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Sensitization of nanoporous TiO_2 electrodes using the naturally occurring chromophores: stentorin and hypericin

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Abstract

This paper compares hypericin and stentorin as possible photosensitizers for transparent, nanoporous, TiO_2-based photovoltaic cells. The absolute photon conversion efficiency (APCE) of stentorin-sensitized nanoporous TiO_2 electrodes was 2%, 20 times greater than that of electrodes sensitized by the structural analog, hypericin (0.1%). We attribute the greater efficiency of the stentorin electrode to the decreased tendency of stentorin to aggregate on the electrode surface. These results suggest that controlling aggregation by making a slight structural modification to the chromophore could be a viable and generalizable method for improving the performance of dye-sensitized electrodes.

Keywords: Hypericin; Stentorin; TiO_2; IPCE; APCE; Photovoltaic

1. Introduction

For photoelectrochemical energy conversion, dye sensitization of wide band-gap semiconductors has enjoyed considerable attention for the past 10 years with the advent of nanoporous high-surface-area TiO_2 electrodes [1–4]. With power conversion efficiencies of ~10%, ruthenium(II) polypyridyl complexes are considered among the most promising candidates for dye photosensitizers [2,5]. Organic dyes and naturally occurring chromophores have also been investigated, however, the observed efficiencies of these have been relatively low [6,7]. Dye aggregation on the semiconductor surface is reported to be one of the major factors responsible for the low photocurrents observed [8]. Among the strategies considered for controlling the extent of aggregation of organic dyes on semiconductor surfaces are structural modification of the dye molecules, and the use of additives [8,9].

We report here on two dye molecules as candidates for the photosensitization of TiO_2. The naturally occurring polycyclic quinones, hypericin and stentorin, have extended π-systems that can act as photosensitizers and efficient excited-state electron donors [10]. Hypericin occurs naturally in the herb St. John's Wort and has been of interest for its photoactivatable antiviral properties [11,12]. The stentorin chromophore is a hypericin analog (Fig. 1) and serves as the primary photosensitizing agent in *Stentor coeruleus*, a photophobic ciliated protozoan [13]. The absorption spectra of both dyes extend into the red (620 nm), giving reasonable overlap with the solar spectrum. The reported lifetimes of the excited states of hypericin and stentorin in aprotic solvents are 5.6 and 5.5 ns, respectively [14], and are well within the time-scale for charge injection into the conduction band of TiO_2 (sub-picosecond) [15–17]. In addition, the presence of quinones in the dye molecules allows for metal ion chelation, and suggests that these dyes will adsorb to nanoporous metal oxide surfaces [18,19]. Similar surface structures on metal oxide surfaces have been reported for anthocyanins [15].

2. Materials and methods

2.1. Chemicals

Cultures of *S. coeruleus* and *Tetrahymena* were acquired from Carolina Biological Supply Company. Hypericin (H-9295, lot #99H1231, Sigma-Aldrich) was 98% pure by HPLC (according to the supplier) and was used without further purification. Propylene carbonate (PC), lithium iodide hydrate, hydrogen hexachloroplatinic acid (HHPA, 8%),

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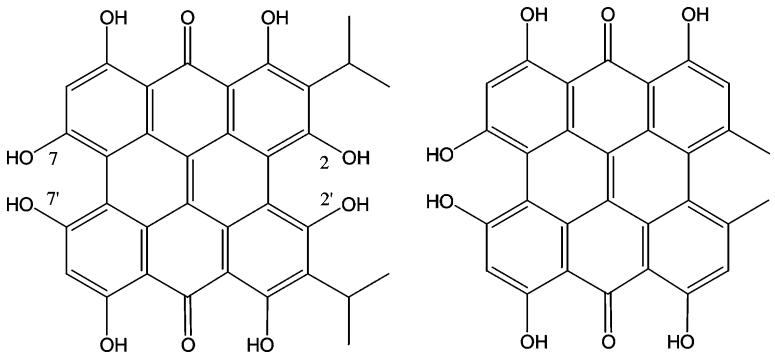

Fig. 1. Structures of hypericin and stentorin.

titanium(IV) isopropoxide, HPLC grade ethanol, and reagent grade dichloromethane were acquired from Aldrich and used as received. Electronics grade isopropanol and HPLC grade acetone were acquired from Fisher Scientific. Indium tin oxide (ITO) films on glass (50 mm × 75 mm × 1.5 mm) were obtained from Delta Technologies (Stillwater, MN, #CG-60IN-S215). ITO was cleaned by sonication for 20 min at 80°C in 80:20 (v/v) water:ethanolamine, and rinsed with 18 MΩ cm water.

2.2. Purification of the stentorin chromophore from S. coeruleus cultures

Stentorin cells were cultivated in 19-liter bottles in a dark room kept at 18–21°C. The growth medium consisted of 0.34 g/l $K_2HPO_4{\cdot}3H_2O$, 0.02 g/l $MgSO_4$, 0.013 g/l $NaNO_3$, pH 7.0. After autoclaving and cooling, 5 ml/l of 0.1 M $CaCO_3$ was added by sterile filtration. The 8–10 liter cultures received biweekly feedings of ∼5 ml *Tetrahymena*, which were cultivated on sterile media: 5 g/l proteose peptone, 5 g/l tryptone, 0.2 g/l $K_2HPO_4{\cdot}3H_2O$, pH 7.2.

Stentorin cells were harvested either by aspirating attached cells from the walls of the cultivation flasks, or by pouring off cultivation media and collecting the flocs that had settled in the flasks. Cells and flocs were concentrated by centrifugation and the supernatant replaced with a volume of absolute ethanol equal to the pellet volume. This dense suspension was extracted by sonication on ice at 50% duty cycle and 30% amplitude with a 600 W microtip probe sonicator. The resulting suspension was centrifuged (10 min at 13,000 rpm), and the supernatant removed. The supernatants of three successive extractions were concentrated by rotoevaporation and purified by two preparative thin layer chromatography steps. Stentorin was eluted from fluorophore-free silica plates using absolute ethanol and had an R_f of 0.90–0.95. Subsequently, stentorin eluted by 85/15 (v/v) dichloromethane/ethanol had an R_f factor of 0–0.10. Care was taken to remove stentorin immediately from the silica to prevent degradation of the dye. A 20-ml cell pellet yielded 1 ml of a stentorin solution in acetone with an absorbance of 0.6 AU at 612 nm measured in a 1-mm pathlength cell.

2.3. Chemical analysis of stentorin

2.3.1. ^1H NMR spectroscopy

The proton shifts observed in the ^1H NMR spectrum of the extracted dye consistent with the published spectrum [20] of Stentorin were as follows: ^1H NMR (400 MHz, DMSO-d_6,): 1.48 (12H, d); 4.04 (2H, sep); 6.57 (2H, s); 14.9 (2H, s); 15.46 (2H, s). The very broad peak previously reported for the hydroxyl groups at positions 2,2′ and 7,7′ was not seen in this study. This was most likely do to proton exchange with water in the DMSO [20].

2.3.2. HPLC analysis

The purity of the stentorin preparation was analyzed by HPLC and compared to that of a commercially available hypericin sample. Each dye (0.3–0.5 mg/ml) was dissolved in DMSO and injected (10 μl) onto a Supelcosil LC-8 analytical HPLC column (25 cm × 4.6 mm, 5 μm particle size) using a Waters 600 HPLC system (Milford, MA). Separations were obtained under isocratic conditions at a flow rate of 1 ml/min, using a 67/33 acetonitrile/water mobile phase containing 0.1% phosphoric acid. Chromatograms were generated by a Waters 996 photodiode array detector, which allowed for a full UV–visible spectral assessment (250–750 nm) of the eluted peaks.

2.4. Preparation of counter and dye-sensitized working electrodes

Platinum counter electrodes were prepared by evaporating 100 μl of 0.008% HHPA in isopropanol onto a 9 mm × 50 mm ITO electrode and sintering for 30 min at 380°C [15]. Between uses, counter electrodes were cleaned with absolute ethanol and stored in the dark.

TiO_2 colloids were prepared by a previously published method [4]. TiO_2 working electrodes were prepared by scoring a 50 mm × 75 mm × 1.5 mm sheet of ITO into 9-mm strips

with a diamond-tipped glass cutter. Two strips of Scotch tape were applied 11 mm apart and perpendicular to the scores. A drop of TiO_2 suspension was spread uniformly between the taped regions with a glass rod. When the TiO_2 had dried to transparency (after 30 min), the tape was removed and the electrodes were separated along the scores and sintered at 450°C for 1 h. Electrodes were stored desiccated in the dark.

2.5. Preparation of dye-sensitized TiO_2 electrodes

TiO_2 electrodes were warmed to 125°C to remove any surface water. After cooling to near room temperature, the electrode was immersed in 0.4 ml of dye/acetone solution with an absorbance of 0.4 AU at λ_{max} (measured in a 1-mm pathlength cell). Electrodes were soaked for 24 h, then rinsed in acetone, air dried, and stored in the dark. Solution absorbances were measured using a Varian Cary 4G UV–Vis spectrophotometer. The absorbance of dye-modified films were measured before and after photocurrent measurements to confirm stability.

2.6. Photocurrent measurements

Photovoltaic cells were assembled by clamping a 130-micron thick teflon gasket between the Pt counter electrode and the modified TiO_2 working electrode. A 9-mm diameter window cut in the gasket defined the 0.64 cm^2 working area of the device. The photovoltaic cells were illuminated by a 150-W Osram XBO 150W xenon lamp filtered by an Oriel #77250 monochromator. Lamp output profiles were acquired with a calibrated International Light IL-1700 radiometer. Photocurrents were acquired using a Keithley 6512 electrometer and measurements were made under white light (using a 395 nm cut-off filter), darkness, and every 10 nm from 400 to 700 nm. Action spectra were obtained by subtracting the dark current from the measured illuminated current and plotting the incident photon conversion efficiency (IPCE) vs. wavelength. The IPCE was calculated from Eq. (1):

$$\mathrm{IPCE}(\lambda) = \frac{(1240\,\mathrm{eV\,nm})I_{ph}}{\lambda P_0} \quad (1)$$

In this equation, I_{ph} is the incident photocurrent density in mA/cm^2, λ the wavelength of incident radiation in nm, and P_0 is photon flux in mW/cm^2. The APCE was calculated by dividing the IPCE by the light harvesting efficiency (LHE) as defined by

$$\mathrm{LHE} = 1 - 10^{-A(\lambda)} \quad (2)$$

where $A(\lambda)$ is the absorbance at λ.

3. Results and discussion

3.1. Isolation and purity of stentorin

The isolation and purification of the stentorin chromophore from *S. coeruleus* cultures was based on modified literature procedures [20]. From the HPLC analysis, both hypericin and stentorin exhibited similar elution profiles and the eluted peaks for each dye had absorbance spectra similar to previously published spectra for each dye [20]. From these analyses, it appeared that the purity of both hypericin and stentorin were greater than 90%.

3.2. Adsorption to TiO_2

Both dye molecules adsorb to TiO_2 films from acetone as characterized by the appearance of UV–Vis absorption peaks from 500 to 700 nm in the spectra of the derivatized TiO_2 films. As shown in Fig. 2, the spectrum of hypericin is noticeably red-shifted and broadened compared to solution, whereas the spectrum of stentorin is only slightly broadened compared to its solution spectrum. The absorbance maximum of the TiO_2 films at λ_{max} for both dyes is ~0.2 at the highest molar concentration used. This gives an LHE of ~45% for these dyes on the TiO_2 electrodes.

3.3. Photovoltaic measurements

Incident photon-to-current efficiencies (IPCEs) were measured in a photovoltaic cell consisting of the derivatized TiO_2 electrode and a Pt-coated ITO electrode in a sandwich

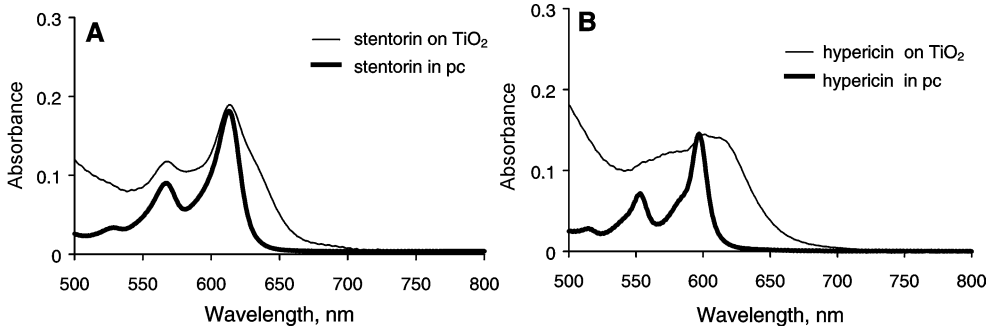

Fig. 2. Absorption spectra of stentorin (A) and hypericin (B) in PC and adsorbed to TiO_2 transparent nanocyrstalline electrodes immersed in PC.

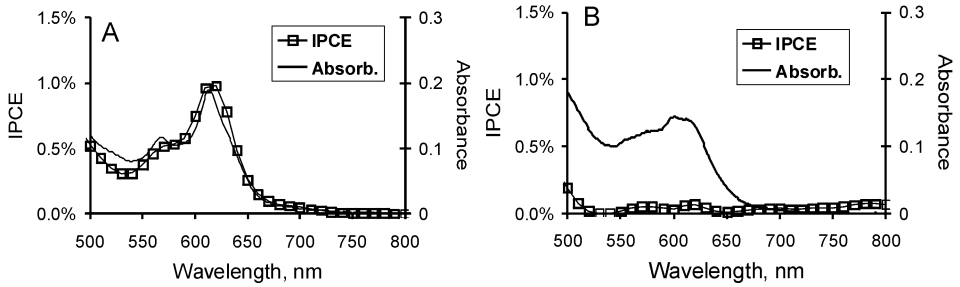

Fig. 3. (A) The photocurrent action spectrum of stentorin on TiO_2 overlaid with the UV–visible spectrum on TiO_2 measured in PC. (B) The photoaction spectrum of hypericin adsorbed onto electrodes overlaid by its UV–visible spectrum on TiO_2 measured in PC. The photoaction spectra were measured in PC 0.5 M in NaI and 0.05 M in I_2 in a thin-layer, two-electrode cell as described in Section 2.6.

configuration. The solvent was PC with LiI (0.5 M) and I_2 (0.05 M). Fig. 3 shows a plot of IPCE vs. excitation wavelength for a stentorin-derivatized TiO_2 electrode. The photoaction spectrum overlaps the absorption spectrum of the molecule adsorbed to TiO_2. Correcting for the harvesting efficiency (LHE) of the derivatized TiO_2 electrode using Eq. (2), the APCE is ~2% at 611 nm (average of three electrodes). On the other hand, the IPCE (and APCE) of hypericin is noticeably smaller by an order of magnitude with IPCE and APCE <0.1% at 598 nm.

Fig. 4 indicates that the sustained excitation at 611 nm of a stentorin-derivatized TiO_2 electrode in a photovoltaic cell displays a gradual drop (5% per 100 s) in photocurrent. The photocurrent is not regenerated in the dark. Both dyes undergo photochemical bleaching in prolonged experiments in the photovoltaic cell as noted by a decrease in absorbance of the dyes in the TiO_2 films before and after use. The dyes are also bleached on TiO_2 when exposed to laboratory lighting over the course of several days.

The red-shift and broadening of the hypericin spectrum on TiO_2 compared to solution suggests that this dye is forming aggregates on the electrode surface. Aggregation of hypericin is characterized by a red-shift and broadening of its spectrum and has been reported in solvents and in sol–gel matrices [21]. Stentorin adsorbed to TiO_2 at similar coverages displays no red-shift and only a slight broadening of the low-energy absorption band compared to solution. Structural differences between the two molecules may account for this effect. Stentorin has bulky isopropyl groups that may prevent aggregation, depending on the nature of the adsorbed layer.

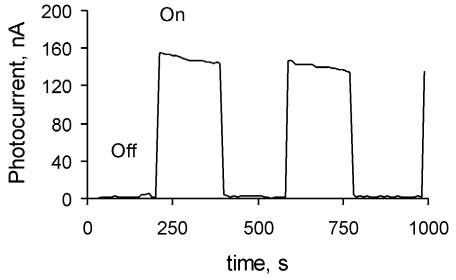

Fig. 4. The photocurrent at 610 nm of a stentorin-derivatized TiO_2 electrode as a function of time and on/off irradiance (8.5×10^{-5} W/cm^2) measured in PC 0.5 M in NaI and 0.05 M in I_2 in a thin-layer, two-electrode cell as described in Section 2.6.

The photocurrent efficiencies of stentorin-sensitized TiO_2 electrodes are comparable to previous electrodes modified by organic dyes. The overlay of the photoaction spectrum with the absorbance spectrum of stentorin is consistent with photoinduced electron transfer from the excited state of the dye molecule to the conduction band of TiO_2. Hypericin and stentorin are known to undergo photoinduced electron transfer with electron acceptors in solution [22]. The redox potential of hypericin in the singlet excited state has been determined to be ~−1.2 V vs. NHE [23] which is sufficiently negative to photoinject in the conduction band of TiO_2 (illustrated in Fig. 5) [3]. The oxidation electrochemistry of hypericin has been reported to be chemically irreversible [23], but with a peak potential at 0.95 V vs. NHE, the resulting radical cation can easily be reduced by the redox mediator. Since both stentorin and hypericin have similar photochemical properties, the origin of the differences in efficiency most likely arises from their differential tendencies to aggregate on the surface. Aggregation

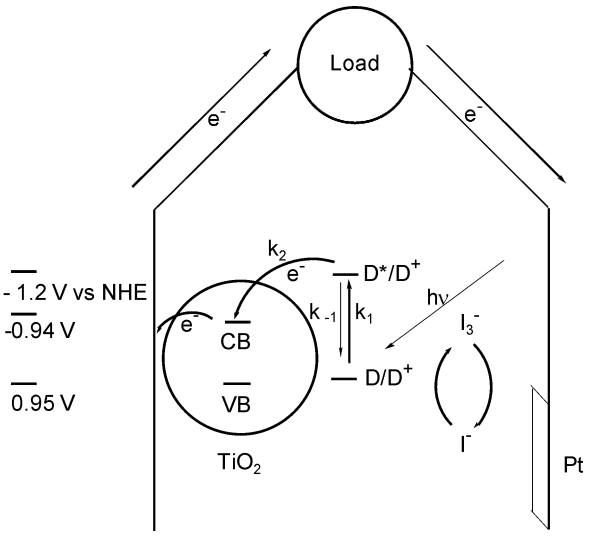

Fig. 5. Generally accepted scheme for dye sensitization of TiO_2 [3].

of organic dyes is known to rapidly deactivate excited states (k_{-1} in Fig. 5), which would compete with photoinduced electron transfer into the semiconductor (k_2 in Fig. 5).

The irreversible nature of both the decrease in the photocurrent and the decrease of absorbance of the dye on the TiO_2 films is consistent with dye degradation. While we have not investigated the mechanism for the observed photobleaching, several mechanisms may account for this observation. Hypericin is known to be a photosensitizer for singlet oxygen with a relatively high quantum yield [24], however, there is little literature precedent that the dye reacts irreversibly with singlet oxygen [10]. Degradation of the dye may also be caused by exhaustive oxidation and re-reduction of the dye. The I^-/I_3^- mediator may not be able to re-reduce the dye efficiently (i.e. a high percentage of the oxidized dye returning to the original reduced state), since the oxidation of hypercin is reported to be chemically irreversible [23].

In conclusion, because the photocurrents measured for the hypericin dye-sensitized TiO_2 electrode are so small, hypericin is an unlikely candidate for commercial dye-sensitized photovoltaic devices. The gradual decay of the photocurrent in prolonged photovoltaic operations for the stentorin-derivatized TiO_2 electrode also makes the use of this dye an unlikely candidate for dye sensitization. However, the more efficient performance of stentorin vs. hypericin is encouraging. The fact that the degree of surface aggregation can be controlled by slight structural modifications is an encouraging result, because it suggests that a similar strategy might be used to improve the photovoltaic performance of electrodes sensitized with other organic dyes.

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