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# Investigation of Green Dye-Sensitized Solar Cells Based on Natural Dyes

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***Abstract*—**Natural dyes, extracted from black carrot and bramble, were utilized as photosensitizers to prepare dye-sensitized solar cells (DSSCs). Spectrophotometric studies of the natural dyes in solution and on a titanium dioxide substrate were carried out in order to assess changes in the status of the dyes. The results show that the bathochromic shift is seen on the photo-electrode substrate. The chemical binding of the natural dyes at the surface photo-electrode were increased by the chelating effect of the Ti(IV) ions. The cyclic voltammetry results showed that all extracts are suitable to be performed in DSSCs. Finally, photochemical performance and stability of DSSCs based on natural dyes were studied. The DSSCs sensitized by black carrot extract have been reported to achieve up to Jsc=1.17 mAcm$^{-2}$, Voc= 0.55 V, FF= 0.52, η=0.34%, whereas Bramble extract can obtain up to Jsc=2.24 mAcm$^{-2}$, Voc= 0.54 V, FF= 0.57, η=0.71%. The power conversion efficiency was obtained from the mixed dyes in DSSCs. The power conversion efficiency of dye-sensitized solar cells using mixed Black carrot and Bramble dye is the average of the their efficiency in single DSSCs.

***Keywords*—**Anthocyanin, dye-sensitized solar cells, green energy, optical materials.

## I. Introduction

DSSCs have more and more attention due to low cost, vast range of materials, transparency and green technology. The photosensitizers have direct effect on photovoltaic properties of DSSCs [1], [2]. The natural dyes, due to low cost, abundant and no environmental treat, are appropriate for using in DSSCs device. Specially, natural dyes have an importance role in green DSSCs [3]. Anthocyanins are derivatives of antocyanidins that, depending on their pH, may appear red, purple or blue. Anthocyanins occur in leaves, stems, roots, flowers and fruits. The bonding between natural dye and photoanode substrate has been formed by carbonyl and hydroxyl groups in anthocyanin molecules. The excited electron of dye molecules has been injected through this bonding [4]. Polo et al. assembled DSSCs cells using two fruits from anthocyanin groups. The results show that the power conversion efficiency of these fruits is 1.5% and 0.95%, respectively [5]. Nishanta et al. used *Kopsia flavida* fruit as natural photosensitizer in DSSCs and achieved η=0.38% [6]. Four natural photosensitizers based on natural photosensitizers have been investigated in dye-sensitized solar cells by Kushwaha et al. and they achieved power conversion efficiency of 0.12%-0.37% [7]. Wongcharee et al. assembled DSSCs based on rosella, blue pea and mixed extracts. The highest power conversion efficiency of 0.37% has been obtained for rosella extract. The results show that the temperature of extraction processing decreased the performance of devices [8]. Fernando et al. fabricated DSSCs cells based on natural dyes extracted from tropical flowers. The highest power conversion efficiency of 1.14% has been obtained for hibiscus flowers [9]. Bathi et al. studied the performance of DSSCs based on *Lawsonia inermis* leaves, sumac/rhus fruits and *Curcuma longa* roots. The highest power conversion efficiency of 1.5% has been obtained for red purple sumac [10]. Ozuomba et al. studied the optical and photovoltaic performance of the DSSCs based on Hibiscus flower. The natural photosensitizer was the member of anthocyanin family. The power conversion efficiency of sensitized DSSCs was 0.58% [11]. Park et al. extracted natural photosensitizer from gardenia yellow and used in DSSCs structure. The maximum absorption and power conversion efficiency of natural dyes were 544 nm and 0.17%, respectively [12].

In this study, two natural dyes, Black carrot and Bramble, have been used as photosensitizers. The UV-Vis spectra of natural dye in solution and on photo-anode substrate were studied and absorption maxima wavelength and intensities of the extraction were also investigated. Finally, these natural extraction and mixture have been used in DSSCs and their photovoltaic behaviors have been studied.

## II. Experimental

### A. Materials and Instruments

All chemical materials and solvents utilized in this study were analytical grade provided by Merck Co. without further purification. The sample of Bramble and Black carrot were collected from natural source in Boshehr city of Iran during 2016 growing seasons. Transparent conducting oxide, FTO (F-doped $SnO_2$, DyeSol), $TiO_2$ pastes, scattering layer (Sharif Solar Co.) were purchased. The UV-Vis spectrophotometry and FTIR spectra were measured with Cecil 9200 double beam transmission spectrophotometer and Perkin-Elmer Lamada 25, respectively.

### B. Sample Preparation

Brambles and Black carrot are members of the anthocyanin group that are appropriate for using in dye-sensitized solar cells structure. Anthocyanin is polar pigment with carbonyl and hydroxyl groups (Fig. 1) that may appear in various colors from pink. These groups can be linked to the photo-anode

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surface in DSSCs structure. The general chemical structure of anthocyanin and picture of the investigated natural dye source are shown in Fig. 1. In this study, the sample of Black carrot and Bramble was collected from underbrush grown in south of Iran. The extract of Black carrot and Bramble were achieved from fresh fruit and their performance is investigated in dye-sensitized solar cells.

### *C. Electrochemical Measurements*

Electrochemical measurements of the synthesized dyes were carried out in solution in acetonitrile. The oxidation potential ($E_{ox}$) was measured using three small-sized electrodes. A quasi reference electrode (QRE) was used as the reference. Platinum wires were used as the working and the counter electrodes. All electrode potentials were calibrated with respect to ferrocene (Fc)/ferrocenium ($Fc^{+}$) redox couplet. An acetonitrile solution (2 ml) of dyes containing tetrabutylammonium perchlorate (0.1 mol $dm^{-3}$) and ferrocene (ca. 1 mmol $dm^{-3}$) was prepared. The electrochemical measurements were performed at a scan rate of 100 mV $s^{-1}$ [13].


Fig. 1 (a) Bramble, (b) black carrot and (c) general structure of anthocyanin

### *D. DSSCs Assembly*

A nanocrystalline $TiO_2$ film was coated on a FTO glass glass support. The dye solutions were adsorbed by dipping the coated glass for overnight in a solution of the dye in ethanol. Finally, the film was washed with an ethanol solvent. The electrolyte was Acetonitrile-ethylenecarbonate (v/v=1:4) containing tetrabutyl ammonium iodide (0.5 mol $dm^{-3}$). The components of DSSCs contain photoanode; Pt counter electrode and electrolyte solution were prepared in sandwich method [14]. Monochromatic light was used to investigate the action spectrum. Illumination with AM 1.5 was utilized for investigating photocurrent-photovoltage curves by a Bunko-Keiki CEP-2000 system.

## III. Results and Discussion

Anthocyanins are the water soluble pigment of natural dyes that adsorb light at the longest wavelength. Anthocyanin molecules have carbonyl and hydroxyl substituents as functional groups that can be linked to the surface of a porous titanium dioxide substrate. This bonding transfers the excited electron of dye molecules to the conduction band (CB) of metal oxide such as $TiO_2$. The KBr plates must be thoroughly cleaned after this procedure to prevent contamination of future samples. The infrared (FT-IR) spectra were studied and the results demonstrated appearance of important peak. The OH group (bonding vibration) has appeared in 3331 $cm^{-1}$ and 3361 $cm^{-1}$ which demonstrated that hydrocyle groups of natural extract contain anthocyanin that causes bonding between metal oxide and functional groups, respectively. The board band centered at 500-600 $cm^{-1}$ is due to the vibration of the Ti-O band in the porous nano anatase titanium dioxide substrate [15], [16].

Anthocyanin compounds exhibit a wide band in UV-Vis region of the spectrum due to charge transfer transition. Table I illustrated the wavelength of maximum absorption ($\lambda_{max}$) and the molar absorpivity ($\varepsilon_{max}$) for the Black carrot and Bramble and UV-Vis absorption spectra for natural dyes shown is in Fig. 2, together with the $\lambda_{max}$ of the corresponding dyes adsorbed on photo-anode substrate. Upon dye adsorption onto a titanium dioxide surface, the wavelength of maximum absorption is shifted by 10 and 13 nm (bathochromic shift) for black carrot and bramble extract, respectively as compared to the corresponding spectra in solution. Their binding can be increased by the chelating effect to the Ti(IV) ions [5]. The attachment to the titanium dioxide surface confirms the exited state, thus shifts toward the lower energy of the absorption maximum [15], [17]. Table I shows the molar extinction coefficients of Black carrot and Bramble extract in solution at their respective $\lambda_{max}$, indicating that these natural dyes have good light harvesting abilities [6].

The cyclic voltammetry method has been used for studying oxidation potential ($E_{ox}$) of natural dye. The cyclic voltammetry spectra illustrate two redox waves that first oxidation wave shows oxidation of the internal standard of ferrocene and second wave indicates the electrochemical oxidation of the dye. Cyclic voltammetry method is an appropriate experimental way for study of oxidation potential of natural dye [6]. The oxidation peak potential ($E_{pa}$) for bramble and black carrot as natural dye can therefore be calculated as 0.66 vs and 0.69 vs $Fc/Fc^{+}$ in solution.

TABLE I
Absorption of the Natural Dyes

| Dye | $\lambda_{max}$ (nm) (in solution) | $\varepsilon$ ($M^{-1}cm^{-1}$) | λmax (nm) (on $TiO_2$) |
|---|---|---|---|
| Black carrot | 489 | 27254 | 491 |
| Bramble | 521 | 27579 | 541 |

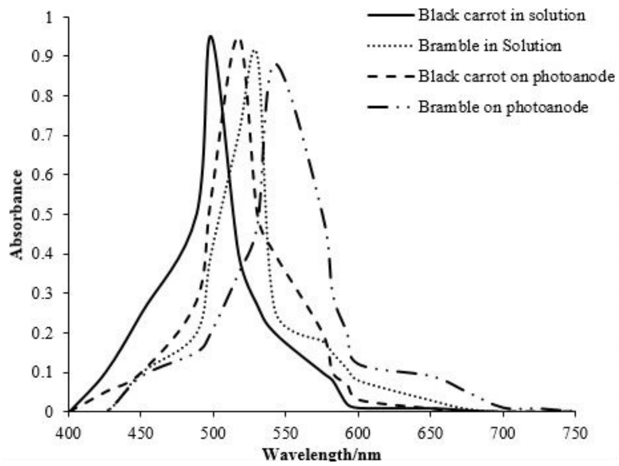


Fig. 2 UV-Vis absorption spectra for natural dyes

No reduction peak was observed for the synthesized dye. Therefore, the $E_{ox}$-$E_{0-0}$ level, where $E_{0-0}$ represents the intersection of normalized absorption and the fluorescence spectra in solution (Fig. 2), was calculated. This is considered to correspond to the reduction potential [16], [18]. The $E_{0-0}$ of organic dye was observed corresponding to 2.01 eV and 2.11 eV, respectively. Therefore, the $E_{ox}$-$E_{0-0}$ level of organic dye is calculated to be –1.33 V and -1.29 V vs $Fc/Fc^+$ in acetonitrile.

We extract anthocyanin from Black carrot and Bramble for making natural photosensitizer for dye-sensitized solar cells. The photocurrent–photovoltage (J–V) diagrams of devices sensitized by natural dyes have been shown in Fig. 3. Photovoltaic parameters of DSSCs based on natural dyes have been presented on Table II.

TABLE II
PHOTOVOLTAIC PERFORMANCE OF DSSCS BASED ON BLACK CARROT AND BRAMBLE

| Dye source | $J_{SC}$ (mA.cm$^{-2}$) | $V_{OC}$ (V) | FF (%) | η (%) |
|---|---|---|---|---|
| Black carrot | 1.17 | 0.55 | 0.52 | 0.34 |
| Bramble | 2.24 | 0.54 | 0.57 | 0.71 |

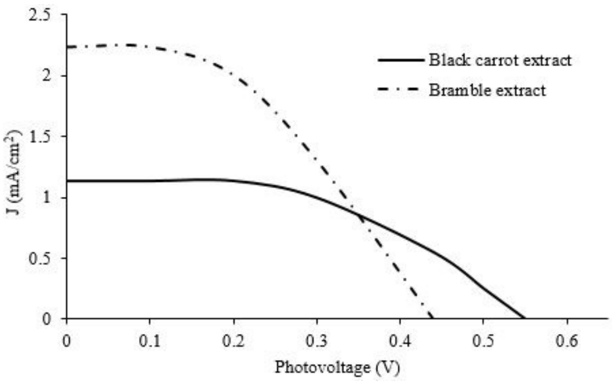


Fig. 3 Current density-voltage characteristics for black carrot and bramble

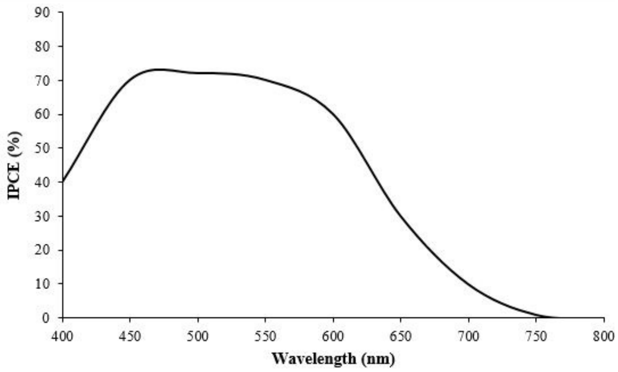


Fig. 4 IPCE spectra of DSSCs based on black carrot extraction

According to the results shown in Table II, the power conversion efficiencies of DSSCs based on Black carrot and Bramble extraction under AM 1.5 are 0.34% and 0.71%, respectively. Bramble extract shows better charge transfer due to higher light absorption; thus, Bramble is better photosensitizer compared to Black carrot [9], [10]. Thus, under similar assembling processing of DSSCs and investigation conditions, power conversion efficiency of Bramble extract is higher than Black carrot.

The photo to current conversion efficiency (IPCE) spectra of DSSC based on black carrot extraction is presented in Fig. 4. The natural dye shows IPCE ranged from 75%. Finally, we fabricated dye-sensitized solar cells using mixer of both natural pigments extracted from Bramble and Black carrot. The short circuit photocurrent ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF) and conversion efficiency (η) of DSSC based on mixture extraction are 1.64 mA cm$^{-2}$, 0.52 V, 0.55% and 0.47%, respectively. The dye-sensitized solar cell sensitized by a mixed Bramble and Black carrot shows a conversion efficiency of 0.47%.

## IV. CONCLUSIONS

Two natural dyes native to Iran were collected and extracted from Bramble and black carrot. The natural dyes, due to low cost, abundant and no environmental treat, are appropriate for using in DSSCs device. The UV-Vis of natural extraction in solution and on photo-anode substrate was investigated. The results show that the absorption maxima wavelength of Black carrot and Bramble are 489 nm and 541 nm, respectively. The photo-anode sensitized by Black carrot and Bramble extraction shows bathochromic phenomena (32 nm and 50 nm) compared to the dye spectra in solution. Finally, dye-sensitized solar cells are synthesized using anthocyanin extracted from Bramble and Black carrot. The power conversion efficiencies of DSSCs based on Black carrot and Bramble are 0.34% and 071%, respectively. The DSSCs have been fabricated using mixed extract. The power conversion efficiency of these devices is 047% (average value of single DSSCs based on two natural dyes). The results show that the Bramble illustrates the best power conversion efficiency due to appropriate interaction between the functional groups of natural dye and photo-anode substrate.

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