of the powder obtained from the comellia sinensis, punica granatum L. var sativa k.maly, morus nigra, rubia tinctorum and brassica oleracea are shown in Fig. 6a-e, respectively.

The main pigment of *camellia sinensis* is (–)-Epigallocatechin gallate, which is the most abundant flavonoid in camellia sinensis leaves (Fig. 7) [29]. In the FT-IR spectrum of *camellia sinensis* 



Fig. 8. Chemical structure of delphinidin 3-glucoside as the most flavonoid in punica granatum fruit skin.



Fig. 9. Cyanidin-3-grucorutinoside and cyanidin 3-rutinoside; two natural dyes in morus nigra fruit.

(Fig. 6a), the strong bands observed at 1639, 1456 and 1034 cm<sup>-1</sup> corresponds to vibrational modes of aromatic C=C and C-O stretching, respectively. The signal corresponds to phenolic hydroxyl appeared at 3377 cm<sup>-1</sup>. Moreover, the bands related to bending and stretching vibrations of meta aromatic rings are shown at 610, 740 and 824 cm<sup>-1</sup> (Fig. 6).

Delphinidin 3-glucoside was identified to be the major anthocyanin present in the pomegranate fruit skin (Fig. 8) [30]. In the IR spectrum of *punica granatum* (Fig. 6b), the stretching frequency of aromatic C=C can be seen at around 1615 and 1448 cm<sup>-1</sup>. The stretching vibration of O–H in phenol ring, C=O and C-O appeared at 3402, 1729 and 1040 cm<sup>-1</sup>, respectively

Cyanidin-3-diglucoside-5-glucoside "cores" as the predominant anthocyanins in *morus nigra* which is non-acylated, mono-acylated or di-acylated with p-coumaric, caffeic, ferulic and sinapic acids. Also, red cabbage includes anthocyanin-enriched concentrates such as pelargonidin-3-glucoside and novel forms of cyanidin-3-O-triglucoside-5-O-glucoside diacylated with hydroxycinnamic acids [31].

In morus nigra, cyanidin-3-grucorutinoside and cyanidin 3-rutinoside are responsible for the fruit coloration (Fig. 9) [32, 33]. In the IR spectrum of morus nigra (Fig. 6c), the stretching vibrations of O-H in phenol cycle and aromatic C=C are shown at 3395 and 1638-1459 cm<sup>-1</sup>, respectively. Besides, the stretching frequency of C=O and C–O is assigned at 1739 and 1046 cm<sup>-1</sup>, respectively.

It was identified that alizarin is the major anthocyanin in the *rubia tinctorum* (Fig. 10) [34]. In the FT-IR spectrum of *rubia tinctorum* (Fig. 6d), the stretching vibration of O–H at 3418 cm<sup>-1</sup>, the C=C stretching at 1600 and 1410 cm<sup>-1</sup>, and the C=O stretching due to anthraquinone group are visible at 1630 cm<sup>-1</sup>.

The major anthocyanins in red cabbage are acylated with aromatic acids, i.e. cyanidin-3, 5-diglucoside, cyaniding 3-sophoroside-5glucoside and cyanidin-3-sophoroside-5-glucoside acylated with sinapic acid [35].

The typical component pigment in red cabbage



Fig. 10. Alizarin; a natural anthraquinone as the major pigment in root of rubia tinctorum.



Fig. 11. Chemical structure of cyanidin-3-sophoroside-5-glucoside as the typical anthocyanin in brassica oleracea leaves.

with the cyanidin unit glycosylated by three glucose units, giving cyanidin-3-sophoroside-5-glucoside is shown in Fig. 11. In the IR spectrum of *brassica oleracea* (Fig. 6e), the stretching frequency of aromatic O-H at 3404 cm<sup>-1</sup>, the stretching vibrations of C=C of aromatic ring at 1624 and 1407 cm<sup>-1</sup>, and stretching frequency of C-O at 1027 cm<sup>-1</sup> are clear.

According to the FT-IR results, all of the natural pigments contain active functional groups such as carbonyl and hydroxyl groups. The interactions of the natural dye molecules via the carbonyl and hydroxyl groups with the hydroxyl groups on TiO, surface lead to the electron transfer from the natural dyes to the conduction bond of TiO<sub>2</sub>. Therefore, it is concluded that the best sensitizer extracted from comellia sinensis, punica granatum L. var sativa k. maly, morus nigra, rubia tinctorum and brassica oleracea belongs brassica oleracea (Red Cabbage) leaves in comparison with the other natural dyes. It could be due to the high concentration of anthocyanins content in the cabbage leaves or the presence of hydroxyl groups in cyanidin natural pigment which can bond to the TiO<sub>2</sub> surface effectively [35].

The DSSCs sensitized with *brasica oleraca* extract shows higher  $V_{\alpha}$  than that of other natural

extracts while natural dyes commonly show low  $V_{oc}$ . Also brasica oleraca and morus nigra show higher  $J_{sc}$  than that of other extracts which relate to the ability of the pigment for charge transfer in the TiO<sub>2</sub>/dye/electrolyte interface [36]. The reason for such low efficiency about other extract can be due to low concentration of anthocyanins content. Also anthocyanins from various plants give different sensitizing performances [23].

Anthocyanins are the core compositions of natural dye and are often found in fruits, flowers and leaves of plants. As anthocyanins exhibited the colour in the range of visible light from red to blue, they are prospected to become high efficient sensitizers for wide band gap semiconductors [37]. In comparison to the obtained results, there are various findings about the application of natural dyes containing anthocyanins in dye sensitized solar cells [38]. In 2010, Chang and Lo [39] investigated the effect of chlorophyll extract from pomegranate leaf and anthocyanin extract from mulberry fruit as the natural dyes for DSSC.

The conversion efficiency of the DSSCs equipped by chlorophyll dyes from extract of pomegranate leaf was 0.597%, with open-circuit voltage  $(V_{oc})$ of 0.56 V, short-circuit current density  $(J_{sc})$  of 2.05 mA/cm<sup>2</sup>, and fill factor (*FF*) of 0.52. While

Dye	Semiconductor	λ <sub>max</sub> (nm)	J₅c (mAcm²)	Voc (V)	FF	п (%)
Flowers						
Begonia [23]	TiO <sub>2</sub>	540	0.63	0.53	72.2	0.24
Chinese rose [23]	TiO <sub>2</sub>	516	0.90	0.48	61.9	0.27
Hibiscus rosasinesis [42]	TiO <sub>2</sub>	534	4.04	0.4	63	1.02
Fruits						
Tangerine peel [23]	TiO <sub>2</sub>	446	0.74	0.59	63.1	0.28
Kopsia flavida [46]	TiO <sub>2</sub>	550	1.20	0.52	0.62	-
Leaves						
Vernonia amygdalin [43]	TiO <sub>2</sub>	400	0.07	0.34	0.81	0.69
Lawsonia inermis [44]	TiO <sub>2</sub>	518	1.87	0.61	0.58	0.66
Seeds						
Coffee [23]	TiO <sub>2</sub>	-	0.85	0.55	68.7	0.33
Black Rice [40]	TiO <sub>2</sub>	560	1.14	0.55	0.52	-

Table 2. Photoelectrochemical parameters of natural dyes based DSSC.

the conversion efficiency of the DSSCs prepared by anthocyanin dyes from mulberry extract was 0.548%, with  $V_{oc}$  of 0.555 V and  $J_{sc}$  of 1.89 mA/ cm<sup>2</sup> and FF of 0.53. The conversion efficiency was 0.722% for chlorophyll and anthocyanin as the dye mixture, with  $V_{oc}$  of 0.53 V,  $J_{sc}$  of 2.8 mA/cm<sup>2</sup>, and FF of 0.49.

Hao *et al.* [40] studied the photoelectric parameters of DSSC sensitized with the extract of capsicum, *erythrina variegata* flower, rosa xanthine. High photoelectrochemical values were obtained from the DSSC sensitized by the natural dye extracts of black rice and *erythrina variegata* flower which contain anthocyanin cores in their molecular structures [40]. The low  $P_{max}$  values come from the DSSC sensitized by the extracts of kelp and capsicum, which ascribes to weakly bond between their dye molecule and TiO<sub>2</sub> film [40].

Although nature dye chlorophyll plays a key role in the photosynthesis ability in plant body, it cannot result in good photo-to-electric conversion in DSSC because of no available bonds between the dye molecules and TiO<sub>2</sub> film to transfer the electrons from excited dye molecules to TiO, film. These results confirm the present observations about the important role of functional groups in natural dyes like anthocyanins in performance of dye-sensitized solar cells. Furthermore, the performance of several natural dye sensitizers in DSSC have been evaluated by open circuit voltage  $(V_{oc})$ , short circuit current  $(J_{sc})$ , fill factor (FF), and energy conversion efficiency  $(\eta)$  in comparison with the results in the literature (Table 2) [5, 6, 16, 17, 41-46].

The intensity and range of absorption light

of the natural extracts also affect the solar cell efficiency. Based on our finding brassica oleracea extract showed broad absorption between 400-700 nm and better sensitization activity. The low efficiencies of the DSSCs prepared by natural dyes depend on the dye structure and its anchoring groups and stability. The anchoring group which is attached to the TiO<sub>2</sub> is responsible for electron transfer from the dye molecules to the conduction band of TiO<sub>2</sub>. The lack of efficient hydroxyl groups in rubia tinctorum pigment leads to low efficiency of the DSSCs sensitized with this extract<sup>46</sup>. Furthermore, natural dyes are less stable than inorganic dyes that resulting decrease in the efficiency of natural dye based DSSCs [25]. The  $V_{\alpha c}$ of some synthetic photosensitizers such as N719 is higher than that of natural ones because of the presence of ACOOH ligands in their molecular structures. The ACOOH ligands can combine with the hydroxyl groups of TiO, surface to generate esters. This interaction enhances coupling effect of electrons on TiO, conduction band to acquire a quick electron-transport rate [40].

#### CONCLUSION

In the present work, the natural extracts from several types of native plants, *comellia sinensis*, *punica granatum* L. var sativa k.maly, *morus nigra*, *rubia tinctorum* and *brassica oleracea* from Kashan area, were used as photosensitizers in DSSCs for the first time. Among these natural dyes, the DSSC fabricated with the extract of *brassica oleracea* with the conversion efficiency of 0.88%, open circuit voltage ( $V_{oc}$ ) of 0.62 V and short-circuit current density ( $J_{ec}$ ) of 2.36 mA/cm<sup>2</sup>,

and fill factor (FF) of 0.60 showed significant higher photocurrent and reasonable efficiency. The improved efficiency of the cell based on the brassica oleracea extract can be related to the presence of the typical anthocyanin with the cyanidin unit glycosylated by three glucose units, named cyanidin-3-sophoroside-5-glucoside. The presence of hydroxyl groups in the anthocyanin molecules improves the interaction of between photosensitizer and TiO, surface. Our studies on the solar cells clearly indicated that the DSSC fabricated with various natural dyes displays good to medium efficiencies because of containing different anthocyanin pigments. Recent developments on various kinds of sensitizers for DSSC devices have led to the use of natural dyes that absorb sunlight within the visible spectrum with higher efficiencies. The nature of the dye used as sensitizers is the main factor affecting the DSSC efficiency. The application of natural dyes as sensitizers in DSSCs provides an alternative source and has several advantages such as low cost, ecofriendliness, availability, and simple manufacturing and usage.

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## **CONFLICT OF INTEREST**

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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