Unusually efficient photosensitization of nanocrystalline TiO_2 films by pomegranate pigments in aqueous medium

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Unusually high photocurrents, with quantum yields up to $\Phi = 0.74$, are obtained using TiO_2 photosensitized by adsorbed natural pigment(s) from pomegranate liquid, with aqueous iodide/iodine acting as charge carriers. An open circuit photovoltage up to 0.45 V is observed. The quantum yield of the photocurrent, the photovoltage and the stability are unusually high for aqueous solutions. In contrast to the intensively investigated $Ru(dcbpy)_2(SCN)_2$ system, increasing the TiO_2 nanocrystallite's diameter from 5 to 18 nm considerably decreases the photocurrent. Apparently, the TiO_2 porous layer functions as a nano-filter for the pigment mixture. The effects of changing charge carrier concentrations and the photocurrent spectrum and yields under various conditions are reported. Ethanol used as solvent for the charge carriers yields comparable results (tested at pH 2.8). Our main observations suggest that it may be possible to construct Graetzel-type cells with no special care to eliminate traces of water.

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] This extension of semiconductors' response spectrum into the solar range has been progressively refined through basic studies of interfacial electron transfer reactions.[2–11] While early versions of dye-sensitized photoelectrochemical cells were inefficient, Graetzel and his coworkers,[12–28] as well as others[29–59] succeeded in achieving 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.[60] The Graetzel cell is based on a dye (S) adsorbed onto a porous TiO_2 layer. The basic photo-physical reactions can be written as:

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

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

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

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

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 nanocrystallite, electron injection into the semiconductor according to reaction (2) can occur on a fast or ultra-fast time scale,[22,37,43,61–84] successfully competing with the deactivation reaction (3). The resulting charge-separated system undergoes 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[16,18–30,36,37,41,42,51] serve as charge carriers. There are only a small number of examples where aqueous solutions have been employed instead of organic solvents. Desilvestro *et al.*,[12] O'Regan *et al.*[15] and Vlachopoulos *et al.*[14] used $Ru(dcbpy)_3{}^{2+}$ as the photosensitizer with the charge carriers hydroquinone (HQ; IPCE = 44%)[12] and I^- (IPCE = 25%[15] and 73%[14]). Liska *et al.*[13] used *cis*-$Ru(dcb)_2(H_2O)_2$ as the photosensitizer and I^- as a reductant (IPCE 60%). However, the aqueous systems were unstable[85] so that with the exception of oxometal phthalocyanines in combination with aqueous HQ[49] (low photocurrent, no yield reported), water has been avoided as a solvent for the charge carriers after 1990, although equilibration of the TiO_2 layers with photosensitizers has been often carried out using water solutions.[31,32,38,50,52–55] The presence of water in the TiO_2 pores was reported to decrease the injection efficiency of most dyes.[18,43,47,48,81] In view of the undesirable effects that have been attributed to water solutions, attempts are often made to avoid even traces of water.

In most cases the photosensitizers used were Ru complexes although other photosensitizers such as osmium complexes,[56] iron complexes,[44] porphyrins,[17,19,38,39,57] phthalocyanines,[38,39,49,52] rhodamine 6G,[34] perylene,[40] mercurochrome,[58] merocyanine,[59] and xanthene[42,58] have also been employed.

Photocurrents were observed also in systems containing natural pigments, including anthocyanins. Tennakone *et al.* studied cyanidin pigments (cyanin without the sugar moiety) from flowers[31,33,35] and santalin from red sandalwood[45] 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.[32] Olea *et al.*[46] studied blackberry 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.*,[23] using water-free ethylene glycol or propylene carbonate as solvents for I^-/I_3^-, reporting an IPCE of 19%. The present work reports photocurrent yields in the photosensitization of a TiO_2 porous layer by pigments adsorbed from seed coats of the pomegranate fruit, using water as a solvent for the charge carriers. Pomegranate is a rich source of anthocyanin pigments,[86] which are responsible for the red color of pomegranate liquid. The chemical formula of cyanidin-3-glucoside, the spectrum of which closely resembles that of the pomegranate pigment mixture, is shown in Scheme 1.

The present study extends earlier works to aqueous solutions, showing good stability (tested for several days) and unusually high photocurrent yields. These features were

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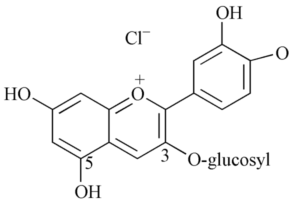

Cyanidin-3-glucoside (as chloride)

Scheme 1

unexpected for such a simple system in a water environment. This manuscript follows a recent preliminary report.[87]

Experimental

Materials

Lithium iodide (99%, Aldrich), potassium iodide (99.7%, Merck), sodium iodide (99.5%, Merck), tetrabutylammonium iodide (99%, Fluka), tetrabutylammonium perchlorate (99.99%, Southwestern Chemicals), 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 a deionizer (Millipore, Milli-Q model). ITO/glass (Geomatec, 10 $\Omega \square^{-1}$) 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.

Photosensitizer

The seed coats of the pomegranate fruit were processed and separated from the solid residue by filtration. The resulting liquid was kept frozen until used (up to one year). 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 to 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 in 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^{-1} was obtained, and the resulting cloudy white dye mixture was used for the preparation of clear TiO_2 layers on ITO.

Transparent TiO_2 layers were prepared on an ITO surface using TiO_2 nanocrystallites dispersed in water at pH 1.8 (100 g L^{-1}) by successive spin coating, followed by heating at 450 °C. The layer thickness was 3.35 ± 0.5 μm, absorbance at 355 nm $D_{355} = 1.05$–1.15. The ITO plate carrying the TiO_2 layers, with dimensions of 0.85×5 cm^2, was coupled with a Pt coated ITO plate of similar dimensions. In some experiments we used SnO_2 coated TiO_2 (generously donated by M. Graetzel). These TiO_2 nanocrystallites were prepared by a similar procedure,[16,18] except that they were heated for 1 day in an autoclave at 220–230 °C, yielding particles of 18 nm diameter. Pt was deposited on the counter electrode by very short (a few seconds) electrolysis of chloroplatinic acid.[88,89] The absorption spectra of the dyes in the TiO_2 layers were recorded and only samples with similar absorptions were used for comparative investigations.

The two plates were separated by a thin Teflon spacer and tightly held together by means of an appropriate slit in the Teflon base at the bottom of a two-window optical cell. Iodide and iodine in water solution or in the natural liquid of the pomegranate fruit were added at the bottom and filled the space between the two plates because of capillary forces. Although the cell was not tightly closed, it was possible to illuminate this setup for several hours without observable loss of solution.

Adsorption of the dye

Unless otherwise stated, the ITO/TiO_2 and SnO_2/TiO_2 electrodes were equilibrated with the pomegranate liquid (natural pH 2.8) to which acid (HCl) or alkali (NaOH) had been added to adjust the pH in the range 1.0–5.6 by shaking 12–24 h, inducing a violet coloration of the film. Prolonged shaking beyond 48 h resulted in decreased photocurrents. The electrode was washed with the appropriate acidic water before illumination. Considerably lower photocurrent yields were observed when the electrodes were initially equilibrated with the natural pomegranate liquid at the natural pH and subsequently washed or shaken with acidic water. This observation is apparently related to the buffer capacity of the $TiO_2/H^+/$dye system, which seems to have been ignored in previous works.

The natural red dye is likely to be a mixture of several pigments. Its spectrum on the TiO_2 layer in the 500–700 nm range resembles that of cyanidin 3-0-β-glucopyranside and cyanidin 3,5-0-β-diglucopyranside, which are among the six pigments identified in pomegranates.[86] Deviations below 500 nm, increasing towards the UV, indicate the presence of additional absorbing materials in the natural dye mixture.

Illumination

Illumination was carried out using a 12 W halogen lamp. A reflector provided a conical shaped 35° light beam. A water filter (1 cm 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 ± 0.15 cm^2. The integrated visible light intensity in the 400–700 nm range was about 2×10^{-7} einstein s^{-1}. Unless otherwise stated, an aqueous solution containing 2.4 M NaI and 0.1 M I_3^- was used to fill the space between the electrodes.

Actinometry and determination of quantum yields

The action spectra were measured with the aid of a B&L monochromator. Calibration of the light source and monochromator system was carried out using a calibrated silicon photodiode (Hamamatsu type c2719). Actinometry was carried out using the ferrioxalate actinometer[90] 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.

Results and discussion

The absorbance spectrum of the red pigment(s) used in this work is shown in Fig. 1. The spectrum is similar to that of pigments isolated from blackberries in aqueous organic solution, although the red shift induced by TiO_2 is much smaller in the latter case.[23] The spectrum in the TiO_2 film is shifted towards the red compared to the absorption of the natural solution. There is only a small effect of pH on the shape of the spectrum in the range 1.0–4.1, although a considerable red shift is observed at pH 5.6 (Fig. 2). The spectral changes, which occur upon adsorption of the pigment onto TiO_2, apparently involve formation of ether-like bonds involving aromatic hydroxyl groups of the pigment. The remaining absorption spectrum of the natural solution after equilibration with the

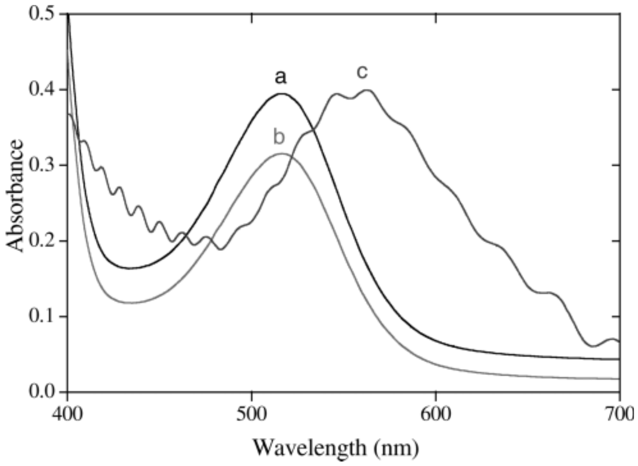

Fig. 1 Spectrum of pomegranate pigments in the natural liquid and adsorbed onto TiO_2. (a) Spectrum of the natural pomegranate liquid, diluted 1 : 10. (b) Spectrum of the natural solution after equilibration with the ITO/TiO_2 electrode, diluted 1 : 10. (c) Spectrum of the ITO/TiO_2 electrode after equilibration with the pomegranate liquid, corrected for the spectrum of the dye-free electrode.

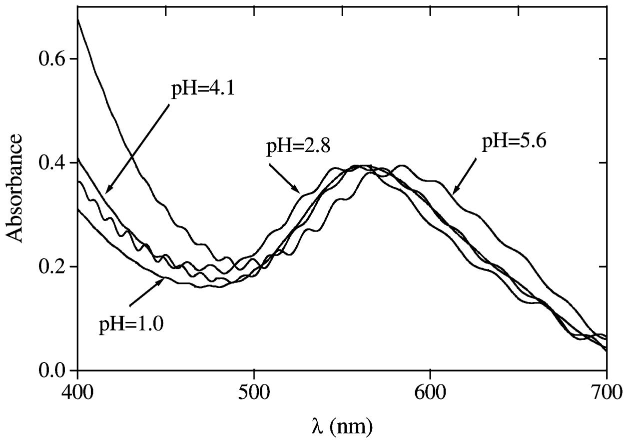

Fig. 2 Spectra of the adsorbed dye at various pH. The TiO_2 electrode was equilibrated with the natural pomegranate liquid at the given pH. The pH was adjusted by addition of HCl or NaOH to the natural pomegranate liquid. The spectra were normalized to the same peak absorption. Results at pH 1.2, 1.4 and 1.8 are very similar to pH 1.0.

electrode is somewhat different from the initial absorption (Fig. 1), indicating selective adsorption to the TiO_2.

Typical short circuit photocurrents and open circuit photovoltages observed upon illumination with the entire visible range of the halogen lamp are presented in Table 1. The photocurrents, which showed a linear dependence on light intensity in the range of measurements, were normalized to the light absorption and show the relative photon-to-current efficiencies. Note that both photocurrents and photovoltages vary somewhat when different TiO_2 samples are used, even when they are made from the same preparation. The differences, usually up to 10%, are due to variations in size (area and thickness of the layer) as well as inhomogeneity of the TiO_2 layer on the ITO surface. In view of the large scatter of results, averages values of at least 5 experiments were used. Results deviating by more that 10% were discarded, although in some cases, when comparative tests involved different TiO_2 preparations, normalization of photocurrents was carried out for convenience of the presentation. The photovoltages are much more reproducible than the photocurrents. Table 1 shows that the aqueous Na^+ counter ion is the most effective in photocurrent generation, although the results in ethanol are not much different. The *t*-butyl ammonium cation is the most effective counter ion with respect to the photovoltage, but it generates considerably lower photocurrent.

Table 1 Photocurrents and photovoltages for various iodides and solvents. TiO_2 layers equilibrated with natural pomegranate liquid at the natural pH for 24 h. Peak absorbance in the layers was 0.4. All systems contain 1 M iodide and 0.1 M iodine. Illumination carried out at 400–700 nm

Counter ion (solvent)	i_π/mA cm^{-3}	Photovoltage/V
Li^+ (H_2O)	0.18	0.30
K^+ (H_2O)	0.46	0.33
Na^+ (H_2O)	0.86	0.44
Na^+ (ethanol)	0.82	0.41
$(t\text{-Bu})_4N^+$ (ethanol)	0.31	0.48

Table 2 Control experiments: relative photocurrents in the absence and presence of NaI and I_2

[NaI]/M[a]	[$(t\text{-Bu})_4NClO_4$]/M[a]	[I_2]/M[a]	% rel. photocurrent[b]
1	–	0.1	100
1	–	–	6
–	–	0.1	27
–	1	–	10

[a] The electrodes were equilibrated with the natural dye liquid at the natural pH, washed with water at pH 2.8, and dried in vacuum before adding the electrolyte/I_2 solution in dry ethanol. Peak absorbance of the dye at the electrode was 0.4. [b] Relative to the photocurrent using 1 M NaI and 0.1 M I_2 in 100% ethanol.

Several control experiments are summarized in Table 2. It can be seen that both iodide and iodine are necessary for the maximum photocurrent, although significant photocurrent is observed also in the absence of iodide. There is relatively very little photocurrent in the absence of iodine. These results indicate the involvement of I^- in the regeneration of S by reaction (5).

$$2S^+ + 3I^- \rightarrow 2S + I_3^- \qquad (5)$$

The observation of a significant photocurrent in the absence of iodide raises the question whether the pigment is being oxidized. In view of this, stability tests were carried out over a period of 48 h, showing no measurable change in photocurrent, except for an initial increase during the first 20 min. The stability of the pigments implies that its oxidation is not an important path in the inhibition of the back reaction (4), at least in the presence of I^-. A simple calculation shows that if oxidation of the pigments was essential for the photocurrent generation, a substantial decrease of photocurrent would have been observed within minutes, in contrast to the stability of the photocurrent (after an initial increase) over days. Oxidation of impurities in the pomegranate liquid serving as a source of energy for the operation of the photoelectrochemical cell is also highly unlikely, since washing of the layers with water leaves only the adsorbed components in the layer. The concentration limit of adsorbed species in the layer is of the order of the adsorbed pigments. Hence, considerable oxidation of the impurities is expected to take place within a time span 2–3 orders of magnitude shorter than the time during which tests show no deterioration of the photocurrent. Therefore, even if oxidation of photosensitizer molecules or impurities may take place in the absence of iodide, the high iodide concentration suppresses these reactions. Note that significant photocurrent is obtained in the absence of iodide also in the Ru(dcb-py)$_2$(SCN)$_2$ system, in pure ethanol solution containing $NaClO_4$ and I_2.[91] Under these conditions impurities are highly unlikely. Evidently, in the presence of iodide, reaction (5) is involved in the generation of most or all of the photocurrent. In summary, the observations described above indicate: (a) at least one of the pigments present in the pomegranate liquid (mostly anthocyanins), adsorbs onto the TiO_2 and injects an electron into the conduction band upon excitation; (b) the resulting oxidized pigment reacts with iodide, although decomposition or reaction with one or more of the chemical components of the natural liquid in competition with reactions (4) and (5) cannot be completely ruled out; (c) since without I_2 only relatively small photocurrents are observed, it is evident that I_2 (in the form of I_3^-) is the predominant electron acceptor at the counter electrode, while the reaction of iodine with the TiO_2 electrons is relatively slow. Since addition of NaI to the pomegranate liquid containing I_2 increases the photocurrent by about threefold, this means that iodide successfully competes with the TiO_2 electrons for the oxidized pigment(s).

The effect of changing iodide and iodine concentrations is shown in Fig. 3 and 4, respectively. Increasing the iodide concentration increases the photocurrent, indicating that reaction (5) does not completely suppress reaction (4). The photocurrent increases from 2.55 mA (short cycle current) to a limiting value of 4.6 mA when a positive potential (0.5 V above the potential of the counter electrode) is applied to the working electrode. This effect apparently involves suppression of reaction (4) by efficient removal of the electrons. The photocurrent in Fig. 4 is determined by the opposing action of iodine, enhancing the photocurrent by reaction with the electrons at the counter electrode, while suppressing it by reaction with the TiO_2 electrons.

The effect of pH on photocurrent is presented in Fig. 5, indicating that the protonated form of the adsorbed cyanin dye is the active photosensitizer. The photovoltage changes only little with pH. Typical values using 2.5 M NaI and 0.1 M I_2 in water solution, and the entire spectral range of the excitation lamp (400–700 nm), vary from 0.40 V at pH 1.0 to 0.46 at pH 2.8.

Fig. 6 shows the photocurrent spectrum, compared to the absorption spectrum of the pigment at $pH = 2.8$. The photocurrent parallels the light absorption although the photocurrent peak is shifted by about 17 nm towards longer wavelengths. This may be caused by the existence of a mixture of similar pigments with different quantum yields. Note that although the light intensity is considerably decreased when passed through the monochromator, the photocurrent yields are expected to change only little.[92]

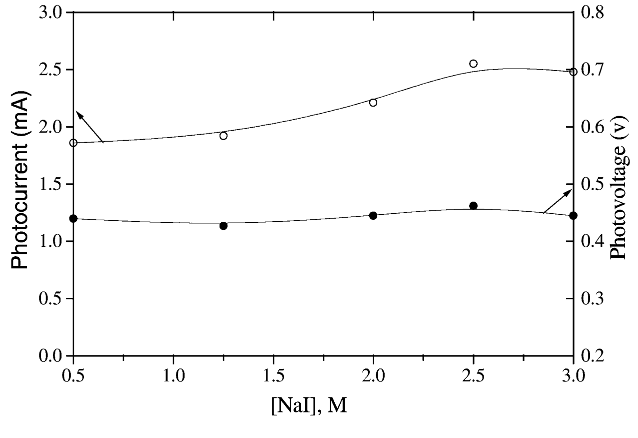

Fig. 3 Effect of $[I^-]$ on the steady state photocurrent and photovoltage. TiO_2 layers equilibrated (24 h) with natural pomegranate liquid at pH 2.8. Charge carrier: 0.1 M iodine in water solution at pH 2.8. The electrode spectrum is similar to that presented in Fig. 1. The 12 W halogen lamp was used with a 400 nm filter. Peak absorbance of the dye in the layer was 0.4.

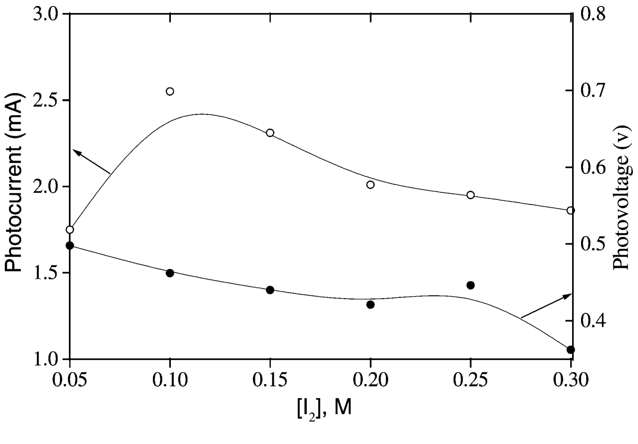

Fig. 4 Effect of $[I_2]$ on the steady state photocurrent and photovoltage. TiO_2 layers equilibrated with natural pomegranate liquid. Electrolyte: 2.5 M sodium iodide in water solution at pH 2.8. Other conditions as in Fig. 3.

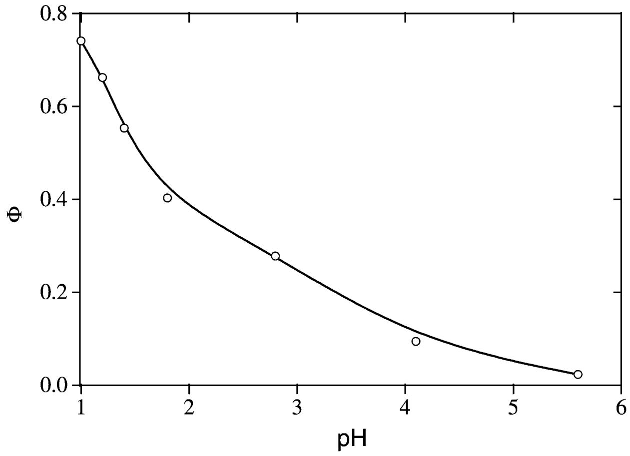

Fig. 5 Effect of pH on the quantum yield of photocurrent. TiO_2 layer equilibrated with natural pomegranate liquid. Charge carriers: 2.5 M sodium iodide and 0.1 M iodine at the given pHs. The photocurrents were measured at 600 nm, at a photon flux of 7.8×10^{-10} einstein s^{-1}.

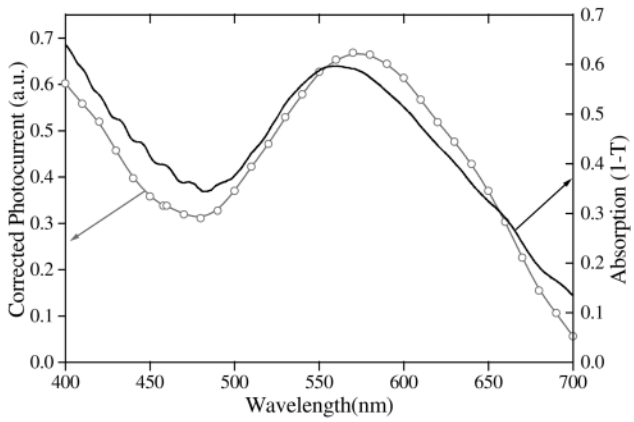

Fig. 6 Comparison of photocurrent (○–○–○) and absorption (——) spectrum. TiO_2 layer equilibrated with natural pomegranate liquid, measured in 2.5 M NaI and 0.1 M iodine dissolved in the natural dye liquid (pH 2.8). Photocurrent at 457.9 nm was 1.5×10^{-10} F s^{-1}. Note that the results correspond to $\Phi = 0.28$ at 600 nm.

Table 3 Photocurrent quantum yields as a function of TiO_2 particle size Natural dye used at pH 2.8. $Ru(dcbpy)_2(SCN)_2$ used in absolute ethanol containing 1.9 M NaI and 0.1 M I_3^-

Photosensitizer	TiO_2 particle diameter/nm	Φ
Natural dye	5	0.28
Natural dye	18	0.13
$Ru(dcbpy)_2(SCN)_2$	5	0.50
$Ru(dcbpy)_2(SCN)_2$	18	0.75

The effect of TiO_2 particle size is summarized in Table 3. Two sizes were compared: the standard 5 nm diameter used in most of the experiments, and TiO_2 layers composed of 18 nm diameter TiO_2.[16,18] In both cases the photosensitizer was adsorbed from the natural liquid and used at the natural pH of 2.8. Comparative experiments using $Ru(dcbpy)_2(SCN)_2$ are also presented. In the natural dye system, the photocurrent quantum yield is considerably higher when the smaller TiO_2 particles are used. These results suggest that smaller nanocrystallites (and consequently, smaller pores in the layer) are required to "filter" out some of the components in the pigment mixture, which decrease the efficiency of the photoelectrochemical cell. Note that the control experiments using $Ru(dcbpy)_2(SCN)_2$ instead of the natural dye show an opposite effect, namely, the photocurrent yields are higher with the larger TiO_2 nanocrystallites. These results apparently reflect the better quality of the large particle layer with respect to electron migration towards the electrode. It is tempting to speculate that considerably higher yields could be achieved by appropriate purified anthocyanins, using the large nanocrystallites.

Conclusions

An open circuit photovoltage of up to 0.45 V and photocurrent quantum yield of up to $\Phi = 0.74$ are observed at pH 1. The quantum yield of the photocurrent, the photovoltage and stability of the photoelectrochemical cell are unusually high for aqueous solutions. Comparative experiments using $Ru(dcbpy)_2(SCN)_2$ with the same kind of TiO_2 layer and iodide/iodine in dry ethanol as charge carriers produce photocurrents corresponding to quantum yields of up to 0.5. This yield is considerably lower than that measured with TiO_2 layers prepared in Graetzel's laboratory, which are composed of considerably larger nanocrystallites.[16,18] Attempts to repeat the experiments using the larger TiO_2 particles show a 50% higher photocurrent in the $Ru(dcbpy)_2(SCN)_2$ system (compared to the our TiO_2 layers), but considerably lower photocurrents were observed in the natural dye systems. These results suggest that smaller nanocrystallites (and consequently, smaller pores in the layer) are required to "filter" out some of the components in the pigment mixture, which decrease the efficiency of the photoelectrochemical cell. Note that the highest quantum yields in the natural dye systems are obtained when the equilibration time of the TiO_2 coated electrodes with the dye solutions is 12–24 h. Under these conditions the peak absorbance of the dye in the TiO_2 layer is relatively small (in the range 0.2–0.4), implying that some of the pigments, which adsorb relatively slowly, compete for the photons, but are inefficient in photocurrent generation.

The present work suggests that using the charge carriers in water solutions does not necessarily poison the photoelectrochemical cell, although a typical Graetzel cell is believed not to function in a water environment. Much more work is required to answer the intriguing question concerning the role of water in the different systems. However, our main observations, including the lack of a strong pH effect on the photovoltage, suggest that it may be possible to prepare Graetzel-type cells with no special care to eliminate traces of water. This conclusion may apply also to some solid charge carriers, which may be relatively easier to prepare inside the TiO_2 pores using water solutions.

Acknowledgements

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