Photosensitization of nanocrystalline TiO$_2$ films by anthocyanin dyes

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Abstract

Reasonably high stable photocurrents, with quantum yields up to $\Phi = 0.52$ are observed using TiO$_2$ photosensitized by adsorbed anthocyanin dyes with iodide/iodine in water at pH 1. The respective yields in pure ethanol are usually somewhat lower, up to $\Phi = 0.33$. Open circuit photovoltage up to 0.47 V in ethanol and 0.38 in water are obtained. The effects of changing charge carrier concentrations and pH, as well as the photocurrent spectra and yields under various conditions are reported. These simple systems show relatively high quantum yields of the photocurrents, as well as good stability when acidic aqueous solutions of the charge carriers are employed. Comparable yields are obtained in ethanol solutions, although some of the dyes quickly deteriorate. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Sensitization of wide band gap semiconductor electrodes by dyes absorbing visible light has been a topic of continuing interest since its introduction by Gerischer in 1972 [1]. While early versions of dye-sensitized photoelectrochemical cells were inefficient, Graetzel and his coworkers [2–18] as well as others [19–49] succeeded to achieve relatively high photon-to-current conversion efficiencies. The preparation and dynamics of interfacial photosensitized charge separation in metal oxides such as TiO$_2$ films has been recently reviewed [50]. The Graetzel cell is based on a dye (S) adsorbed to a porous TiO$_2$ layer. The basic photo-physical reactions can be written as

$$S + h\nu \rightarrow S^* \tag{1}$$

$$S^* + TiO_2 \rightarrow S^+ + e_{TiO_2}^- \tag{2}$$

$$S^* \rightarrow S \tag{3}$$

$$S^+ + e_{TiO_2}^- \rightarrow S + TiO_2 \tag{4}$$

$$2S^+ + 3I^- \rightarrow 2S + I_3^- \tag{5}$$

The dye (S) is excited with visible light ($h\nu$) to the electronically excited state S*. If this state lies energetically above the conduction band edge of a semiconductor nano-crystallite, electron injection to the semiconductor according to reaction (2) can occur on a fast or ultra-fast

time scale [12,26,33,51–75], successfully competing with the deactivation reaction (3). The resulting charge-separated systems undergo relaxation and recombination processes (reaction (4)) with typical time constants in the range from 10 fs up to 500 μs.

In a typical Graetzel cell, I$^-$/I$_3^-$ ions in organic solvents serve as charge carriers. Oxidation of iodide according to reaction (5) must effectively compete with the recombination reaction (4) in order to achieve high photocurrent. Aqueous solutions have been rarely employed [2,4,5], being unstable [76] or show low efficiency [7,33,37,39, 40,71].

Many photosensitizers other than Ru complexes have also been reported, such as osmium complexes [46], Fe complexes [34], Re and Rh polynuclear complexes [75], porphyrins [8,9,27,30,47], phthalocyanines [27,30,37,42], rhodamine 6G [24] perylene, [28, #14], mercurochrome [48], merocyanine [49], xanthene [32,48]. Photocurrents were observed also in systems containing natural pigments, including anthocyanins. Tennakone et al. [21,22,29] studied cyanidin pigments from flowers and santalin from red sandalwood [35] in a TiO$_2$/CuI or TiO$_2$/CuSCN solid layer, and tannins as well as related phenolic pigments from tea in TiO$_2$ layers [23]. Olea et al. [36] studied blackberries pigments as photosensitizers (TiO$_2$). Photocurrents were observed in non-aqueous systems, although the efficiency of the photoelectrochemical cells has not been reported. Cyanin dyes, extracted from blackberries, have been recently studied by Cherepy et al. [13] using water-free ethylene glycol or propylene carbonate as solvents for I$^-$/I$_3^-$, reporting IPCE = 19%.

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Recently, we have observed unusually high photocurrent yields in a system based on a natural cyanidin dye from pomegranate liquid, which is known to be a rich source of anthocyanin pigments [77]. The high photocurrent was observed in an aqueous medium, yet, no desorption of the dye was noticeable. This unusual observation called for more detailed work on related pigments which can be obtained in a pure state. The results are reported in the present manuscript.
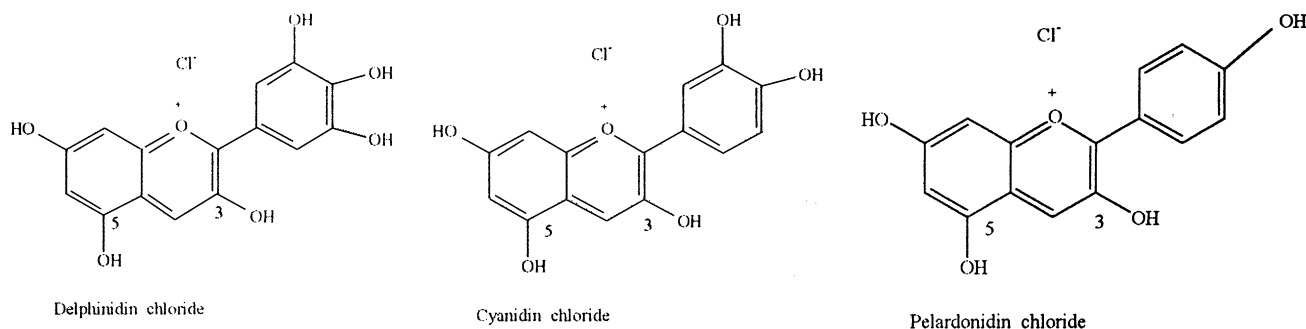
2. Experimental

2.1. Materials

Lithium iodide (99%, Aldrich), sodium iodide (99.5%, Merck), potassium iodide (99.7%, Merck), Cesium iodide (99.5%, Aldrich), tetrabutylammonium iodide (99%, Fluka), iodine (99.985%, Mallinckrodt), titanium isopropoxide (97%, Aldrich), 2-propanol (99.5%, Frutarom), absolute ethanol (99.9%, J.T. Baker), sodium hydroxide (97%, Frutarom) and nitric acid (69%, Frutarom) were used as received. Water was passed through deionizer (Millipore, Milli-Q model). ITO/glass (Geomatec's, $10\,\Omega$ per square) was washed with detergent, rinsed with de-ionized water and ethanol and dried with a fan. The pH was adjusted by adding HCl or NaOH.

2.2. Photosensitizers

Delphinidin (Dp), cyanidin (Cy) and pelargonidin (Pg) were purchased from Extrasynthese, delphinidin-3-glucoside (Dp-3-glc), cyaniding-3-glucoside (Cy-3-glc), cyaniding-3:5-diglucoside (Cy-3,5-diglc), pelargonidin-3-glucoside (Pg-3-glc), and pelargonidin-3:5-diglucodide (Pg-3,5-diglc) were purchased from Polyphenols Laboratories AS, all as chloride salts, and used as received. The chemical structures of cyanidin, delphinidin and pelargonidin chlorides are shown in Scheme 1. All the dyes investigated in this work are soluble in both water and ethanol, although relatively lower solubility is observed for some of the glucosides.

2.3. TiO$_2$ layers

Transparent TiO$_2$ layers were prepared on ITO surface using TiO$_2$ nanocrystallites dispersed in water at pH 1.8 (100 g/l) by successive spin coatings followed by heating at 450 °C. Layer thickness was $3.35 \pm 0.5\,\mu$m, absorbance at 355 nm, $D_{355} = 1.05 - 1.15$. The TiO$_2$ colloid was prepared by hydrolysis of titanium isopropoxide. A small amount (16 cm^3) of 2-propanol was added to the isopropoxide (100 cm^3), and the resulting solution added dropwise to 600 cm^3 water containing 0.11 M HNO$_3$ at 0–5 °C under Ar gas while vigorously stirring. The reaction mixture was then heated to 80 °C for a period of 5–7 days, until a transparent solution was obtained. The TiO$_2$ colloidal solution was filtered through a 0.45 μm filter (Acrodisc LC13, Gelman), resulting with a clear solution of particles with average diameter of 5 nm as determined by electron microscopy. The water solution was vacuum distilled until a concentration of 100 g/l was obtained, and the resulting cloud dye–white mixture used for the preparation of clear TiO$_2$ layers on ITO. The ITO plate carrying the TiO$_2$ layers, with the dimensions 0.85×5 cm^2, coupled with Pt-coated ITO plate of similar dimensions. Pt was deposited on the counter electrode by very short (a few seconds) electrolysis of chloroplatinic acid [78,79]. The working and counter electrodes where separated by a thin Teflon spacer and tightly held together by means of an appropriate slit at the Teflon base at the bottom of a two windows optical cell. Iodide and iodine in water or ethanol solution was added at the bottom filled the space between the two plates because of capillary forces.

2.4. Adsorption of the dye

Unless otherwise will be stated, the ITO/TiO$_2$ was equilibrated with the dye solutions by shaking 1 h, inducing coloration of the film.

2.5. Illumination

Illumination was carried out using a 12 W halogen lamp with a 400 nm cutoff and with water filter. A reflector provided a conical shaped 35° light beam. Water filter (1 cm

Scheme 1. Chemical structure of the photosensitizers.

light path) was placed between the lamp and the cell, which was at a distance of 7 cm from the light source. The illuminated area was $(2.55 \pm 0.15)\,cm^2$. The integrated visible light intensity in the range 400–700 nm was about 2×10^{-7} Einstein/s. Unless otherwise will be stated, aqueous solution containing 2.45 M CsI and 0.05 M I_3^- filled the space between the electrodes.

2.6. Actinometry and determination of quantum yields

The action spectra were measured with the aid of B&L monochromator. Calibration of the light source and monochromator system was carried out using a calibrated silicon photo-diode, product of Hamamatsu type c2719. Actinometry was carried out using the ferri-oxalate actinometer [80] at 457.9 nm. The light intensity at other wavelengths was calculated from the calibrated light source spectrum, and the total light intensity of the visible range was calculated by integration.

3. Results and discussion

3.1. Absorption spectra

The absorbance spectrum of the delphinidin and cyanidin dyes in acidic aqueous solution and in TiO_2 layer is presented in Figs. 1 and 2. In water solutions, the absorption bands at pH 2.8 are somewhat broader than at pH 1, although the peak positions vary only little, if at all, between pH 1 and 2.8. The spectra in layers are red shifted by 10–40 nm compared to the respective aqueous solutions. The peak positions in both water and ethanol solutions and the respective layers are summarized in Table 1, together with spectra of pelardonidin dyes. The latter do not adsorb to TiO_2 from
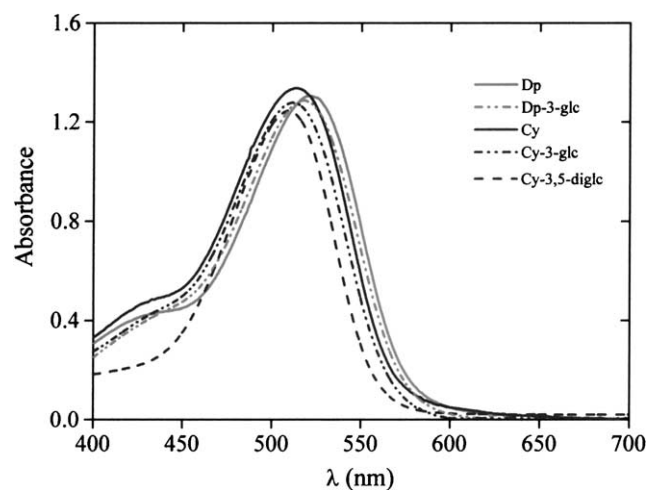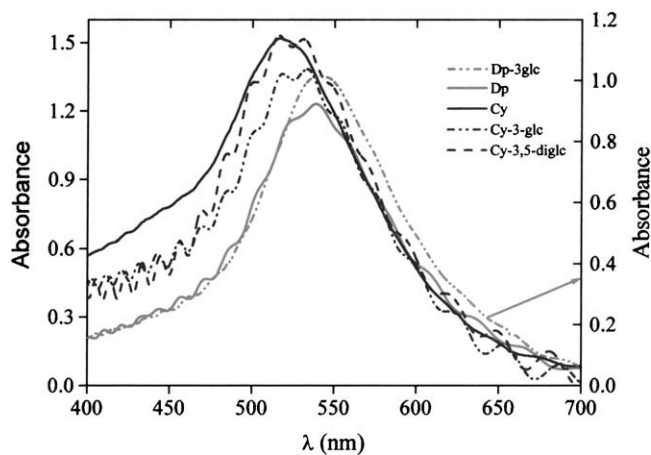

Fig. 2. Spectra of delphinidin and cyanidin dyes in the TiO_2 layers. The TiO_2 electrodes equilibrated with the respective dye solutions at pH = 1.0. 5×10^{-4} M of Dp, Cy and Cy-3,5-diglc, saturated solutions of Dp-3-glc and Cy-3-glc.

water solution and therefore were studied only in ethanol. The adsorption of the pigment to the TiO_2, apparently involves formation of ether like bond with the aromatic hydroxyl groups, according to the following reactions:

$$(6)$$

$$(7)$$
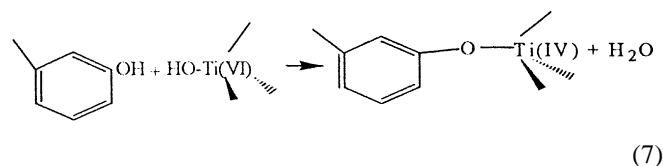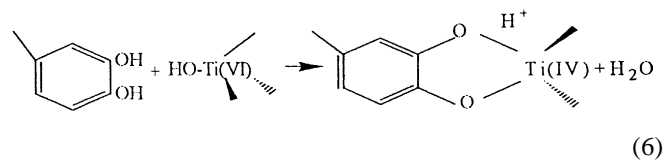
The spectra of all eight dyes in ethanol are shown in Fig. 3. These spectra are red shifted compared to the respective spectra in aqueous solution. The spectra of the dyes in TiO_2 layer adsorbed from the respective ethanol solution are shown in Fig. 4. In the ethanol systems, a blue shift is observed in the TiO_2 layers in Dp, Cy and Pg. The glucosides, on the other hand, show red shift (Table 1).

3.2. Effect of counter ion

Typical short circuit photocurrents and open circuit photovoltages observed upon illumination with the entire visible range of the halogen lamp are presented in Table 2 for delphinidin chloride, using different iodide salts as charge carriers. Table 2 shows that the aqueous Cs^+ counter ion is the most effective in photocurrent generation, and the efficiency decreases systematically from Cs^+ to Li^+. The Cs^+ counter ion was chosen for comparison between the different dyes in water, while the Na^+ counter ion was

Fig. 1. Spectra of aqueous delphinidin and cyanidin dyes at pH 1.0. 1×10^{-4} M Dp, Cy and Cy-3,5-diglc, 40% of the saturation concentration of Dp-3-glc and Cy-3-glc.

Table 1
Visible peak positions of anthocyanin dyes in the solution and the TiO$_2$ layers (nm)

Dye	Solution			Layer		
	Water		Ethanol (pure)	Water[a]		Ethanol[a] (pure)
	pH 1.0	pH 2.8		pH 1.0	pH 2.8	
Dp	520	520	541, 574[b], 624	539	557	540
Dp-3-glc	517	517	533, 570[b], 627	541	559	590
Cy	513	514	427, 558[b], 597	517	536	541
Cy-3-glc	512	511	543	533	544	562
Cy-3,5-diglc	509	509	532	516	555	567
Pg			431, 534[b]			421, 530[a]
Pg-3-glc			436, 514[b]			536
Pg-3,5-diglc			419, 514[b]			521

[a] The TiO$_2$ layer equilibrated with the solution at the given pH.
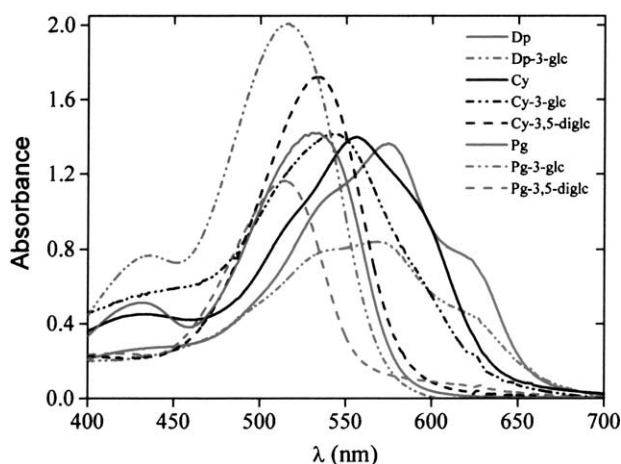[b] The main peak position.

Fig. 3. Spectra of anthocyanin dyes in ethanol solutions. Dp, Cy and Pg at 1×10^{-4} M, Dp-3-glc, Cy-3-glc, Cy-3,5-diglc, Pg-3-glc and Pg-3,5-diglc in saturated solution.
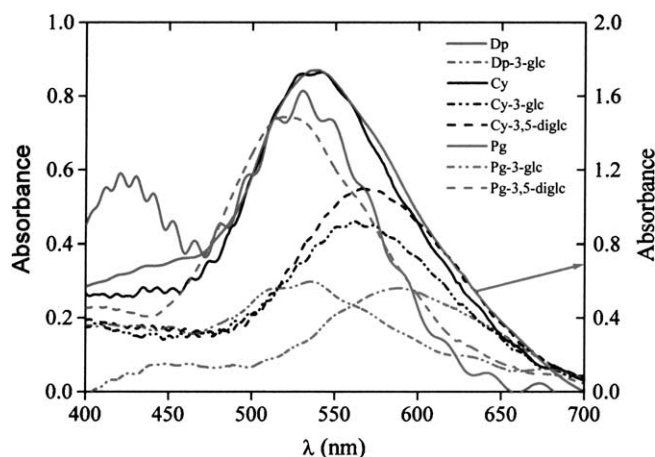

Fig. 4. Spectra of anthocyanin dyes in TiO$_2$ layer. The TiO$_2$ electrodes equilibrated with the respective dye in ethanol solutions. Dp, Cy and Pg at 5×10^{-4} M, Dp-3-glc, Cy-3-glc, Cy-3,5-diglc, Pg-3-glc and Pg-3,5-diglc in saturated solution.

chosen for ethanol solutions. The results are summarized in Table 3.

3.3. Quantum yields

The quantum yields and open circuit photovoltages of the dyes in the TiO$_2$ layers are summarized in Table 3. As will be seen later, the quantum yield of a given dye depends on excitation wavelength, although in the aqueous systems at pH 1, where the yields are usually the highest, the photocurrent

follows the light absorption of the main visible band. The quantum yields measured at 600 nm are reported in Table 3. In general, the yields in the water systems increase with [H$^+$] (compare results at pH 1 and 2.8). In most cases, ethanol solutions of the charge carriers show lower yields compared to the respective aqueous solutions. Anthocyanin molecules with two or three adjacent hydroxyl groups, namely, the delphinidins and cyanidins, show higher yields as well as higher stability compared to the pelargonidins. This is attributed to the double binding involving the formation of

Table 2
Photocurrents and photovoltages for various iodides and solvents[a]

Counter ion	Li$^+$ (H$_2$O)	Na$^+$ (H$_2$O)	K$^+$ (H$_2$O)	Cs$^+$ (H$_2$O)	Na$^+$ (ethanol)	(t-Butyl)$_4$N$^+$ (ethanol)
Photocurrent (mA)	1.75	2.8	3.1	3.9	2.2	0.9
Photovoltage (V)	0.30	0.29	0.31	0.38	0.41	0.47

[a] Aqueous solutions: 2.5 M iodide and 0.05 M iodine at pH 1.0; ethanol solutions: 2.0 M iodide and 0.05 M iodine at neutral pH; peak absorbance of the dyes in the TiO$_2$ layers was 1.20. Illumination was carried out at 400–700 nm.

Table 3
Quantum Yields and photovoltages[a]

Dye	Solvent	pH	Φ	Photovoltage (V)
Dp	Water	1.0	0.33	0.38
Dp-3-glc	Water	1.0	0.52	0.36
Cy	Water	1.0	0.28	0.31
Cy-3-glc	Water	1.0	0.52	0.33
Cy-3,5-diglc	Water	1.0	0.38	0.34
Dp	Water	2.8	0.004	0.11
Dp-3-glc	Water	2.8	0.002	0.18
Cy	Water	2.8	0.004	0.03
Cy-3-glc	Water	2.8	0.003	0.13
Cy-3,5-diglc	Water	2.8	0.016	0.16
Dp	Ethanol	Pure	0.30	0.41
Dp-3-glc	Ethanol	Pure	0.24	0.34
Cy	Ethanol	Pure	0.33	0.39
Cy-3-glc	Ethanol	Pure	0.033	0.36
Cy-3,5-diglc[b]	Ethanol	Pure	1[c]	0.38[c]
Pg	Ethanol	Pure	0.21	0.38
Pg-3-glc	Ethanol	Pure	0.33	0.37
Pg-3,5-diglc	Ethanol	Pure	0.090	0.36

[a] Water solutions: 2.5 M CsI and 0.05 M iodine; ethanol solutions: 2.0 M NaI and 0.05 M iodine; the TiO$_2$ electrodes were equilibrated with 5×10^{-4} M dye at pH 1.0, or with the saturated dye solution when solubility was lower than 5×10^{-4} M. The quantum yields were measured at 600 nm. Open circuit photovoltage generated at 400–700 nm.

[b] Unstable during measurements.

[c] Maximum value.

a quinonoidal structure in the case of delphinidins and cyanidins [13]. In contrast, the pelargonidins have isolated hydroxyl groups, which produce a single bond to the TiO$_2$.

3.4. Effect of [I$^-$]

The effect of changing iodide concentrations is shown in Fig. 5. Delphinidin chloride has been chosen as a typical example.
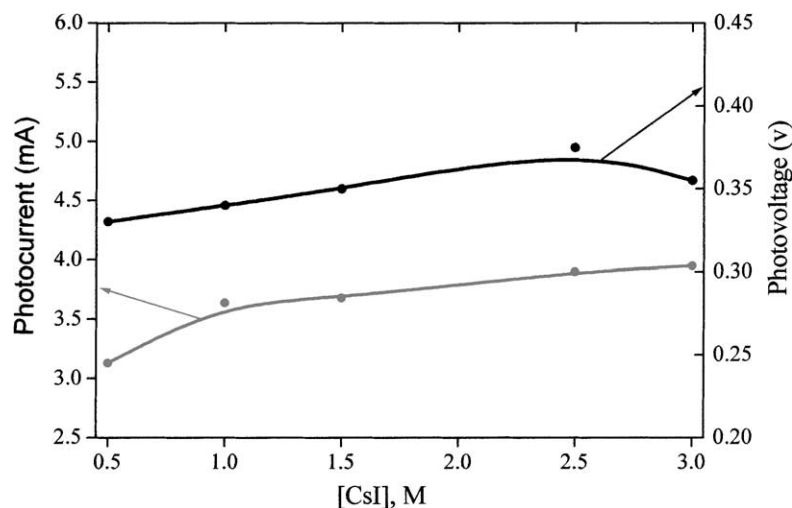
Other dyes behave similarly, although the observed photocurrents and photovoltages vary as can be seen in Table 3. Increasing the iodide concentration increases the photocurrent relatively little, indicating that reaction (5) successfully competes with reaction (4). The limiting photocurrent corresponds to $\Phi = 0.33$ (Table 3). However, the yield is more than doubled upon application of +0.5 V to the working electrode, indicating that under the conditions of Fig. 5, the electron injection efficiency determines the quantum yield. The effect of pH in the aqueous solutions is remarkable. The quantum yields decrease by an order of magnitude, as the pH varies from 1 to 2.8. The closed circuit photovoltages decreases typically by 0.1 V (not shown in the table). Electron injection from the excited dye may be more favorable at lower pH, because of the positive effect on the redox potential of the TiO$_2$ electron. This results with increasing the driving force for electron injection (reaction (2)) and decreasing the driving force of the back reactions.

3.5. The effect of [I$_2$]

The effect of I$_2$ on photocurrent and photovoltage is shown in Fig. 6 for delphinidin chloride. Such behavior is typical to all the investigated dyes. The relatively moderate effect of [I$_2$] on the photocurrent indicates that reduction of iodine is not important under the conditions of this work.

3.6. Photocurrent spectra

Fig. 7a and b shows the photocurrent spectra, compared to the absorption spectra of delphinidin chloride and delphinidin-3-glucoside chloride, respectively, at pH = 1.0. The photocurrents parallel the light absorption reasonably well at $500 < \lambda < 700$ nm, however, a clear increase of photocurrent relative to the absorption is observed at $\lambda <$
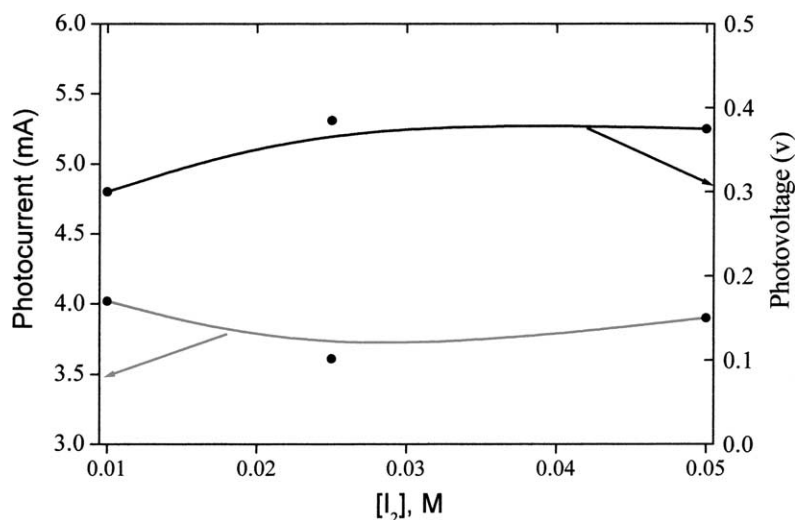

Fig. 5. Effect of [I$^-$] on the steady state photocurrent and photovoltage. TiO$_2$ layer equilibrated with aqueous 5×10^{-4} M delphinidin chloride at pH 1.0, and used with 0.05 M iodine in water at pH = 1.0.

Fig. 6. Effect of [I_2] on the steady-state photocurrent and photovoltage. [CsI] = 2.5 M. Other conditions are as in Fig. 5.

450 nm. This observation is typical to all the dyes studied at pH 1, indicating that excitation at the absorption shoulder below 450 nm results with higher electron injection yields [34].

The results at pH 2.8 are not very accurate because of the low photocurrents. The photocurrent spectra are clearly different from the absorption spectra in the five dye systems, probably related to the broadening of the absorption band, apparently because of the contribution of ionic dissociation. The results suggest that different absorption bands, although with overlapping energies, have different electron injection efficiencies. A similar phenomenon has been observed in the ethanol systems, where the photocurrents are much higher than in the pH 2.8 aqueous solutions. Examples are shown in Fig. 8. To summarize: (a) photocurrents fairly closely parallel the light absorption of Pg and Pg-3-glc at $\lambda > 450$ nm, increasing below 450 nm towards the shorter wavelengths, while the absorption changes only little. (b) Dp and Dp-3-glc behave similarly, significant deviations observed at $\lambda <$

500 nm are smaller in the Dp-3-glc system. (c) Cy shows a photocurrent peak at 590 nm, while the absorption has peak at 541 nm. Again, an increase in photocurrent is observed at $\lambda < 450$ nm, while the absorption remains unchanged. (d) Cy-3-glc, Cy-3,5-glc and Pg-3,5-glc show a pronounced increase of photocurrent below 500 nm, although the absorption decreases or remains unchanged. These results suggest that different absorption bands have different efficiencies concerning electron injection to the TiO_2 layer. Note that the spectral measurements in the TiO_2 layers require subtraction of control spectra (namely, TiO_2 layer without dye). Moderate deviations may arise from small changes in the TiO_2 during dye adsorption and measurements. However, the considerable deviations observed at both pH 2.8 (water) and pure alcohol solutions are related to the photochemistry and photophysics of the adsorbed dyes. Much more detailed work is required to obtain a comprehensive set of results, which will provide information about the role of different absorption bands.
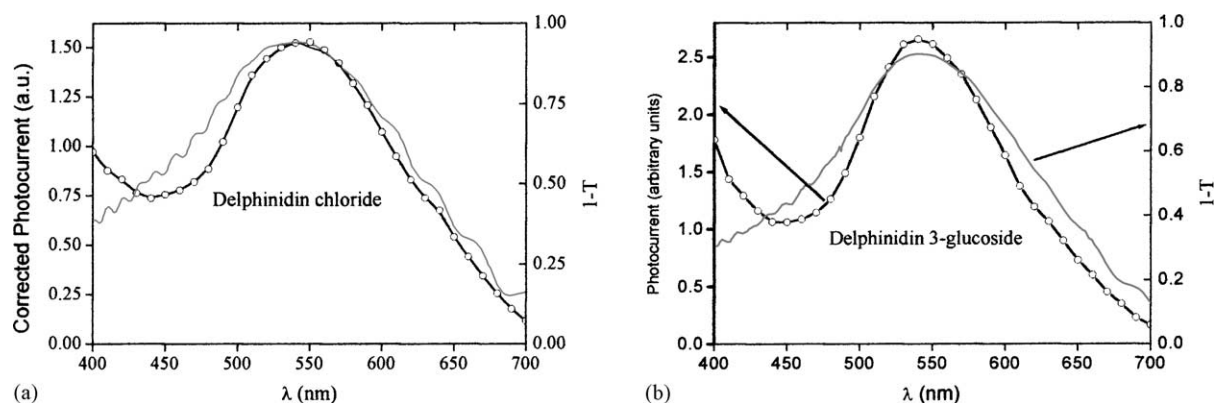

Fig. 7. Comparison of photocurrent and absorption spectrum. Charge carriers: 2.5 M CsI and 0.05 M iodine in water at pH 1.0. Photocurrent at 600 nm was: (a) 2.8×10^{-10} F/s, corresponding to $\Phi = 0.33$; (b) 4.5×10^{-10} F/s, corresponding to $\Phi = 0.52$.
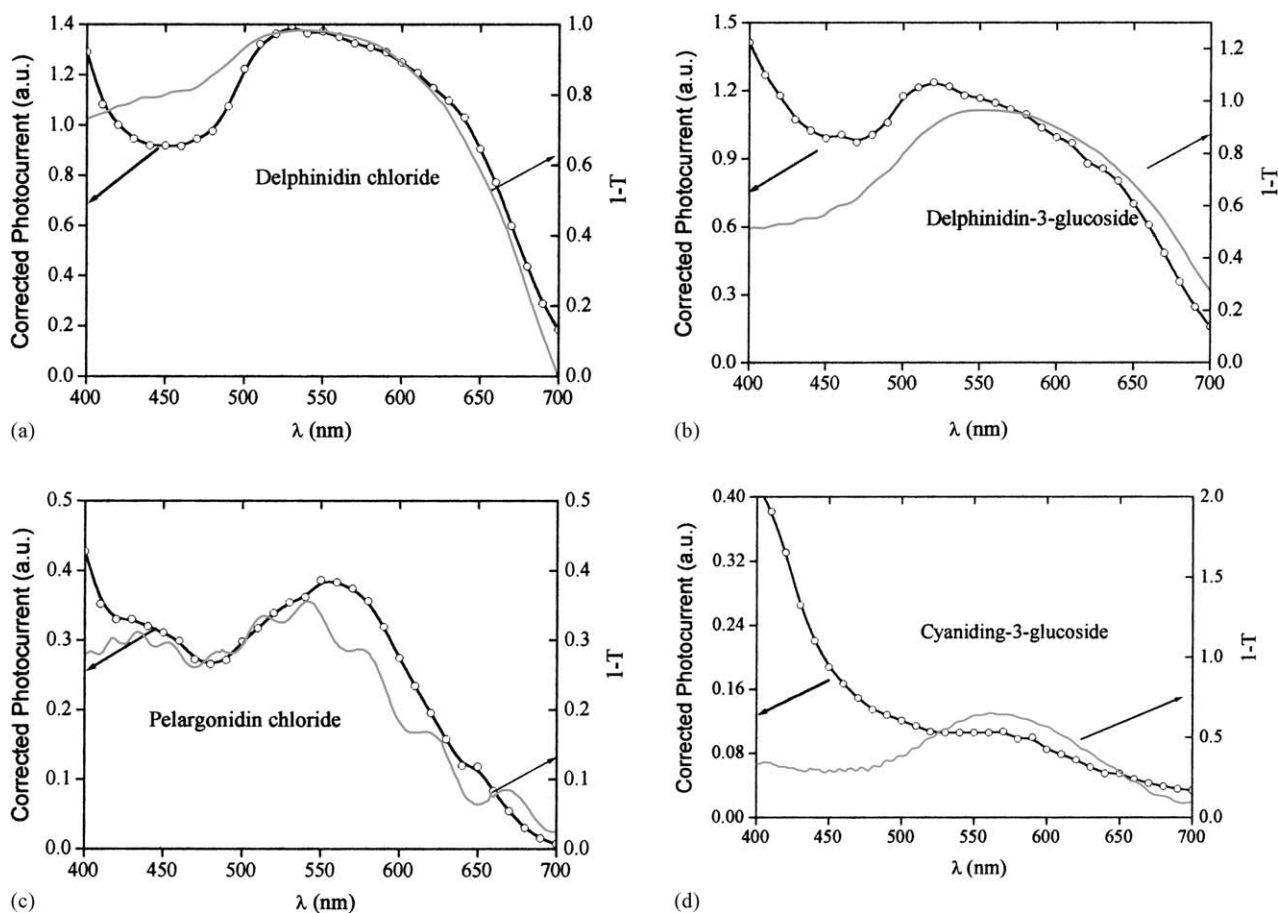
Fig. 8. Photocurrent spectra for the ethanol systems. Charge carriers: 2.0 M NaI and 0.05 M I_2 in ethanol. Photocurrent at 600 nm was: (a) 2.6×10^{-10} F/s, corresponding to $\Phi = 0.30$; (b) 2.1×10^{-10} F/s, corresponding to $\Phi = 0.24$; (c) 1.8×10^{-10} F/s, corresponding to $\Phi = 0.21$; (d) 2.8×10^{-11} F/s, corresponding to $\Phi = 0.03$.

4. Conclusions

Photocurrents with quantum yields up to $\Phi = 0.52$ are observed using TiO_2 photosensitized by adsorbed anthocyanin dyes with iodide/iodine in water (pH 1) or pure ethanol acting as charge carriers. Open circuit photovoltage up to 0.47 V in ethanol and 0.38 in water are obtained. Photocurrent yield, photovoltage and stabilities are high compared to most other aqueous systems.

In aqueous environment at pH 1 the spectra of the photocurrents are similar to the visible absorption of the photosensitizers, although higher quantum yields are observed below 450 nm. Deviations between absorption and photocurrent spectra are very pronounced in most ethanol systems. These observations are attributed to differences in electron injection yields from different energy states of the dyes.

Acknowledgements

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