compounds, but in the fully substituted compounds AX_4 etc., where the segregation mechanism is somewhat restrained by symmetry, the s orbital contributions are again higher, though not so high as in the hydrides themselves. The inability of the perturbation model to deal with features of molecular structure such as the tendency for s orbital density to be heavily utilized in a nonbonding role stands out clearly, there being no tendency for the s and p orbital contributions to bonding in A–X and A–H bonds to vary at all with change of substituent once H has been replaced by X.

Results of A–H and A–X overlap population comparisons in AH_2X and AHX group molecules are not given. At the optimum geometries of the molecules in these series the bond angles are close enough to 90° to ensure that the central-atom s orbital is almost fully occupied, the contribution to the overlap populations of both A–X and A–H bonds being small and usually negative. The possibility of negative involvement in bonding cannot be accommodated in the perturbation theory model, and the results do not conform to the Walsh–Bent rule.

Comparisons on an intermolecular basis are now considered. Most may be made from entries in Tables I–III. Data in apparent conformity with the hypothesis are encountered in a few cases, but most are like those described in the previous paragraph for intramolecular comparisons. Similarly, it is hard to discern any trends in the data for the fully substituted AX_3 and AX_2 series compounds that could be construed in favor of the hypothesis. (The relevant results appear in Tables VII and VIII.)

The infrequency of comparisons that conform to the Bent–Walsh rule is easily predicted from the earlier results. The inability of the perturbation theory treatment to accommodate the important nonbonding role of the central-atom s orbital has already

been noted. In addition, there is the difficulty that overlap integrals of both the s and p orbitals together with the orbital energies must all enter the reckoning when relative s and p orbital usage is being estimated; the difficulty of accounting for this with a single parameter, electronegativity, is obvious. Although there is a relationship between bond angle and s and p orbital utilization, the nature of the relationship invalidates any argument that uses geometrical data to estimate participation of s and p orbitals in bonding.

Dye-Loaded Polymer Electrodes. 2. Photoelectrochemical Sensitization of Croconate Violet in Polymer Films

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Abstract: Enhanced sensitized photoelectrochemical effects are observed upon dispersal of croconate violet (**1**), an anionic pseudooxocarbon dye, in an adherent polymer coating (poly(4-vinylpyridine)) on a highly doped tin oxide electrode. Benzoquinone, functioning as a supersensitizer, enhanced cathodic photocurrent generation by an order of magnitude. Characteristics of a photoelectrochemical cell employing such a dye-loaded polymer electrode have been investigated. Evidence is presented that the dye-loaded polymer coating can mediate electron transfer between the electrode surface and a dissolved redox couple.

Introduction

Exploration of novel photoelectrochemical systems for solar energy conversion has been a subject of great interest. Marked improvements in photostability and efficiency of solar energy conversions have been made with light-responsive inorganic semiconductors[1] and with chemically modified electrodes.[2]

An attractive technique for the extension of the absorptive range of such materials involves the attachment of organic dyes of high extinction coefficients to the irradiated electrode surface, and

several studies seeking to examine the performance of photovoltaic systems involving organic dyes have been reported.[3-6] When the dyes are reversibly adsorbed onto the electrode, however, energy losses from the excited state and photoinduced instability often limit practical applications of these systems. Structural modifications of the absorptive dye or environmental changes at the interface could, in principle, obviate some of these problems.[7] For

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example, recent work in our laboratory has shown that the fluorescence yield of an anionic oxocarbon dye could be increased (by nearly an order of magnitude) by microencaging the dye within a polymer.[8] We reasoned that by judicious synthetic control of the environment at the electrode–electrolyte interface we might achieve improved photoelectrochemical efficiencies. To guide such efforts, we require a more complete understanding of the basic photoprocesses and of the mechanism of generation of photocurrents in these systems.

The absorption and redox properties of a new class of dyes, condensation derivatives of oxocarbons, have been reported recently.[9,10] Of these, croconate, e.g., **1–3**, and squarylium, e.g., **4**, dyes also have been found to have excellent semiconductor

1

croconate violet

2

croconate blue

3

lithium croconate

4

squarate yellow
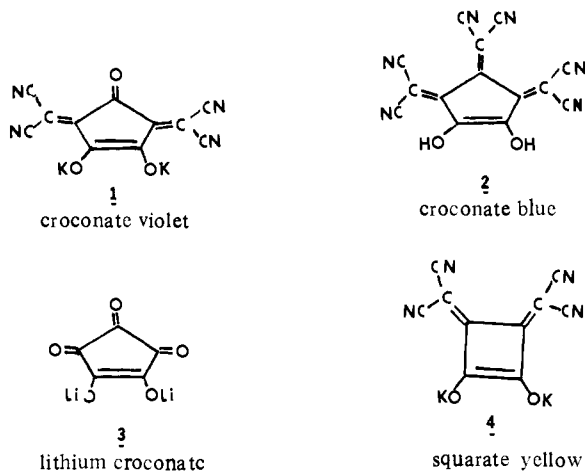
properties and strong absorption in the visible.[10] Even with ideal chemical properties, a dye can function as an effective photosensitizer only when it is strongly adsorbed onto the surface of the electrode. Since oxocarbons **1–4** are highly soluble in water and in many nonaqueous solvents, their use has been restricted. We have recently reported, however, that croconate violet (**1**) can be incorporated into a protonated poly(4-vinylpyridine) film. Such a dye-loaded film, when coated on a SnO_2 electrode, was stable and electroactive in the aqueous medium and exhibited some interesting electrocatalytic properties.[11]

We now report that we can use such dye-loaded polymers to increase the photoelectrochemical responsiveness of large-band-gap semiconductors. We describe here an extremely simple route for holding sufficient quantities of dye for effective sensitization near the electrode surface. Our investigation of the electrochemical properties of these dye-loaded, polymer-coated semiconductors and their use as sensitizers for photoelectrochemical effects represent the first study of anionic organic dye sensitization of polymer-coated electrodes. A detailed discussion of the photoelectrochemistry of this dye–polymer system follows.

Experimental Section

Materials. The synthesis and purification of the croconate and squarylium dyes have been reported earlier.[9] Poly(4-vinylpyridine) (PVP) from Polysciences Inc. was used as supplied. Ethanol was USP reagent grade. Millipore water was used to prepare all aqueous solutions. Unless otherwise stated, all solutions were deoxygenated by purging with N_2 for 15–20 min. All other chemicals were analytical reagents.

Preparation of Dye-Loaded Polymer Electrodes. n-SnO_2 electrodes were cut from antimony-doped NESA glass (PPG Industries) and were cleaned successively in HNO_3 (24 h), Alconox detergent solution (30 min), 2-propanol (5 min), distilled water (30 min), and saturated NaOH (24 h).[12] Electrodes were washed thoroughly with water and dried in

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an oven at 120 °C for 24 h. The conductive surface of the glass plate was then polymer-coated by applying a solution of 1% PVP in ethanol and allowing the solvent to evaporate. Attempts to prepare thicker films by this technique gave unevenly coated electrodes which in turn gave irreproducible behavior. The PVP-coated electrode (SnO_2/PVP) was then soaked for 15 min in an aqueous solution of the dye (ca. 1 mM) buffered to pH 3.3 with 0.1 M CF_3CONa and CF_3COOH. The electrode was then removed and was washed with Millipore-filtered water. Coloration of the polymer film confirmed the incorporation of the dye. Such an electrode will be referred to as SnO_2/PVP/dye. The thickness of the dry film, determined with a Sloan Dektak surface profilometer, was 0.1 μm. Typically, a surface coverage of approximately 4–8 × 10^{-9} mol/cm^2 of dye (except with croconate blue where the incorporation of the dye was very poor) in the polymer film is obtained by this procedure. Dye concentrations of up to 0.8 M can be attained in the film.

Electrochemical and Photoelectrochemical Measurements. The electrochemical cell was a standard three-compartment cell with Pt foil (2 cm^2) as counterelectrode and a saturated calomel electrode (SCE) as reference. Photovoltages and photocurrents were measured with Kiethley (Model 177) digital multimeter. Cyclic voltammograms were recorded with a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat, a PAR Model 175 universal programmer, and a Houston Instruments x-y recorder. The light source for photoelectrochemical measurements was a collimated beam from a 250-W halogen lamp, filtered with a 460-nm Corning cutoff filter. Light intensity at the cell face was 120 mW/cm^2. For excitation with selected wavelengths, a Bausch and Lomb high-intensity grating monochromator was inserted into the path of the illumination beam.

Spectroelectrochemical Measurements. A Teflon block was machined to accommodate an 0.5 cm × 3 cm SnO_2 plate (working electrode), a Pt wire (counterelectrode), and Ag wire (reference). This Teflon block also had provision for bubbling N_2 into the cell. The whole assembly could be inserted into the sample chamber of the fluorimeter. Fluorescence of SnO_2/PVP/**1** was measured at front face at various applied potentials.

Results

Photoelectrochemical sensitization by croconate violet (**1**) has been investigated in a systematic way. Where possible, a comparison with other oxocarbon derivatives **2–4** has also been made. Such an approach should facilitate exploration of desirable characteristics of other organic systems as sensitizers in solar energy conversion.

Electrochemistry of 1. When considering organic dyes as potential photovoltaic transducers, it is important to have characterized their electrochemical properties. Redox potentials and chemical reversibility of several oxocarbon dyes at metal electrodes have already been reported.[10,13] In this section we consider how this electrochemical behavior is altered by incorporating the dyes into a PVP film precoated on a semiconductor electrode. At pH 3, the pendant pyridines are highly protonated, and anionic dyes should be strongly held within the polymer matrix by strong electrostatic interactions. Only croconate blue, the largest and most heavily substituted of these dyes, was not efficiently taken up into the polymer coating. Hence, electrostatic interactions between the anionic dyes and cationic PVP are probably very significant for binding within the polymer matrix.

Cyclic voltammograms of various dye-loaded polymer electrodes are given in Figure 1. These characteristics were similar to the cyclic voltammograms in homogeneous solution at metal electrodes;[11,13] i.e., incorporation of the dyes into the film did not dramatically alter their usual electrochemical properties. However, significant protonation of the PVP film was required in order to attain complete electroactivity of the incorporated dye. Similar effects have been discussed by Anson and co-workers in their electrochemical studies of inorganic complexes held electrostatically in polymer films.[14]

Croconate violet (**1**) and squarate yellow (**4**) exhibited quasireversible oxidation–reduction current peaks at about +0.6 V vs. SCE. Pen-width reproducibility of repeated cyclic voltammetric scans confirmed the stability of these electrodes. However, on cycling SnO_2/PVP/croconate blue, (**2**), reversible oxidation–reduction peak currents could be seen only in the initial scan. When

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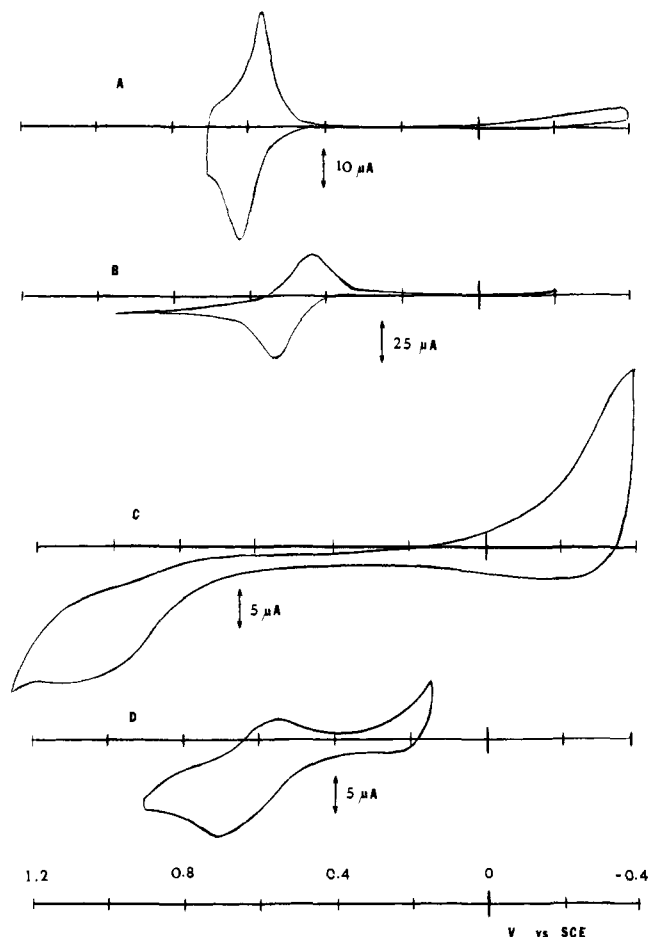
Dye-Loaded Polymer Electrodes

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Figure 1. Cyclic voltammograms of dye-loaded PVP-coated SnO₂ electrodes: (A) **1**, (B) **4**, (C) **3**, (D) **2** (film thickness, 0.1 μm; electrolyte, 0.1 M CF₃COONa, pH 3).

Figure 2. Cyclic voltammograms for the quinone (Q)/hydroquinone (H₂Q) couple at n-SnO₂ at various stages of modification of 0.1 M CF₃COONa, pH 3: (A) n-SnO₂/PVP/**1** with no Q/H₂Q; (B) n-SnO₂ in 4 × 10⁻⁵ M H₂Q; (C) n-SnO₂/PVP in 4 × 10⁻⁵ M H₂Q; (D) n-SnO₂/PVP/**1** in 4 × 10⁻⁵ M H₂Q.

scanned successively, these current peaks quickly disappeared, indicating the depletion of **2** from the polymer film. Lithium croconate (**3**), though successfully incorporated into the protonated PVP film, exhibited irreversible oxidation waves at +1.0 V vs. SCE. This irreversibility will limit the utility of **2** and **3** in dye-loaded polymer electrodes.

Mediated Electrochemical Reactions. Many different interesting properties of polymer-coated electrodes have been discovered recently.[11,15-18] In particular, the possibility that such materials might mediate electron transfer between the electrode surface and a dissolved redox couple is particularly intriguing. We find that mediated electron transfer for the oxidation of dissolved hydroquinone (H₂Q) can be achieved on our dye-loaded polymer-coated electrode (SnO₂/PVP/**1**).

Figure 2A shows the cyclic voltammogram of SnO₂/PVP/**1** in an aqueous solution of 0.1 M CF₃COONa (pH 3.3). Figures 2B and 2C show the oxidation of hydroquinone at a native SnO₂ and at a SnO₂/PVP electrode, respectively. The presence of a protonated PVP film on SnO₂ resulted in shift of oxidation of H₂Q to more positive potentials. Such a shift in oxidation peak should be expected if the PVP film coated on the electrode acts as a barrier for the diffusion of H₂Q from solution to the electrode surface. When SnO₂/PVP/**1** was scanned in the same solution, oxidation of H₂Q occurred rapidly at the potential at which dye **1** is oxidized. The anodic peak current in Figure 2D was ap-
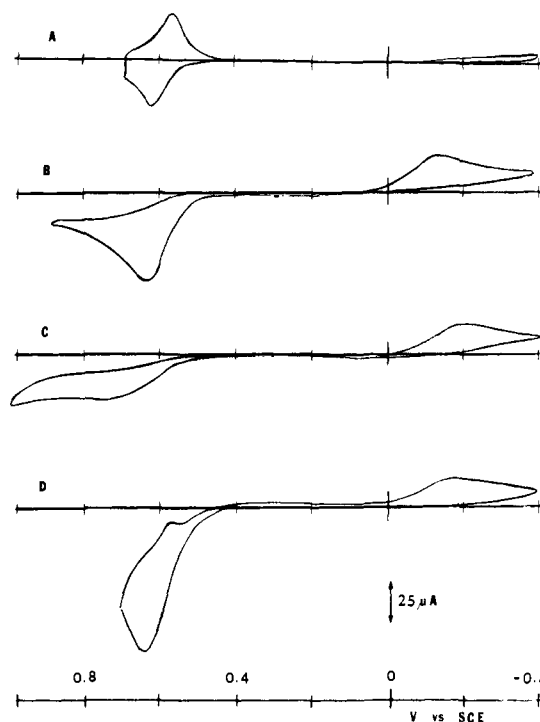
proximately equal to the sum of the analogous currents observed in Figures 2A and 2B. No reduction peak corresponding to the reduction of oxidized dye **1** (as seen in Figure 2A) could be seen in the reverse scan. This clearly demonstrated that the oxidized dye in the polymer film was able to oxidize H₂Q. Similar behavior has also been reported by Oyama and Anson for the oxidation–reduction of Feⁱⁱ/Feⁱⁱⁱ at a pyrolytic graphite electrode coated with PVP and loaded with IrCl₆³⁻.[19] SnO₂/PVP/**1** was also found to mediate electron transfer during the oxidation of Feⁱⁱⁱ by electrochemical cycling. The capability of similar dye-loaded polymer films in mediating electron transfer could find practical applications in the mechanistic interpretations of supersensitization or in defining electrocatalysis or electron transport in membranes.

Spectroelectrochemistry of 1. The fate of excited states of dye molecules held within a polymer matrix adsorbed on a semiconductor electrode poised at various applied potentials is unknown. The reversible electrochemical behavior of SnO₂/PVP/**1** makes it an ideal candidate for such a study. Accordingly, SnO₂/PVP/**1** was subjected to various anodic potentials while simultaneously monitoring the fluorescence from the excited dye **1**. Emission and excitation spectra of SnO₂/PVP/**1** at 0.45 V vs. Ag are shown in Figure 3. No distinct changes in the excitation or emission maxima could be seen at applied potentials ranging between 0.45 V (corresponding to the oxidation peak of **1** in PVP film) and 0 V vs. Ag. Thus, the absorption and emission characteristics of the oxidized form of dyes **1** are not significantly shifted from those of the dye itself. However, an increase in the fluorescence intensity was seen as **1** became oxidized. Apparently, therefore, the oxidized form of **1** has a higher fluorescence efficiency than does **1** itself. A typical plot of fluorescence intensity against applied potential as the electrode is reversibly cycled between 0 and 0.5 V is shown in Figure 4. As **1** in the PVP film was oxidized electrochemically, an increase in the fluorescence yield was seen, and in the reverse scan when the oxidized form of **1** was reduced, the original level of fluorescence was recovered. This observation was parallel to the cyclic voltammetric behavior seen with SnO₂/PVP/**1** under identical conditions. Similar spectroelectrochemical observations

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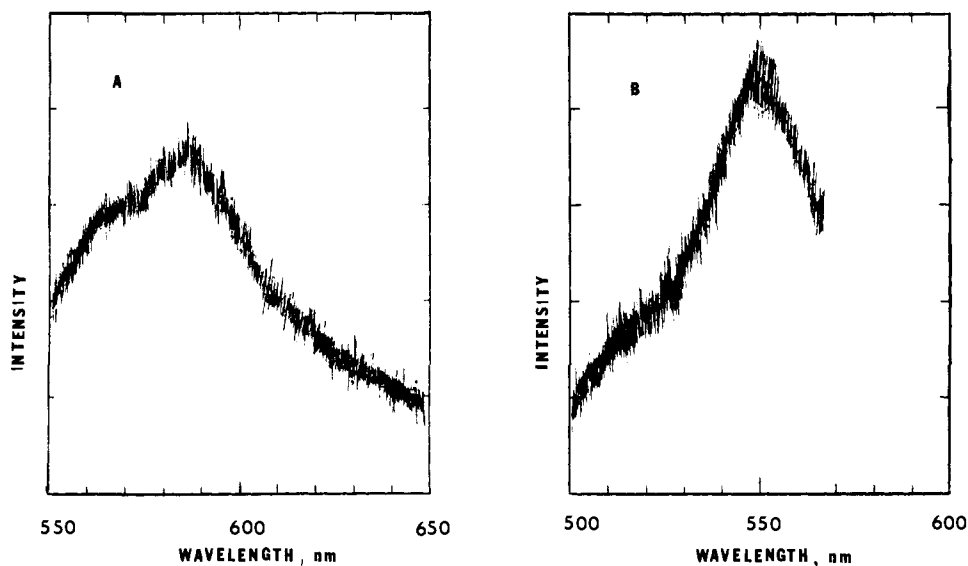(19) Oyama, N.; Anson, F. C. *Anal. Chem.* **1980**, *52*, 1192.

Figure 3. (A) Emission spectrum (ex: 530 nm) and (B) excitation spectrum (em: 600 nm) of $SnO_2/PVP/1$ at an applied potential of 0.45 V vs. Ag wire (electrolyte: 0.1 M CF_3COONa, pH 3).

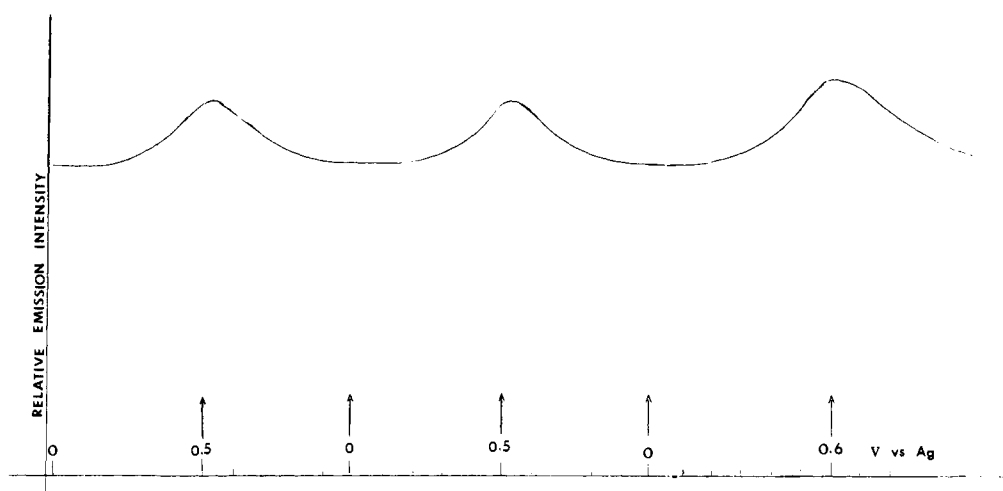**Figure 4.** Fluorescence emission of $SnO_2/PVP/1$ vs. applied electrode potential cycled between 0 and 0.5 V (vs. Ag) with front face measurements (electrolyte: 0.1 M CF_3COONa, pH 3; ex, 550 nm; em, 580 nm; scan rate 2 mV/S).

have been reported by Buttry and Anson with $Ru(bpy)_3^{2+}$–loaded Nafion films coated on SnO_2.[20] More detailed experiments are necessary to understand the details of photo- and electrocoupled processes at modified electrodes, but this preliminary observation establishes that spectral monitoring of emission behavior can provide useful adjunct information on redox reversibility.

Photoelectrochemistry of 1 in Dye-Loaded Polymer Coatings. Of the many organic semiconductors considered so far, merocyanine and squarylium dyes are thought to display attractive photovoltaic properties,[6] and phthalocyanine films coated on conductive surfaces[21] have been reported to exhibit useful photoelectrochemical features. Quantum conversion efficiencies of these organic photovoltaic devices, however, have remained unfortunately low.

The usual method for forming the sensitizing films has involved either vacuum sublimation or evaporation of the solvent after applying dye solution on a conductive surface. One of the major problems encountered in these techniques is the unavoidable aggregation of the dye. This association often leads to undesirable photophysical properties, e.g., self-quenching and excited-state annihilation.[22]

Another technique which has been employed successfully recently involves covalent attachment of the sensitizing dye to the electrode surface.[12,23] This method, though quite useful for inducing electrochemical effects and for studying mechanisms of catalysis, is not effective for attaching sensitizing dyes since covalent bonding leads to only monolayer coverage and hence to relatively inefficient light gathering near the electrode surface.

Our present technique, the loading of highly absorptive dyes into polymer coatings on electrodes, could in principle bring useful quantities of the sensitizing dye to the electroactive surface while simultaneously solving problems induced by dye aggregation. By incorporating the anionic dyes into a protonated polymer film precoated on a conducting SnO_2 surface, we effectively minimize interaction between dye molecules. The resulting films can be regarded as statistical equivalents of several monolayers, an aggregate in which charge transfer might occur by electron hopping,[15-18] and the mediated electrochemical reactions discussed above show that our surface modifications still allow for normal levels of electroactivity.

With this surface modification technique, we can also employ water-soluble dyes. With the usual vacuum deposition techniques, water-soluble species would not adhere to the surface after in-

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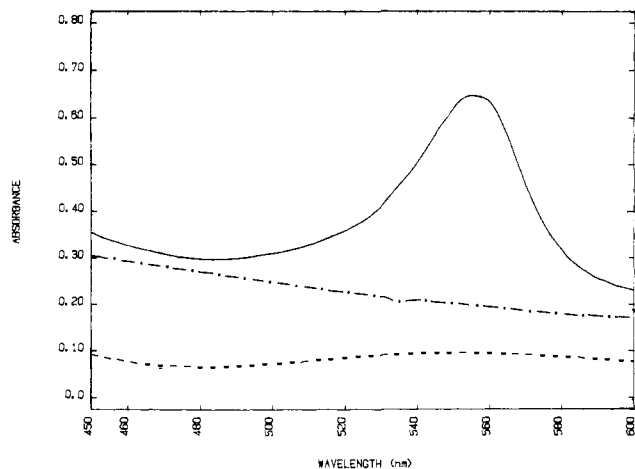
Figure 5. Absorption spectra of transparent n-SnO$_2$ electrodes at various stages of modification: (- -) native SnO$_2$; (-·-) SnO$_2$/PVP; (—) SnO$_2$/PVP/1.

Table I, Photoelectrochemical Effects at Dye-Loaded PVP Film Coated on n-SnO$_2$ Electrodes[a]

dye[b]	photo-potential, ΔV, mV	short-circuit current, Δi, μA
no dye	~0	~0
croconate violet	50	0.1
squarate yellow	45	0.08
croconate blue[c]	−30	−0.05
lithium croconate	~2	<0.01

[a] Electrode (2 cm^2) was illuminated with λ >460 nm (120 mW/cm^2) without applied bias. [b] Electrolyte was 0.1 M CF$_3$COONa (pH 3). [c] Very little dye was incorporated into the film.

Table II, Effect of Dye Concentration in the Polymer Film Coated on n-SnO$_2$

surface coverage[a] of 1 × 10^{-9} mol/cm^2	photovoltage, ΔV, mV	photocurrent, Δi, μA	
		front face	back face
1	60	0.5	0.5
4	60	3.0	3.0
6	52	3.5	3.8

[a] Film thickness = 0.1 μ. [b] Electrolyte: 10^{-2} M benzoquinone, 10^{-5} M hydroquinone, 0.1 M CF$_3$COONa (pH 3).

troducing aqueous electrolytes, and electrochemical or photoelectrochemical catalysis would be obviated. Since our dyes are electrostatically bound to the strongly adsorbed polymer, however, the dyes can be effectively localized near the electrode even in the presence of aqueous electrolytes, and electrochemical effects can be observed.

A typical absorption spectrum of SnO$_2$/PVP/1 is shown in Figure 5. The absorption spectrum of dye 1 incorporated into the polymer film closely resembles that observed in solution. Aggregation in these films was minimal, since its absorption band is unbroadened. However, the absorption maximum of SnO$_2$/PVP/1 (560 nm) is red-shifted compared with that observed for the dye in ethanol. The effect of the polymeric environment on the emission and absorption characteristics of the dye has been discussed elsewhere.[8]

Photoelectrochemical effects observed with our oxocarbon dyes loaded into poly(vinylpyridine)-coated tin oxide are given in Table I. Croconate violet (1) and squarate yellow (4) both exhibited photocurrent and photovoltage values of about 0.1 μA and ~50 mV, respectively, in the absence of any added redox couples. Much smaller currents were observed with lithium croconate (3), probably because of poor light absorption by 3 at wavelengths longer than 460 nm. Except with croconate blue (2), these dye-loaded polymeric coatings produced cathodic currents upon excitation. The anodic photocurrent observed with 2 is consistent with the weak interaction with PVP with 2 described above, and

the mechanics of generation of photocurrent is apparently different from that observed with the other members of this series. Croconate violet (1) was taken as the representative of these oxocarbon dyes, and the photoelectrochemistry of SnO$_2$/PVP/1 was examined in greater detail.

More stable photocurrents were seen when a redox couple such as O$_2$, Fe^{III}/Fe^{II}, or benzoquinone/hydroquinone (BQ/H$_2$Q) was present in solution. Figure 6 shows the response of photocurrent to illumination in the presence of Q. Generation of photocurrent was instantaneous and was quite steady during a short period of illumination. Over a longer period of illumination a slow decay in photocurrent was seen. A decrease of 30% in short circuit current was noted when the illumination was extended for 30 min. On interrupting the illumination, the photocurrent decayed back to the original dark current value.

Increasing concentrations of the dye in the film resulted in improved photoelectrochemical effects (Table II) with dye surface coverages between 1 and 4 × 10^{-1} M. However, only a much smaller increase in photocurrents could be seen at higher dye concentrations in a 0.1 μm thick PVP film. Since nearly identical photocurrents were observed upon illuminating the front and back
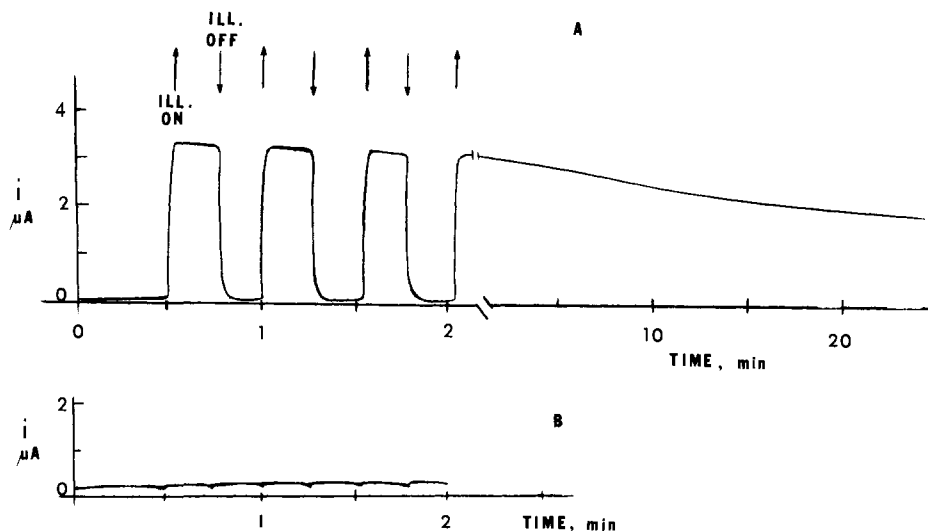

Figure 6. Response of photocurrent at (A) SnO$_2$/PVP/1 and (B) SnO$_2$/PVP to illumination and its stability over an extended period of illumination (film thickness, 0.1 μm; surface coverage of 1 = 4 × 10^{-9} mol/cm^2; electrode area = 2 cm^2; electrolyte, 10^{-2} M benzoquinone, 10^{-5} M hydroquinone, 0.1 M CF$_3$COONa, pH 3).

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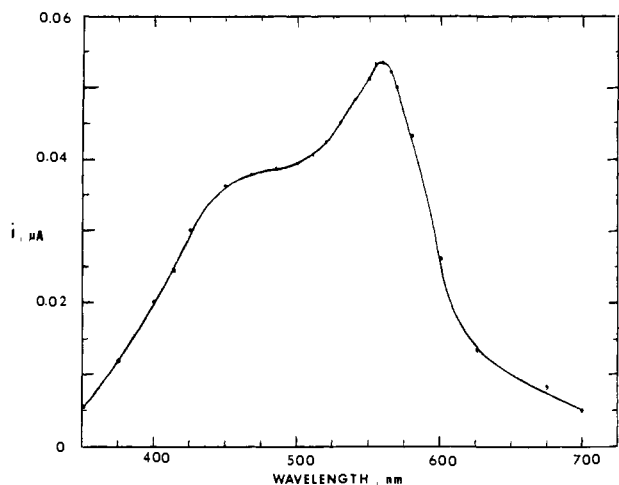
Figure 7. Photocurrent action spectrum of n-SnO$_2$/PVP/1 (film thickness, 0.1 μm; surface coverage of **1** = 4 × 10^{-9} mol/cm^2; electrode area = 2 cm^2; electrolyte; 10^{-2} M benzoquinone, 10^{-5} M hydroquinone, 0.1 M CF$_3$COONa, pH 3).

Figure 8. Light-intensity dependence of short-circuit photocurrent (*i*) and open circuit photovoltage ($V_{o.c.}$) of a photoelectrochemical cell employing n-SnO$_2$/PVP/1 (film thickness, 0. μm; surface coverage of **1** = 4 × 10^{-9} mol/cm^2; electrode area = 2 cm^2; electrolyte: 10^{-2} M benzoquinone, 10^{-5} M hydroquinone, 0.1 M CF$_3$COONa, pH 3).

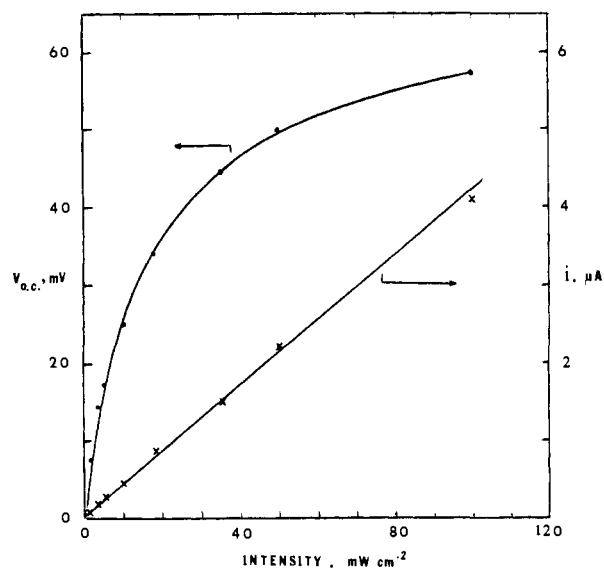faces of the electrode, we infer that excitation or electron transfer within the polymer layer must be highly efficient.

Photocurrent Action Spectrum. Figure 7 shows the action spectrum of the photocurrent observed at SnO$_2$/PVP/**1**. The photocurrent maximum at 560 nm coincided with the absorption maximum (S$_0$-S$_1$, Figure 5). This confirmed our assumption that the observed photoelectrochemical effect was initiated by dye excitation. The observed photocurrent maximum is rather broad and is attributed to the widened band (15 nm) employed for excitation.

Light-Intensity Dependence. The dependence of the photocurrent and photovoltages on light intensity are shown in Figure 8. The photocurrent varied linearly, while photovoltage increased exponentially with the intensity of the incident beam. Linear dependence of photocurrent on light intensity is commonly observed in thin films because of efficient sensitization or supersensitization. Increased thickness of the film is expected to increase the chance of encounter with a recombination center, thereby decreasing the efficiency of charge separation and causing a sublinear dependence of photocurrent on incident light intensity. In the present case, the observed linear dependence of photocurrent on incident intensity indicated that the dye-loaded polymer film

Table III. Photoelectrochemical Effects at n-SnO$_2$ with Various Stages of Modification

electrode	photovoltage, ΔV, mV	photocurrent, Δi, μA
1. 10^{-2} Benzoquinone, 10^{-5} M Hydroquinone, 0.1 M CF$_3$COONa (pH 3)		
SnO$_2$	−5	−0.01
SnO$_2$/PVP	−15	−0.06
SnO$_2$/1 (ads)	10	0.05
SnO$_2$/PVP/1^a	50	3.0
2. 2.5 × 10^{-5} M Croconate Violet, 10^{-2} M Benzoquinone, 10^{-5} M Hydroquinone, 0.1 M CF$_3$COONa (pH 3)		
SnO$_2$	15	0.2
SnO$_2$/PVP	10	0.4
SnO$_2$/1 (ads)	20	0.6
SnO$_2$PVP/1^a	55	6.0

^{a} Surface coverage of 1 = 4 × 10^{-9} mol/cm^2.

Table IV. Photoelectrochemical Effects at SnO$_2$/PVP and SnO$_2$/PVP/1 in the Presence of Various Redox Couples

redox couple	$V_{o.d.}$,^{a} V	photovoltage, ΔV, mV	photocurrent, Δi, μA
1. SnO$_2$/PVP			
none	0	0	0
O$_2$ (aerated)	0.275	0	0
Q/H$_2$Q^b	0.310	−15	−0.06
Fe^{III}/Fe^{II} ^{c}	0.440	5	0.02
2. SnO$_2$/PVP/1			
none	0	70	0.035
O$_2$ (aerated)	0.275	50	0.1
O$_2$ (sat)	0.295	40	0.09
Q/H$_2$Q^b	0.310	60	3.0
Fe^{III}/Fe^{II} ^{c}	0.440	15	0.5

^{a} Open-circuit voltage with respect to SCE in dark. ^{b} 10^{-2} M benzoquinone, 10^{-5} M hydroquinone, 0.1 M CF$_3$COONa, pH 3. ^{c} 10^{-2} M Fe(NO$_3$)$_3$ and 10^{-2} M FeSO$_4$, 0.1 M CF$_3$COONa, pH 3.

up to a thickness of 0.1 μm retained the desirable properties of thin films.

Influence of Redox Couples. The influence of various stages of modification of n-SnO$_2$ and of supersensitizing redox couples present in the electrolyte is summarized in Tables III and IV, respectively. Distinctly higher photocurrents and photovoltages were observed with dye-loaded polymer films than could be attained with other forms of dye attachment (Table III). The very small photocurrents seen at bare n-SnO$_2$ or at SnO$_2$/PVP in the absence of dye can be attributed to trailing absorption by the semiconductor.

When no dye was present in the solution, these electrodes exhibited small anodic photocurrents as are typically seen with n-type semiconductors. Anodic photopotential generation is also seen with SnO$_2$/PVP/1 in contact with inert electrolyte upon monitoring current transients with laser coulostatic techniques.[24] The excursion of the anodic photopotential during the first few microseconds following pulse excitation (Nd:YAG laser, 532 nm, pulse width 10 ns) indicates injection of an electron into the conduction band as a primary step of photosensitization.

In the presence of redox couples, however, cathodic photocurrents are observed. Of the various redox couples employed, benzoquinone/hydroquinone gave the highest photocurrents and the best long-term stability (Table IV). As will be discussed later, these redox couples assist in in photocurrent generation by providing routes for supersensitization.

Mechanism of Generation of Photoelectrochemical Effects. Sensitization of lightly doped large-band semiconductors usually proceeds either by electron injection into the conduction band or by hole injection into the valence band by the excited state of the dye. A choice between these paths is governed by the energy levels of the semiconductor bands and the excited-state oxidation and

(24) Kamat, P. V.; Fox, M. A. *J. Phys. Chem.* **1983**, *87*, 59.

reduction potentials of the sensitizer. At low dopant concentrations, electron injection into the conduction band, inducing anodic photocurrents, is usually seen with n-type semiconductors.
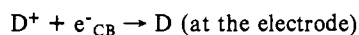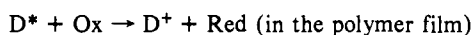
At pH 3, the energy level of the conduction band of an n-type tin oxide electrode lies at about −0.5 V vs. SCE, which is below the estimated donor levels of excited **1**. (The oxidation of **1** occurs at about +0.6 V; excitation at 530 nm provides ∼2.3 V). Electron injection from the excited state should therefore be favorable. Since the valence band lies at substantially lower energy (approximately +2.5 V), however, hole injection from excited **1** is highly unlikely. Anodic photocurrents would therefore be anticipated. Consistent with this view, very small anodic photocurrents are observed with adsorbed dye in the absence of dissolved redox couples in the electrolyte. Analogous results have previously been reported at unmodified n-type SnO_2[23,25] and at n-ZnO.[26]

Cathodic photocurrents are observed, however, on SnO_2/PVP/**1** under steady-state illumination. The SnO_2 electrodes employed in this study were highly doped and, accordingly, highly conductive. The space charge layer in such highly doped electrodes is very thin and efficient electron tunneling through the layer is sometimes observed.[4,25] Generation of a hole at +0.6 V by excitation of the dye molecules contained within the adsorbed polymer layer induces electron flow from the semiconductor to the dye. The resulting radical ion can then act as a reductant, converting a dissolved redox couple of appropriate potential to its reduced form. Alternately, the excited state of the dye can interact with the couple, generating the reduced couple and the oxidized form of the dye. The dye radical cation, perhaps stabilized by electron donation from the electron-rich pyridine groups pendent from the backbone of the polymer film, then accepts an electron from the highly doped conduction band and initiates a cathodic current. Thus benzoquinone is reduced to hydroquinone at the irradiated electrode, and a cathodic current flows.
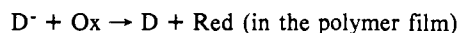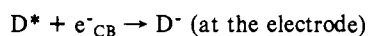
Such an effect is photogalvanic and requires equilibration. Consistent with this expectation, reproducible and steady cathodic photocurrents were observed at SnO_2/PVP/**1** only after a short induction period. Stable currents could then be observed for longer periods, and the values reported in Tables III and IV are those obtained after 5 min of continuous irradiation.

Memming and co-workers have observed similar cathodic photocurrents on highly doped, unmodified n-SnO_2 sensitized by $Ru(bpy)_3^{2+}$. At even very low concentrations of oxygen, substantial cathodic photocurrents were observed.[27]

On our modified electrodes, several redox couples (O_2, benzoquinone/hydroquinone, Fe^{III}/Fe^{II}, etc.) significantly enhanced the observed cathodic photocurrents. The overall supersensitization process occurring at the illuminated cathode can therefore be summarized as

$$D \rightarrow D^*$$

$$D^* + Ox \rightarrow D^+ + Red \text{ (in the polymer film)}$$

$$D^+ + e^-_{CB} \rightarrow D \text{ (at the electrode)}$$

or

$$D \rightarrow D^*$$

$$D^* + e^-_{CB} \rightarrow D^- \text{ (at the electrode)}$$

$$D^- + Ox \rightarrow D + Red \text{ (in the polymer film)}$$

where D is the sensitizing dye and Ox/Red are the oxidized and reduced forms, respectively, of the dissolved couple. The enhanced currents can be attributed to the unique stabilization of radical ions by the highly charged polymer matrix.

We showed earlier that **1**-loaded PVP can mediate electron transfer between a poised electrode and a solution redox couple, i.e., an exchange of electrons between adjacent oxidized and reduced dye molecules contained within the film. The ease of propagation of charge within the polymer film also facilitates supersensitization. That is, the dye radical ion formed by electron-transfer interception of the excited state can ultimately transfer its charge to the solution phase through electron hopping. The results summarized in Table III clearly show that more than an order of magnitude enhancement of photocurrent is achieved in the sensitization of photocurrent when the dye is incorporated into the polymer film. Among the possible reasonable explanations for this enhancement are an extended lifetime of the excited state of the dye in the polymer matrix,[8,22] the stabilization of mechanistically important radical ions within the charged film, the promotion of mediated charge transfer through the film, and/or the spatial arrangement of useful concentrations of dye under conditions where self-quenching can be limited. Thus, dye-loaded polymer coatings function as intriguing environments for supersensitization of large-band-gap semiconductors.

Sunlight Engineering Efficiency. The maximum power obtained in the photoelectrochemical cell employing SnO_2/PVP/**1** was 0.06 $\mu W/cm^2$ at an incident white light intensity of 120 mW/cm^2. The engineering efficiency of this solar energy conversion can be calculated as in the following equation.

$$\text{sunlight engineering efficiency} = \frac{0.06 \times 10^{-6} \text{ W}}{120 \times 10^{-3} \text{ W} \times 100\%} = 5 \times 10^{-5}\%$$

Because of absorption mismatching of the spectrum of the dye ($\lambda_{max} \sim 560$ nm) with the solar spectrum, more than 80% of the incident light is not utilized for the direct conversion into electricity. Although this efficiency is two orders of magnitude higher than that achieved by direct dispersal of the dye on the n-SnO_2 electrode, it remains grossly inefficient.

Future studies will be directed toward understanding the mechanistic details of the several possible steps involved in the generation of sensitized photoelectrochemical effects at dye-loaded films held at the semiconductor–electrolyte interface.

Conclusions

We have investigated the photoelectrochemical effects sensitized by several oxocarbon dyes. A simple technique in which anionic dyes are incorporated into a cationic polymer film allowed for production of materials which exhibited electroactivity, longer lived excited states, and sensitization of photocurrents. Excitation of the dye-loaded polymer films in the absorption band of the dye led to cathodic photoelectrochemical effects. Dissolved redox couplex served as supersensitizers and improved the performance and durability of the photoelectrochemical cell. The work presented here could serve as a model for exploring new organic systems or for improving the performance of existing organic energy conversion devices.

Registry No. 1, 66888-99-1; **2**, 72893-87-9; **3**, 66888-97-9; **4**, 7565-48-7; PVP, 25232-41-1; benzoquinone, 106-51-4; SnO_2, 18282-10-5.

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