Photovoltaic response of carotenoid-sensitized electrode in aqueous solution: ITO coated with a mixture of TiO_2 nanoparticles, carotenoid, and polyvinylcarbazole

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Photovoltaic responses were observed upon irradiating (>420 nm) an ITO electrode spin-coated with a mixture of TiO_2 nanoparticles, polyvinylcarbazole, and carotenoid (canthaxanthin or β-carotene, Car) and immersed in an aqueous KCl solution also containing hydroquinone (QH_2). The anodic photocurrent involves electron transfer from the excited state of the carotenoid (Car*) to the TiO_2 conduction band; the resulting carotenoid radical cation ($\mathrm{Car}^{\cdot+}$) is reduced by QH_2. The photocurrent was nearly constant during one hour of continuous irradiation, which indicates that these carotenoids are stable at the electrode/electrolyte interface, presumably because of rapid regeneration of Car from $\mathrm{Car}^{\cdot+}$ during the electron transfer cycle. In contrast, when the aqueous electrolyte solution was saturated with O_2, a cathodic photocurrent was observed; this reversal of polarity is attributed to electron transfer from Car* to O_2, and subsequent reduction of the resulting $\mathrm{Car}^{\cdot+}$ by electrons from the TiO_2 conduction band.

Introduction

Although the lifetime of the S_1 excited state of carotenoid pigments in solution is generally very short (10–50 ps),[1,2] carotenoids can undergo photochemical reactions such as unimolecular isomerization,[3,4] quenching of triplet or singlet states of other molecules through energy transfer,[5] intramolecular charge-transfer,[6] charge separation in synthetic molecular dyads and triads,[7,8] and photoinduced electron-transfer to solvent molecules.[9] It has also been shown recently that electrons can be transferred from excited states of a carotenoid to the conduction band of semiconductor particles, and cause enhanced photodegradation and photoisomerization of the carotenoids depending on the properties of both carotenoid and semiconductor.[10] Further, it is well established that carotenoids serve as light-harvesting accessory pigments in photosynthetic plants by transferring the singlet excitation energy to chlorophyll a (Chl a). They also act as 'triplet valves' to harmlessly dissipate the energy of Chl triplets and are scavengers of singlet oxygen which can destroy Chl.[11] In addition, the highly conjugated carotenoids can function as short molecular wires that mediate electron transfer in donor–acceptor complexes and membranes.[12,13] Photoconduction properties of carotenoids were systematically studied, and effective production of charge carriers by excitation of carotenoid absorption bands was observed.[14–16] These properties, together with their characteristic light absorption in the range of 380–520 nm and molar extinction coefficients larger than 10^5, make certain carotenoids potential sensitizer materials in solar photovoltaic cells and other artificial photochemical devices.

Sandwich cells of the type (Al|Chl a|mixture of Chl a and canthaxanthin|Chl a|Ag) have been used in measurements of photovoltaic currents.[17] A photocurrent, generated by irradiation with light that is in the canthaxanthin absorption region, was attributed to energy transfer from canthaxanthin to Chl a. It was also suggested that the long conjugated chain of canthaxanthin may behave as a photoconductor and serve to reduce the internal resistance of the cells.[17] To overcome the kinetic limitation of efficient charge-transfer imposed by the short singlet excited state lifetime, carotenoids should be incorporated into a structure in which ultrafast photoinduced electron transfer can occur. One strategy to accomplish this is to form an organized assembly of the carotenoid pigments in contact with a conducting or semiconducting electrode so that electron transfer between the pigment and the electrode can effectively compete with the decay of the carotenoid excited state. Indium tin oxide (ITO) electrodes coated with LB (Langmuir–Blodgett) films of 7′-apo-7′-(4-carboxyphenyl)-β-carotene and immersed in an electrolyte solution also containing benzoquinone (Q) or hydroquinone (QH_2) have been shown to be photoactive.[18] The results of photocurrent (2 nA cm^{-2}) and action spectra measurements implicated the excited carotenoid pigment as the photoactive species in the electron transfer process. However, these methods for studying the photochemical properties of carotenoids are limited to carotenoids containing certain terminal groups such as carboxylic acid functionalities that can be attached to the ITO surface to form LB films.

During the past decade, the utilization of semiconductors as catalysts in solar energy conversion, photochemical transformations of organic and inorganic compounds, and photodegradation of organic pollutants has seen a tremendous growth.[19] Among the many semiconductors used in past and present research in photocatalysis, titanium dioxide (TiO_2) features prominently. Recently application of dye-sensitized semiconductor electrodes to a new type of photovoltaic cell, the dye-sensitized TiO_2 nanocrystalline solar cell or Graetzel cell,[20] has stimulated much interest.[21] Photosensitization, which is achieved by adsorption of dye molecules on the surface of a large bandgap semiconductor, such as TiO_2, and injection of an electron into its conduction band upon visible excitation, provides an efficient wet chemical method for converting sunlight into chemical or electrical energy, and overcomes the limitation of non-coated metal oxide semiconductors that are only photoactive when exposed to UV light. Although many organic dyes, *e.g.*, Ru complexes,[22,23] erythrosin B,[24] eosin,[25] phthalocyanines,[26] oxazines,[27] and squaraine,[28] have been studied for sensitization of large-bandgap semiconductors, development of new semiconductor sensitizers which produce higher conversion efficiency and low cost solar photovoltaic dye cells is a long-term task.

Studies indicate that electron transfer from the electronically

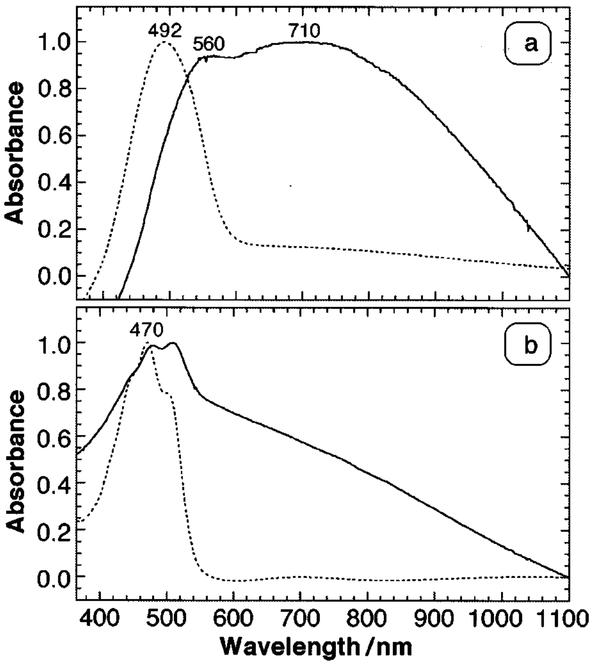


Fig. 1 Optical absorption spectra of ITOs coated with a mixture of (a) canthaxanthin–PVK–TiO_2 (solid line) and canthaxanthin–PVK (dotted line), and (b) β-carotene–PVK–TiO_2 (solid line) and β-carotene–PVK (dotted line).

excited photosensitizer *cis*-$(H_2O)_2$bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II), adsorbed on the surface of TiO_2 nanocrystals, to TiO_2 is a very fast process (<7 ps).[20] This may imply that, given the lifetime (10–50 ps) of the S_1 excited state of carotenoid (Car*), the electron transfer from Car* to TiO_2 could also occur. To date photochemical studies of the Car/TiO_2 system are still lacking.

In this study, ITO electrodes coated with a mixture of TiO_2 nanoparticles, β-carotene or canthaxanthin, and polyvinylcarbazole (PVK) (a material that can be made into a hole doped semiconductor) immersed in aqueous KCl solution also containing hydroquinone (5 mM) as electron donor and a platinum wire counter electrode were irradiated with visible (>420 nm) light. The photovoltaic properties of this cell and the effect of dissolved oxygen on the photocurrent were investigated.

Results and discussion

Optical absorption spectra of carotenoid, TiO_2, and PVK mixture

The optical absorption spectrum ($\lambda_{max} = 492$ nm) of an ITO coated with a canthaxanthin–PVK film is shown in Fig. 1a, dotted line. Compared to the spectrum of canthaxanthin measured in dichloromethane ($\lambda_{max} = 465$ nm), a 27 nm red-shift of the absorption maximum occurs. This behavior suggests that canthaxanthin may form aggregates in the PVK medium on the ITO surface. For the canthaxanthin–PVK film also containing TiO_2 (Fig. 1a, solid line), the short-wavelength absorption is further red-shifted to 560 nm, and additional absorption occurs at longer wavelength with a maximum near 710 nm. However, due to reflection and diffusion of the incident light by larger TiO_2 particles which were bonded together by smaller TiO_2 particles, the solid line in Fig. 1a may not reflect the real absorption spectrum of canthaxanthin–PVK film containing TiO_2 particles.

The spectra of β-carotene films on ITO are shown in Fig. 1b. The spectrum of β-carotene in the presence of only PVK (dotted line, $\lambda_{max} = 470$ nm) is similar to that of β-carotene measured in dichloromethane ($\lambda_{max} = 450$ nm), the fine structure is preserved, but the absorption maximum is red-shifted by 20 nm. As for canthaxanthin, this may indicate that β-carotene forms aggregates in the PVK medium. For the β-carotene–PVK–TiO_2 film, a further red-shift of the absorption maximum can be observed; the long-wavelength absorption tail extension is also due to the diffuse reflection of the larger TiO_2 particles in the film.

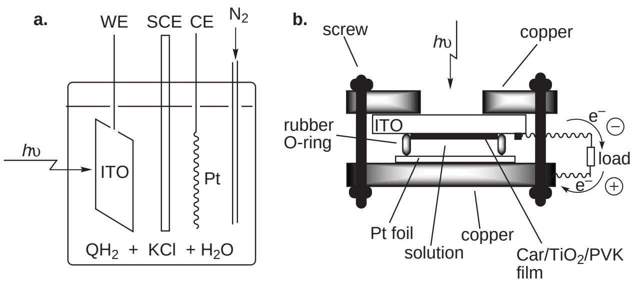


Fig. 2 Schematic of (a) the photoelectrochemical cell and (b) the cross section of the sandwich cell used for photoelectrochemical and photovoltaic measurements.

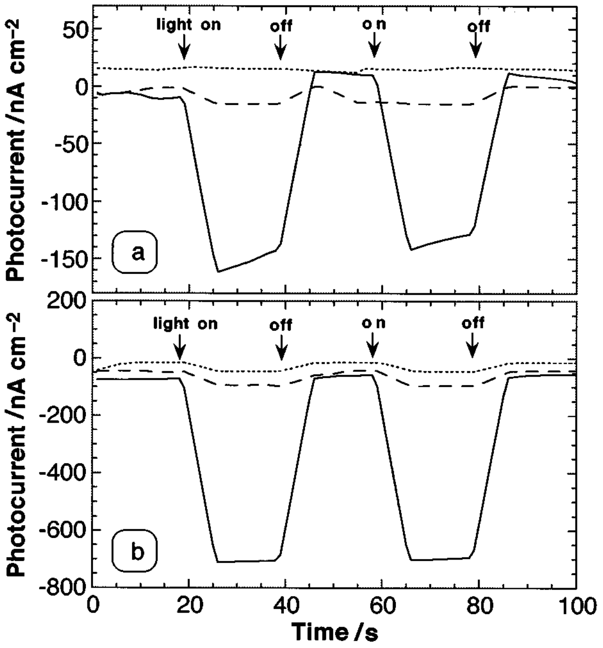


Fig. 3 Photocurrent response of ITO electrodes coated with canthaxanthin–PVK (dotted line), PVK–TiO_2 (dashed line) and canthaxanthin–PVK–TiO_2 (solid line) as the irradiation was turned on or off; the electrode potentials were fixed at (a) 0 mV and (b) 100 mV *vs.* SCE. 0.1 M KCl and 5 mM QH_2 aqueous solution, pre-purged with N_2 for 20 min. The anodic current polarity is negative.

Photoelectrochemistry at fixed electrode potential

Fig. 3a shows the photoresponse of an ITO electrode coated with a canthaxanthin–PVK–TiO_2 film (solid line) and immersed in an aqueous solution containing 0.1 M KCl and 5 mM QH_2 upon irradiation with visible light. The photoelectrochemical cell shown in Fig. 2a was used and the working electrode (ITO) was adjusted to 0.0 V *vs.* SCE using the potentiostat of the BAS-100W. Upon irradiation, the photocurrent (the anodic current polarity is negative) increased and rapidly reached an approximately steady-state value. The photocurrent returned to the low level after irradiation was terminated. Under the same conditions, but with ITOs coated with only canthaxanthin–PVK (Fig. 3a, dotted line) or only PVK–TiO_2 (Fig. 3a, dashed line) films, no or only very small photocurrents were detected; therefore the origin of the photocurrent must be attributed to the excitation of canthaxanthin. Photocurrent responses in Fig. 3b were measured using the same conditions as in Fig. 3a, except that an electrode potential of 0.1 V was applied. The photocurrent increased as a more positive potential was applied (Fig. 3b, solid line). A similar photoresponse was observed for ITO coated with β-carotene–PVK–TiO_2 as shown in Fig. 4. The dependence of the photoresponse on the applied potential is shown in Fig. 5, solid line, for the canthaxanthin–PVK–TiO_2 film and dotted line for β-carotene–PVK–TiO_2.

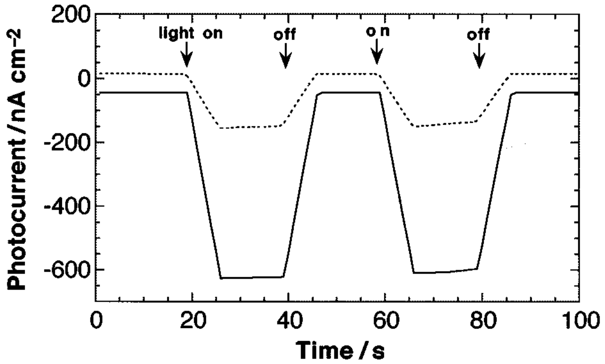


Fig. 4 Photocurrent response of ITO electrode coated with β-carotene–PVK–TiO_2 as the irradiation was turned on or off; electrode potentials were fixed at 0 mV (dotted line) and 100 mV (solid line) *vs.* SCE, respectively. 0.1 M KCl and 5 mM QH_2 aqueous solution, pre-purged with N_2 for 20 min.

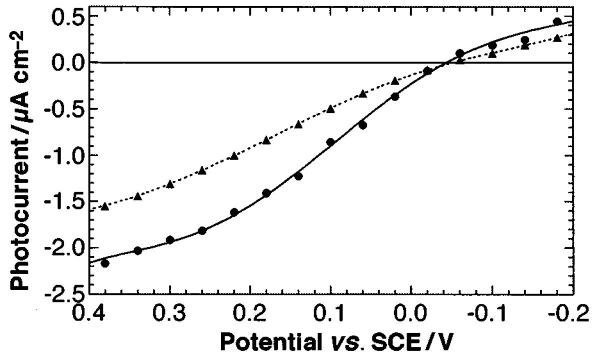


Fig. 5 Photocurrent *vs.* electrode potential for ITO electrode coated with canthaxanthin–PVK–TiO_2 (solid line) and β-carotene–PVK–TiO_2 (dotted line). 0.1 M KCl and 5 mM QH_2 aqueous solution, pre-purged with N_2 for 20 min.

Photovoltaic response

To confirm that photovoltaic currents were generated upon excitation of the ITO electrodes coated with carotenoid–PVK–TiO_2 films using the above mentioned photoelectrochemical cell, the working electrode (ITO) and counter electrode (Pt) were directly connected *via* a 75 KΩ resistor instead of using a potentiostat. Upon irradiation of the system, the photogenerated electrons flow from anode (−) to Pt cathode (+) (the photocurrent flows in the opposite direction) and deliver electric power to the load. Measurements of the photogenerated voltage upon the load permits evaluation of the photocurrent. The photocurrent readouts as a function of irradiation time are shown in Fig. 6. The negative sign of the photocurrents indicates that the current is anodic for the working electrode, ITO–carotenoid–PVK–TiO_2. For both ITO–canthaxanthin–PVK–TiO_2 (solid line) and ITO–β-carotene–PVK–TiO_2 (dotted line) electrodes, the photocurrents rise rapidly and reach a nearly steady-state value (about 90 and 40 nA cm^{-2}, respectively). The photocurrents were almost constant during one hour of continuous irradiation, with an output voltage of about 22 mV for the canthaxanthin–PVK–TiO_2 electrode and 10 mV for the β-carotene–PVK–TiO_2 electrode.

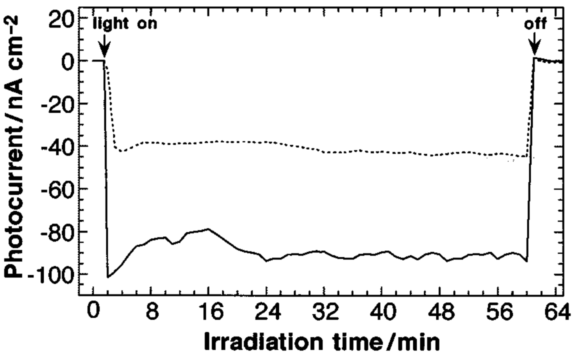


Fig. 6 Photovoltaic response of ITO electrodes coated with canthaxanthin–PVK–TiO_2 (solid line) and β-carotene–PVK–TiO_2 (dotted line) as the irradiation was turned on or off; the ITO working electrode (−) and the Pt counter electrode (+) were connected *via* a 75 KΩ resistor, using the photoelectrochemical cell shown in Fig. 2a. 0.1 M KCl and 5 mM QH_2 aqueous solution, pre-purged with N_2 for 20 min.

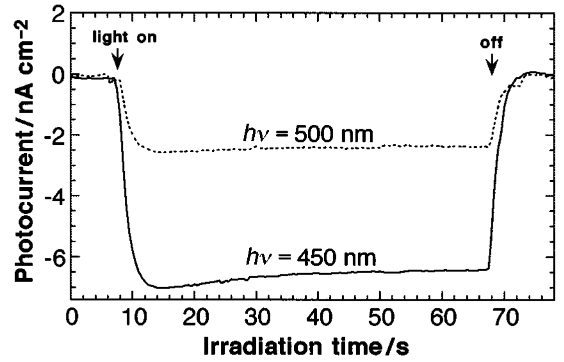


Fig. 7 Photovoltaic response of ITO electrode coated with canthaxanthin–PVK–TiO_2 as the 450 nm (solid line) and 500 nm (dotted line) monochromatic irradiation was turned on or off; a sandwich cell shown in Fig. 2b was used; the ITO working electrode (−) and the Pt counter electrode (+) were connected *via* a 75 KΩ resistor; 0.1 M KCl and 50 mM QH_2 aqueous solution pre-purged with N_2 for 20 min were injected into the cell.

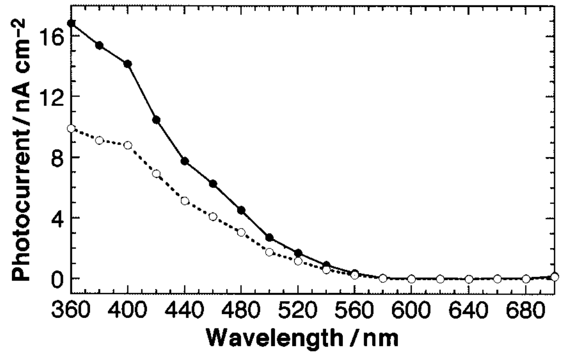
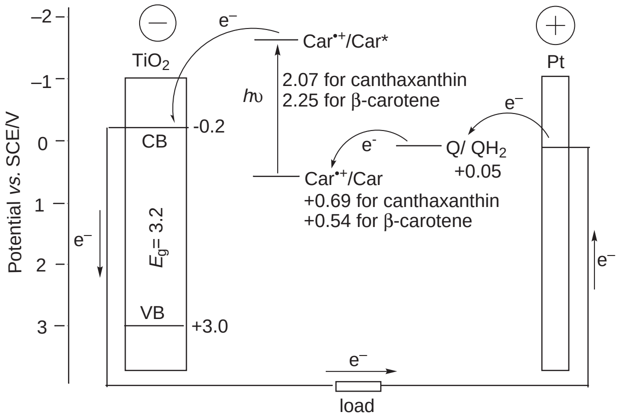


Fig. 8 Action spectra of ITO electrodes coated with canthaxanthin–PVK–TiO_2 (solid line) and β-carotene–PVK–TiO_2 (dotted line), 0.1 M KCl and 50 mM QH_2 aqueous solution pre-purged with N_2 for 20 min.

A sandwich cell was also employed to demonstrate the photovoltaic currents. As shown in Fig. 2b, the cell consists of an ITO–carotenoid–PVK–TiO_2 photoanode (−) and a Pt cathode (+) which were connected *via* a 75 KΩ resistor as load. Although the generated photocurrents are small, the cell is indeed sensitive to low-intensity monochromatic light. Fig. 7 shows the photovoltaic response of the canthaxanthin–PVK–TiO_2 sandwich cell when intermittently exposed to 450 nm (solid line) and 500 nm (dotted line) light. The β-carotene–PVK–TiO_2 cell exhibits a similar response. The action spectra obtained by monochromatic illumination of the cells using canthaxanthin–PVK–TiO_2 and β-carotene–PVK–TiO_2 electrodes, respectively, are shown in Fig. 8.

Carotenoid-sensitized TiO_2 photoelectrode mechanism

It was recently shown that illumination of a mixture of carotenoids and semiconductor (CdS, ZnO, and TiO_2) particles can induce electron transfer from carotenoids to semiconductors to form carotenoid radical cations.[10,29] We have now directly observed the generated photocurrent. Our results demonstrate that a photocurrent is indeed produced upon excitation of the carotenoid within the carotenoid–PVK–TiO_2 film followed by quenching of its excited state by electron injection into the TiO_2 conduction band, or by a carotenoid-sensitization process. Scheme 1 illustrates the proposed mechanism of this process.



Scheme 1 Schematic representation of the principle of carotenoid-sensitized TiO_2 photovoltaic response in the presence of an electron donor.

Upon irradiation of the cell, the carotenoid molecules are electronically excited and inject electrons into the TiO_2 conduction band. These injected electrons traverse the TiO_2–PVK film and are collected at the back contact (ITO electrode). After passing through the external circuit and delivering power to a load, the electrons re-enter the cell at the counter electrode, reduce the quinone to QH_2 ($Q + 2H^+ + 2e^- \rightleftharpoons QH_2$, 0.05 V *vs.* SCE at pH 7 in aqueous solution), which then reduces the photo-oxidized carotenoid ($Car^{\bullet +}$) back to its original state. The fact that the photocurrent was nearly constant during one hour of continuous irradiation indicates that these carotenoids are stable at the electrode/electrolyte interface, presumably because of rapid regeneration of Car from $Car^{\bullet +}$ during the electron transfer cycle.

Back reactions such as recombination of the injected electron with the oxidized form of the carotenoid ($Car^{\bullet +}$) could occur and would reduce the cell efficiency. Other factors leading to low efficiency of such a cell include (1) slow electron injection rate compared to the relaxation of the carotenoid excited state and (2) the PVK (which is essentially an insulator) dispersed in the TiO_2–carotenoid film would render the photoinjection, traverse, and collection processes of the electron at the back contact inefficient. If it were not for the carotenoid conjugated structure serving as 'molecular wires' or 'electron mediators' and its photoconduction properties in the films,[12,13] such a cell would not work. Direct coordination of a carotenoid substituted with a terminal carboxylate ligand to the TiO_2 surface *via* formation of covalent bond would facilitate the photoinjection and movement of electrons and therefore increase the cell efficiency; this aspect is being investigated, and much higher quantum efficiency has been obtained, as expected.[30]

Influence of oxygen as electron acceptor

In contrast to the generation of an anodic photocurrent when the solution contains the electron donating QH_2, cathodic photocurrents were observed when the electron accepting O_2 was present. Fig. 9 shows the photoresponse of ITO electrodes coated with PVK–TiO_2 (dotted line), canthaxanthin–PVK–TiO_2 (solid line), and β-carotene–PVK–TiO_2 (dashed line) immersed in an aqueous solution containing 0.1 M KCl and saturated with oxygen. The photoelectrochemical cell shown in Fig. 2a was used and the working electrode was adjusted to 0.0 V *vs.* SCE. For ITO coated with PVK–TiO_2, there was essentially no photoresponse upon illumination. For ITO coated with canthaxanthin–PVK–TiO_2, however, a cathodic photocurrent (the cathodic current polarity is positive) was generated and rapidly reached an approximately steady-state value. The photocurrent quickly returned to the low level after irradiation was stopped. Under the same conditions but with ITO coated with β-carotene–PVK–TiO_2, a similar photocurrent response, but of smaller magnitude, was observed. The mechanism shown in Scheme 2 could account for the cathodic photocurrent generation.

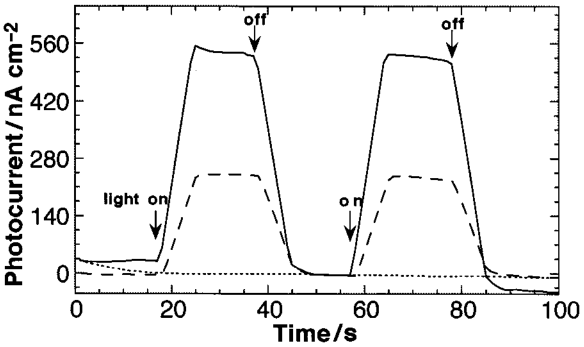
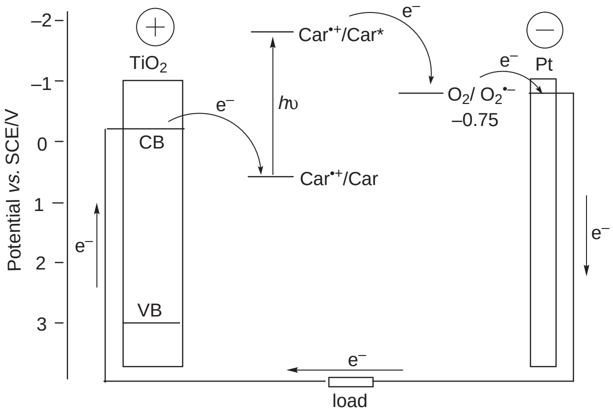


Fig. 9 Photocurrent response of ITO electrodes coated with PVK–TiO_2 (dotted line), canthaxanthin–PVK–TiO_2 (solid line), and β-carotene–PVK–TiO_2 (dashed line) as the irradiation was turned on or off; the electrode potentials were fixed at 0 mV *vs.* SCE. 0.1 M KCl aqueous solution saturated with oxygen for 20 min. The cathodic current polarity is positive.



Scheme 2 Schematic representation of the principle of carotenoid-sensitized TiO_2 photovoltaic response in the presence of an electron acceptor.

Upon illumination of the photoelectrode, the carotenoid molecules are electronically excited and transfer electrons to oxygen molecules to form superoxide radical ions $O_2^{\bullet -}$ ($O_2 + e^- \rightleftharpoons O_2^{\bullet -}$, −0.75 V *vs.* SCE), which are oxidized at the Pt counter electrode. After passing through the external circuit and delivering power to the load the electrons re-enter the cell at the ITO electrode and then reduce the oxidized carotenoid ($Car^{\bullet +}$) to the neutral compound. Therefore the photocurrent polarity depends on the nature of the redox couples in the electrolyte solution. The absence of a photoresponse upon irradiation of ITO coated with only PVK–TiO_2 (Fig. 9, dotted line) under otherwise the same conditions confirms that carotenoids are the sensitizer species.

Conclusions

We have demonstrated that anodic photovoltaic currents are generated upon illumination (>420 nm) of ITO electrodes spin-coated with carotenoid–PVK–TiO_2 films immersed in aqueous electrolyte solution containing hydroquinone (QH_2). In the presence of oxygen as electron scavenger, however, a cathodic photocurrent is observed. In both cases carotenoid-sensitization processes on the TiO_2 surface account for the generation of these photocurrents. This method extends the photoelectrochemical study of carotenoid modified electrodes to carotenoids that do not form LB films on semiconductor surface.

Experimental

All-*trans* canthaxanthin and β-carotene were purchased from Fluka. Cyclohexanone, poly(9-vinylcarbazole) (PVK), potassium chloride (99.99%), and hydroquinone (99+%) (QH_2) were purchased from Aldrich. Titanium(IV) oxide nanoparticles (30 nm, ST-1, anatase) were purchased from the Ishihara Sangyo Kaisha Corporation (Japan). Highly purified water (Millipore Milli-Q, 16 MΩ cm), provided by Professor Metzger of the University of Alabama, was used to prepare electrolyte solutions.

Transparent glass plates (1.5 × 6 cm^2) coated with InO_2–SnO_2 (ITO) were soaked in potassium hydroxide saturated ethanol solution for 24 h, rinsed thoroughly with deionized water, soaked in pure water for 2 h, dried at 110 °C for 10 h, and then stored in a desiccator over Drierite at room temperature. The ITO working electrodes were spin-coated with a mixture of TiO_2 nanoparticles, carotenoid, and PVK according to the following procedure. A mixture of 250 mg PVK and 50 mL cyclohexanone was stirred for 48 h; the resulting solution was stored for later use. 2 mL PVK solution was transferred to a 5 mL vial containing 25 mg TiO_2 particles and 10 mg carotenoid, mixed well, and left to stand for 1 h before making the film. 0.5 mL of the above mixture was applied to the ITO surface (conducting side), and the plate was spun at 1000 rpm for 5 min. The film thickness was about 1.2 μm as estimated by the weight change and size of the ITO plate before and after coating. The ITO film electrode was used immediately after preparation.

Electrochemical measurements of the photocurrent at a fixed electrode potential were carried out using the BioAnalytical Systems BAS-100W electrochemical analyzer. The reference and counter electrodes were a saturated calomel electrode (SCE) and a platinum wire, respectively. The homemade electrochemical cell consisted of a 100 mL glass vessel with a flat quartz glass window used for irradiation of the ITO surface (Fig. 2a). The electrode area exposed to the irradiation was 3.2 cm^2. An 80 mL aqueous solution of 5 mM QH_2 and 0.1 M KCl was added to the cell and then purged with N_2 for 25 min to remove O_2 before measurement. Alternatively a homemade sandwich cell (Fig. 2b) was used for photovoltaic voltage and current measurements; in this assembly a Pt foil served as anode (counter electrode); the volume was about 400 μL. An aqueous solution of 50 mM QH_2 and 0.1 M KCl pre-purged with N_2 for 25 min was injected through the rubber O-ring into the cell with a syringe. The irradiation area of the sandwich cell was 2.5 cm^2. A 75 KΩ resistor was used as the load. The photovoltage was measured by an electronic multimeter (Hewlett Packard, 3478A).

Optical absorption spectra in the range of 190 to 1100 nm were measured using a Shimadzu UV-1601 UV-vis spectrophotometer. Absorption spectra of ITO spin-coated with a film of carotenoid–PVK or carotenoid–PVK–TiO_2 were measured in air using a blank ITO as reference. A 250 W xenon lamp (ILC Technology) at a distance of 30 cm was used to irradiate the photoelectrodes. Deionized water contained in a cylindrical glass cell (path length, 10 cm) was used as an IR cut-off filter. A longpass glass optical filter (Edmund Scientific Company, 2 × 2 in^2) was used to cut off light below 420 nm. The photoenergy at the external surface of the cell, measured with a Newport power meter (Model 818-SL), was 0.8 W cm^{-2}. For monochromatic irradiation, a monochromator (Kratos Schoeffel Instruments, GM 252, 180–800 nm, slit 5 nm) was used together with the 250 W xenon lamp.

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