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Natural Dyes Extracted from Black Carrot and Bramble for Dye-Sensitized Solar Cells

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ABSTRACT

Two different natural dyes containing anthocyanin extracted from black carrot and bramble from Iran. Spectrophotometric evaluations of the natural dyes in solution and on a TiO_2 substrate were carried out in order to assess changes in the status of the natural dyes. The results show that the natural dyes indicate bathochromic shift on the TiO_2 substrates. The chemical adsorption of natural dyes present at the surface of TiO_2 substrate that their chemical binding can be increased by the chelating effect to the Ti(IV) ions. Finally, dye sensitized solar cells were fabricated in order to determine the photovoltaic behavior and conversion efficiencies of each dyes and mixture of extracts. Such evaluations demonstrate conversion efficiencies of 0.33%, 0.69% and 0.47% for black carrot, bramble and mixed extract, respectively. Natural dyes are suitable alternative photosensitizers for dye-sensitized solar cells due to simple preparation method, low cost, environmentally friendly and widely available. Prog. Color Colorants Coat. 8 (2015), 153-158 © Institute for Color Science and Technology.

1. Introduction

Dye-sensitized solar cells (DSSCs or Grätzel cells) have more and more attention due to low cost, vast range of materials, transparency and green technology [1]. The performance of the solar cells depends on a structure dye utilized as sensitizers [2]. Inorganic complexes have shown good conversion efficiency in DSSCs when adsorbed on TiO_2 nanoparticles [3] but, the main disadvantage of inorganic dyes is their high

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cost [2]. Natural dyes have importance in comparison with inorganic dye molecules by their applicability to green chemistry in DSSCs [4, 5]. The advantages of natural dyes include their availability and low cost [6] and various natural dyes have been examined over the last two decades as suitable sensitizers [7]. The anthocyanins belong to the major group of natural dyes that is responsible for cyanic colors ranging from salmon pink through red and violet to dark blue of most flowers, fruits and leaves [7, 8] sometimes, they are present in other plant tissues such as roots, tubers and stems [9]. Carbonyl and hydroxyl groups present in the anthocyanin molecules can be bonded to the surface of a porous nanoanatase TiO_2 substrate. This links makes injection excitation electron from anthocyanin molecule to the conduction band (CB) of TiO_2 [2, 6]. Polo et al. utilized the natural dyes based on anthocyanin as sensitizer in DSSC and have been reported to achieve up to η=1.5% for Jaboticaba extract and η=0.95% for calafate extract [10]. Nishanta et al. fabricated DSSC with natural dye based on anthocyanin and presented η=0.38% for KopsiaFlavida fruit [11].

In the present investigation, two natural dye containing anthocyanin extracted from black carrot and bramble that grown in Iran as sensitizers for the first time. The spectrophotometric properties of the prepared natural dyes in solution and on a nanoanatase TiO_2 substrate were examined. The absorption maxima and intensities of the resultant natural dyes were also obtained. Finally, Dye sensitized solar cells were fabricated utilizing these natural dyes and mixture of extracts and their photovoltaic behaviors were determined.

2. Experimental

2.1.Materials and instruments

The sample of brambles used in this study were obtained from ten-years-old bramble tree are grown in Iran. The samples of black carrot and bramble were collected at random from natural source. The samples were harvested during the 2014 growing seasons. UV-visible spectrophotometry were carried out on a Cecil 9200 double beam transmission spectrophotometer.The FTIR spectra were measured with Perkin-Elmer Lamada 25. The samples were pressed pellets of a mixture of the powder with KBr.

2.2. Sample preparation

Fresh black carrot or bramble of 1 g was extracted in 100 ml of water at 80 ºC for 30 min. Solid residues were filtrated out to obtain clear dye solutions. A mixed dye was prepared by mixing black carrot and bramble solutions at a ratio of 1:1 by volume.

2.3. Dye-sensitized solar cells (DSSCs) assembly and photovoltaic characteristics of the resultant solar cells

TiO_2 nanoparticles were obtained commercially from nanomahan Company in Iran. An organic paste containing TiO_2 nanoparticles, a binder and a solvent was printed on conducting glass substrates (FTO glass) by doctor blading, followed by heating in hot-air stream at 350 °C for 30 min. Then, a 50mM aqueous solution of $TiCl_4$ was dropped onto the TiO2 films and kept at 25°C for 20h, followed calcining at 450°C for 30 min in air. The natural dyeswere adsorbed by dipping the coated glass for 18 hours in aqueous solution of the each dye. Finally, the film was washed with an anhydrous ethanol. The iodide electrolyte solution (0.5M potassium iodide mixed with 0.05M iodine in water-free ethylene glycol) was used as an electrolyte. The dye-adsorbed TiO_2 electrode, the Pt counter electrode and the electrolyte solution were assembled into a sealed sandwich type solar cell [12, 13].

An action spectrum was measured under monochromatic light with a constant photon number (5×10^{15} photon cm^{-2} s^{-1}). J-V characteristics were measured under illumination with AM 1.5 simulated sun light (1000 mW cm^{-2}) through a shading mast (5.0 mm×4 mm) by using a Bunko-Keiki CEP-2000 system.

3. Results and discussion

Anthocyanins are the most abundant and palmate those adsorb light at the longest wavelength [7]. Carbonyl and hydroxyl groups present in the anthocyanin molecules can be bonded to the surface of a porous nanoanatase TiO_2 substrate. This links makes injection excitation electron from anthocyanin molecule to the conduction band (CB) of TiO_2 [6]. Infrared absorption spectra were obtained using a mixture of the powder KBr. The infrared spectra are studied and showed appearance of some peak. The peak 3327 Cm^{-1} and 3356 Cm^{-1} that related to OH groups (OH vibration) mentioned to hydroxyl groups in extract anthocyanin dyes and natural dye coated on TiO_2, respectively. The board band centered at 500-600

Cm^{-1} is due to the vibration of the Ti-O band in the porous nanoanatase TiO_2 substrate.

Anthocyanin compounds exhibit a wide band in UV-Vis region of the spectrum due to charge transfer transition [14]. The wavelength of maximum absorption (λ_{max}) and the molar extinction coefficients (ε_{max}) for the two natural dyes and mixed extract are listed in Table 1 and shown in Figure1, together with the λ_{max} of the corresponding dyes adsorbed on TiO_2 films. Upon dye adsorption on to a TiO_2 surface, the wavelength of maximum absorption is bathochromicallyshifted by 10, 13 and 13 nm for black carrot,brambleand mixed extract,respectively as compared to the corresponding spectra in solution. Chemical adsorption of these natural dyes is due to alcoholic bound protons which condensewith the hydroxyl groups present at the surface of nanostructured TiO_2 film. Their binding can be increased by the chelating effect to the Ti(IV) ions [10]. The attachment to the TiO_2 surface avouches the exited state, thus shifts toward the lower energy of the absorption maximum [10, 15]. The molar extinction coefficients of black carrot and bramble extract in solution at their respective λ_{max} are also shown in Table 1, indicating that these natural dyes have good light harvesting abilities [16].

Table 1: Absorption of the natural dyes.

Dye	λ_{max}(nm) (in solution)	ε ($M^{-1}cm^{-1}$)	λ_{max}(nm) (on TiO_2)
Black carrot	488	26452	498
Bramble	517	27145	530
Mixed extract	503	25789	516

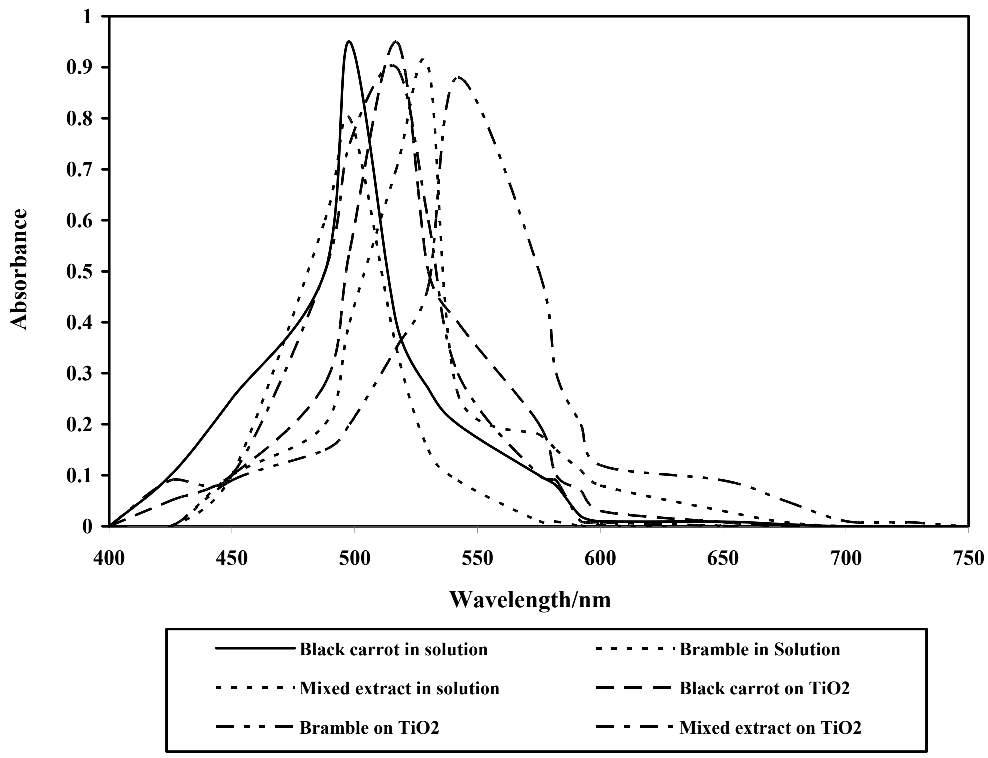

Figure 1: UV-Vis absorption spectra for natural dyes.

Dye-sensitized solar cells (DSSCs) were constructed and compared in order to clarify the relationships between the sensitizing behaviors of natural dyes molecules. The DSSCs utilized these natural dyes as sensitizers for nanocrystallineanatase TiO_2. A typical photocurrent–photovoltage (J–V) curve for cells based on natural dyes and a mixture of extract is depicted in Figure 2. Table 2 presents the detailed photovoltaic parameters of DSSCs in terms of short-circuit photocurrent (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and conversion efficiency (η).

According to the results shown in Table 2, under the standard global AM 1.5 solar condition, the conversion efficiencies of cells containing black carrot, bramble and mixtureextract are 0.33%, 0.69% and 0.47%, respectively. The larger conversion efficiency of bramble extract sensitizer is probably due to higher intensity and broader range of the light absorption of the extract on TiO_2 and higher interaction between TiO_2 and anthocyanin in bramble extract leads to a better charge transfer [17]. A DSSCs sensitized by a mixed extract had a conversion efficiency of around the average value of those sensitized with black carrot and bramble extracts. This result is in agreement with the results by Wongcharee et al. [2]. Under similar fabrication DSSCs and irradiation conditions, the DSSCs sensitized by bramble extract showed a good performance to the DSSCs prepared from other natural dyes based on anthocyanin [7, 18].

Table 2: Photovoltaic performance of DSSCs based on black carrot, bramble and mixed extract.

Dye source	J_{SC} (mA.cm^{-1})	V_{OC} (V)	FF (%)	η (%)
Black carrot	1.14	0.55	0.52	0.33
Bramble	2.23	0.54	0.57	0.69
Mixed	1.64	0.52	0.55	0.47

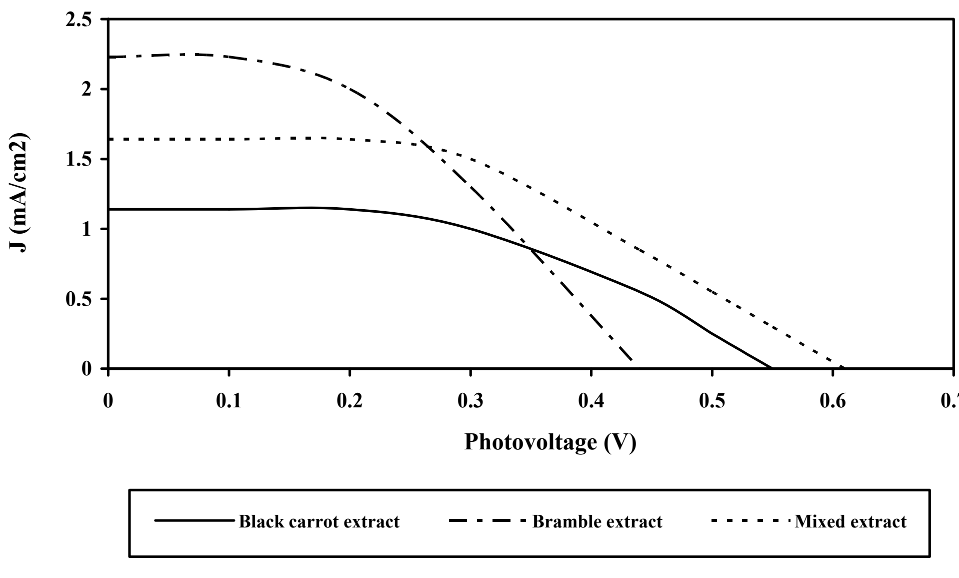

Figure 2: Current density-voltage characteristics for black carrot, bramble and mixed extract.

4. Conclusions

Two different natural dyes were extracted from black carrot and bramble that are grown in Iran. Natural dyes are environmentally friendly and low cost source as sensitizer for dye-sensitized solar cells. The spectrophotometric properties of the natural dyes in solution and on TiO_2 substrate were examined. According to the results, black carrot and bramble extracts showed absorption maxima in solution at 488nm and 517nm, respectively. The absorption maxima of both natural dyes separately applied on TiO_2 films gave bathochromic shifts compared to the corresponding dye spectra in solutions. Finally, the natural extract dyes were utilized in constructed DSSCs and their photovoltaic behaviors were assessed. A solar energy to electricity conversion efficiency of 0.33%, 0.69% and 0.47% were achieved for black carrot, bramble and mixed extract, respectively. The mixed extract has a conversion efficiency of around the average value of those sensitized with black carrot and bramble extracts. From these experimental results and discussion, it was found that bramble extract presents the best photosensitized effect in dye-sensitized solar cells, which is due to the better interaction between the carbonyl and hydroxyl groups of anthocyanin on bramble extract and the TiO_2 substrate in DSSCs.

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