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Dye-sensitized solar cells based on nanocrystalline TiO_2 and natural pigments

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We report the fabrication of solar cells based on nanocrystalline TiO_2 sensitized with anthocyanins extracted from various plants, such as red cabbage and red onion, in an attempt to recycle residues from the food industry. We vary the solvent and the conditions in which the dye is extracted and analyze their effect on the solar cell performance. We find that all the extracts present light harvesting properties and perform charge transfer sensitization of the TiO_2 semiconducting layer. The current-voltage curves have the expected shape for a photovoltaic device and the values of the fill-factors are relatively good, some in excess of 0.57. The efficiency, measured under standard AM 1.5 conditions, is 0.17 or lower, which is typical for most natural extracts tested so far.

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1. Introduction

Since the announcement in 1991 of the first dye sensitized solar cell (DSSC) with an efficiency of over 7% [1], these photovoltaic systems have attracted significant attention as low-cost alternatives to conventional solid-state devices [2]. The most commonly studied cells employ mostly ruthenium polypyridyl complexes as charge-transfer sensitizers, yielding over 11% solar-to-electric power conversion efficiencies in standard global air mass (AM) 1.5 sunlight [3].

Despite their high efficiency, the ruthenium complexes are expensive, instable in the presence of water and not environmental friendly [4]. To widen the choice for this critical component of the DSSC, several groups have developed metal-free sensitizers leading to widely varying efficiencies [5,6,7,8]. There are several basic requirements for an efficient sensitizer. The energy of the excited-state should be above the energy of the conduction band edge of the oxide. Light excitation should be associated with a net electron flow from the dye toward the surface of the semiconductor. And, finally, a strong conjugation across the donor and anchoring groups and good electronic coupling between the lowest unoccupied molecular orbital (LUMO) of the dye and the TiO_2 conduction band should exist, to ensure high electron-transfer rates [9].

Among the organic dyes, porphyrins and phthalocyanines attract particular attention, the former because of the analogy with natural photosynthetic processes, the latter because of their photochemical and phototherapeutic applications [10]. However, porphyrins cannot compete with the Ru-based dye sensitizer due to their lack of red and near IR absorption. Phthalaocyanines do show intense absorption bands in this spectral region. However, problems with aggregation and the unsuitable energetic position of the LUMO level, which is sometimes too low for electron transfer to the TiO_2 conduction band have turned out to be intractable so far [10].

Another strategy to obtain a broad optical absorption extending throughout the visible and near IR region is to use a combination of two dyes which complement each other in their spectral features. Such dye combinations have already been applied to mesoporous TiO_2 films in the form of mixtures of porphyrines and phthalocyanines [11].

The search for alternative sensitizing dyes was also inspired by natural processes, especially by photosynthesis, in an effort to develop environmental friendly energy solutions at low technological costs [12]. Natural dyes have been considered as alternative sensitizers for DSSCs because of the wide availability, simple preparation technique, and low cost [13]. Among vegetal pigments, the natural compounds which give the color of flowers, fruits, and leaves, chlorophyll [14] and anthocyanins [15-18]have been explored as sensitizers of wide band gap semiconductors for DSSCs, the efficiencies obtained varying widely, in some cases also because of the use of noncalibrated light sources [15-18].

Building upon previous DSSC studies [19], we report here the fabrication of solar cells based on nanocrystalline TiO_2 sensitized with anthocyanins extracted from widely spread plants such as red cabbage and red onion, in an attempt to recycle residues from the food industry. We vary the solvent and the conditions in which the dye is extracted and analyze their effect on the solar cell performance. The current-voltage curves on which the efficiency was determined were measured under standard AM 1.5 conditions, using a homemade class A small area solar simulator [20].

2. Experimental

2.1. Materials and material preparation

Anthocyanins, sugar-bound polyphenols found in all land plants, are water-soluble pigments, that may appear red, purple, or blue according to the pH of the solution, being responsible for the red and purple colors of many fruits and flowers. Most naturally occurring anthocyanins arise as a glycoside and contain one of the several aglycone cores. Anthocyanidins are the aglycones of anthocyanins, obtained by hydrolysis. A wide repertoire of colors in the red-blue range is available to anthocyanins as a result of their complexation with other polyphenols, pectins, and metal ions. Anthocyanins are being used in organic solar cells because of their ability to absorb light and convert it into electrons [21].

Red cabbage (*Brassica olercea* var. *capitata* f. *rubra*) and red onion (*Allium cepa*) are red colored vegetables, containing anthocyans as natural pigments. The aglycone portion of most anthocyanins of red cabbage and red onion pigments has been identified to be cyanidine [22] (see Fig. 1) which is attached to carbohydrate moiety at both 3 and 5 positions [22,23].

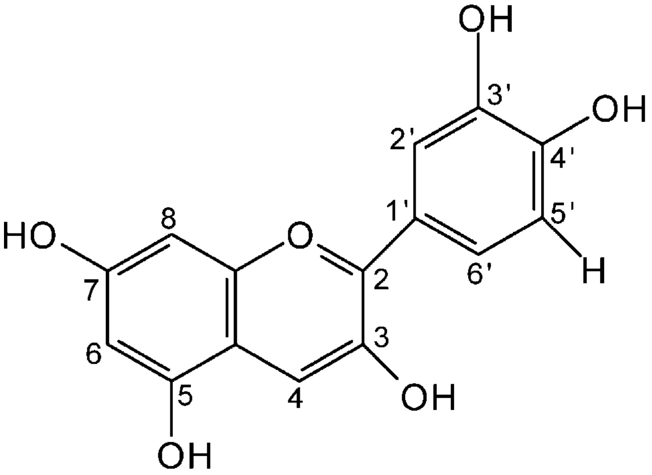

Fig. 1. Molecular structure of cyanidin, the common anthocyanin aglycone core present in red cabbage and red onion.

This aglycone core can exist as a positively charged oxonium ion and termed as a flavylium cation in acidic solution. The flavylium cation can exist in equilibrium with a colorless pseudo-base form (quinoidal form) in basic pH. In an acidic solution, the oxonium ion results in an extended conjugation of double bonds through three rings of the aglycone moiety, which helps in the absorption of photons in the visible spectra. Addition of a base disrupts the conjugation of double bonds between the second and third rings and results in absorption of photons in the UV range rather than in the visible range. The effect of pH change on increasing the number of conjugated double bonds in the molecule lowers the energy level of the electronic transition between the ground state and the excited states, and in turn results in the absorption of photons at greater wavelength [22,23].

The extracts of red cabbage leaves and red onion skins were obtained from fresh biological materials. The solvents (water, methanol, methanol solution 40%, ethanol) were acidulated with HCl (pH=3) and added over the small pieces of clean leaves of red cabbages, respective the skins of red onions (10 mL of solvent for 1 g of vegetal material). The mixtures were kept in the dark for 24 hours and then filtered. All resulted solutions were protected from direct light exposure.

The red cabbage juice was obtained using a blender, the resulting mixture being then filtered. During the filtering, two differently colored types of juice were obtained, first a purple (pH = 6) and than a dark blue (pH = 7) juice, which were collected separately. Both of them were turned into red juice by adding HCl till pH = 3.

2.2. Device fabrication

For preparation of the nanocrystalline TiO_2 photoelectrode, a small amount of TiO_2 suspension (Ti nanoxide-T: colloidal anatase, particle size of ~13 nm, Solaronix, Switzerland) was applied onto a conductive glass by doctor blading using adhesive tape (thickness ~50 μm) as a frame and spacer. The conductive glass substrate (Solaronix) consisted of a soda lime glass sheet of 2.2 mm thickness, with a conductive layer of F-doped SnO_2 (sheet resistance: 15 Ω/square), and an optical transmission greater than or equal to 80%, in the 400-700 nm region. After the evaporation of the solvent from the deposited suspension, the substrate was sintered for 30 minutes at 450 °C in the oven. The resulting plate was then immersed into the dye solution and then washed to remove any dye that has not been absorbed by the TiO_2 layer and then heated in an oven at 40 ^{o}C for one hour. The counter electrode consisted of a thermally platinized conductive glass, 5 mM H_2PtCl_6 (Solaronix) in dry isopropanol, heated at 380°C on the same type of conductive glass substrate for 10 minutes. The two electrodes were clipped together to make a sandwich type cell. The electrolyte, an iodide based high boiling point electrolyte with 50 mM of tri-iodide in Tetraglyme (TG-50, Solaronix), was injected into the space between the electrodes and filled the space through capillary action.

2.3. Measurements

The UV-VIS absorption spectra of dye solutions and dye adsorbed on the TiO_2 surface were recorded in the range 200–900 nm, on a Jasco V 550 spectrometer. Efficiencies of the cells were measured under global AM 1.5 standard sun conditions (1000 W/m^2) at 25^{o}C, using a class A homemade small area solar simulator [20]. The cell surface was exposed to light through a circular slit of 10 mm diameter, resulting in a useful area of about 0.785cm^2. The current and voltage values were measured using two digital bench multimeters (Mastech MS8050) and a precision decadic resistance box. All measurements were made at about 45 s intervals, allowing time for each reading to stabilize.

3. Results and discussion

3.1. Electronic spectra of the extracted dyes

In the visible range (see Fig. 2), the red onion skin extracts present a strong absorption band at about 500 nm (520 nm for aqueous solution), characteristic for cyanin. The band is solvent sensitive, with a local maximum shifted toward higher wavelengths from methanol (510 nm), to water (520 nm) and to ethanol (532 nm), respectively. For the methanolic extract, the band is most intense, broader with a shoulder at higher wavelengths. The presence of the extra feature may also be due to self-association into supermolecular structures, which lower the energy based on stronger interactions with other anthocyanins and/or metal ions [24].

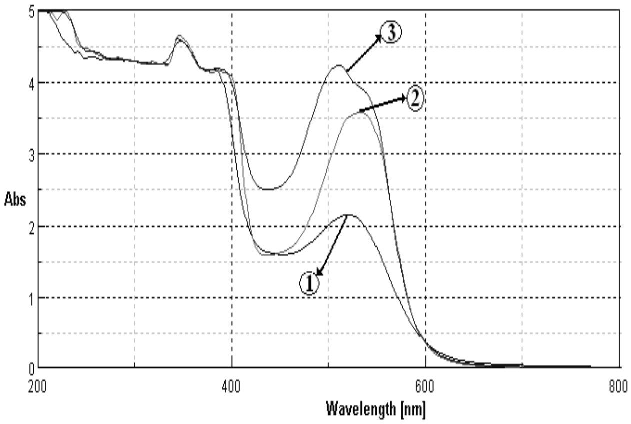

Fig. 2. The electronic absorption spectra for red onion skin extracts in water (1), ethanol (2), and methanol (3).

Fig. 3 displays the absorption spectra of the extract in solution and adsorbed onto the TiO_2 nanoporous layer. In the coordinated form, the absorption bands of the dyes are broader, less intense and red shifted, when compared to the corresponding uncoordinated pigment. The most obvious broadening and red shift is in the case of ethanol solution. The red shift of the bands may be due the coordination of organic compounds, in deprotonated form, to Ti(IV) ions, probably as bidentate chelating ligands, through oxygen atoms [**Error! Bookmark not defined.**]. Such effects were observed for anthocianins upon complexation with metal ions, including aluminum, iron, tin, titanium, and chromium[25].

From Fig. 3 we also note a shoulder in the near UV region of the spectrum. This feature can be assigned to ligand-metal charge transfer [26]. The electrons are transferred from the HOMO (highest occupied molecular orbital), localized on the chromophore end of the complex, to the LUMO, localized on the titanium side of the complex [24].

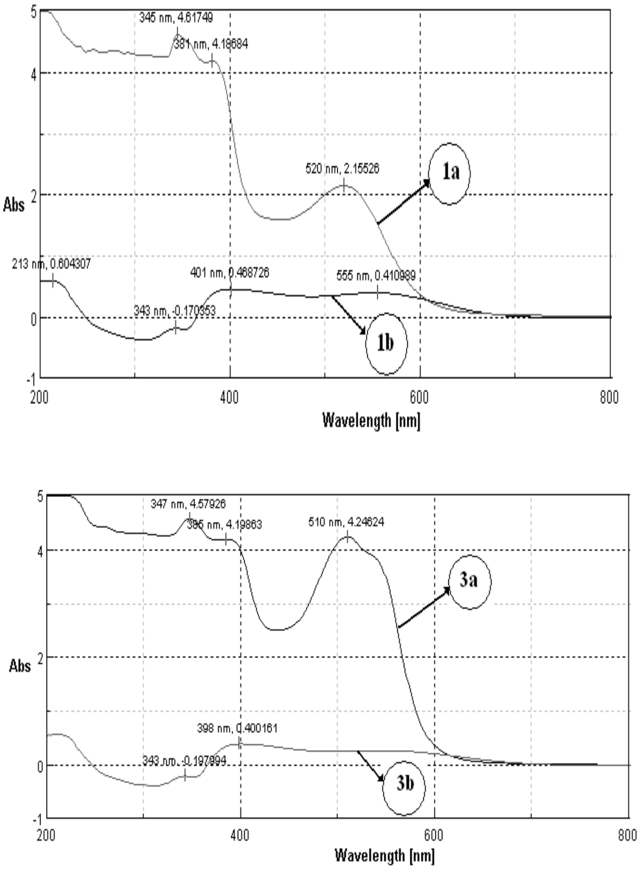

Fig. 3. Electronic absorption spectra of the red onion extract solution (a) and absorbed onto the TiO_2 photoanode (b) in water (top), ethanol (center), and methanol (bottom).

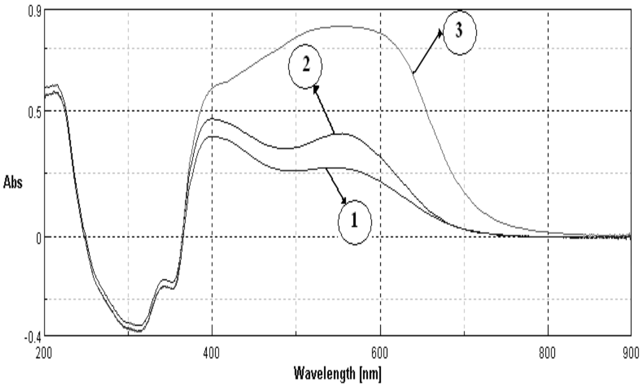

Fig. 4. Electronic absorption spectra of the methanolic (1), water (2), and ethanolic (3) red onion extracts adsorbed onto the TiO_2 photoanode.

A comparison between the electronic spectra of the three red onion skin extracts adsorbed on the TiO_2 film (Fig. 4) shows that the better coordination with the metal occurs for the ethanolic extract, although the more concentrated extract was obtained using methanol.

Similar absorption in the visible range can be seen in Fig. 5 for the red cabbage extracts, with peaks between 500 and 545 nm. The absorption is solvent sensitive, with a narrow band in the case of water (centered at 537 nm) and methanol (double peak at 510 and 534 nm) and wider, double-feature bands for ethanol and methanol in water. Therefore, light harvesting takes place over a broader range in the latter two cases.

Fig. 6 displays the absorption spectra of the extract both in solution and adsorbed onto the TiO_2 nanoporous layer. In the deprotonated coordinated form, the absorption bands of the dyes are broader, less intense and red shifted. The absorption bands of the two types of extracts have various strengths and breadths for different solvents, red cabbage having wider and more intense bands for ethanol and water.

Interesting for the red cabbage are also the differences between the absorption spectra of the juices (diluted in water in a 1:4 ratio), each with a different pH (see Fig. 7). The peak in the absorption band differ by almost 100 nm between the pH =3 (red juice) and pH = 7 (blue juice), whereas the intensity is significantly lower for pH = 6 (purple juice).

Fig. 8 displays the electronic absorption spectra of red cabbage extracts and juices absorbed onto the TiO_2 photoanode. The largest absorption was observed for juices, especially the blue juice (pH = 7), (2) red juice (3) purple juice, fact easily observable due to the intense coloration of the sensitized photoanods. Among the extracts, the one obtained in water has the largest absorption, about twice the intensity of the other solvents at 570 nm.

In all cases, the shift of the absorption bands toward larger wavelengths suggests [24] that the binding between the dye and the semiconducting oxide takes place through the carbonyl and hydroxyl groups present in the cyanine-based dyes in the natural pigments, which are capable of chelating to the titanium sites, in the same way as for the red onion extracts (as seen in Fig. 3).

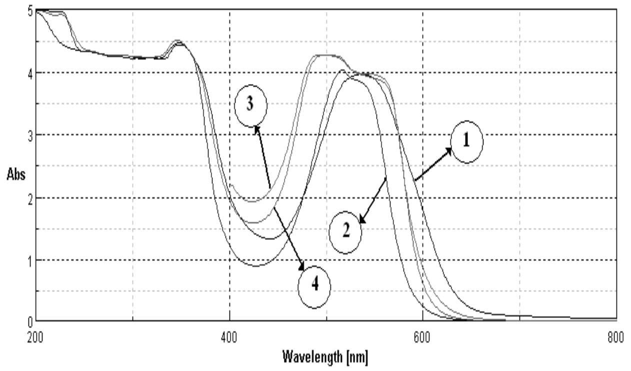

Fig. 5. Electronic absorption spectra of the red cabbage extracts in water (1), methanol (2), methanolic solution in water (40%) (3), and ethanol (4).

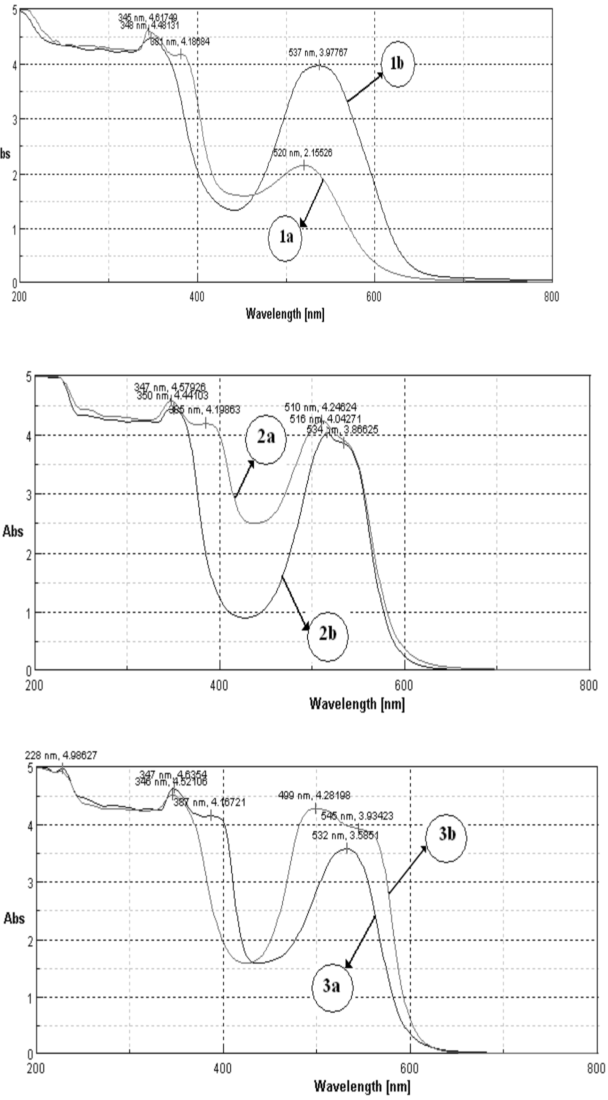

Fig. 6. Electronic spectra of the extracts of red onion (a) and red cabbage (b) in: water (top), methanol (center),and ethanol (bottom).

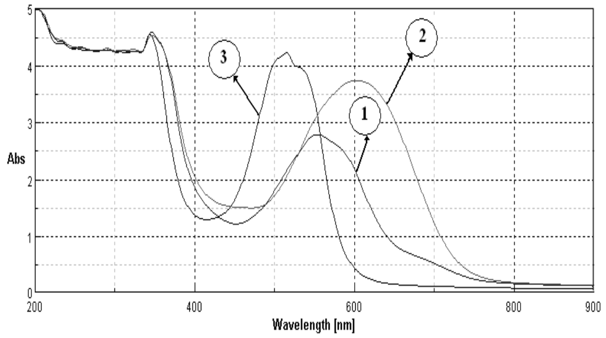

Fig. 7. Electronic absorption spectra of the red cabbage juices: purple, pH = 6, (1), blue, pH = 7, (2), red, pH=3, (3).

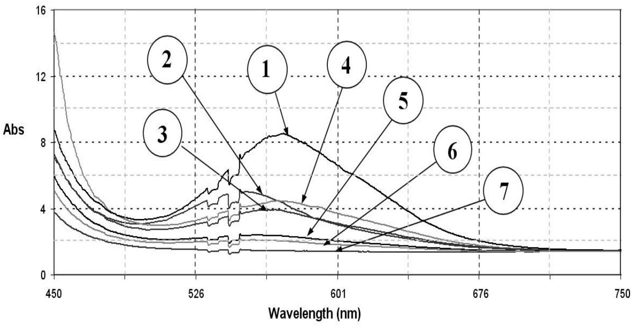

Fig. 8. Electronic absorption spectra for red cabbage extracts and juices absorbed onto the TiO_2 photoanode: (1) blue juice, (2) red juice (3) purple juice, (4) water extract, (5) 40% methanol solution, (6) ethanol extract and, (7) methanol extract.

3.2. Electro-optical characterization of the DSSC

The current density – voltage (*I-V*) curves obtained for the solar cells with TiO_2 films sensitized with vegetal extracts are presented in Figs. 9 and 10 for red onion and red cabbage, respectively. All *I-V* curves have the typical aspect of a photovoltaic device, which proves that all the extracts display light harvesting properties and perform charge transfer sensitization of the TiO_2 semiconducting film.

The values of the short-circuit current density and open-circuit voltage are in the range of other reports on natural extracts as dyes [15-18]. Differences occur between the various photovoltaic cells, depending on the dye used, despite being fabricated and tested in similar, standard conditions [20].

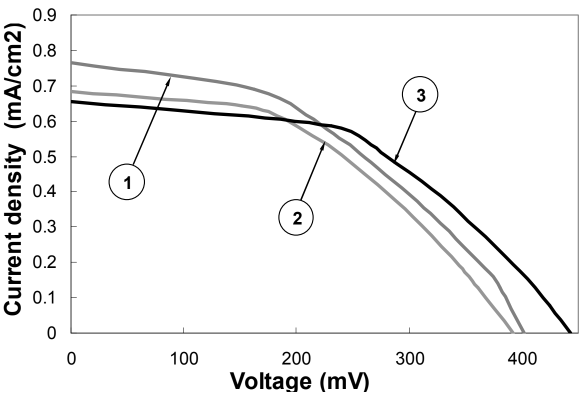

Fig. 9. Current density – voltage characteristics of solar cells sensitized with red onion extracts in water (1), ethanol (2), and methanol (3).

Table 1 presents the values of the short-circuit current (I_{sc}), open-circuit voltage (V_{oc}), maximum power (P_{max}), fill-factor (*FF*) and external quantum efficiency [19] obtained for solar cells using TiO_2 sensitized by different anthocyanins extracted from red cabbage leaves and red onion skin. In the case of the red onion extracts (see Fig. 9) the fill-factor values are lower, between about 0.43 and 0.48, while for red cabbage it ranges higher, from 0.48 to 0.57. The differences are relatively small for the DSSCs based on red onion extracts, although even in this case we note that I_{sc} and V_{oc} vary in opposite directions.

In the case of DSSCs sensitized with anthocyanins from red cabbage the differences are more spectacular. Although the values of the open-circuit voltage vary in a small range (from 341 to 421 mV), the short-circuit current density varies more widely, the value for the water extract being three times larger than that for the ethanol extract, which performed the worst.

On average, the DSSCs fabricated with red cabbage juice performed worse than those with the extract, despite the good adsorption on the oxide layer and the strong and broad absorption band in the visible range. Moreover, the time stability of the photovoltaic cells sensitized with natural plant juice was found to be lower, with samples degrading after less than a month (without any sealing of the device).

The acidity of the juice influences the device quality, better efficiencies being obtained for pH = 3. This result is consistent with reports by other groups [27], which claim for other organic sensitizing dyes that better results are obtained for solutions with pH = 2.8.

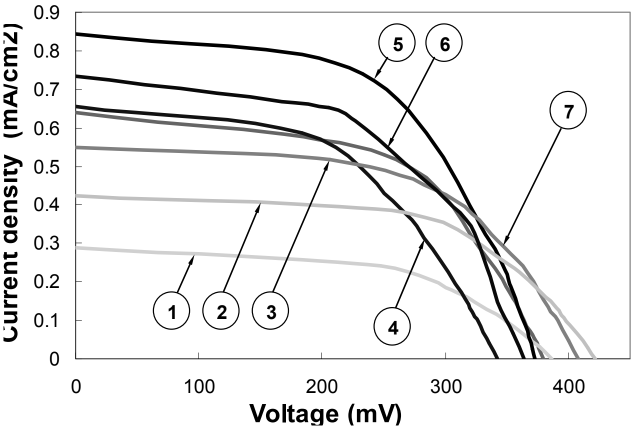

Fig. 10. Current density – voltage characteristics of solar cells sensitized with red cabbage: (1) ethanol extract, (2) blue juice, (3) purple juice, (4) 40% methanol extract, (5) water extract, (6) ethanol extract and (7) red juice.

Table 1 Short-circuit current (I_{sc}), open-circuit voltage (V_{oc}), maximum power (P_{max}), fill-factor (FF) and efficiency measured under standard global air-mass 1.5 illumination at 25°C, using a calibrated small area solar simulator[28].

Pigment used	I_{sc} (mA)	V_{oc} (mV)	P_{max} (mW)	FF	Efficiency (%)
Red cabbage extracts					
blue juice	0.332	421.60	79.51	0.568	0.101
purple juice	0.430	407.45	100.44	0.573	0.128
red juice	0.502	379.36	104.10	0.546	0.133
MeOH extract	0.226	386.46	46.97	0.538	0.060
40% MeOH solution	0.514	341.95	84.69	0.482	0.108
EtOH extract	0.577	363.67	109.91	0.524	0.140
water extract	0.662	372.79	135.61	0.549	0.173
Red onion extracts					
EtOH extract	0.536	391.8	94.72	0.451	0.121
Water extract	0.600	402.0	103.10	0.427	0.131
MeOH extract	0.515	443.3	110.41	0.484	0.141

Consistent with other reports that organic dyes in water solutions can lead to relatively high efficiencies [28], we found that the best efficiency was obtained with the water extract, contrary to reports that for devices sensitized with ruthenium-based dyes water has a negative impact on the pigment, the electrolyte, and the quality of the nanoporous oxidic film [4].

5. Conclusions

We fabricated and tested under standard illumination conditions DSSCs with nanocrystalline TiO_2 sensitized with anthocyanins extracted from food red cabbage laves and red onion skin, in an attempt to recycle residues from the food industry. We varied the solvent and the conditions in which the dye was extracted and studied the effect on the overall solar cell performance. We found that all the extracts present light harvesting properties and perform charge transfer sensitization of the TiO_2 semiconducting layer. The *I-V* curves have the expected shape for a photovoltaic device and the values of the fill-factors are consistent with studies on other similar materials. The efficiency is relatively low, which is typical for most natural extracts tested so far.

On average, the DSSCs fabricated with red cabbage performed better than those from red onion. Also the devices obtained by sensitizing the oxide with red cabbage juice performed worse than those with the extract, despite the good adsorption on the oxide layer and the strong and broad absorption band in the visible range. Moreover, the time stability of the photovoltaic cells sensitized with natural plant juice was found to be lower. The acidity of the juice influences the device quality, better efficiencies being obtained for lower pH, around 3. The best devices were made with the red cabbage extract in water, consistent with other reports that organic dyes in water solutions can lead to relatively high efficiencies.

Although overall, compared to the ruthenium dyes, the efficiency is very low, our results show that the vegetal extracts, adsorbed onto the surface of TiO_2 semiconductor, absorb visible light and promote electron transfer across the dye/semiconductor interface. When used in regenerative photoelectrochemical solar cells, the extracts convert visible light into electricity, the shape of the I-V curve and the values of the fill-factor being encouraging. The use of a natural source for the semiconductor sensitizer enables a faster, simpler and environmentally friendlier production of solar cells. These are compelling arguments to search for better organic dyes despite the low efficiency obtained so far.

Acknowledgments

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