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Betalain pigments for dye-sensitized solar cells

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Abstract

A dye-sensitized solar cell based on natural betalain pigments from red beet roots is described. Reddish-purple betanin is an easily oxidized, water-soluble pigment with strong visible light absorption, having a maximum molar absorptivity of about 65,000 M^{-1} cm^{-1} at 535 nm. A photoanode was fabricated from nanocrystalline TiO_2 on transparent conductive glass, treated with ethanolic HCl solution, then sensitized with raw beet extract or a betanin solution from which yellow betaxanthin pigments were removed by column chromatography. The betanin-sensitized film when employed in a dye-sensitized solar cell gave a maximum photocurrent of 2.42 mA/cm^2 and open-circuit photovoltage of 0.44 V in the presence of methoxypropionitrile containing I^-/I_3^- redox mediator. Photocurrents and photovoltages are also reported for the DSSC sensitized with yellow betaxanthin and a brown betalain-derived oxidation product. Wavelength-dependent incident photon-to-electron conversion efficiencies (IPCEs) show maximum values of 14% and 8% for betaxanthin- and betanin-based solar cells, respectively.
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Keywords: Dye-sensitized solar cell; Plant pigments; Betalains

1. Introduction

Solar energy conversion based on dye-sensitization of wide band gap nanocrystalline semiconductor films is an area of intense investigation [1–5]. The most efficient dye-sensitized solar cells (DSSCs) to date are based on ruthenium-containing metallorganic dyes adsorbed on nanocrystalline TiO_2, the best of which have been reported to convert solar energy to electrical energy with an efficiency of 10–11% [5–7]. A key aspect of optimizing the sensitizer for solar energy conversion is the ratio of the rates of forward (injection) and reverse (recombination) electron transfer [8,9]. The high energy conversion efficiency of the widely used N3 sensitizer and other related Ru-bipyridyl based dyes derives from the spatial separation of the donor LUMO orbital, which is close to the TiO_2 surface, and the acceptor HOMO, resulting in injection which is much faster then recombination. Another important parameter is the rate at which the oxidized sensitizer reacts with the reduced form of the redox mediator, which is typically I^-/I_3^-. Osmium analogues of commonly used Ru-based dyes, for example, react much less rapidly with I^-resulting in lower efficiency [10]. The advantages of Ru-based sensitizers are offset by their expense and tendency to undergo photochemical degradation in the presence of water. Since the efficiencies of DSSCs have not yet approached the theoretical limit and are not competitive with the more expensive silicon-based solar cells, their main advantage of cost-effectiveness depends on the utilization of cheap and readily available sensitizer dyes. The use of nontoxic natural pigments as sensitizers would definitely enhance the environmental and economic benefits of this alternative form of solar energy conversion.

Natural pigments from plants, such as chlorophyll [11,12] and anthocyanins [13–17], have been extensively investigated as sensitizers for the DSSC. Though the former have inherent limitations as solar energy sensitizers owing to weak absorption of green wavelengths, the absorption spectra of the latter have more favorable overlap with the solar spectrum. The anthocyanins are water soluble flavonoids responsible for the red and blue colors of many fruits and leaves and may serve as photoprotective agents, antioxidants and osmotic regulators [18,19]. The

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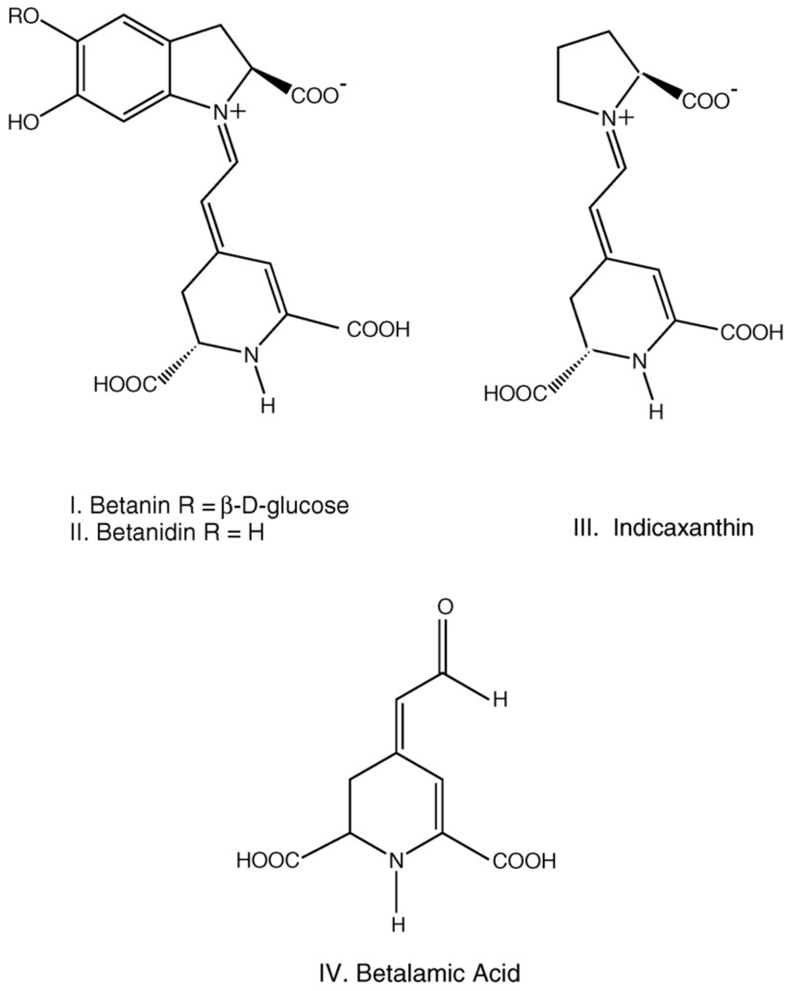
flowering plants of the order *Caryophyllales*, on the other hand, derive their colors from nitrogen-containing betalain pigments rather than anthocyanins [20–22]. The efficiencies η of solar energy conversion by anthocyanins are rather low, for example 0.56% for a DSSC based on cyanin from blackberries [13]. To our knowledge, the betalain pigments have not been previously evaluated as dye sensitizers, except for a preliminary report on natural sensitizer dyes that included red beet pigment [23]. Like the anthocyanins, the betalains have favorable light absorbing and antioxidant properties, are capable of complexing metal ions, and exist in nature in association with various copigments which modify their light absorption properties. Betalains possess the requisite functional group (–COOH) to bind to TiO_2. In contrast, the adsorption of anthocyanins onto TiO_2 in their quinoidal form depends on the existence of two –OH groups *ortho* to one another on an aromatic ring, a motif that in general leads to strong electronic coupling and rapid forward *and* reverse electron transfer.

The betalain pigments (Fig. 1) comprise the red-purple betacyanins, betanin (**I**) and betanidin (**II**), with maximum absorptivity at λ_{max} about 535 nm, and the yellow betaxanthins with λ_{max} near 480 nm. The structure of indicaxanthin (**III**), a common betaxanthin found in beet root, is shown in Fig. 1.

Table 1
Wavelengths of maximum absorption, molar absorptivities, and first and second pK_a of betalains

	λ_{max} (nm)	ε (M^{-1} cm^{-1})	pK_{a1}	pK_{a2}
Betanin	535	65,000	−2.4	6.9
Betanidin	542	54,000	−2.4	6.9
Indicaxanthin	482	42,600	−2.4	10.1
Betalamic acid	424	24,000	1.7	10.2

Betanin, the red-purple pigment distributed in beets, is the 5-*O*-β-glucoside of betanidin. The aglycone betanidin has a slightly red-shifted absorption spectrum compared to betanin. Table 1 lists the literature values of λ_{max} and molar absorptivity ε for common beet pigments taken from Refs. [24,25], along with calculated pK_a values taken from SciFinder Scholar. While it is difficult to assess the quality of the calculated pK_a's, they are in qualitative agreement with those of similar carboxylic acid derivatives (see for example Ref. [26]), and the second pK_a of betanin is in excellent agreement with the observed changes in the optical absorption spectrum reported here. Interest in betalain pigments from beets and other plants, such as prickly pear [25], bougainvillea [27], amaranth [28], and other species [29,30] derives from their potential applications as natural food colors



I. Betanin R = β-D-glucose
II. Betanidin R = H

III. Indicaxanthin

IV. Betalamic Acid

Fig. 1. Betalain pigments.

[31] and antioxidants [20]. However, these two properties are at cross-purposes to one another as limited stability of betalain pigments has hindered their applications as food colorants. An early report by von Elbe and Attoe [32] focused on the redox chemistry of betanin and betanidin. The redox measurements were made on aqueous solutions containing the pigment in its reduced form only, rather than an equimolar mixture of reduced and oxidized forms. The redox potential of betanin was found to vary from about 0.27 V at pH 3 to 0.32 V at pH 6, versus a normal hydrogen electrode at the same pH. Corrected to the normal hydrogen electrode (NHE) at a pH of 0, this translates to a nonstandard redox potential for betanin that ranges from 0.45 to 0.67 V as pH ranges from 3 to 6. The redox potential of betanidin was reported in Ref. [32] to be slightly lower than that of betanin and equal to the redox potential of ascorbic acid at the same pH. Thus betanidin is more easily oxidized than betanin and the similar redox potentials of betanidin and ascorbic acid implicate the enediol group as the site of oxidation for the aglycone. More recently, Butera et al. [25] reported redox potentials for betanin and indicaxanthin at pH 7.4 determined using cyclic voltammetry. Though problems with reversibility were noted as in Ref. [32], the use of differential pulse voltammetry for betanin at pH 7.4 resulted in anodic waves at 0.62, 0.84 and 1.22 V versus NHE. Indicaxanthin, on the other hand, gave two anodic waves at 0.83 and 1.12 V. The similarity of second and third redox potentials of betanin to the two redox potentials of indicaxanthin may indicate that the first oxidation of betanin takes place at the aromatic ring.

The redox potential of a dye is an important parameter when considering it as a sensitizer for solar energy conversion. For electron injection to be thermodynamically favorable, the excited state redox potential energy, obtained by subtracting the 0–0 energy for electronic excitation from the ground state redox potential energy, must be lower than the TiO_2 conduction band. In contact with water, the standard redox potential of TiO_2 in volts is given by −0.16 to 0.06 pH versus NHE [3]. Making a rough estimate of $E_{00} \approx 1.9$ eV from the onset of the visible absorption band at about 650 nm, the excited state redox potential of betanin at neutral pH is estimated to be $0.6– 1.9 = -1.3$ V which is more negative than the redox potential of TiO_2 of about −0.6 V. Electron injection from the excited state of betanin to the TiO_2 conduction band is thus thermodynamically favored, at least in water at pH 7. As will be shown here, nonaqueous solvents for the electrolyte in the DSSC, acetonitrile (ACN) and methoxypropionitrile (MPN) give better energy conversion.

Reversibility of redox chemistry and stability in general are important considerations for a potential dye sensitizer. The stability of the red-purple betanin pigment has been the subject of many studies owing to its approved use as food colorant [33–35]. The degradation of betanin into betalamic acid and cyclo DOPA 5-*O*- β-D-glucoside was reported to be partially reversible [34]. Pedreño and Escribano [33] found betanin to be much more stable at pH 3.5 than pH 8.5. Light and oxygen are known to influence the stability of betanin and ascorbic acid is widely used as a preservative to protect betanin from oxidation.

This paper is the first detailed report of the use of betalain pigments in dye-sensitized solar energy conversion. Though rather modest energy conversion efficiencies are determined, the betalain pigments present rich possibilities for exploring the molecular basis for dye-sensitization of metal oxide nanoparticles.

2. Experimental section

High pigment beet extract containing about 1.2% betanin was obtained from Seneca foods and either used as received (referred to as “raw” beet extract below) or after column chromatography (“purified” beet extract) to remove the yellow betaxanthins as indicated in the text. Two different chromatographic procedures were applied, using either a Waters MCX ion-exchange column or Sephadex G25 and 0.1 M HCl in ethanol as the eluting solvent. Absorption spectroscopy was used to monitor the betaxanthin content as described below. TiO_2 films were cast from dispersions of Degussa P25 TiO_2 in ethanol onto fluorine-doped SnO_2 conductive glass (Hartford Glass) as described in Ref. [36]. Electrolyte solutions were prepared with 0.5 M $I_2$and 0.05 M LiI in 3-methoxypropionitrile (MPN). In some experiments, as indicated below, 0.5 M *tert*-butylpyridine (TBP) was used in the electrolyte solution to improve the maximum photovoltage. The counter electrode consisted of platinum-sputtered conductive glass.

Absorption spectra were recorded using a Shimadzu UV-2501 spectrometer. Spectra of dyes adsorbed on TiO_2 were recorded in air using glass substrates and thinner, more transparent TiO_2 films than those used for photocurrent measurements. The reference was a TiO_2 film without sensitizer. Buffers used in pH-dependent experiments were borax, for pH 11 to 8.5, KH_2PO_4 for pH 8 to 6, and potassium hydrogen phthalate for pH 5.5 to 4.

Betanin was only weakly adsorbed on an untreated TiO_2 film, regardless of the pH of the sensitizing solution. However, after soaking the film for 6 h in 0.5 M HCl in ethanol and after column chromatography, good adsorption of betanin on TiO_2 was achieved.

Dye-sensitized solar cells were illuminated with incident power of about 100 mW/cm^2 from a 75 W Xenon lamp using an illumination area of 0.196 cm^2 and UV and IR filters in front of the sample. Current and voltage were measured using a Keithley 2400 source meter, and the incident light power was measured using a Melles Griot bolometer. The incident light power was varied using neutral density filters in front of the cell. Reported power conversion efficiencies are based on the incident light and are not corrected for the absorption of the conductive glass. Wavelength-dependent incident photon-to-current quantum efficiencies, IPCE(λ) were measured using an adaptation of a PTI Quanta Master fluorimeter, consisting of 75 W Xe arc lamp source filtered by the instrument’s excitation monochromator, with 1200 l/mm grating, using a slit bandpass of 20 nm, and a final illumination area of about 0.15 cm^2. Incident wavelengths were scanned from 400 to 770 nm twice: first to record the incident light power and the second time to measure the short-circuit photocurrent, both of which were recorded every 10 nm. The lamp intensity spectrum was determined with a ThorLabs Optical Power Meter PM120 (50 nW lower detection limit), and recorded using the analog output to a Keithley 2400 source meter, which was also used to directly measure the photocurrent. The lamp intensity was estimated to fluctuate by ±5% setting a lower limit for the relative error in the IPCE. All calculations were handled using programs built in National Instruments LabView. The measurement technique was validated by determining IPCE(λ) for a DSSC cell containing the well-studied Ru-based N3 dye in a solar cell prepared as described above but using N3 purchased from Solaronix as the sensitizer. The resulting photocurrent action spectrum was found to be in good agreement with the literature [1,4], giving maximum IPCE values ranging from about 0.50 to 0.90 in replicate measurements using different N3-sensitized photoanodes.

3. Results

3.1. *Absorption spectroscopy*

Fig. 2 shows the absorption spectrum of raw beet extract diluted in water and buffered at pH values between 4 and 11. The absorption maximum shifts to the red and decreases in intensity as the pH is raised. An apparent isosbestic point at about 560 nm suggests an equilibrium between two forms of betanin. Since betanin (Bt), betanidin (Bd) and indicaxanthin (In) all have a negative pK_{a1} value, we assume the –COOH on the five-membered ring to be the most acidic of the three carboxylic acid groups on Bt, Bn or In, consistent with the zwitterionic structures depicted in Fig. 1. The rapid shift in the absorption spectrum of Fig. 2 at pH values near 6.8 is consistent with the pK_{a2} given in Table 1. The second acid dissociation constant, probably involving a carboxylic acid function on the dihydropyridine ring, is evidently more facile for Bt and Bd than for In and betalamic acid, consistent with greater resonance stabilization of the conjugate base for the pigments containing aromatic rings. Following Ref. [25], the indicaxanthin concentration [In] in μM is estimated from the absorbance at 482 and 536 nm from

$$[\mathrm{In}] = 23.8A_{482} - 7.7A_{536} \tag{1}$$

For the pH 7 spectrum in Fig. 2, this gives $[\mathrm{In}] \approx 0.35\,\mu\mathrm{M}$ compared to the betanin concentration [Bn] of about 1.0 μM.

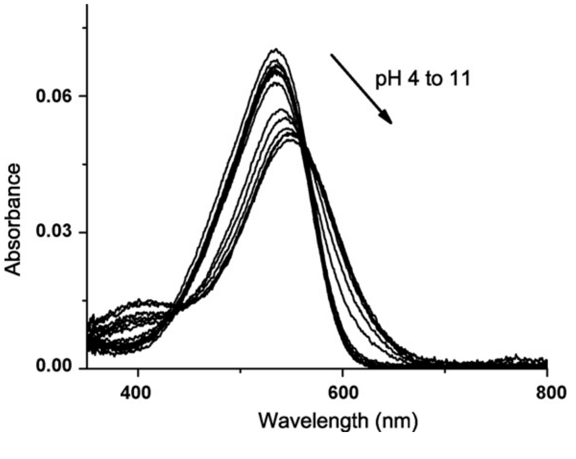


Fig. 2. Absorption spectra of beet extract in water from pH 4 to 11. The absorption maximum shifts from 535 to 550 nm as the pH is increased.

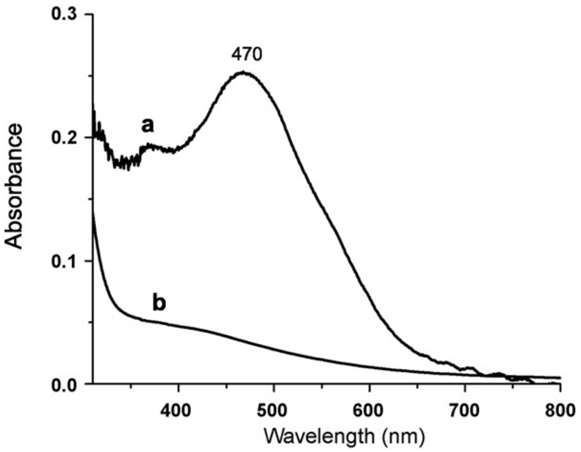


Fig. 3. Absorption spectrum of TiO_2 films sensitized by raw beet extract (a) freshly prepared, and (b) after exposure to air.

Fig. 3 shows the absorption spectrum of TiO_2 films sensitized by soaking in raw beet extract at neutral pH. The initially prepared film shows a strong absorbance peak at 470 nm suggesting the yellow betaxanthin compounds are more strongly absorbed than betanin or betanidin. Confirming this, Fig. 4 shows the absorption spectrum of the beet extract before and after the TiO_2 film was dipped into it. Using Eq. (1), the data of Fig. 4 suggests that there is preferential adsorption of indicaxanthin over betanin on the TiO_2 film. The difference spectrum shown in the inset to Fig. 4 shows a peak at about 475 nm, close to the expected absorption maximum of betaxanthin. After exposure to air, the film acquires a brown color and the absorption spectrum shown in Fig. 3 b is obtained, presumed to result from melanin-like polymer of *cyclo*-DOPA [37]. The brown oxidation product can also be formed by heating the raw beet extract as shown in Fig. 5. As the solution is heated the absorption peak at 535 nm diminishes and absorption bands at 450 and 270 nm grow in, consistent with cleavage of betanin into betalamic acid and *cyclo*-DOPA along with possible formation of indicaxanthin as well. Eventually after exposure to air the solution acquires

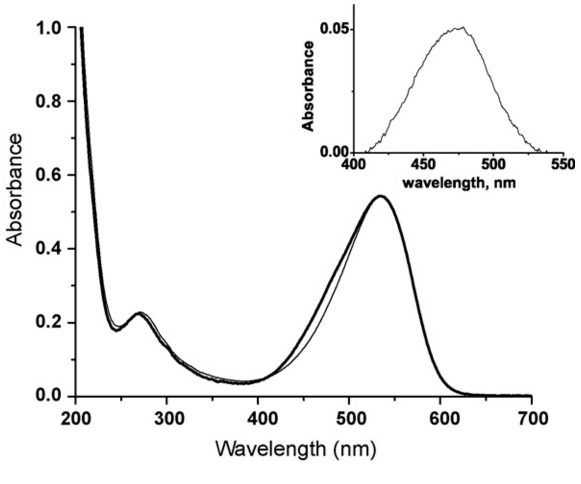


Fig. 4. Absorption spectrum of beet extract in water before (thick line) and after (thin line) dipping a TiO_2 film in the extract. The inset shows the difference spectrum.

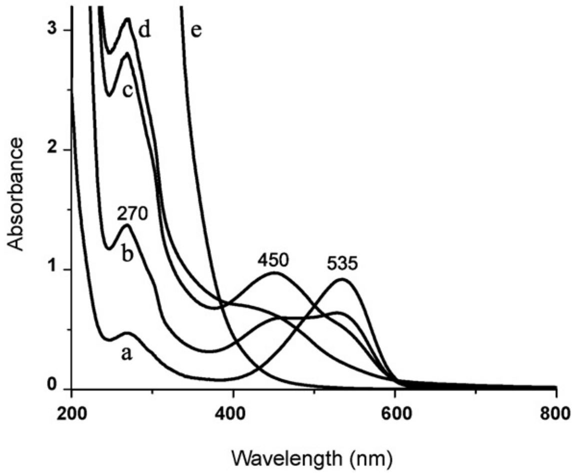


Fig. 5. Absorption spectrum of beet extract after heating at 65 ° C for (a) 0 min, (b) 20 min, (c) 40 min, (d) 60 min and (e) after 6 days in air at room temperature.

strong UV absorption, shown in Fig. 5 e, as expected for the melanin-like brown polymer.

In order to obtain TiO_2 films sensitized with betanin, it was necessary to first separate the betaxanthin compounds using column chromatography, and to use an acid-treated TiO_2 film. The ratio of Bt to In was increased from about 3:1 in the raw beet extract to about 3.5:1 in the column purified extract. Untreated TiO_2 was still only weakly stained by the column effluent, though a faint pink color of the film could be achieved after soaking in acidic purified beet extract. It was found that acid pretreatment of the TiO_2 film by ethanolic HCl led to a more darkly colored film as shown in Fig. 6. The increased ratio of A_{536} to A_{482} in the spectrum of the treated film suggests less adsorption of residual In. In either case the absorption maximum is about 560 nm. Slight red-shifts of the absorption spectrum of various dyes adsorbed on TiO_2 have frequently been observed and attributed to electronic coupling of the sensitizer and the semiconductor. The acid treatment probably leads to a net positive charge on the TiO_2 film and may facilitate the adsorption of betanin through the COO^- group.

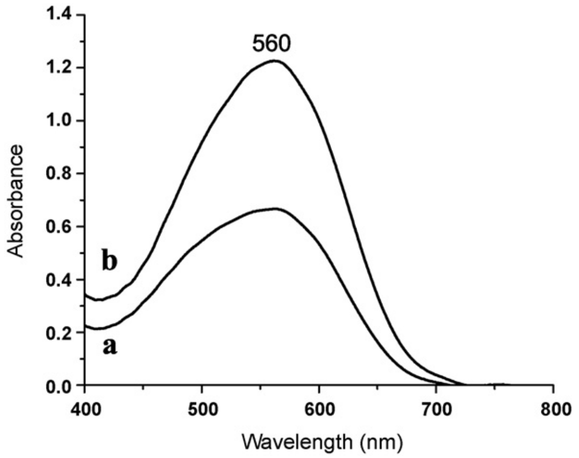


Fig. 6. Absorption spectrum of TiO_2 film sensitized by column-purified beet extract before (a) and after (b) treatment of the film with ethanolic HCl.

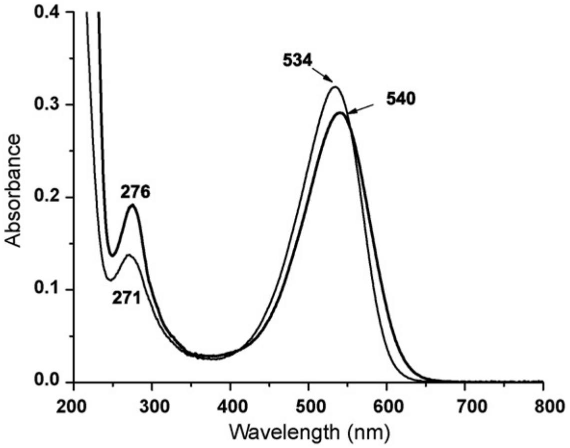


Fig. 7. Absorption spectrum of aqueous beet extract at neutral pH (absorption maxima at 271 and 534 nm), and that of the same sample following conversion of betanin to betanidin by β-glucosidase at pH 3.5 (absorption maxima at 276 and 540 nm).

Fig. 7 shows the spectrum of raw beet extract before and after reaction with β-glucosidase to convert betanin to betanidin. The resulting solution was then used to sensitize an untreated TiO_2 film. As shown in Fig. 8, betanidin adsorbs strongly on TiO_2 film as would be expected based on the presence of two *ortho*–OH groups on the aromatic ring. The use of phosphate buffer interferes with the adsorption of betanidin onto TiO_2, so the betanidin-sensitized film was obtained by the addition of the enzyme in the absence of buffer. The absorption spectrum of betanidin is red-shifted on TiO_2 with a maximum at about 555 nm compared to 540 nm in solution. Along with the observed increase in spectral width, this red shift is indicative of strong electronic coupling of Bd and TiO_2.

3.2. *Photocurrent and photovoltage measurements*

Four different betalain-derived sensitizers were investigated. Films sensitized by raw beet extract are referred to here as betaxanthin-sensitized, owing to preferential adsorption of yel-

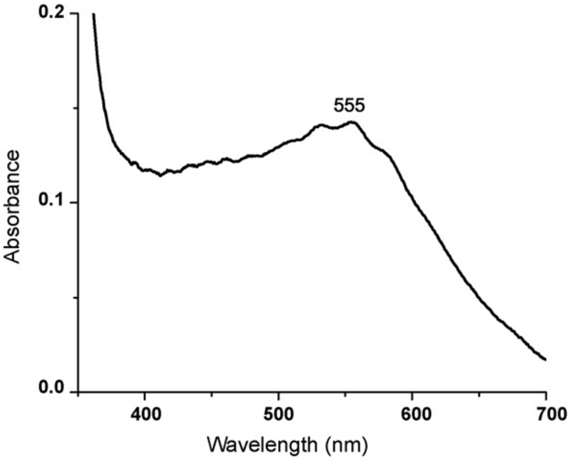


Fig. 8. Absorption spectrum of TiO_2 film stained by beet extract solution following conversion of betanin to betanidin.

Table 2
Comparison of DSSCs using three different betalain pigments

Sensitizer	I_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
Betaxanthin	2.00	0.22	0.51	0.19
Betanin	0.51	0.27	0.47	0.07
Melanin	0.75	0.23	0.35	0.05

Electrolyte solution consisted of 0.5 M LiI and 0.05 M I_2 in acetonitrile, and incident light power was 99.8 mW/cm^2.

low betalains, while those sensitized by purified beet extract will be called betanin-sensitized. (These designations are for convenience and are not meant to imply the complete absence of the other pigment.) A DSSC based on the brown oxidation product was also found to give small photocurrent and is referred to below as melanin-sensitized. Finally, the betanidin-sensitized solar cell obtained by soaking the TiO_2 film in raw beet extract after enzymatic removal of the sugar group was tested, but negligible photocurrents were obtained. Reported in this section are the short-circuit photocurrent I_{sc}, the open-circuit voltage V_{oc}, the fill factor FF, and the energy conversion efficiency η.

Table 2 summarizes the results for betaxanthin, betanin, and melanin as sensitizers on untreated TiO_2 and in the absence of TBP. The data of Table 2 are for ACN-electrolyte. The highest efficiency in this series was obtained for the betaxanthin-sensitized solar cell. We also tried ethanol as a solvent (data not shown) but much lower photocurrents and efficiencies were obtained as in our previous studies using the ruthenium-based N3 sensitizer [38]. Interestingly, the melanin-sensitized film produced rather large photocurrent considering its poor light-harvesting properties. (See Fig. 3.) The results in this case are similar to those reported in Ref. [39], where a synthetic eumelanin compound derived from dihydroxyindole was used as a broadband sensitizer for the DSSC. We found the betalain-derived melanin adsorbed on TiO_2 film to be very stable over long time.

Table 3
Performance of betanin-sensitized DSSC using MPN as solvent

TBP (M)	HCl (h)	I_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
0.5	6	2.42	0.44	0.63	0.67
0	6	1.43	0.42	0.56	0.34
0.5	0	1.35	0.45	0.65	0.40
0	0	0.89	0.26	0.47	0.11

Electrolyte solution consisted of 0.5 M LiI and 0.05 M I_2 in methoxypropionitrile and incident light power was 99.8 mW/cm^2.

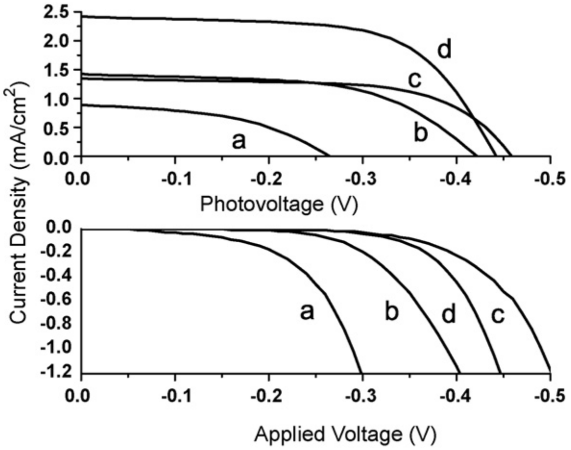


Fig. 9. Photocurrent vs. photovoltage (top) and dark current vs. applied voltage (bottom) for betanin-sensitized DSSC using MPN as solvent: (a) no HCl treatment or TBP added, (b) HCl treatment, no TBP (c) TBP, no HCl treatment, and (d) HCl treatment and TBP added.

Further studies of the betanin-sensitized solar cell were pursued using MPN as the solvent for the electrolyte. The influence of acid pretreatment and TBP were explored and the results are shown in Table 3 and Fig. 9. The highest efficiency is obtained using both acid pretreatment and TBP which leads to larger current. The maximum voltage is highest for the DSSC containing TBP and untreated TiO_2, consistent with the lowest dark current as shown in the lower part of Fig. 9. Note that addition of TBP improves both the photocurrent and photovoltage in contrast to its effect on the N3-sensitized DSSC where there is little effect of TBP on the photocurrent. The maximum photovoltage V_{oc} is a function of the flux of injected electrons I_{inj} and the recombination current I_0 [40,41]:

$$V_{oc} = \frac{mk_BT}{e} \ln\left(\frac{I_{inj}}{I_0}\right) \quad (2)$$

where m is the diode quality factor. The maximum possible V_{oc} is the difference in the Fermi level of the semiconductor and the I^-/I_3^- redox potential, but recombination and less than maximum yield of electron injection limits open-circuit voltage. The best values of V_{oc} for the Bt-sensitized DSSC are about 0.44 V, compared to about 0.7 V for the N3-sensitized DSSC [1–5]. The lowered photovoltages for Bt as compared to N3 as sensitizer result from lower injection yields and higher recombination current. Acid treatment alone improves both I_{sc} and V_{oc} by virtue of increasing the dye loading, as expected, but TBP alone (no acid treatment) also improves photocurrent and photovoltage. TBP is believed to reduce recombination, thereby improving the maximum photovoltage [43,44]. In the case of N3-sensitized films, recombination is dominated by electron capture by I_3^-, since the oxidized dye is rapidly reduced by I^-. In the present study, the injected electrons probably also recombine with oxidized Bt, resulting in lower I_{sc} and V_{oc}.

Recombination of electrons with $I_3^-$is revealed by the dark current as a function of applied potential as shown in the lower part of Fig. 9. The onset potential for dark current should be set by the difference in the Fermi level of TiO_2 versus the I^-/I_3^-redox potential. The latter is expected not to vary as it is a function of the solvent, thus the data in the lower part of Fig. 9 reveal changes in the TiO_2 conduction band with acid treatment and TBP. Interestingly, the acid treatment alone results in a shift in the onset value for dark current to larger magnitude of applied voltage. Acid pretreatment of the TiO_2 film might have been expected to cause a shift in the conduction band to more positive potential, based on shifts in the TiO_2 redox potential with pH, leading to a shift to less negative onset potential, opposite to what is observed. Acid treatment also permits higher dye loading which helps to reduce recombination [45]. On comparing the dark currents for the two films treated by TBP (c and d in the lower part of Fig. 9), the onset potential for dark current is the same and suggests that TBP raises the conduction band energy of TiO_2 as previously reported [43].

The kinetics of regeneration of the sensitizer by reaction of the oxidized form with I^- is also important to consider. As shown on the left hand side of Fig. 10, the photocurrent produced by the Bt-sensitized solar cell was found to be a linear function of the incident light power. This suggests that reaction of oxidized Bt with I^-does not limit the flow of current. We also attempted to check the stability of the dye by measuring the absorption spectrum of the sensitized film before and after the measurement of the photocurrents. The measurement is made difficult by the inhomogeneity of the sensitized films, but the results indicate there is some degradation of Bt during the photocurrent measurements, corresponding to about 10% decrease in absorbance. To check the rectifying properties of the Bt-sensitized solar cell, the open-circuit voltage was plotted as a function of the natural log of I_{sc}, from data at different incident light powers, as shown on the right hand side of Fig. 10. From the slope of this graph the diode quality factor m for DSSCs using the acid pretreatment was found to be about 1.3 in the presence of TBP and 1.7 in the absence of TBP, indicating better rectification in the presence of TBP. The recombination current I_0 was also decreased from 2.3×10^{-5} mA/cm^{-2} in the absence of TBP to 1.7×10^{-6} mA/cm^{-2} in the presence of TBP. While the quality factors obtained here are similar to those found for N3-sensitized solar cells [36], the recombination currents are much larger.

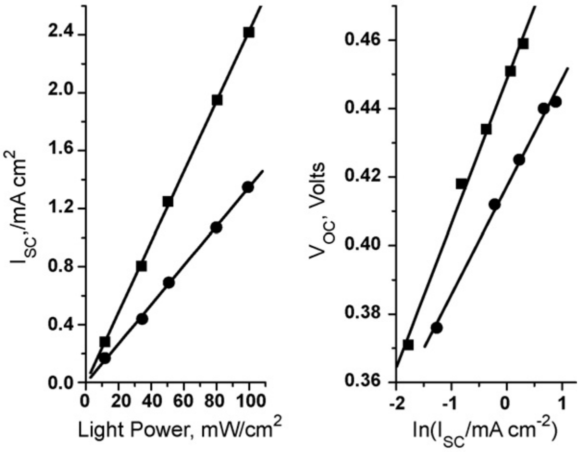


Fig. 10. Short-circuit photocurrent I_{sc} vs. incident light power (left) and open-circuit voltage V_{oc} vs. ln(I_{sc}) (right) for Bt-sensitized solar cell using MPN solvent and acid pretreatment, with (squares) and without (circles) TPB.

3.3. Incident photon-to-electron conversion efficiencies

Incident photon-to-electron conversion efficiencies, IPCE(λ), were recorded as a function of incident wavelength for the betaxanthin-sensitized and the betanin-sensitized solar cell. IPCE(λ), also called the photocurrent action spectrum, is the ratio of the number of electrons produced in the external circuit to the number of photons incident upon the cell and is the product of three efficiencies:

$$\mathrm{IPCE}(\lambda) = (1 - 10^{-A})\phi_{\mathrm{inj}}\eta_{\mathrm{c}} = \frac{I_{\mathrm{sc}}hc}{P_0\lambda e} \tag{3}$$

where $1 - 10^{-A}$ is the light harvesting efficiency based on the absorbance A at wavelength λ, ϕ_{inj} is the quantum efficiency for electron injection defined as number of electrons transferred per photon absorbed, and η_{c} is the collection efficiency. IPCE(λ) is determined experimentally from a measurement of the short-circuit photocurrent density I_{sc} under illumination at wavelength λ with power density P_0. Fig. 11 shows IPCE(λ) for a DSSC sensitized with raw beet extract (“Bx-sensitized”) and a “Bt-sensitized” DSSC based on an acid-treated TiO_2 film sensitized with beet extract following column chromatography. IPCE(λ) for the Bt-sensitized DSSC bears a close resemblance to the absorption spectrum of a Bt-sensitized TiO_2 film as shown in Fig. 6, with a maximum IPCE of about 8% at a wavelength of about 560 nm. The Bx-sensitized DSSC shows a slightly higher peak IPCE of about 14%. The shape of IPCE(λ) is somewhat different from the absorption spectrum of the Bx-sensitized TiO_2 film shown in Fig. 3 a, perhaps a result of the adsorption of more than one pigment when an untreated film is exposed to raw beet juice.

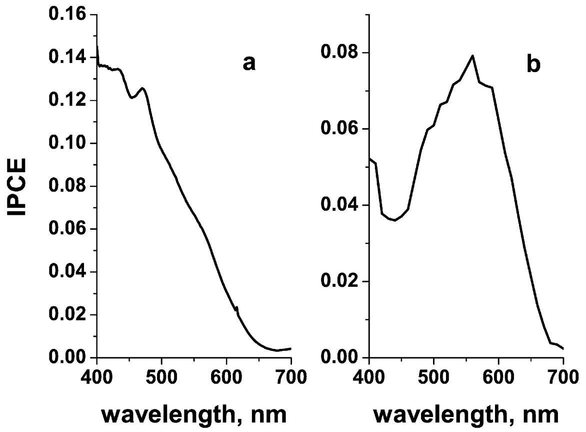


Fig. 11. IPCE(λ) for (a) betaxanthin-sensitized and (b) betanin-sensitized DSSC. Electrolyte solution consisted of 0.5 M LiI and 0.05 M I_2in MPN.

4. Discussion

First, we consider the basis for the preferential adsorption of indicaxanthin over betanin in the case of untreated TiO_2. The molar concentration of Bt in raw beet extract is about three times that of In, yet the visible spectrum of the sensitized film is dominated by In. P25 is a mixture of anatase (about 75%) and rutile forms of TiO_2. The zeta potential of anatase has been reported to be about 6.2 while that of anatase is 4.7 [42]. Thus at pH 7 the surface of P25–TiO_2 is negatively charged and adsorption of negatively charged components is unfavorable. In a solution of In and Bt at pH 7, In is expected to have zero net charge while Bt exists in an approximately 50:50 mixture of zwitterionic and anionic forms. Acid pretreatment of the TiO_2 film may result in a net positive charge which facilitates adsorption of anionic Bt.

The acid pretreatment employed here is similar to that reported in Ref. [46], for which the sensitizer was the ruthenium-containing black dye. In that work, HCl pretreatment was found not to have a large effect on the onset potential for generation of dark current, in contrast to the present work. Instead, acid treatment in Ref. [46] led to a small decrease in dark current and increase in V_{oc}. A more striking contrast between the present work and Ref. [46] is the much larger dark current observed in our study. Possible sources of this difference could be the use of deoxycholic acid in Ref. [46] to suppress recombination as well as dye aggregation, and $TiCl_4$ treatment of the electrode to block recombination at the conductive glass substrate. This suggests that more can be done to improve the performance of betalain-sensitized solar cells by optimizing the film preparation and suppressing recombination.

The influence of TBP on the performance of the betanin-sensitized solar cell is different from what is seen using N3 as sensitizer [43], in that the photocurrent is enhanced in the former but not the latter. This could be a result of a lower quantum yield for electron injection in the case of Bt. The driving force for electron injection is larger for Bt than for N3, presumably leading to faster electron injection. Evidently, the rate of reverse electron transfer is also faster for Bt than for N3, such that suppression of recombination leads to an increase in the photocurrent. In the case of N3 as sensitizer, the quantum yield for electron injection is already near 100%, so that TBP serves to suppress only the recombination of conduction band electrons with I_3^-, since oxidized N3 reacts rapidly with I^-. This suggests that the performance of Bt as a dye sensitizer could be enhanced by finding a redox mediator which reacts more rapidly with oxidized Bt.

The photocurrent action spectrum of a DSSC sensitized with yellow betaxanthin shows higher maximum IPCE than that of a DSSC sensitized with purple betanin. Though the light-harvesting properties of the yellow pigments are less favorable for solar energy conversion as compared to purple betanin, the higher photocurrents obtained with the former result in higher energy conversion efficiency. For both Bx- and Bt-based DSSCs, the less than 100% IPCE values at wavelengths well within the absorption band of the adsorbed dye reflect the detrimental consequences of recombination and possibly also the less than maximally efficient quantum yield for electron injection.

5. Conclusions

This is the first detailed report on the use of betalains for dye-sensitized solar energy conversion. Compared to anthocyanins as dye sensitizers, slightly higher maximum photocurrents and power conversion efficiencies are obtained under full spectrum illumination of 100 mW/cm^2. Though anthocyanins and betalains share a similar biological niche, the presence of carboxylic acid functions in the latter presents an advantage for anchoring the dye to the TiO_2 surface by manipulating the surface acid–base chemistry. Future work will be directed at optimizing the performance of betalain-sensitized solar cells by exploring variations in the electrolyte composition and film properties, as well as the use of purified betalain extracts from various plant sources.

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