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Improving optical absorptivity of natural dyes for fabrication of efficient dye-sensitized solar cells

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Abstract

Efficient and cheap dye-sensitized solar cells (DSSCs) were fabricated using natural dyes from *Pastinaca sativa* and *Beta vulgaris*. Natural dyes are environmentally and economically superior to ruthenium-based dyes because they are nontoxic and cheap. However, the conversion efficiency of dye-sensitized solar cells based on natural dyes is low. One way to improve the DSSC performance is to enhance the absorptivity of extracted dyes. We investigated the influence of various factors in the extraction process, such as utilization of different extraction approaches, the acidity of extraction solvent, and different compounds of solvents on the optical absorption spectra. It was found that we could considerably enhance the optical absorptivity of dye and consequently the performance of DSSC by choosing a proper mixture of ethanol and water for extracting solvent and also the acidity of dye solution.

Keywords: Dye sensitized solar cell; Optical absorption; Natural dye; Betalains

Background

One of the greatest challenges in the next 50 years is the production of clean and renewable energy [1]. Our current energy consumption predominately relies on fossil fuels that generate greenhouse gases, most notably carbon dioxide. Greenhouse gases are directly implicated in the rise of average global temperature over the last century, which has widespread effects on ocean levels, biodiversity, crop production, natural disasters, and other aspects of the ecosystem [2]. Among the renewable energy technologies, solar cells utilizing solar energy are considered as the most promising ones. First-generation solar cells are based on silicon materials [3]. Second-generation solar cells rely on thin films such as cadmium telluride and copper indium selenide. However, indium, tellurium, and selenium are relatively scarce. Cadmium is a highly toxic heavy metal, and mining of these metals causes various environmental hazards [4]. Because of the high cost of solar cells, we must look for other technologies if solar cells become environmentally and economically competitive with fossil fuels.

Dye-sensitized solar cells (DSSCs) are third-generation solar cells that exhibit many advantages over the previous generations of solar cells [5,6]. In an environmental comparison of electricity generation from a DSSC system and a natural gas combined cycle power plant, the gas power plan would result in 450 g CO_2/kW h and DSSCs would result in between 19 and 47 g CO_2/kW h [7-9]. One of the key materials in DSSCs is the sensitizer. Ruthenium complex dyes are capable of delivering DSSCs with high conversion efficiencies [10]. However, ruthenium dyes are not suitable for environmentally friendly photovoltaic systems. Ruthenium is expensive and environmentally hazardous. Ruthenium compounds are treated as highly toxic and carcinogenic. When ruthenium compounds are heated in the presence of air, they form ruthenium tetroxide, which is a highly volatile and toxic compound that damages the eyes and upper respiratory system [4].

Natural dyes such as pigments used in food coloring are easily and safely extracted from plants [11]. It means that they do not require complex synthesis or toxicity test [12] and can be used in DSSCs. Since natural dyes have low cost of synthesis and are environmentally friendly, they are considered as a viable option for dye-sensitized solar cells in future research [13]. Natural dyes in DSSCs have shown overall conversion efficiencies below 1%. Until now, several natural dyes such as betalains [14,15], anthocyanins [16,17], and carotenes [18] have been used as sensitizers in DSSCs. Betalains are water-soluble pigments that can be found in roots, fruits,

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and flowers. Betalain definition embraces all compounds with structures based on the general formula shown in Figure 1. Betalains have the requisite functional groups (-COOH) to bind better to the TiO_2 nanostructure [19]. In this work, we developed an effective approach for extraction of dyes from *Beta vulgaris* and *Pastinaca sativa* in such a way that we could modify the optical absorption spectra of the extracted dye. To this end, we examined the influence of several parameters such as extraction solvents, acidity of solutions, and mixture of the extraction solvents on the absorptivity of the extracted dyes. Then, we used these dyes to fabricate DSSC under analogous conditions.

Mechanism of dye-sensitized solar cell

DSSC is composed of five elements: two transparent conductive substrates, nanostructured titanium dioxide layer, Pt layer, dye molecules, and electrolyte. Transparent conductive substrates are coated with a thin layer of TiO_2 and Pt nanostructures, respectively. The mechanism of this type of solar cell is similar to the photosynthesis process in plants [20]. In photosynthesis, light is converted into chemical energy. Photons with different energies in sunlight strike on the cell and penetrate into the dye layer since both the fluorine-doped tin oxide (FTO) layer with glass substrate and the TiO_2 nanocrystals are transparent to visible light. If photon energy is close to the energy gap of the dye molecule, namely the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), it will be absorbed by the dye, promoting one electron from HOMO to LUMO [21,22]. The excited electron will then be injected into the conduction band of TiO_2 through the interfacial bonds between the dye and the TiO_2, then be transported, and finally collected by the FTO (working electrode). The hole which was generated by photon excitation remains on the molecule during the process since the HOMO of dye is separated from all other energy levels. The hole eventually will be filled up by electrons from electrolyte ions. At the same time, reduction of oxidized dye by iodide produces triiodide. The triiodide diffuses to a counter electrode and accepts electrons from external load, regenerating the iodides. The overall process will provide electron flow from the working electrode to the outer circuit [23,24]. The dye would be regenerated by the electrolyte solution and would get ready for the next photon [24]. The general structure of a DSSC is illustrated in Figure 2.

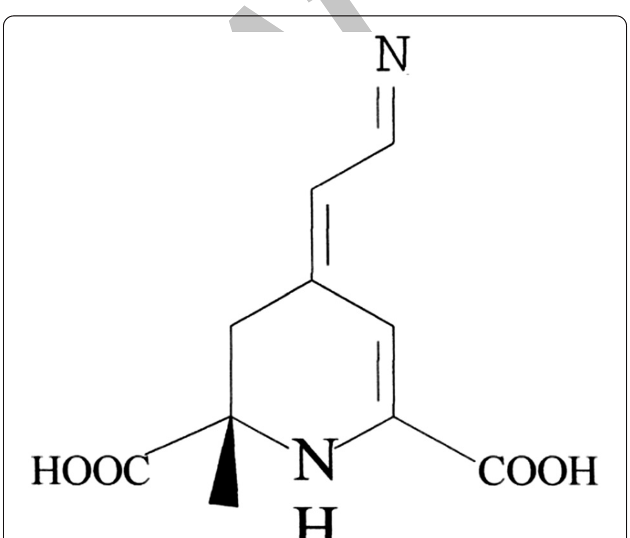

Figure 1 General formula of betalain [19].

Experimental details

Preparation of natural dye as sensitizer

The extracts of *P. sativa* and *B. vulgaris* were obtained from fresh materials. The solvents extracted from *P. sativa* (ethanol and water extract) were added over the small pieces of clean *P. sativa* in a solvent of 0.1 and 1 N HCl. The dyes extracted from *B. vulgaris* were obtained by immersing the *B. vulgaris* slice in HCl (0.1 and 1 N) solution (ethanol extract). The mixtures were kept overnight, and the resulting extracts were filtered to remove any solid residue and were used for sensitization. All solutions were protected from direct light and stored in the refrigerator at about +5°C; the dye solutions were stable for more than 12 months. The features of solutions extracted from *P. sativa* and *B. vulgaris* are listed in Table 1.

Fabrication of dye-sensitized solar cell

For the fabrication of dye-sensitized solar cells, the FTO conductive glass with a resistance of 8 Ω was used. TiO_2 paste with nanoparticle sizes ranging from 15 to 20 nm was deposited on the FTO conductive glass with doctor blade technique [25], and then TiO_2 paste with particle

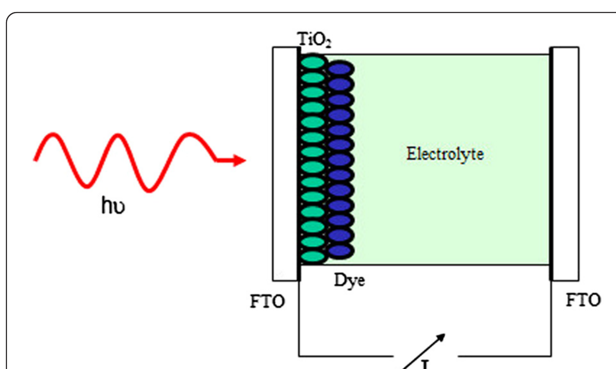

Figure 2 Schematic of DSSC.

Table 1 Chemical characteristics of the extracted solutions

Plant	Solvent	Diluted	Name
Pastinaca sativa	0.1 N HCl	Water	A
Pastinaca sativa	1 N HCl	Ethanol	B
Pastinaca sativa	0.1 N HCl	Ethanol	C
Pastinaca sativa	1 N HCl	Water	D
Pastinaca sativa	0.1 N HCl	Mixture of water and ethanol	E
Beta vulgaris	0.1 N HCl	Ethanol	F
Beta vulgaris	1 N HCl	Ethanol	G

sizes ranging from 100 to 200 nm as a scatterer layer was used. The TiO_2 film was sintered at 500°C for 30 min. After cooling, the TiO_2 electrode was immersed in a solution of dye for a time period varying from 6 to 24 h; TiO_2 film and substrates were rinsed in ethanol. The dye-covered TiO_2 electrode and Pt counter electrode was assembled into a sandwich type cell and sealed with a sealing spacer. The electrolyte solution was prepared by dissolving 2.07 g of KI and 0.19 g of I_2 in 25 ml ethylene glycol. After injection of the electrolyte, the hole in the counter electrode was sealed using a sealing spacer.

Result and discussion

Sensitizers for DSSCs need to fulfill important requirements such as absorption in the visible and near-infrared regions of the solar spectrum and should be strongly chelated to the semiconductor oxide surface. Moreover, the LUMO of the dye should lie at a higher energy level than the conduction band of the semiconductor so that, upon excitation, the dye injects electrons into the conduction band of the TiO_2. The HOMO energy level of the dye needs to be more positive than the redox potential of the couple (I^-/I_3^-) [5]. In this study, sensitizers such as dye extracted from *B. vulgaris*, *P. sativa* were used to fabricate DSSCs.

Betalains in acidic environments have strong absorption in the 400- to 600-nm range due to the color combination of yellow-orange betaxanthins and red-pink betacyanins [26]. Since the destruction of the environment and nonacidic betalains occurs very quickly, the acidic environment was an important factor for the extracted betalain dyes as previously observed by Zhang et al. [27]. The acid concentration in aqueous extract was changed from its initial value of 0.1 to 1 N for extracted dye from *P. sativa* and *B. vulgaris*. In addition to the significant increase of absorption intensity, this change has caused variation in the electrical current of the cells. Figure 3 shows the absorption spectra of four dyes extracted from *P. sativa* in which two of them were diluted in water and the others were diluted in ethanol.

The intensity of absorptions is approximately equal for water and ethanol extracts. An explanation for these results may come from the difference between compositions of the extracts. In the water extract, the concentration of dyes is expected to be higher than in ethanolic extracts, probably because of a higher solubility. Figure 4 shows the absorption spectrum of natural dyes extracted from *P. sativa* diluted in water and ethanol.

Consequently, although the UV-vis spectra of the extracts indicated the most suitable dye of the ethanolic extract, the performance of the DSSCs suggested that the proper sensitizer is the one obtained from the water extract. The acidity of the extract likely influences the solubility of various dyes, leading to extracts with different compositions. Although the absorption intensity of

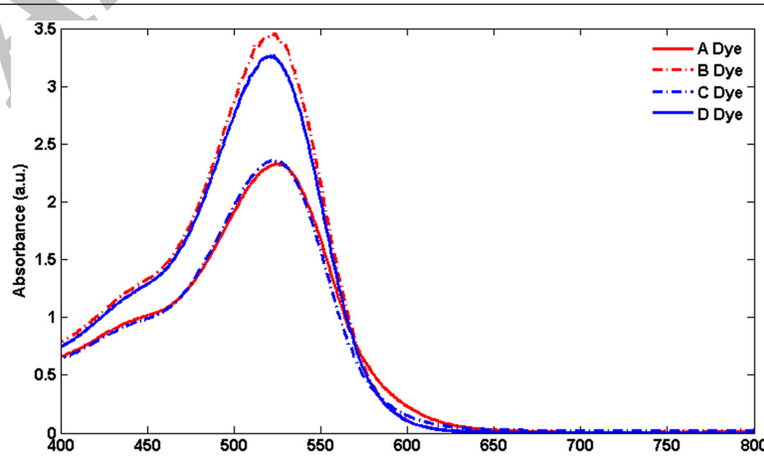

Figure 3 Absorption spectra of *P. sativa* extracts in acidic medium and other extracts. Water extract (dyes A and D) and ethanol extracts (dyes B and C).

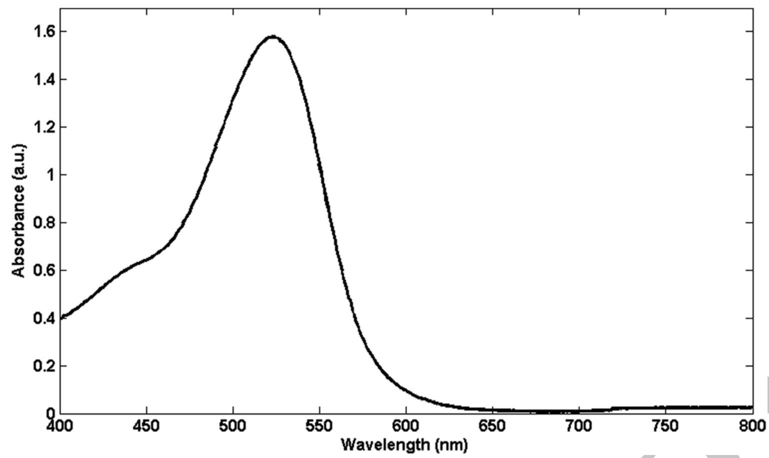

Figure 4 UV absorption spectra of dye solution extracted from *P. sativa*. In acidic solution diluted in a mixture of water and ethanol (E solution).

dye E, that is the mixture of A and C, is low, it indicates better performance in DSSCs. Figure 5 shows the absorption spectrum of dyes E, C, and A.

Changes which were made in the synthesis of natural dyes cause increase in absorption intensity which directly affects the rate of increase in some other parameters such as excited state lifetime of the dye molecules. We have shown that changing the acidity of the solution to extracted dye from *B. vulgaris* had an extensive effect on the absorption spectra. Figure 6 shows the effects of acidic solution in the absorption spectra of dye extracted from *B. vulgaris*.

Under equal preparation and irradiation conditions, the performance of DSSCs with eight different extracts was examined. The experimental setup for measuring the performance of DSSCs using natural dyes was built using a xenon lamp as solar simulator with full spectrum in the visible light. The first four ones correspond to extracts obtained from *P. sativa*, the other two ones were extracted from *B. vulgaris*, and the last one was obtained from *P. sativa* in acidic solution diluted in ethanol and water mixture. Table 2 summarizes the results for the extracts. In this table, the short-circuit photocurrent density (J_{SC}), the open-circuit voltage (V_{OC}) and the fill factor (FF) are reported.

We achieved a better sensitization activity using the dye extracted from *P. sativa* compared to the dye extracted from *B. vulgaris*. It was found that the best results were recorded for *P. sativa*. This is because these extracts both have betaxanthins and betacyanins, each with an absorption at different wavelengths, helping the cell to capture photons of two different energies. The best FF was obtained by the *P. sativa* extract (dye B), showing V_{OC} and J_{SC} values of 0.39 V and 7 mA/cm^2,

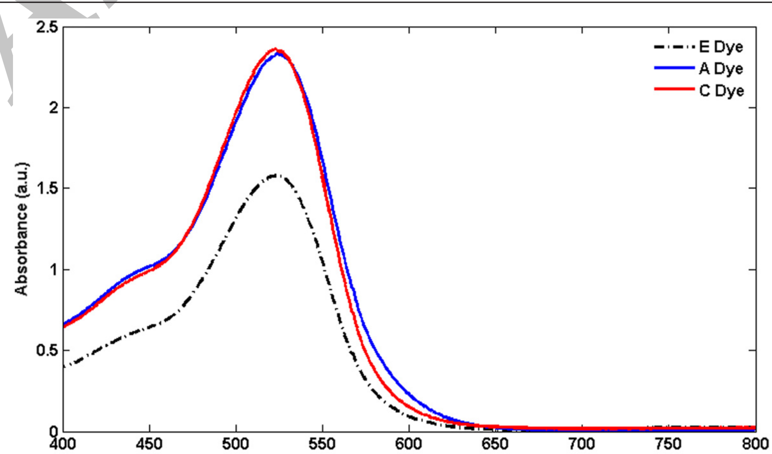

Figure 5 Absorption spectra of *P. sativa* extracts in 0.1 N HCl solution and other extracts. Water extract (dye A), ethanol extract (dye C), and ethanol and water extracts (dye E).

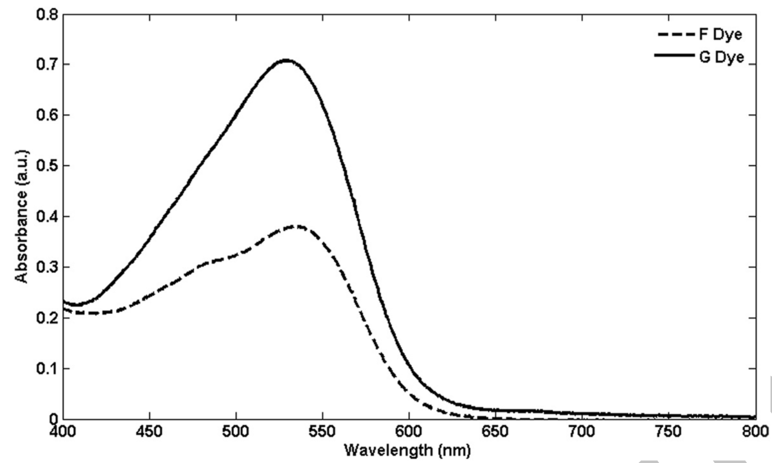

Figure 6 Absorption spectra of dye solutions extracted from *B. vulgaris.* In acidic medium, 0.1 N HCl (dye F) and 1 N HCl (dye G).

respectively, with an active area = 0.9 cm^2. Dye extracted from *P. sativa* (dye D) displays a promising photoelectrochemical performance showing a $J_{SC} = 7.2$ mA/cm^2, a $V_{OC} = 0.42$ V, a fill factor = 0.9, and an active area = 0.9 cm^2. Despite a maximum FF value of 0.95, the DSSC equipped with *B. vulgaris* extract (dye G) shows a $J_{SC} =$ 3.45 mA/cm^2, a $V_{OC} = 0.46$ V, an FF = 0.9, and an active area = 0.9 cm^2. These values are in agreement with those obtained in [14-16]. The current-voltage curve obtained with solar cells using *P. sativa* (dye B) as sensitizer is presented in Figure 7. Fill factor values from 0.4 to 0.95 were obtained with the natural dye extracted. The best values of FF for DSSCs using betalain dyes are less than 0.7 [28], significantly smaller than our best FF value of 0.95. Calogero et al. reported that a maximum FF of 0.57 was obtained using betalain dye extracted from *Bougainvillea* as sensitizer. They also reported that using *B. vulgaris rubra* as sensitizer for DSSC with maximum conversion efficiency has an FF of 0.37 [15], while we achieved a maximum FF of 0.9 (B solution). Betalains extracts from Sicilian prickly pear are employed as sensitizer for DSSCs with the highest performance reported by Calogero et al. at 0.62 [16]. In particular, the use of betalains gives a promising result with an FF of 0.95 which we know to be among the highest one so far that is reported with natural dyes. From the above results, it is seen that most of the natural dyes based DSSCs extracted from *B. vulgaris* and *P. sativa*, with the fill factor is enhanced with the increase of extract acidity. We have found that the dye extracted from *P. sativa* shows the highest solar energy conversion efficiency. Enhancement of performance of DSSCs has been successfully accomplished using extracts of the *B. vulgaris* and *P. sativa* plants as natural sensitizers. The dye extracts present good light harvesting properties and sensitize the charge transfer of TiO_2. The use of natural sources for the sensitizer simplifies the points involved in the simple and environmentally friendly production of DSSCs, providing an interesting alternative to commonly used organic and inorganic dyes.

Table 2 Photo electrochemical properties of dye extracted from *B. vulgaris* and *P. sativa* in DSSCs

Dye	J_{SC} (mA/cm^2)	V_{OC} (v)	FF
Pastinaca sativa (A)	3.75	0.43	0.83
Pastinaca sativa (B)	7	0.42	0.95
Pastinaca sativa (C)	3.55	0.26	0.68
Pastinaca sativa (D)	7.2	0.42	0.9
Pastinaca sativa (E)	6.9	0.41	0.82
Beta vulgaris (F)	2.51	0.36	0.4
Beta vulgaris (G)	3.45	0.46	0.9

Conclusions

We studied the use of dye extracted from *B. vulgaris* and *P. sativa* for DSSCs considering the improvement of natural pigment use. In our study, we tried to enhance the performance of DSSCs using natural dyes. The increase of acidity of dyes extracted from *B. vulgaris* and *P. sativa* leads to an increase of the DSSC performance. The simple extraction procedure, low cost, and environmentally friendly nature make natural dyes promising sources of sensitizers for DSSCs. The efficiency increases after the acidity of the extracts increased. The open-circuit voltage has small differences, but the current density varies significantly. Our experimental results show that the short-circuit current density and the efficiency of the DSSCs increased by the acidification of dye extracted from *B. vulgaris* and *P. sativa*. We observed that the nature of solvent has an effect on the performance of DSSCs using the solvent as sensitizer. Although

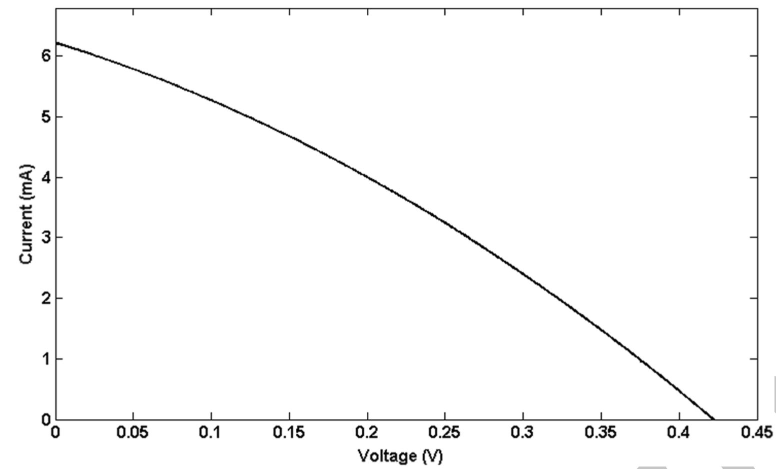

Figure 7 Current-voltage curve obtained for photoelectrochemical solar cell sensitized by *P. sativa* (B).

the spectrum of the extracts is considered as the most suitable dye of the ethanolic extract, the performance of the cells suggested that the proper solvent as sensitizer was obtained from the water extract in acidic solution. We stress that these results are achieved by optimization of the extraction dyes and enhance the optical absorption of natural dyes. The results are encouraging and may boost additional studies to search for new natural dyes and to optimize DSSCs with natural dyes.

Competing interests
The authors declare that have no competing interests.

Authors' contributions
AM participated in the design of the study and drafted the manuscript. Both authors, AM and RH, had the same participation in any section of the article. Both authors read and approved the final manuscript.

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RH is an MSc student of Physics at Persian Gulf University. AM is an assistant professor of Physics at Persian Gulf University.

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