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Three Fresh Plant Seeds as Natural Dye Sensitizers for Titanium Dioxide Based Dye Sensitized Solar Cells

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

In this paper, we used the extracts of three fresh plant seeds as photosensitizers for DSSCs based on TiO_2 nanopowder as a semiconducting material. Ethanol was used to extract the dyes from the seeds. The fill factors of the cells sensitized with the seeds of *Raphanus raphanistrum*, *Lepidium sativum* and *Dianthus barbatus* were 0.45, 0.40, and 0.48, respectively, whereas the efficiencies were 0.05, 0.03, and 0.15. The performance of the DSSC sensitized with *Dianthus barbatus* was investigated at various pH values of the dye solution and found to have a considerable effect of the cell efficiency.

Keywords: Dye sensitized solar cells; plant seeds; efficiency; pH.

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1. INTRODUCTION

Innovative scientific research is needed to satisfy the increasing energy demand in the world. This demand is expected to double by the year 2050 and triple by the end of the century. Natural energy sources are expected to play a vital role in the energy crisis solution. The solar energy reaching the earth from the sun is estimated as 3×10^{24} J/year which is about 104 times the current power consumption in the world. This means that in order to meet the current energy needs, 0.1% of the earth surface should be covered by solar cells with a conversion efficiency of 10%. Solar cells are devices used to convert sun light into electric current. One of the interesting developments of solar cell technology is dye-sensitized solar cell (DSSC) invented by Brian O'Regan and Michael Grätzel in 1991 [1]. DSSCs and organic cells are considered the third generation of photovoltaic cells [2-5]. DSSCs are promising and have many advantages over silicon solar cells such as low cost and green energy photovoltaic devices. Moreover, fabrication of DSSCs does not need high purity or advanced techniques. A DSSC consists of nanocrystalline wide-band gap semiconductor oxide film (e.g. TiO_2 and ZnO) coated on a transparent conducting glass electrode (fluorine-doped tin oxide, FTO). The semiconductor is used in nanostructure form because it offers a large surface area for dye anchoring. A platinum (Pt) thin film is used as a counter electrode with an electrolyte normally containing I^-/I_3^- redox. The redox is sandwiched between the dye monolayer and the platinum film. Natural dyes, which can be simply extracted from plant flowers, seeds, roots and leaves, have attracted much more interest [5-20]. In these works, it has been emphasized that efficient dyes can be extracted from natural products and used as photosensitizers for efficient DSSCs. The principle of operation of DSSCs is relatively simple. The dye molecules are excited by absorbing sun light. The charge injection takes place from the excited dye molecules to the conduction band of the metal oxide. Then, the charge separation takes place at the interface due to the photo-induced electron injection from the sensitizer to the metal oxide. In silicon based solar cells, the semiconductor performs both the task of light absorption and charge separation. The dye molecules are regenerated by the redox system which is regenerated at the counter electrode by electrons passing from the transparent conducting glass electrode to the load. The operating principle of DSSCs is illustrated schematically in Fig. 1.

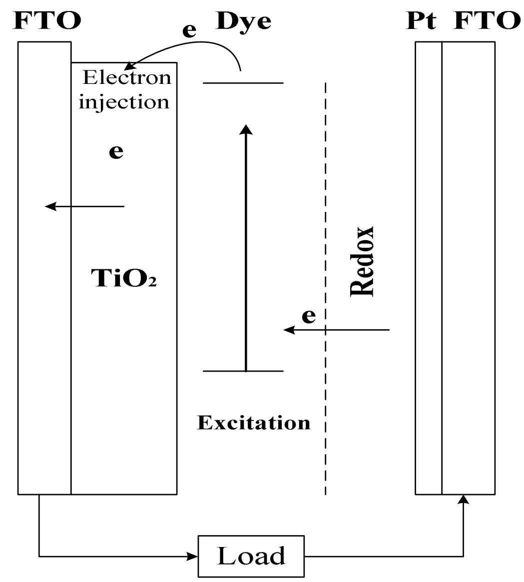

Fig. 1. Principle of operation of DSSCs

Natural dyes have been used as sensitizers for DSSCs. Natural dyes extracted from fresh and dried plants have been studied [8]. It was found that spinach oleracea extract has a better performance after drying where the efficiency of the cell prepared with ZnO thin film layer reached 0.29% [6,8]. Plant seeds have been examined as sensitizers and it was found that extracts from onion, rapa and Eruca sativa seeds have efficiencies of 0.875%, 0.86%, and 0.725%, respectively [10]. A conversion efficiency of 0.66% was obtained using red Sicilian orange juice dye as a sensitizer [21]. Rosella was used as a sensitizer for DSSCs with efficiency of 0.70% [22]. Roy et al. indicated that using Rose Bengal dye resulted in 2.09% conversion efficiency [23]. Furthermore, Wang et al. [24] carried out a modified structure of coumarin derivative dye as sensitizer in their DSSC, which provided an efficiency of 7.6%.

In this work, natural dyes were extracted from three fresh plant seeds (*Raphanus raphanistrum*, *Lepidium sativum* and *Dianthus barbatus*) and used as photosensitizers for DSSCs. The extracts were characterized by UV-Vis absorption spectroscopy. The DSSCs were fabricated using TiO_2 nanopowder. The J-V characteristic curves of the fabricated DSSCs were conducted. The performance of the DSSC sensitized with *Dianthus barbatus* was examined with the pH of the extract solution.

2. EXPERIMENTAL

2.1 Preparation of Natural Dye Sensitizers

Fresh seeds of *Raphanus raphanistrum*, *Lepidium sativum* and *Dianthus barbatus* were collected and crushed into tiny pits using a ceramic pestle and mortal. These seeds have been chosen because they have no nutritional use, cheap, and popularly grown in Palestine. One gram of the crushed sample was weighed and immersed in 80 ml of ethanol solvent for 24 hrs. Solid residues were filtered out to obtain clear dye solutions. The extracted solutions were evaporated at 70℃ by using a hot plate to increase the concentration of the dye to the solvent. Elucidation of the extracted dyes was not carried out since the aim of our work was to use them as available in the plant seeds without any isolation. The performance of the fabricated DSSCs was examined with the pH of dye solution by adjusting pH of 5.1 using 0.1M HCl solution to four different pHs (1.4, 2.9, 3.8 and 4.5).

2.2 Preparation of TiO_2 Electrode (Photoanode)

The photoanode is usually constructed from TiO_2 film. A TiO_2 homogenous paste was prepared by mixing TiO_2 nanopowder (P25) of ca. 0.2 g, polyethylene glycol (MW10,000) of ca. 0.4 g and one drop of acetate (CA) -acetone solution (0.1M). The blend was well mixed using an ultrasonic bath for 0.5 h. A TiO_2 film electrode was prepared by spreading the paste over the FTO coated glass. The TiO_2 film was then sintered at 450ºC for 1 h. The thickness of the sintered films was measured using Olympus polarizing microscope BX53-P equipped with DP73 camera and it was found to be about 22µm. The dyes were adsorbed on the TiO_2 surface by immersing the coated electrodes in the aqueous solution of each dye for 24 h. The non-attached dye was washed up with anhydrous ethanol. The cells were assembled by fixing the working electrode and the counter electrode by paper clips with a spacer between the electrodes. The redox electrolyte solution was composed of 2 mL acetonitrile (ACN), 8 mL propylene carbonate (p-carbonate), 0.663 g (LiI). The redox electrolyte solution was sandwiched between the two electrodes.

2.3 Characterization and Measurement

The absorption spectra of all dye solutions and *Dianthus barbatus* dye adsorbed on TiO_2 surface were recorded using a UV–Vis spectrophotometer (GENESYS 6, Thermo Scientific, USA) in the spectral range from 350 nm to 800 nm. The current density–voltage (J–V) curves were measured using National Instruments data acquisition card (USB NI 6251) in combination of the LabVIEW program, under simulated sunlight (AM1.5, 100mW/cm^2). Based on a J–V curve, the fill factor (*FF*) is given by

$$FF = \frac{J_{\max} V_{\max}}{J_{sc} V_{oc}}, \quad (1)$$

where $J_{\max}$ and $V_{\max}$ are the current density and voltage for maximum output power ($P_{\max}$), and J_{sc} and V_{oc} are the short-circuit current density and open-circuit voltage, respectively. The overall energy conversion efficiency (η) is defined as

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}}, \quad (2)$$

where P_{in} is the power of incident light.

3. RESULTS AND DISCUSSION

3.1 Absorption of Natural Dyes

Fig. 2 shows the UV–Vis absorption spectra of *Raphanus raphanistrum* (A), *Lepidium sativum* (B) and *Dianthus barbatus* (C) seeds. It was found that the three extracts have absorption bands in the spectral range between 300 nm and 400 nm. There is an absorption knee of *Raphanus raphanistrum* extract at about 440 nm. Moreover, a small peak of *Lepidium sativum* extract was found at about 680 nm. The difference in the absorption characteristics is due to the different types of anthocyanins and colors of the extracts. The absorption peaks observed in the spectral range between 300 nm and 400 nm represent high energy transition in the UV region. They are not of interest in the application of DSSCs since the visible solar spectrum lies in the range between 400 nm and 800 nm.

After immersion of the TiO_2 coated electrode in the *Dianthus barbatus* extract, observable colors of TiO_2 films turned to dark green. In this case, an absorption peak of photoanode is broader than that of the dye solution as shown in Fig. 3

with a shift to a higher wavelength from 660 to 690nm. The difference in the absorption peak is due to the binding of anthocyanin in the extract to the oxide surface [14].

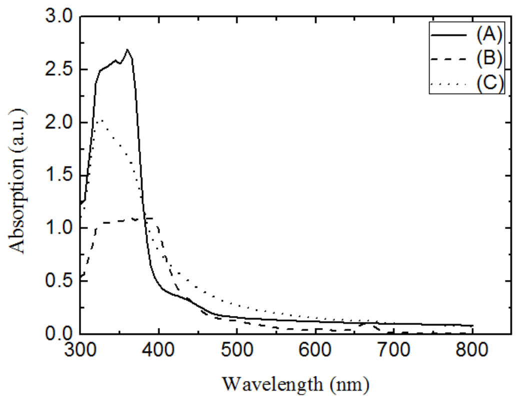

Fig. 2. Absorption spectrum of *Raphanus raphanistrum* (A), *Lepidium sativum* (B) and *Dianthus barbatus* (C) seeds using ethanol as a solvent

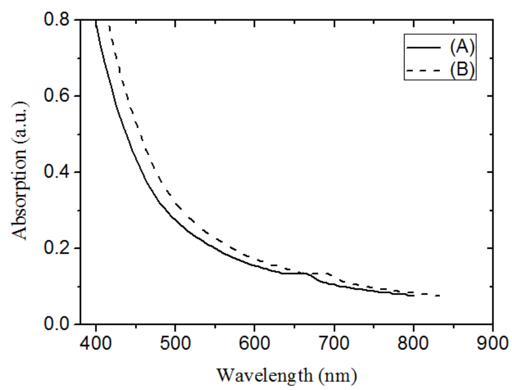

Fig. 3. Absorption spectra of the extract of *Dianthus barbatus* (A) and dye adsorbed on TiO_2 (B)

3.2 Photoelectrochemical Properties

Fig. 4 shows the current density–voltage (J–V) curves for the illuminated DSSCs sensitized with *Raphanus raphanistrum* (A), *Dianthus barbatus* (B) and *Lepidium sativum* (C) extracts. The DSSC output power was calculated as $P = JV$ using the J - V data corresponding to each cell. The output power plotted as a function of V is shown in Fig. 5 for the three DSSCs. The photocurrent density (J_{max}) and photovoltage (V_{max}) corresponding to the maximum power point (P_{max}) were then obtained for each cell from the P - V curve. Table 1 presents the performance of the DSSCs in terms of short circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and energy conversion efficiency (η). As shown in the table, the short-circuit current density had the values 0.23, 0.19, and 0.53 for cells sensitized with *Raphanus raphanistrum*, *Lepidium sativum* and *Dianthus barbatus*, respectively. The open-circuit voltage ranged from 0.51 V for the DSSC sensitized with *Lepidium sativum* to 0.58 V for that sensitized with *Dianthus barbatus*. The open-circuit voltage of the DSSC sensitized with *Raphanus raphanistrum* was 0.57 V. The fill factor had the values 0.45, 0.40, and 0.48 for cells sensitized with *Raphanus raphanistrum*, *Lepidium sativum* and *Dianthus barbatus*, respectively. The overall energy conversion efficiency ranged from 0.40% to 0.48%. Obviously, the efficiency of the cell sensitized with the *Dianthus barbatus* extract was significantly higher than those sensitized with the *Raphanus raphanistrum* and *Lepidium sativum* extracts. To make sure that the current density obtained in the fabricated cells relates to the electron generation of the dyes, a cell was fabricated using bare TiO_2 without any dye and the J-V curve of the cell was conducted. A current of only few microamperes was obtained.

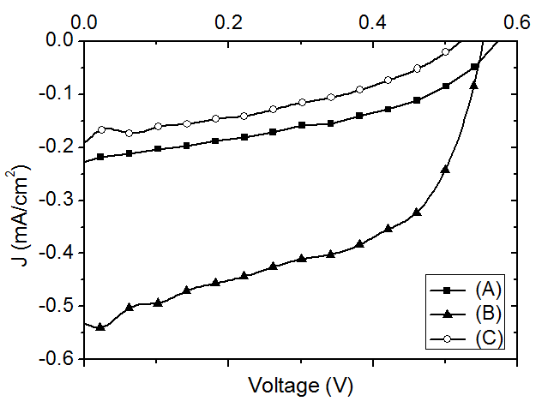

Fig. 4. J-V characteristic curves for the DSSCs sensitized with *Raphanus raphanistrum* (A), *Dianthus barbatus* (B) and *Lepidium sativum* (C) seeds, at an intensity of 1000 W/m^2

3.3 Effect of pH of *Dianthus barbatus* Extract Solutions

The effect of pH of *Dianthus barbatus* extract solutions on the fabricated DSSC parameters was also investigated in this study. The original pH of the extract solution of *Dianthus barbatus* was measured using a calibrated pH meter and found to be 5.1. Fig. 6 shows the absorption spectra of various *Dianthus barbatus* dye solutions whose pH was controlled by adding 0.1M HCl. Five different pH values ranging from 1.4 to 5.1 were examined. When pH was 3.8, a relatively high and wide absorption peak was observed. The J-V characteristic curves of the DSSCs fabricated at different pHs were investigated. The photo electrochemical parameters of these cells are summarized in Table 2. It is obvious that the extract solution pH has a noteworthy effect on the performance of the fabricated cells. The short circuit current density and the open circuit voltage are crucially dependent on the pH of the extract solution. The efficiency was found to increase with decreasing pH until it peaks at a specific value of pH. Then the efficiency decreases if the pH continues to decrease below this value. We can conclude that there is an optimum value of the pH of the extract solution at which the DSSC exhibits its best performance. This may be attributed to the fact that at this pH value, the photoanode made from the *Dianthus barbatus* extract adsorbed on TiO_2 can absorb more light. This is indicated by the wide peak intensity as shown in Fig. 6. It was reported that there is better DSSC stability as pH decreases because anthocyanin existed as flavylium ion, which is stable form of anthocyanin [15]. An increasing pH hydrates this ion to quinonoidal bases.

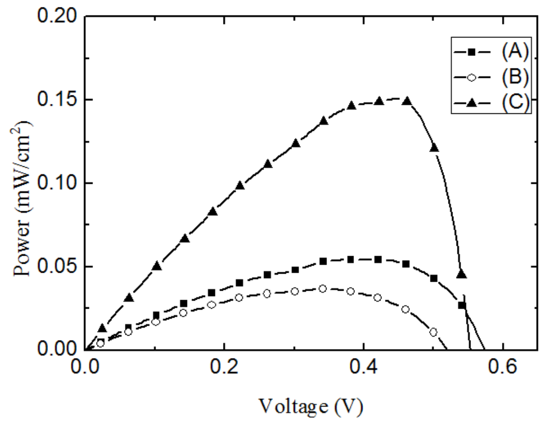

Fig. 5. P-V characteristic curves for the DSSCs sensitized with *Raphanus raphanistrum* (A), *Lepidium sativum* (B) and *Dianthus barbatus* (C) seeds, at an intensity of 1000W/m^2

Table 1. The parameters of the fabricated DSSCs

Extract	λ_{max} (nm)	J_{sc} (mA/cm^2)	V_{oc} (V)	J_{max} (mA/cm^2)	V_{max} (V)	P_{max} (mW/cm^2)	*FF*	η %
Raphanus raphanistrum	440	0.23	0.57	0.135	0.425	0.056	0.45	0.05
Lepidium sativum	600-680	0.19	0.51	0.11	0.34	0.03	0.40	0.03
Dianthus barbatus	660	0.53	0.58	0.35	0.42	0.14	0.48	0.15

Table 2. Effect of pH of extract solutions on the performance of DSSC sensitized with *Dianthus barbatus*

pH	J_{sc} (mA/cm^2)	V_{oc} (V)	P_{max} (mW/cm^2)	*FF*	η %
1.4	0.644	0.561	0.176	0.40	0.145
2.9	0.703	0.499	0.188	0.42	0.147
3.8	0.588	0.558	0.164	0.58	0.190
4.5	0.560	0.557	0.159	0.55	0.170
5.1	0.53	0.58	0.14	0.48	0.150

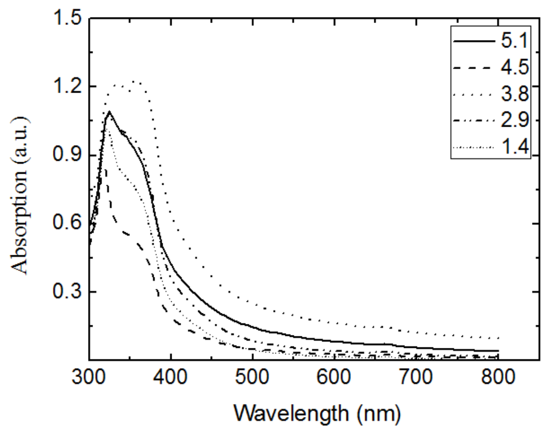

Fig. 6. Absorption spectra of dye solutions extract of *Dianthus barbatus* with different pH. The legend shows the pH of *Dianthus barbatus* extract solutions

4. CONCLUSION

In conclusion, the extracts of *Raphanus raphanistrum*, *Lepidium sativum* and *Dianthus barbatus* seeds were investgated as photosensitizers for DSSCs based on TiO_2 metal oxide. The three extracts were found to have absorption bands in the spectral range between 300 nm and 400 nm. A small peak was also found for the extract of *Lepidium sativum* at about 680 nm. The short-circuit current density was found to have the values 0.23, 0.19, and 0.53 for DSSCs sensitized with *Raphanus raphanistrum*, *Lepidium sativum* and *Dianthus barbatus*, respectively. The open-circuit voltage was found to have the range from 0.51 V for the DSSC sensitized with *Lepidium sativum* to 0.58 V for that sensitized with *Dianthus barbatus*. The best performance was found for the DSSC sensitized with *Dianthus barbatus* with a fill factor and efficiency of 0.48 and 0.15, respectively. The effect of pH of *Dianthus barbatus* extract solutions on the performance of the DSSCs was examined. Five different pH values ranging from 1.4 to 5.1 were examined. The conversion efficiency of the fabricated cells was found to increase with decreasing pH until it peaks when the pH was 3.8. Then the efficiency decreases if the pH continues to decrease below this value. We can conclude that the conversion efficiency of DSSCs can be improved by adjusting the pH of the extract.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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