

TOWARD A MORE EFFICIENT UTILISATION OF BETALAINS AS PIGMENTS FOR DYE-SENSITIZED SOLAR CELLS

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We report on the use of natural dyes, betalains, as pigments for Dye-Sensitized Solar Cells (DSSC). Time-Dependent Density Functional Theory calculations provide the electronic spectra of the various types of betalain dyes and allow a discussion of their matching to the solar spectrum. Experimentally, we vary parameters such as the nature of the extracting solvent, the pH and the composition of the extract, to optimize the fabrication of DSSCs using betalains. Based on UV-Vis spectra correlated with electro-optic measurements providing the photovoltaic conversion efficiency under standard AM1.5 conditions we find that the decrease of the pH of the dye solution leads to an increase of the DSSC performance, likely due to the increasing ratios of betacyanins with respect to betaxanthins in the extracts as well as the possible hydrolysis of betanin to betanidin. In order to fabricate better DSSCs using betalain natural dyes, we propose to use water as extracting solvent, to increase the content in betacyanins on the photoanode by a preliminary purification and to raise the stability of the dyes preferably by using anti-oxidizing copigments that do not interact with the substrate.

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1. Introduction

Dye-Sensitized Solar Cells (DSSCs) [1,2], one of the most convenient sources for future clean energy, consist of an electrode with a porous layer of a nanocrystalline wide band gap semiconductor, such as TiO₂, sensitized with a light absorbing dye, a redox electrolyte (e.g. I₃/I⁻) and a counter electrode for instance platinized conductive glass. The working principle of the device is based on light absorption in the dye anchored to the TiO₂ nanoparticles, followed by transfer of the resulting photoelectron from the excited level of the dye into the conduction band of TiO₂, and through the electrode into the external circuit. The electrolyte facilitates the transport of the electron and the regeneration of the sensitizer, through reduction of the triiodide ion at the counter electrode, followed by oxidation of the iodide ion at the dye [2,3].

DSSCs have as main advantage with respect to the usual solar cells the use of relatively inexpensive materials and technologies [2]. The use of natural pigments may be a convenient alternative to ruthenium complexes [4], despite the lower efficiency, because they are easy to obtain. The cost-effectiveness of DSSCs (defined as the ratio between the conversion efficiency and the cost of the dye) using, for instance, anthocyanins extracted from red cabbage is 50 times

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larger than in the case of ruthenium complexes [5]. It is also expected that the DSSCs with nontoxic natural pigments (like anthocyanins [6,7,8,9], chlorophylls [10,11], and hypericin [12]) as sensitizers would definitely enhance the environmental benefits of this form of solar energy conversion. But until now, the efficiencies of solar energy conversion by anthocyanins (the most used as pigments for DSSCs) and chlorophylls are rather low; e.g. 0.56% for a DSSC based on anthocyanins extracted from blackberries [8] or 0.17% from red cabbage and red onion [9].

Betalains are a class of vegetal pigments, isolated mainly from plants of the order Caryophyllales. The main chromophore of betalains is the betalamic acid (**ba**, see Fig. 1). The two categories of betalains are: the reddish to violet betacyanins, in which **ba** is associated to *cyclo*-DOPA, and the yellow to orange betaxanthins, in which **ba** is associated to an amino acid or an imino compound. The simplest natural betacyanins are the non-glycosylated betanidin (**bd**) or isobetanidin chromophores obtained by the condensation of *cyclo*-DOPA with betalamic acid. Betanin (5-*O*- β -D-glucoside of betanidin, **bn**, the major red beet pigment) and gomphrenin (betanidin 6-*O*-D-glucopyranoside, a rare pigment) are two structural isomeric glucosides of betanidin [13].

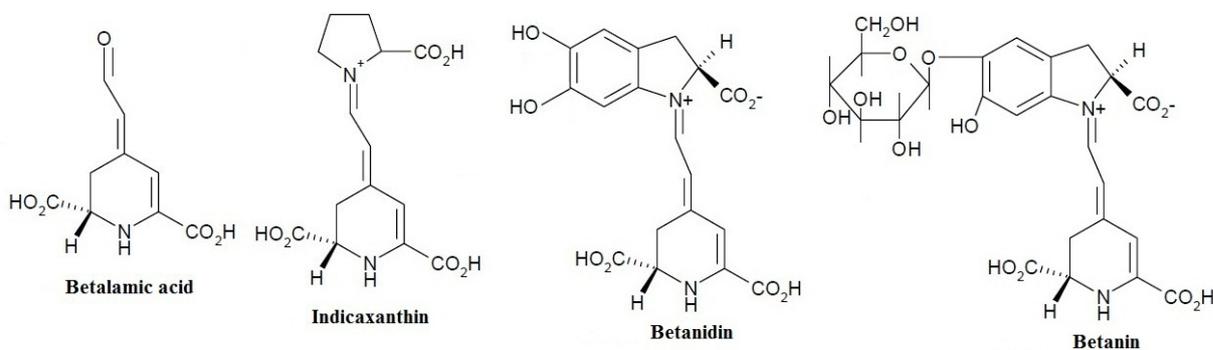


Fig. 1. Chemical structure of betalamic acid (**ba**), indicaxanthin (**in**), betanidin (**bd**) and betanin (**bn**).

The most important source of betanin, the most studied betalain, is the red beet (*Beta vulgaris* subsp. *vulgaris*) root. Betanin is used as a food colouring agent, and the colour is sensitive to pH; in solution, upon heating, was found to hydrolyze to betalamic acid and *cyclo*-DOPA-5-*O*-glycoside [14]. A pH of about 3 - 4 stabilises the betalain pigments and protects against oxidation. Pigment extracts must be protected from direct sun light and should be kept in a cool and dark place [15,16].

To qualify as a good candidate for DSSC photosensitizers, a dye should verify several essential requirements, such as the matching of the absorption spectrum with the solar spectrum, especially in the visible region and part of the infrared, and the presence of anchoring groups (-COOH, -PO₃H₂, -SO₃H, etc.) to strongly bind the dye onto the semiconductor surface [17]. The betalains have favourable light absorption, existing in nature in association with various copigments which modify their light absorption properties, and are capable to complex metal ions, possessing the requisite functional group (-COOH) to bind also to TiO₂. Although the betalain dyes fulfil the criteria mentioned above, they have not been sufficiently studied as dye sensitizers [18,19,20,21]. Moreover, previous reports seem contradictory, as in two such studies [18,20] the purification of the extracts is claimed to lead to higher photovoltaic conversion efficiencies, whereas the third concludes that better results are obtained with natural extracts, without purification [21].

We report here on the fabrication and electro-optical characterization of DSSCs using betalains as TiO₂ sensitizers. To improve the efficiency of DSSCs we studied the influence of several factors: extraction solvent, pH of the solutions, purification, use of copigments, treatment of titania plates. Some of these factors are expected to influence the number of active sites on the TiO₂ surface, hence the adsorbed amount of pigment and cations. It was shown [22,23] that adsorption of specific cations (such as H⁺) on TiO₂ nanoparticles affects the conduction band edge and the ability of molecular sensitizers to inject electrons into the semiconductor. Here, we emphasize the role of extract purification and discuss how adsorption affects the efficiency of the devices.

2. Experimental

2.1. Preparation of dye solutions

All the solvents and the chemicals employed for the experiments were of reagent or spectrophotometric grade.

The pigment N719 (Ruthenium 535-bisTBA, $(\text{Bu}_4\text{N})_2[\text{Ru}(4\text{-carboxy-4'-carboxylato-2,2'-bipyridine})_2(\text{NCS})_2]$), from Solaronix, was dissolved (60 mg) in 100 mL of anhydrous ethanol [24], in order to fabricate a reference DSSC.

The extracts of red beet roots were obtained from fresh biological materials. The solvents (water, methanol and, respective, ethanol) were added over the small pieces of clean red beet roots (10 mL of solvent for each 1 g of vegetal material). The pH of the mixture was adjusted in the range 1.0 – 4.0 by adding hydrochloric acid. The mixtures were kept for 24 hours (regardless of solvent) in dark places, and then filtered. The red beet juice was obtained using a blender, the resulting mixture being then filtered. We used juice at pH 6 and 2 (after acidulation with hydrochloric acid). The pigments were separated using a homebuilt medium pressure liquid chromatography (MPLC) apparatus with silica gel 60 (particle size 0.040 – 0.063 mm) as the stationary phase and a mobile phase of 0.1 M HCl solution in the extraction solvent. The column length was 20 cm and the flow rate was 0.5 mL/min. In order to increase the stability of the extracts, we used as copigments citric acid, ascorbic acid and gallic acid, with a resulted pH in the range 2.0 – 4.0.

All resulted solutions were protected from direct light exposure.

2.2. Preparation of electrodes

The conductive glass substrate consists of a soda lime glass sheet of 2.2 mm thickness, with a conductive layer of F-doped SnO_2 with sheet resistance of $15 \Omega/\text{cm}^2$ (Solaronix), and an optical transmission greater than or equal to 80%, in the 400-700 nm region.

The TiO_2 porous film was obtained by using the sol-gel method, starting from the commercial anatase TiO_2 nanopowder (P25, Sigma-Aldrich) and titanium isopropoxide (Sigma-Aldrich) [25]. The conductive glass substrates were pre-treated by immersing in a TiCl_4 40 mM solution and kept for 40 min at 70°C , to increase the short-circuit photocurrent [26]. The FTO substrates were subject to the coating of a porous film by the “doctor-blade” technique with TiO_2 paste. Layers were sintered at 450°C for 1h. The IR spectra of semiconductor layers (cm^{-1} : $\nu(\text{OH})$, 3410 vw , $\nu(\text{Ti-O})$ 582 vs) showed that the plates are coated with TiO_2 [27], and confirmed that there are no impurities in the titania layers, e.g. titanium isopropoxide or other impurities, which could be detected. The resulting photoanodes were used without a subsequent treatment (untreated plates) or were treated in two ways: (i) they were immersed in a HCl 0.5 M and kept for 6 hours (acidulated plates) [18], and (ii) they were immersed in a TiCl_4 0.2 M solution, kept overnight and sintered at 450°C for 1h (TiCl_4 post-treated plates) [24]. The titania plates were immersed in extracts overnight at room temperature. For the reference cells, the photoanode plates were stained in N719 dye solution by soaking for 2 h at 70°C . The non-adsorbed dye were washed away with proper solvents until the rinse liquid was colourless and then dried at 80°C for 30 min.

Platinum counter electrodes were prepared by spreading a few drops of 5 mM $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$ solution in 2-propanol on the FTO glass, followed by drying at 100°C for 10 min and then at 385°C for 30 min [28].

2.3. Preparation of electrolyte and assembly of DSSCs

The electrolyte solution for natural DSSCs was prepared dissolving KI (0.5 M) and I_2 (0.05 M) in mixed solvents of ethylene glycol and acetonitrile (4:1 in the volume ratio) [6]. For the N719 DSSC the Iodolyte TG-50 (50 mM of tri-iodide in Tetraglyme) from Solaronix was used.

DSSCs were assembled following the procedure described in the literature [29], the catalyst-coated counter electrode being placed on the top, so that the conductive side of the counter

electrode faced the TiO₂ film. The iodide electrolyte solution was placed at the edges of the plates. The liquid was drawn into the space between the electrodes by capillary action. Two binder clips were used to hold the electrodes together.

2.4. Characterisation and measurement

The UV-VIS absorption spectra of dye solutions and dyes adsorbed onto TiO₂ surface were recorded in the range 200–900 nm and respectively 220–850 nm, on a Jasco V 550 spectrophotometer, either in quartz cuvettes in absorption mode or in an integrating sphere. IR spectra were recorded with a Jasco FT-IR 4200 spectrometer from KBr pellets, in the range 400–4000 cm⁻¹, and by diamond crystal attenuated total reflection - Fourier transform IR spectroscopy (ATR-FTIR).

The electro-optical parameters of the DSSCs, the short circuit current, I_{SC} , the open circuit voltage, V_{OC} , the fill factor, FF , and the photovoltaic conversion efficiency, η , were measured under AM 1.5 G standard conditions (1000W/m²) at 25°C, using a homemade class A small area solar simulator [30]. The cell surface was exposed to light through a circular slit of 10 mm diameter, resulting in a useful area of about 0.785cm². The current and voltage values were measured using two digital bench multimeters (Mastech MS8050) and a decadic resistance box. All measurements were made at intervals of 45s, allowing for each reading to stabilize.

We compared the performance of betalains-based DSSCs to the standard DSSCs prepared with N719 dye, using the photoanodes pre- and post-treated with TiCl₄, which lead to a solar energy conversion efficiency of 2.26%.

2.5. Computational details

The structures of betalain natural dyes presented in Fig. 1 (the betalamic acid, indicaxanthin, betanidin, and betanin) were optimized using Density Functional Theory (DFT) calculations [31], with the B3LYP exchange-correlation functional [32,33] and the 6-31G(d) basis set [34]. Vibrational analysis was performed at the same level of theory to check the stability of all optimized structures, and to obtain the zero-point corrections to the total electronic energies. All calculations were performed with the GAUSSIAN03 package [35].

3. Results and discussion

The performance of betalain extracts as pigments for DSSCs was studied varying the nature of the solvent, the pH and composition of extracts. In order to discuss more clearly the experimental data, particularly the UV-Vis spectra, we proceed, however, with our theoretical results.

3.1. Calculated electronic spectra

To better understand the UV-Vis spectra we note first that the natural red beet extracts are likely a mixture of several pigments. The betalain pigments are characterised by a maximum absorbance at about 535 nm (λ_{max}) for the red-purple betacyanins (betanin with λ_{max} = 535 nm and betanidin with λ_{max} = 542 nm) and near 480 nm for the yellow betaxanthins (indicaxanthin, the common betaxanthin found in red beet root with λ_{max} = 482 nm); for the betalamic acid λ_{max} = 424 nm [18].

The simulated UV-Vis spectra were obtained after performing geometry optimizations of all dyes. Optimized geometrical structures of betanidin and betanin dyes were previously reported [36]; we extend this study to the betalamic acid and indicaxanthin and, furthermore, compute proton affinities in gas phase and aqueous solvent. The vibrational analysis was performed on all optimized structures to ensure their stable character and to provide zero-point corrections to proton affinities. We performed electronic structure calculations at DFT/B3LYP/6-31+G(d) level, followed by TD-DFT simulations, providing the electronic absorption spectra for the first 20 singlet-singlet transitions for protonated species (see Fig. 2).

For the protonated **bd**⁺ and **bn**⁺ dyes an intense absorption band is found in the visible range with a strong maximum at 537.4 nm and 526.9 nm, respectively. For both dyes a second, less intense absorption band peaks at about 419 nm. The other two dyes, **ba**⁺ and **in**⁺, have weaker absorption in the visible range, with peaks at shorter wavelengths, at 402.8 nm and 429.6 nm, respectively. The spectral line composition analysis reveals that the most intense band is associated with a transition between the highest occupied and the lowest unoccupied molecular orbital (HOMO → LUMO) for all four species. The next bands consist of HOMO-1 → LUMO transitions. The orbitals involved in all the transitions mentioned above have π and π^* character, respectively.

The best matching with the solar irradiation spectrum is observed for **bd** and **bn**. Taking into account the similar binding to the substrate and charge transfer channels and the better matching with the solar spectrum, **bd** and **bn** seem more likely to lead to higher photovoltaic conversion efficiencies than the other betalain dyes.

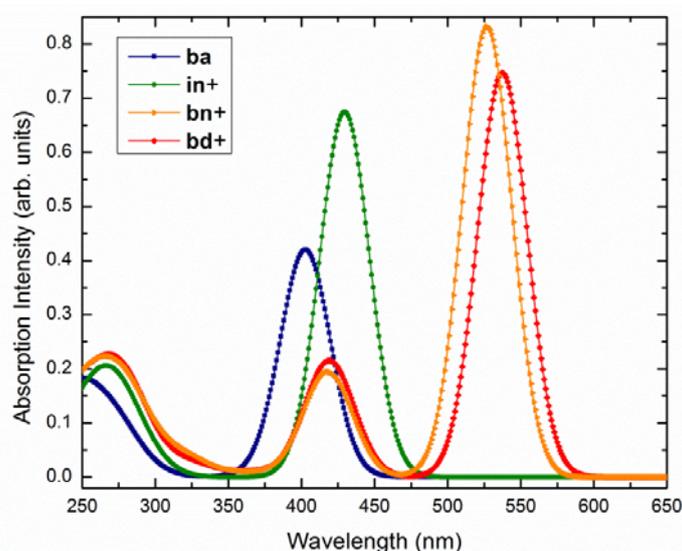


Fig. 2. Simulated electronic absorption spectra of the protonated betalain dyes, calculated by TD-DFT. The spectral lines were convoluted with Gaussian distributions of 40 nm line width at half maximum.

3.2. Effect of the solvent on DSSC's efficiency

The electronic spectra of the extracts and the pigments adsorbed onto the semiconducting layers are displayed in Fig. 3. In the case of the dye solutions, we note that in the visible range the red beet juice presents a strong absorption band at about 530 nm, characteristic for betanin. The absorption band for extracts obtained in the same conditions (pH 2) is solvent sensitive, with a local maximum shifted toward longer wavelengths from ethanol (532 nm), to water (542 nm) and to methanol (544 nm), respectively. Taking into account the positions of the peaks in Fig. 2, we can argue that the absorption maxima may be due to the presence mainly of betanin in the ethanolic extract, or of betanidin in the methanolic and aqueous extracts, respectively. The intensity of absorptions is approximately equal for the aqueous and methanolic extracts, higher than for the ethanolic extract.

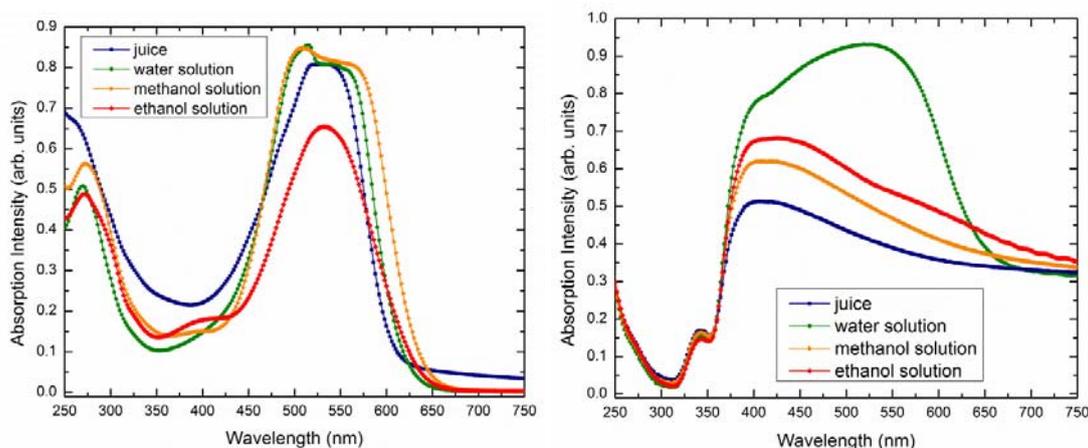


Fig. 3. UV-Vis absorption spectra of the red beet juice/extracts (left) and the red beet juice/extracts adsorbed onto the TiO_2 photoanode (right).

For the methanolic and aqueous extracts we found two absorption bands which are partially overlapped. The second band has an absorption maximum at 509 nm for methanolic extract, and at 515 nm for aqueous extract. These second bands are more intense than the bands at 540 nm. The presence of the extra feature may also be due to self-association into supramolecular structures or to interactions with other organic compounds and/or metal ions [8]. These bands are associated with high concentration of extracts and they disappear in diluted solutions. A possible explanation for such behaviour may be the formation of supramolecular structures in concentrated solutions.

The TiO_2 electrodes were equilibrated with the natural extracts, inducing a red-violet or brown coloration of the film, as seen in Fig. 3. This observation is likely related to the buffer capacity of the TiO_2/H^+ /dye system, which is often ignored in the case of pH-dependent natural dyes [37]. The shifting of the absorption bands for pigments adsorbed onto the TiO_2 nanoporous layer (Fig. 3) may be due the bonding of organic compounds to the TiO_2 surface, through oxygen atoms. Such effects had been observed for other pigments, like anthocyanins, upon complexation with metal ions, including aluminium, iron, tin, titanium, and chromium [38].

The electronic spectra of photoanodes depict that the indicaxanthin is the component adsorbed preferentially, from all extracts used. The relatively small molecules of indicaxanthin, having good coordinating properties, are likely to reach the titania mesopores. The electronic spectrum of indicaxanthin indicates that it is the least suitable pigment as DSSC sensitizer among betalains.

A comparison between the electronic spectra of the extracts and juice adsorbed on the TiO_2 film (Fig. 3) shows that (i) for methanolic and aqueous extracts the intensity of absorption and the shape of spectrum were similar and (ii) the better absorption on TiO_2 and, probably, the better linkage, occurs for the aqueous extract. Moreover, the energies of absorption maxima, and implicit the colours of adsorbed dyes, are different.

An explanation for these results may come from the differences between the compositions of the extracts. In the aqueous extract the concentration of betanidin is expected to be higher than in ethanolic extracts, probably because of a higher solubility. Furthermore, the possibility of hydrolysis of **bn** in water leads to a relative increase in the **bd** content. On the substrate, **bd** is a better ligand, having in addition to the three carboxylic groups, two more hydroxyl groups in *ortho* position, through which can act as a chelating agent [18]. Also, **bd** is a smaller molecule, with a lower steric hindrance compared with **bn**. Another explanation may be that the alcohols are also adsorbed onto the TiO_2 surface [39], and the process may interfere with the adsorption of the betalain pigments.

Consequently, although the UV-Vis spectra of the extracts indicated as most suitable pigment the methanolic extract, the spectra of the sensitised TiO_2 layers suggested that the proper photoanode is the one obtained from the aqueous extract.

In conclusion, we observed that the nature of solvent has an influence on the light absorption of the extract. Previous reports on anthocyanins [40] showed that the extracting solvent has an

effect on the efficiency of DSSCs. In the solvent in which the betalains are more soluble (as shown the electronic spectra the betalains, unlike anthocyanins [41], are expected to be more soluble in water and methanol) it is likely to obtain a higher photovoltaic conversion efficiency, because of a better dispersion of dye molecules on the oxide surface.

Table 1. Typical values of the short circuit current (I_{sc} , in mA, for an active area of 0.785 cm^2), open circuit voltage (V_{oc} , in mV), fill factor (FF), and photovoltaic conversion efficiency (η , in %), determined for solar cells fabricated with TiO_2 sensitized with betalain extracts in different solvents, at the same pH.

Treatment of TiO_2 electrode Extract	Non-acidulated		Acidulated	
	Water extract, pH = 2	$I_{sc} = 0.164$	$V_{oc} = 370$	$I_{sc} = 0.195$
FF = 0.618		$\eta = 0.048$	FF = 0.671	$\eta = 0.070$
Methanolic extract, pH = 2	$I_{sc} = 0.062$	$V_{oc} = 346$	$I_{sc} = 0.091$	$V_{oc} = 357$
	FF = 0.613	$\eta = 0.017$	FF = 0.651	$\eta = 0.027$
Ethanolic extract, pH = 2	$I_{sc} = 0.054$	$V_{oc} = 302$	$I_{sc} = 0.125$	$V_{oc} = 330$
	FF = 0.541	$\eta = 0.011$	FF = 0.611	$\eta = 0.032$

The performance of various DSSCs, fabricated in different conditions, is reported in Table 1. In otherwise identical conditions (pH 2), the best results were recorded for aqueous extracts. The efficiencies are decreasing with the increasing of solvent mass and with the decreasing of polarity. The solvent polarity may be correlated, besides the solubility, with the polarisation of the carboxyl group and with the possibility of deprotonation, possibly leading to a better linkage to the substrate.

The cells sensitised with natural juices, even in acidulated form (pH 2) have low efficiencies (FF = 0.628, $\eta = 0.0249$) probably due to their composition, as they contain various other compounds, different from the betalain dyes. The dissolved molecules on the photoanode surface, may act as a filter, restricting the access of the pigment molecules to Ti(IV) centres, process that also influences the colour ranges of the photoanodes.

3.3. Effect of the pH of the extract

To investigate the effect of the pH on the performance of betalains extracts as photosensitizers for the titania mesoporous layers we fabricated DSSCs using various dye solutions. Since the pH affects the colour of the solution [42], with the bright bluish-red, at a pH of 4 to 5 becoming blue-violet as the pH increases, different light absorption means different efficiency, everything else being equal. Moreover, once the pH reaches alkaline levels betalains degrade by hydrolysis, resulting in a yellow-brown colour. They keep their appearance over a broad pH range from 3 to 7, but degrade below pH 2 and above pH 9 [42].

The original pH of the betalains extracts in water was around 6. We varied the pH for aqueous extract from its initial value of 6.4 to 1, using HCl, and to 9, using NH_3 . The extracts with pH 9 had brown colour and did not coloured the TiO_2 layers, suggesting very poor adherence to the substrate. The absorption bands of the aqueous extracts at different pH are shown in Fig. 4. The pH of the extract likely influences the solubility of the various betalains, leading to the extracts with different compositions. The colour variations can be correlated with changing ratios of betaxanthin and betacyanin content [42]. For instance, the ratio of **in:bn:bd** concentration (resulted from the absorbance values at 482 nm, 535 nm, and 542 nm, respectively, [43]) is 0.900:1.00:1.005 at pH 1, 0.978:1.000:0.981 at pH 2, and 1.034:1.000: 0.988 at pH 6 (Fig. 4).

Keeping in mind the calculated spectra of Fig. 2, which indicated that betacyanins absorb at higher wavelengths than betaxanthines, we can interpret the results displayed in Fig. 4 as indicating that higher pH means lower betacyanin to betaxanthin ratio.

Based solely on the absorption spectra of Fig. 4 we would expect a higher photovoltaic conversion efficiency of the DSSC at lower pH. Indeed, the pH of the pigment solution has a significant effect on the performance of DSSCs, the efficiency increasing with decreasing pH, as shown in Table 2. A maximum efficiency is obtained at the optimum pH of 2. This result might be due to the fact that at pH 2, the photoanode made from the red beet aqueous extract can absorb more light, as indicated the peak intensity in electronic spectra.

Even the increasing of pH with one unit (pH 3) has as a consequence the decreasing of fill factor and efficiency and using neutral extracts the performances of cells are worst.

Chemically, during the processing of the extraction, isomerisation, decarboxylation, or bond cleavage of betacyanins in an acidic medium (or due to heat) may occur. For example, in the acidic medium the betanin can isomerise to isobetanin or neobetanin; in strong acids the betanin can hydrolyse to betanidin. The concentration of betanidin relative to betanin decreased with increasing pH from 1.005 (pH 1) to 0.981 (pH 2) and then slightly changed (0.988) at pH 6. In alkaline medium the betanin can hydrolyse to *cyclo-dopa-5-O-glycoside* and betalamic acid.[18] Through the transformation of betanidin glycosides to their respective aglycones, a bathochromic shift of 4–6 nm is observed. However, these aglycones are chemically more labile and prone to further oxidation which will result in the loss of red colour and subsequent browning, the latter masking the hue of red beet [42]. It is, therefore, possible that at lower pH values, in aqueous extracts, the betanin to be hydrolysed and the main betacyanine in the extracts remains betanidin. However, this behaviour is characteristic for water as solvent and, likely, does not occur in alcoholic solvents.

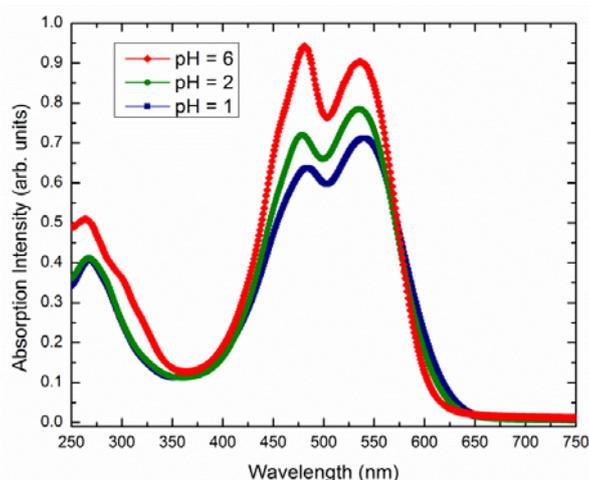


Fig. 4. The absorption bands for aqueous extracts at various values of pH.

Table 2. Typical values of the short circuit current (I_{sc} , in mA, for an active area of 0.785 cm²), open circuit voltage (V_{oc} , in mV), fill factor (FF), and photovoltaic conversion efficiency (η , in %), determined for solar cells fabricated with TiO₂ sensitized with betalain extracts in water solutions of various pH values.

Treatment of TiO ₂ Extracts	Non-acidulated		Acidulated	
	Water extract, pH = 2	$I_{sc} = 0.164$ FF = 0.618	$V_{oc} = 370$ $\eta = 0.048$	$I_{sc} = 0.195$ FF = 0.671
Water extract, pH = 3	-	-	$I_{sc} = 0.046$ FF = 0.568	$V_{oc} = 309$ $\eta = 0.010$
Water extract, pH = 6	$I_{sc} = 0.046$ FF = 0.387	$V_{oc} = 291$ $\eta = 0.0076$	$I_{sc} = 0.042$ FF = 0.544	$V_{oc} = 283$ $\eta = 0.008$

For the titania plates, the pH variation influences also the acid – base equilibrium, which has as effect the protonation of nanocrystalline titania.

The higher performance of the cells using extracts with pH 2 may be due to the form in which exist the betacyanins, probably in an aglyconic and protonated form.

3.4. Effect of extracts purification

The conclusion drawn from Fig. 4 was that the extracts have different compositions depending on pH, with various ratios of betacyanins to betaxanthins. Based on the conclusions drawn from Fig. 2 we attempted to remove the betaxanthines from the mixtures, by means of a prior purification of the extracts using a MPLC method. As expected, after purification the UV-Vis absorption bands showed increased intensity at higher wavelengths. The concentration of indicaxanthin reported to betanin decreased from 0.975:1.000 to 0.606:1.000 for aqueous extracts, but had a slight variation for methanol (from 0.952:1.000 to 0.852:1.000) and ethanol (from 0.742:1.000 to 0.639:1.000) extracts. During the purification of water extracts the concentration of betalamic acid, expressed as **ba:bn** concentration ratio, have a also strong decreasing (from 0.903:1.000 to 0.168:1.000).

As we can see in Table 3, the efficiencies for DSSCs sensitised with purified extracts are higher compared with raw extracts, in otherwise identical conditions. This result is in agreement with previous reports of McHale and coworkers [18,20] and in contradiction with the claims of Calogero *et al.* [21]. We can, therefore, conclude that a preliminary separation of betaxanthines leads to better DSSC performance (see also Fig. 5). The separation of betaxanthines from extracts was only very recently reported [20] as beneficial, as in the first report McHale and coworkers [18] had claimed that betaxanthines lead to higher efficiencies.

Table 3. Typical values of the short circuit current (I_{sc} , in mA, for an active area of 0.785 cm²), open circuit voltage (V_{oc} , in mV), fill factor (FF), and photovoltaic conversion efficiency (η , in %), determined for solar cells fabricated with TiO₂ sensitized with betalain extracts in various solvents, with or without purification, and with various electrode treatments.

Treatment of TiO ₂ Extract	Non-acidulated		Acidulated		Post-treated	
	I_{sc}	V_{oc}	I_{sc}	V_{oc}	I_{sc}	V_{oc}
Water extract, pH = 2	$I_{sc} = 0.164$	$V_{oc} = 370$	$I_{sc} = 0.195$	$V_{oc} = 420$	$I_{sc} = 0.38$	$V_{oc} = 358$
	FF = 0.618	$\eta = 0.048$	FF = 0.671	$\eta = 0.070$	FF = 0.687	$\eta = 0.119$
Purified water extract, pH = 2	$I_{sc} = 0.305$	$V_{oc} = 314$	$I_{sc} = 0.324$	$V_{oc} = 389$	$I_{sc} = 2.95$	$V_{oc} = 357$
	FF = 0.347	$\eta = 0.042$	FF = 0.666	$\eta = 0.107$	FF = 0.300	$\eta = 0.402$
Methanol extract, pH = 2	$I_{sc} = 0.062$	$V_{oc} = 346$	$I_{sc} = 0.091$	$V_{oc} = 357$	-	-
	FF = 0.613	$\eta = 0.017$	FF = 0.651	$\eta = 0.027$	-	-
Purified methanol extract, pH = 2	$I_{sc} = 0.187$	$V_{oc} = 306$	$I_{sc} = 0.16$	$V_{oc} = 367$	$I_{sc} = 0.198$	$V_{oc} = 432$
	FF = 0.258	$\eta = 0.019$	FF = 0.647	$\eta = 0.048$	FF = 0.692	$\eta = 0.075$
Ethanol extract, pH = 2	$I_{sc} = 0.054$	$V_{oc} = 302$	$I_{sc} = 0.125$	$V_{oc} = 330$	-	-
	FF = 0.541	$\eta = 0.011$	FF = 0.611	$\eta = 0.032$	-	-
Purified ethanol extract, pH = 2	$I_{sc} = 0.062$	$V_{oc} = 299$	$I_{sc} = 0.165$	$V_{oc} = 370$	-	-
	FF = 0.496	$\eta = 0.012$	FF = 0.649	$\eta = 0.051$	-	-

In contrast, Calogero *et al.* [21] argued that, compared to raw betalains extracts, purified betanins are rather poor TiO₂ sensitizers, despite the extended spectral absorption at lower energy. In their opinion, the raw natural dye mixtures exhibit better performance than commercial or

purified analogues due to the presence in the natural extract of specific pools of ancillary molecules (i.e., alcohols, organic acids, etc.) which act as coadsorbates, suppressing the recombination with the electrolyte, reducing dye aggregation and favouring charge injection [21].

In summary, we observed, in agreement with previous studies [18,21] that the betaxanthines are adsorbed preferentially onto titania layers. However, we consider that the presence of adsorbed betaxanthines is likely causing lower efficiencies for the solar cells and that a even slight preliminary purification of the extract can increase the efficiency.

3.5. Effect of photoanode treatment on DSSC's efficiency

As already seen in Table 3, in this study we used photoanodes prepared in three different ways. The acidulation of TiO_2 layer led to better results (higher cells efficiencies) in almost all cases. This is a general behaviour for the cells with natural pigments. The TiO_2 surface is positively charged, which increases the amount of active sites for dye adsorption (may facilitate the adsorption of betanin through the COO^- group [18]) and consequently the efficiency. Specific adsorption of H^+ ions on the TiO_2 surface will lead to a positive shift (on the scale relative to NHE) of flat band potential for TiO_2 ; this change will be favourable to electron injection and reduce back electron transfer [22]. Practically, in our study, most experiments were developed in acidic media and the acidity of extracts may have a comparable influence on titania as a preliminary acidulation.

The treatment of TiO_2 layer with a TiCl_4 solution led also to better efficiencies (see Fig. 5), probably because after the treatment the pores of semiconductor layers are smaller and the natural extracts pass through a process similar to filtration, and the extract is purified [44]. This feature may explain the preference for adsorption of small molecules.

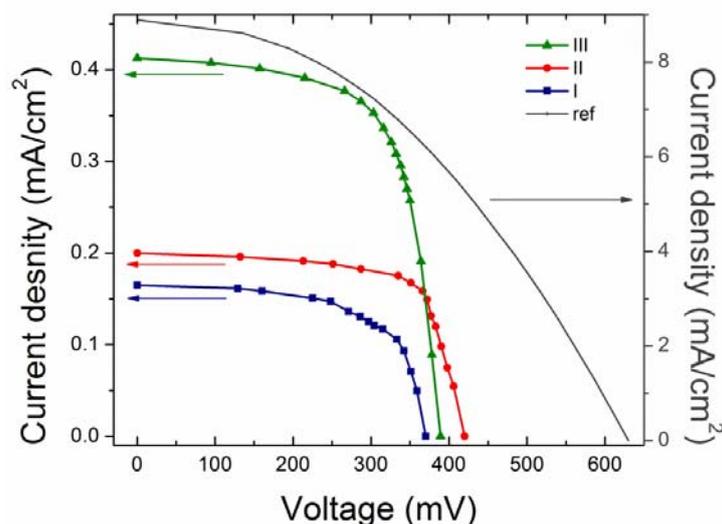


Fig. 5. Current-voltage curves of DSSCs fabricated using water extracts of $\text{pH} = 2$, with various photoanode treatments: I – non-acidulated, II – acidulated, III – post-treated. Right axis is for the reference DSSC, fabricated with the N3 dye [24].

3.6. Effect of copigment addition on the efficiency and stability of DSSCs

A problem for DSSCs is the low stability of the betalains absorbed onto TiO_2 layers, possibly due to the photocatalytic decomposition of betalains by TiO_2 [21], evidenced by the discolouring of the anode. The anode becomes paler and brownish after exposure to sunlight, likely due to a melanin-like polymer of *cyclo*-DOPA. The brown oxidation product can also be formed by heating the raw beet extract [18].

To increase the pigment stability, we used some organic acids (citric acid, which is widely used as a preservative to protect betanin from oxidation [18], ascorbic acid, gallic acid) as

copigments in aqueous extracts (Table 3). The use of citric acid in higher concentrations (for lower pH) lead to devices that did not display photovoltaic behaviour, probably because of the competitive adsorption of copigment onto the semiconductor layer [45]. For ascorbic acid the efficiencies were approximately equal (0.105% at pH 2.6), with typical HCl solutions (0.1191 at pH 2) and the cells were most stable in time. With the gallic acid the pH value cannot be decreased below 3.3 and the efficiency remains comparable with those of a typical HCl extract.

The stability of cells was studied in time, over a few weeks. We observed that the lifetime of the solar cells fabricated using organic copigments was higher in comparison with the extracts without copigments. The efficiency of the solar cells decrease steadily in time, by about 30% in the first week of light exposure, and by less than 15% during the next couple of weeks.

The instability of betalains is materialized in decarboxylation, hydrolysis and oxidation (which makes betalains natural antioxidants). The low thermal stability through decarboxylation of betalains extract, even in the adsorbed form, is confirmed by the IR spectra of the photoanodes. The intensity of the absorption band at 2360cm^{-1} (assigned to C-O asymmetric stretching, ν_3 , of CO_2 [46]) increased with temperature during the heating of betalains sensitized photoanode. The release of CO_2 may be due to the decarboxylation of betalains during the heating [41,42].

Table 4. Typical values of the short circuit current (I_{sc} , for an active area of 0.785 cm^2), open circuit voltage (V_{oc}), maximum power (P_{max}), fill factor (FF), and photovoltaic conversion efficiency (η), determined for solar cells fabricated with TiO_2 sensitized with various betalain pigments stabilised with copigments under different conditions regarding the dye solutions and photoelectrode preparation.

No.	Copigment used	I_{sc} (mA)	V_{oc} (mV)	P_{max} (mW)	FF	Efficiency (%)
Citric acid						
1.	pH = 2	no photovoltaic effect				
2.	pH = 4	0.09	343	11.5	0.373	0.0146
Ascorbic acid						
3.	pH = 2.6	0.385	348	82.8	0.618	0.1055
4.	purified, pH = 2	0.42	404	94.99	0.560	0.1210
5.	pH = 4	0.075	363	16.072	0.590	0.0205
Gallic acid						
6.	pH = 3.3	0.142	413	31.512	0.537	0.0401
7.	pH = 4	0.124	375	22.695	0.488	0.0289
Hydrochloric acid						
8.	pH = 2	0.38	358	62.056	0.687	0.1191
9.	pH = 4	0.08	372	17.174	0.577	0.0219

4. Conclusions

We studied the use of betalains from red beet as pigments for DSSCs having in view the possibility to improve the use of natural pigments. In our study we tried to clarify some contradicting results reported in the literature, regarding the use of betalains as sensitizing dyes for solar cells.

Time-Dependent DFT calculations provided the electronic spectra of the various types of betalain dyes. The better matching to the solar spectrum displayed by the betacyanins recommends them as better TiO_2 sensitizers than the betaxanthins.

UV-Vis absorption spectra of the betalain dyes adsorbed on the semiconducting substrate suggested, based on strong absorption bands around 400 nm, that indicaxanthin is adsorbed preferentially on the semiconductor, likely due to its smaller volume and lower steric hindrance. However, the light absorption of indicaxanthin is poor and the cells have low performance. To improve the device performance we tried to minimize the indicaxanthin content in the dye solution, by purification through a column of silica gel and we observed that the purified extracts led to better cell performances. Moreover, the use of a proper solvent, i.e. water, increases

adsorption of pigments onto titania and the overall photovoltaic efficiency of the device.

The decrease of the pH of dye solution leads to an increase of the DSSC performance due to the increasing ratios of betacyanins with respect to betaxanthins. Additionally the likely hydrolysis of betanin to betanidin at low pH increases the concentration of betanidin, which is probably the sterically preferred betacyanin. Also, the betanidin may be adsorbed strongly on TiO₂ film compared with betanin because of the presence of two *ortho*-OH groups on the aromatic ring. One drawback of betanidin, however, is the low stability, leading to relatively rapid degradation of the device. The use of copigments to prevent oxidation and increase the stability of betalains does not consistently increase the efficiency, one possible reason being the adsorption onto the TiO₂ substrate at competition with the dye, but increase the lifetime of DSSCs.

In order to fabricate better DSSCs using natural dyes, we propose to increase the content in betacyanins on the photoanode, to raise the stability of the dyes preferably by using anti-oxidizing copigments, that do not interact with the substrate.

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