

LETTERS

Insights into Dye-Sensitization of Planar TiO₂: Evidence for Involvement of a Protonated Surface State

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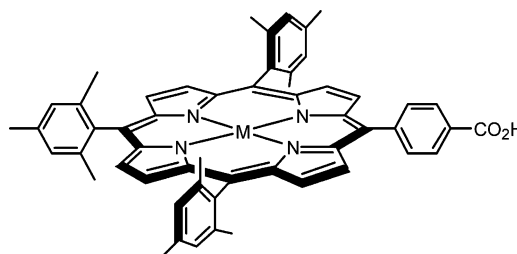
Received: June 24, 2003; In Final Form: August 20, 2003

The pH dependence of sensitized photocurrent for porphyrin-derivatized planar TiO₂ films in regenerative photoelectrochemical cells is reported. The porphyrin sensitizers 5-(4-carboxyphenyl)-10,15,20-trimesitylporphinatozinc(II) (**1**), 5-(4-carboxyphenyl)-10,15,20-trimesitylporphine (**2**), and 5-(4-carboxyphenyl)-10,15,20-trimesitylporphinatoptin(II) (**3**) were studied. The TiO₂ conduction band edge potential (E_{CB}) shifted from -0.43 V to $+0.16$ V vs Ag/AgCl_(aq) from pH 12 to pH 2, a shift of 59 ± 2 mV per pH unit. Excited-state potentials ($E_{1/2}^{+/*}$) of **1–3** ranged from -1.57 to -0.91 V vs Ag/AgCl_(aq), well negative of E_{CB} . Nonetheless, for all three porphyrins a 10-fold increase in the magnitude of sensitized photocurrent was observed upon acidification of the electrolyte from pH 12 to pH 2. Photocurrent vs pH data did not depend on the sensitizer excited-state potential. A model is proposed wherein protonation of a surface state is required for charge compensation and photocurrent production. Therefore, the magnitude of sensitized photocurrent is determined by surface protonation/deprotonation equilibria.

Electron-transfer processes at the semiconductor/electrolyte interface are fundamental to the operation of photoelectrochemical cells.^{1–7} The composition of the electrolyte is known to have profound effects on semiconductor energetics and the efficiency of interfacial electron-transfer processes.^{8–10} Understanding and controlling these effects is important with regard to optimizing the overall efficiency of photoelectrochemical cells. Here we report the photoelectrochemical properties of planar TiO₂ electrodes sensitized to visible light with porphyrin compounds. The results provide compelling evidence for the involvement of a protonated surface state in the light-to-electrical energy conversion process.

The porphyrin sensitizers utilized are shown in Chart 1. Their syntheses will be reported in a separate manuscript. Single-crystal rutile TiO₂ (100) was purchased from Princeton Scientific. Thin films of TiO₂ were prepared by adaptation of the method of Ting et al.^{11,12} Titanium was sputter deposited onto FTO-coated glass (8–20 Ω /square, Libby Owens Ford) at room

CHART 1: Structures of the Porphyrin Sensitizers, 1: M = Zn(II), 2: M = H₂, and 3: M = Pt(II).



temperature followed by oxidation at 450 °C for 30–60 min in air. Photoelectrochemical measurements were made in a 3-electrode, single-compartment cell with a TiO₂ working electrode, Pt mesh or Pt-coated FTO counter electrode, and Ag/AgCl_(aq) NaCl (3 M) reference or Ag pseudoreference electrode. The electrolyte was 0.1 M aqueous Na₂B₄O₇, the pH of which was

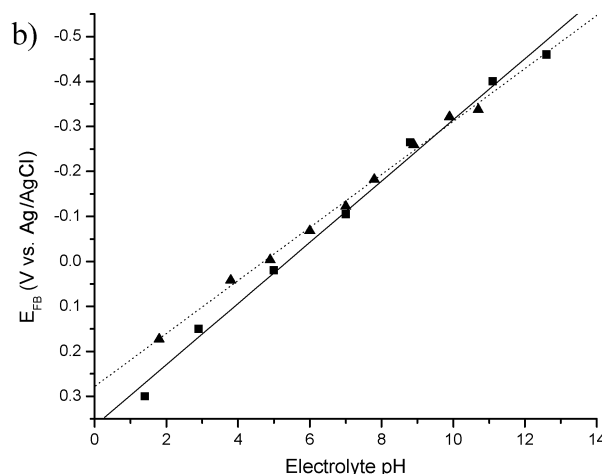
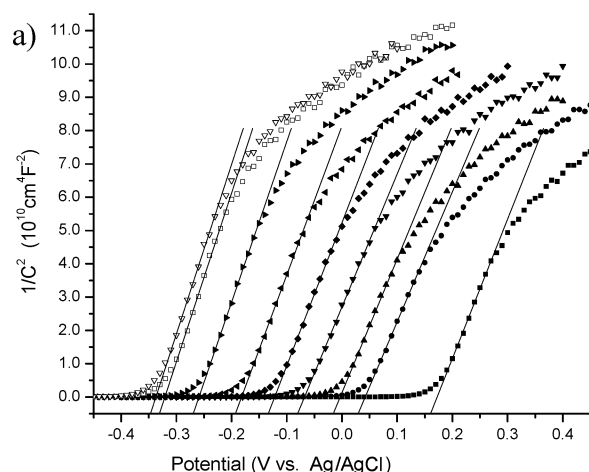


Figure 1. (a) Mott–Schottky plots for an underivatized TiO_2 film with frequency of 100 Hz and peak-to-peak voltage oscillation of 3 mV. Electrolyte pH = 1.8 (■), 3.8 (●), 4.9 (▲), 6.0 (▼), 7.0 (◆), 7.8 (left-pointing solid triangle), 8.9 (right-pointing solid triangle), 9.9 (□), and 10.7 (▽). Superimposed are linear fits of the data. (b) TiO_2 flat-band potential (E_{FB}) vs electrolyte pH for an underivatized TiO_2 film. E_{FB} was estimated from the onset potentials of band gap photocurrent (■, slope = 68 ± 3 mV/pH) and from the x -intercepts of Mott–Schottky plots (▲, slope = 59 ± 2 mV/pH).

adjusted with HCl and NaOH. Sensitized photocurrents were measured with 0.05 M hydroquinone as an electron donor. Photocurrent action spectra were measured at constant positive bias at potentials corresponding to saturation sensitized photocurrent, as determined from linear sweep voltammetry measurements under chopped (~ 1 Hz) Soret band illumination.

Flat-band potentials (E_{FB}) of TiO_2 films were estimated from Mott–Schottky analysis of impedance spectroscopy data^{13,14} (Figure 1a) and from photocurrent onsets. E_{FB} values determined from the two methods were in close agreement. Mott–Schottky plots ($1/C_p^2$ vs V) were obtained at 100 and 10 Hz frequencies, which fall within the capacitive regime of the Bode plot for each electrolyte pH. Donor densities on the order of 10^{18} cm^{-3} were calculated from Mott–Schottky slopes, implying that the conduction band edge potential (E_{CB}) lies within 120 mV of E_{FB} .^{15–17} E_{FB} varied linearly with electrolyte pH, with the expected Nernstian slope of 59 ± 2 mV/pH (Figure 1b). E_{FB} varied from +0.16 to -0.43 V vs Ag/AgCl from pH 2 to 12.

Adsorption isotherms for porphyrin binding to TiO_2 were measured in toluene and were well described by the Langmuir adsorption isotherm model,¹⁸ yielding surface adduct formation constants of 10^5 M^{-1} and saturation surface coverages of $5\text{--}10 \times 10^{-10} \text{ mol/cm}^2$. Attempts to adsorb the tetramesityl analogue of **1** yielded no measurable surface coverage. Absorption spectra of porphyrin-modified TiO_2 slides immersed in aqueous solution were pH independent, indicating that the porphyrins were stable toward desorption or diacid formation.^{19,20}

The reduction potential ($E_{1/2}^{+/0}$) of surface-bound porphyrin **1** was pH dependent, shifting 15 ± 6 mV/pH, consistent with previous measurements of phthalocyanine dyes attached to nanocrystalline TiO_2 .²¹ The excited-state reduction potential ($E_{1/2}^{+/*}$) was estimated by the standard Rehm–Weller equation using the emission spectra of the porphyrins bound to ZrO_2 to estimate E_{00} . The $E_{1/2}^{+/*}$ values of **1–3** span a range of 660 mV. The potential difference between $E_{1/2}^{+/*}$ and E_{CB} determines the thermodynamic favorability of electron injection. For all three porphyrins, $E_{1/2}^{+/*}$ is more than 400 mV negative of E_{CB} , even at basic pH's where E_{CB} is shifted most negative. Therefore, assuming a total reorganization energy of 200 meV,¹⁷ activationless pH-independent, excited-state electron injection is theoretically expected for all the porphyrins.

In contrast to this expectation, the magnitude of the photocurrent was found to increase by about 10-fold at pH < 5, independent of which porphyrin or TiO_2 material (thin film or

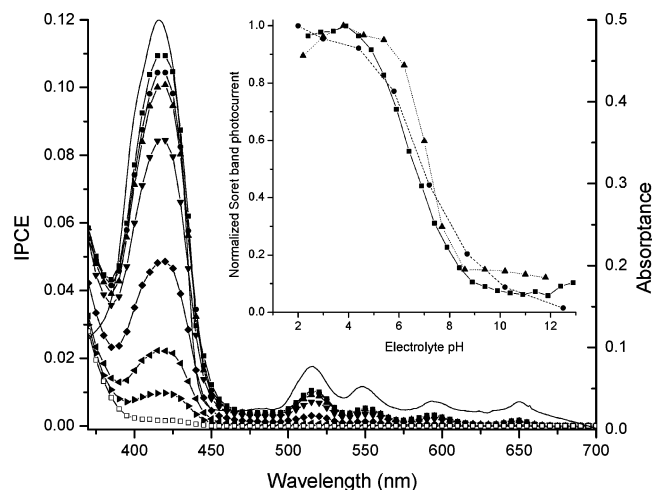


Figure 2. Photocurrent action spectra of a **2**-modified planar TiO_2 film at electrolyte pH's of 2.0 (■), 3.0 (●), 4.4 (▲), 5.8 (▼), 7.2 (◆), 8.7 (left-pointing solid triangle), 10.2 (right-pointing solid triangle), and 12.5 (□). Superimposed is the absorbance spectrum of the film (—). IPCE = Incident photon to current efficiency. *Inset:* Plots of Soret band photocurrent vs electrolyte pH for **1** (■), **2** (●), and **3** (▲).

TABLE 1: Summary of Sensitizer Energetics

sensitizer	$E_{1/2}^{+/0}$ (V) ^{a,b}	E_{00} (eV)	$E_{1/2}^{+/*}$ (V) ^{a,b}
1	+0.54	2.11	−1.57
2	+1.09	2.10	−1.01
3	+1.08	1.99	−0.91

^a For **1**, pH 12 data are reported. For **2** and **3**, the potentials were measured in CH_3CN . ^b Potentials are reported vs Ag/AgCl_(aq).

single crystal) was used (Figure 2 inset). Photocurrent action spectra (Figure 2) agreed with the measured absorbance spectra and were also pH independent. The observed proton dependencies were reversible and independent of hydroquinone donor concentration. The decrease in photocurrent at basic pH's cannot be attributed to decreased hydroquinone oxidation kinetics, because hydroquinone oxidation is more favorable at high pH.²² Control experiments using porphyrin-modified TiO_2 with iodide as the electron donor revealed the same pH dependence.

The observation of sensitizer-independent photocurrent vs pH plots (where no proton dependence is expected thermodynamically) is at odds with the accepted dye sensitization mechanism. Clark and Sutin also reported significant enhancement of

photocurrent efficiency at low pH when none was expected.¹⁷ To rationalize these observations, one must invoke a mechanism that incorporates a proton dependence of something other than the conduction band edge potential or sensitizer excited-state potential. Lyon and Hupp have reported that electrochemical reduction of nanocrystalline anatase TiO₂ films is accompanied by reversible proton uptake from aqueous solution.^{23,24} They attribute the effect to proton adsorption or intercalation driven by charge compensation of conduction band electron density. Similarly, we propose that protonation of a surface site is required for charge compensation of injected electrons. Therefore, the data presented in Figure 2 represent a Bronsted acid–base titration of a localized surface state abbreviated as Ti^{IV}–OH₂⁺/Ti^{IV}–OH. The midpoint of the sensitized photocurrent onset data corresponds to the pK_{a1} of Ti^{IV}–OH₂⁺. A pK_{a1} value of approximately 6.5 is in reasonable agreement with Schindler and Gämsjäger's value of 5.0.²⁵ Reduction of the Ti^{IV}–OH₂⁺ state is necessary for efficient charge compensation and photocurrent production. If this state is within the forbidden energy gap, reduction almost certainly occurs by a conduction band electron. However, our data are more consistent with a mechanism in which the excited state directly reduces a protonated surface state whose energy lies well above E_{CB}.

In conclusion, we have reported pH-dependent sensitized photocurrents for porphyrin-derivatized planar TiO₂ films. Sensitized photocurrent was “turned off” at electrolyte pH's above 12, even though activationless electron injection was energetically favored. Plots of photocurrent vs electrolyte pH were invariant with respect to the sensitizer excited-state reduction potential. These observations are most consistent with the sensitized photoreduction of a protonated surface state. The proton is apparently required for charge compensation and photocurrent production. Therefore, the charge collection efficiency is directly related to protonation/deprotonation equilibria of the TiO₂ surface. Future studies will focus on identifying the energetic position of this protonated state and the details by which it is reduced.

Acknowledgment. The porphyrin complexes **1** and **2** were provided by Prof. J. S. Lindsey. We thank Profs. Lindsey, D. Holten, and D.F. Bocian for helpful insight. This research was funded by the National Renewable Energy Laboratory.

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