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Semiconductor Electrodes. 40. Photoassisted Hydrogen Evolution at Poly(benzyl viologen)-Coated p-Type Silicon Electrodes

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Abstract: Poly(benzyl viologen) (PBV) shows two reduction waves in aqueous (at -0.37 and -0.88 V vs. SSCE) or N,N-dimethylformamide (at -0.22 and -0.64 V vs. SSCE) solutions. A film of PBV on the surface of a p-type silicon electrode can be photoreduced at more positive potentials. When metallic Pt is incorporated into the film, the photoproduction of hydrogen occurs with an underpotential of ca. 0.4 V. The decrease in the photocurrent with time suggests that slow decomposition of the viologen occurs.

The recent interest in the photoproduction of hydrogen by light characteristic of the solar spectrum has led to a number of recent reports using homogeneous and heterogeneous systems.[1-16] The systems employed usually involve a light-absorbing center to effect electron–hole pair formation and a catalyst which promotes the hydrogen evolution reaction. Often, a "sacrificial electron donor" (such as triethanolamine) is used to scavenge the photogenerated hole. An aqueous solution at pH <6 of the reduced form of N,N'-dimethyl-4,4'-bipyridinium (methyl viologen, MV^{2+}, or paraquat) will rapidly evolve H_2 in the presence of either platinum suspensions or hydrogenase (eq 1). This system has thus been

$$2H_2O + 2 MV^+ \cdot \rightarrow 2MV^{2+} + H_2 + 2OH^- \qquad (1)$$
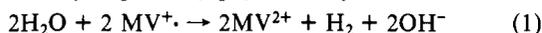
used in several approaches for the photodissociation of water. A well-studied system[1-3,5-10,12,13] involves MV^{2+} and Pt along with a sensitizer such as $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) or proflavin and an external reductant such as triethanolamine or EDTA. In this system, MV^{2+} is reduced by electron-transfer quenching of the excited state of the sensitizer to produce $MV^+ \cdot$ and the oxidized form of the sensitizer. The sacrificial donor is irreversibly oxidized to regenerate the active form of the sensitizer (in competition with the energy-wasting back electron transfer process). The catalyzed reaction between $MV^+ \cdot$ and H_2O at Pt, eq 1, then follows. Long-term hydrogen production in a MV^{2+}-based system is hindered by slow hydrogenation of the intermediates.[13,17-19]

The MV^{2+} system has also been employed in semiconductor electrode photoelectrochemical cells employing p-Si[20,21] or p-GaAs.[22] In these cells, photogenerated electrons produced at the p-type semiconductor surface reduce dissolved MV^{2+}; the $MV^+ \cdot$ in solution produces H_2 via catalysis by colloidal Pt.[22] The production of H_2 at the illuminated semiconductors occurs at an "underpotential", i.e., at potentials less negative than the reversible potential for H_2 evolution at that pH. Hydrogen evolution does not occur readily at uncatalyzed p-type semiconductors. An extension of this approach has been described by Wrighton and co-workers[23] in which the MV^{2+} was covalently attached via a silanization procedure to the semiconductor electrode surface and the Pt incorporated into this layer.

An alternative method, described here, involves the use of an electrode coated with a thin (500 Å to 2 μm) layer of an electroactive polymer. Following the first descriptions of such electrodes,[24] a number of studies[25] and applications have been reported. These electrodes have the advantages of easy preparation (e.g., by spin or dip coating, electrodeposition, and electroinitiated polymerization), a wide choice of electroactive materials, and the possibility of stabilization of the semiconductor surface against photodecomposition by the polymer layer.[26] We describe here the behavior of poly(benzyl viologen) (PBV) layers on electrodes and their use with p-Si to catalyze the photoassisted evolution of H_2.

PBV
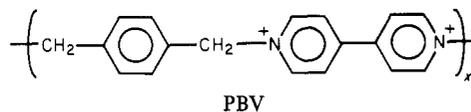
Experimental Section

Boron-doped single-crystal p-Si electrodes (1–2 Ω cm) with an electrodeposited gold ohmic contact were silver epoxied to a copper lead and mounted on 6-mm-bore glass tubing. The electrodes were masked with 5-min epoxy cement except for the face to be illuminated (typically an area of 0.05 to 0.1 cm²). Prior to use, the electrodes were etched in concentrated (48%) HF for 30 s and thoroughly rinsed with distilled water.

Electrochemical experiments were performed with a Princeton Applied Research Model 173 potentiostat in conjunction with a Model 179 digital

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coulometer and a Model 175 signal generator. Cyclic voltammograms were recorded with a Houston Instruments Model 2000 X-Y recorder for sweep rates, v, below 0.5 V/s or a Nicolet Explorer digital oscilloscope (for higher sweep rates). All solutions were deaerated by bubbling with high purity nitrogen for 20 min; a positive pressure of N_2 was maintained throughout the experiment.

Electrochemical experiments were conducted in conventional cells with a Pt counterelectrode and a sodium-saturated calomel electrode (SSCE) as a reference. The electrodes were illuminated by either an Oriel 450-W Xe lamp with a water filter and a 590-nm cutoff filter or a Spectra Physics 1.6-mW He/Ne laser.

Acetonitrile and dimethylformamide were dried with 4-Å molecular sieves. Aqueous solutions were made with triply distilled water. Tetra-n-butylammonium perchlorate was thrice recrystallized from ethyl acetate/pentane and dried in vacuo for 24 h. All other reagents were of at least reagent grade quality and were used without further purification. The bromide salt of poly(benzyl viologen) was synthesized according to a published procedure which yields polymers with a molecular weight of ca. 11 000.[27] This material was washed thoroughly with methanol and ether and dried in vacuo for 24 h. The hexafluorophosphate salt was prepared by dissolving the bromide salt in water and adding a saturated aqueous solution of NH_4PF_6. The white precipitate was collected, dried with ether, recrystallized twice from CH_3CN/Et_2O, and dried in vacuo for 24 h.

The coating of poly(benzyl viologen) onto the surface of p-Si electrodes was accomplished by two methods. In the first, 3 drops of an acetonitrile solution containing 0.168 mg/mL of the PF_6^- salt of the viologen polymer were allowed to evaporate on the surface of the electrode. The same experiment was conducted on a Pt electrode, and by integration of the charge under the voltammetric waves, a coverage of ca. 1×10^{-8} mol/cm² was determined. The second was an electrodeposition procedure accomplished by the photoreduction at p-Si of an aqueous 0.1 M KBr solution containing 1 mg/mL of the bromide salt of the viologen polymer. The reduced form of the polymer precipitates on the surface (vide infra), thus effectively immobilizing it. After deposition, the electrode was disconnected and allowed to dry. A slightly yellowish tint (characteristic of the bromide salt) could be seen on the surface of the electrode. The electrodeposited amount corresponds to a coverage of ca. $(1–5) \times 10^{-8}$ mol/cm². When incorporation of Pt into the polymer layer was desired, a drop of H_2PtCl_6 (12 mg of Pt/mL) was allowed to remain on the surface of the polymer-coated electrode for 20 min. The electrode was then rinsed with distilled water. The $PtCl_6^{2-}$ was converted to Pt^0 in the polymer layer by photoreduction.[28]

Results

Electrochemical Behavior of Poly(benzyl viologen) on Pt Electrodes.

Prior to its use on semiconductor electrodes, the electrochemical behavior of poly(benzyl viologen) was investigated in both aqueous and nonaqueous systems. A cyclic voltammogram obtained from an aqueous solution (pH 9) containing 0.1 M KBr and the dissolved bromide salt of PBV (1 mg/mL) (Figure 1A) exhibits two reduction waves with peak potentials (E_p) at -0.37 and -0.88 V vs. SSCE. The shape of the waves on scan reversal shows that the reduced forms are insoluble and precipitate on the electrode surface. Upon continuous cycling, the waves get increasingly larger, indicating the accumulation of material on the electrode. The bluish-purple color of the reduced form (PBV$^+$·) is clearly visible at potentials negative of the first reduction wave. Qualitatively, the same behavior is observed if only the first reduction wave is scanned.

The electrochemical behavior of the PF_6^- salt of the polymer in DMF solution containing 0.1 M TBAP is shown in Figure 1B. Again, two well-developed waves can be seen with E_p values of -0.22 and -0.64 V vs. SSCE. As in water, if the potential is scanned over both reduction waves, the reverse scan shows evidence of precipitation of the reduced form. If, however, the potential is only scanned over the first reduction wave, the extent of precipitation is greatly diminished, and the wave has all of the characteristics of a reversible diffusion-controlled wave. The peak current for the cathodic branch of the wave (i_{pc}) is proportional to $v^{1/2}$ for sweep rates (v) from 5 mV/s to 50 V/s (Figure 2A). However, at sweep rates lower than 20 mV/s, the anodic wave gets increasingly sharp, indicative of some precipitation (Figure
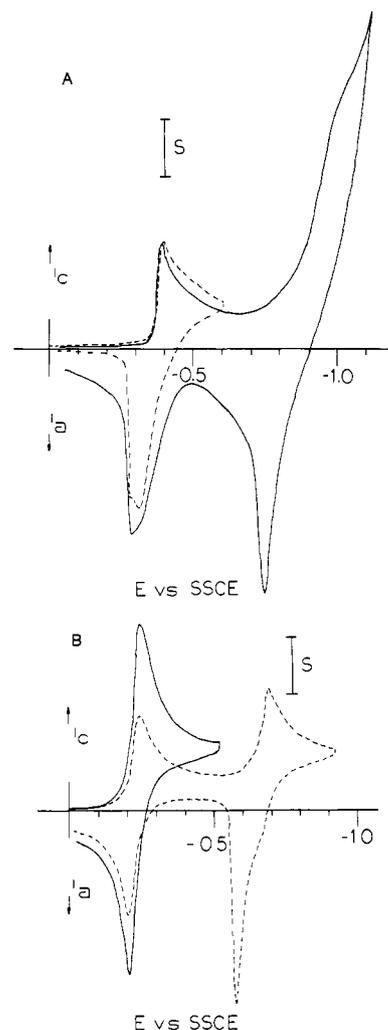
Figure 1. (A) Cyclic voltammogram on Pt of poly(benzyl viologen) (1 mg/mL) in aqueous (pH 9.0) 0.1 M KBr solution. Sweep rate = 100 mV/s. Dashed curve = scan reversal after first wave. $S = 20~\mu A$. (B) Cyclic voltammogram on Pt of poly(benzyl viologen) (1 mg/mL) in DMF/0.1 M TBAP solution. Sweep rate = 100 mV/s. Solid curve = scan reversal after first wave. Solid curve: $S = 5~\mu A$, dashed curve: $S = 10~\mu A$.

2B). Controlled potential electrolysis can be performed, and coulometric n values (number of faradays of electricity passed per mole of viologen center) of 0.97 and 0.95 were obtained for reduction and reoxidation, respectively, at the first wave, indicating that the system is also chemically stable. The fact that relatively clean coulometry can be performed precludes any extensive precipitation of the reduced polymer. The sharpness of the anodic portion of the wave at slow sweep rates might indicate slow adsorption or precipitation of the monoreduced form.

Photoelectrochemical Behavior of p-Si Electrodes Coated with Poly(benzyl viologen) and Pt.

Cyclic voltammograms of freshly etched p-Si electrodes in the dark and under illumination in aqueous solution containing 0.2 M $LiClO_4$/0.2 M NaTFA (where TFA$^-$ is trifluoroacetate) at pH 2.1 are shown in Figure 3A. Note that the ClO_4^- forms of both MV^{2+} and MV$^+$· are insoluble in aqueous solutions (as opposed to the soluble Br$^-$ salt of MV^{2+} described in the preceding section). As expected, very little current flows in the dark since few minority carriers (electrons) are available at the electrode surface.[29] Upon illumination, one observes a small increase in the cathodic current attributed to the photogeneration of electrons which move to the surface by the potential gradient in the space-charge region. However, the

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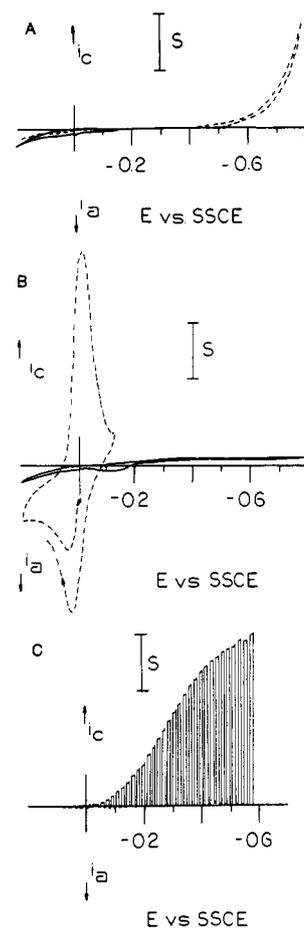(28) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 4317.

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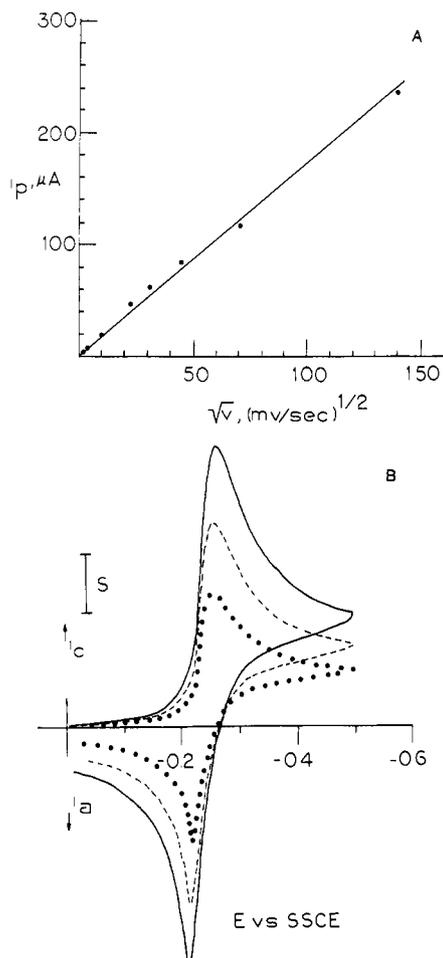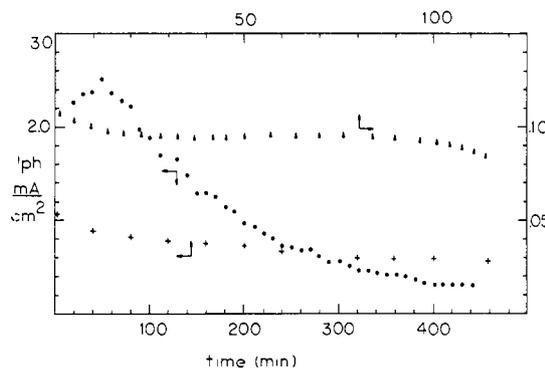
Figure 2. (A) i_p vs. $v^{1/2}$ for the cathodic branch of the first reduction of poly(benzyl viologen) on Pt in DMF/0.1 M TBAP solution. (B) Cyclic voltammograms on Pt for poly(benzyl viologen) in DMF/0.1 M TBAP at different sweep rates. Solid curve = 200, dashed curve = 50, dotted curve = 20 mV/s. $S = 5$ μA.

Figure 3. Electrochemical response in the dark (solid curve) and under illumination (dashed curve) for (A) bare p-Si, $S = 5$ μA; (B) p-Si/poly(benzyl viologen), $S = 5$ μA; (C) p-Si/poly(benzyl viologen)/Pt⁰ under chopped illumination, $S = 100$ μA. Conditions: deaerated aqueous solution 0.2 M sodium trifluoroacetate, pH 2.1, 0.2 M LiClO₄). Sweep rate = 50 mV/s except for part C (10 mV/s). Illumination using a 450-W Xe lamp with a 590-nm cutoff filter (input power density ca. 100 mW/cm²).

current density is small, and the onset for this photocurrent is near the potential for H₂ evolution at a reversible electrode at this pH. This is consistent with the known high overpotential for H₂ evolution at p-Si electrodes.[25,30] This can be contrasted to the behavior of p-Si electrodes coated with poly(benzyl viologen) (Figure 3B). In the dark, the behavior is quite similar to that of bare p-Si. However, upon illumination, a well-developed cathodic wave at E_p = +0.02 V vs. SSCE is observed. The fact that the electrode gets visibly purple under illumination is a verification that the process is the reduction of the surface-confined PBV. Since the formal potential for the poly(benzyl viologen) (+2/+1) couple is –0.38 V vs. SSCE as measured at a Pt electrode, this represents an underpotential of 0.40 V. Thus, under illumination one can drive the electrochemical reaction at potentials 0.40 V more positive than the formal potential of the couple. The underpotential for reduction of dissolved methyl viologen at p-Si in CH₃CN is 0.5 V.[21]

Incorporation of Pt into the PBV layer causes a dramatic change in the behavior. The response under chopped illumination of a p-Si electrode coated with poly(benzyl viologen) and treated with H₂PtCl₆ (Figure 3C) is characterized by an increase in the current which attains a plateau rather than a peak at ca –0.30 V. Moreover, there is visible evolution of gas from the surface of the p-Si electrode. These processes are consistent with the photoassisted evolution of H₂ at the surface of p-Si mediated by the PBV⁺·/Pt⁰ system; the Pt⁰ is generated on the surface by the light-induced reduction of PtCl₆²⁻. At the pH involved (2.1), H₂

Figure 4. Long-term operation of surface-modified p-Si electrodes for H₂ evolution. Conditions: thoroughly degassed aqueous 0.2 M NaTFA, pH 2.1, 0.2 M LiClO₄. Illumination by 450-W Xe lamp with 590-nm cutoff filter (intensity ca. 110 mW/cm²). Applied bias: (▲) –0.1 V, (●) –0.175 V, (+) –0.1 V.

evolution at a reversible electrode would take place at –0.37 V vs. SSCE so the onset represents an underpotential of ca. 0.4 V for H₂ evolution.

To assess the stability of these systems, we have carried out long-term irradiation studies at a small applied cathodic bias (to drive the H₂ evolution reaction at a reasonable rate). Representative results are shown in Table I and Figure 4. In general, the electrodes are most stable at small current densities. Current densities of 2.5 mA/cm² at potentials 250 mV more positive than

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Table I. Results from Long-Term Operation of Surface-Modified p-Si Electrodes for the Photoassisted Evolution of H₂

E_{appl}	$i_{photo_{max}}$, mA/cm²	stability
−0.1 V vs. SSCE	0.1	10% decay in 3 h
−0.175 V vs. SSCE	2.6	50% decay in 3 h
		90% decay in 8 h
−0.1 V vs. SSCE	1.1	50% decay in 2 h

the reversible potential for hydrogen evolution at this pH can be achieved, but the electrodes degrade upon long-term operation. After long-term irradiation, all electrodes were coated with a black film. A similar black film was found on electrodes modified only with the PBV (lacking Pt). This decomposition of the viologen polymer probably occurs either by hydrogenation[17] (as reported in previous studies[13,18,19]) or to reaction with trace O₂.[31] The viologen polymer coated Pt electrodes can be cycled repetitively with very small decrease in current (<5% after 3 h). This result suggests that the polymer itself is chemically robust. That a black film is formed on the coated p-Si electrodes in the presence or absence of Pt would imply that a process other than hydrogenation may be responsible, at least in part, for the decomposition; this

could very well be due to reactions with trace O₂. Reactions at the silicon/polymer interface may also account for the decrease in photocurrent.

Conclusions

Coating of a p-Si electrode with a thin film of poly(benzyl viologen) and Pt promotes the photoevolution of hydrogen. Although the system is stable at low light intensities for several hours, the film eventually degrades with a decrease in photocurrent. The results of a number of studies of semiconductor electrodes and powders with the purpose of driving desired chemical reactions (e.g., H₂ or O₂ evolution) under illumination have shown that one requires not only the semiconductor system, whch provides for photon capture and electron–hole pair separation, but also catalysts. Polymer films provide a useful approach to incorporation of such catalyst systems on a semiconductor surface. Poly(benzyl viologen) films may also be useful in electrochromic (EC) displays.[32] Those on p-Si (or other p-type semiconductor) electrodes are examples of photoaddressable EC displays, as described earlier for heptylviologen bromide on p-GaAs.[33]

(31) A similar effect (i.e., black film formation) has been observed by Murray upon scanning a Pt electrode modified with a viologen polymer reagent. They found that this process was considerably suppressed by rigorous exclusion of O₂. Murray, R. W., private communication.

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Photocatalysis. 6.[1] On the Mechanism of the Cyclotrimerization of *trans*-Cycloheptene, Catalyzed by Copper(I) Triflate

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Contribution from the Institute for Organic Chemistry TNO, 3502 JA Utrecht, The Netherlands. Received January 16, 1981. Revised Manuscript Received June 24, 1981

Abstract: The *trans*-cycloheptene ligand in the copper(I) triflate–*trans*-cycloheptene complex cyclotrimerizes at 60 °C in the presence of *cis*-cycloheptene. With use of cycloheptene-d_4 or *trans*-cyclooctene it was established that cyclotrimerization is a process involving *trans*-cycloheptene molecules only. No *cis*-cycloheptene or *trans*-cyclooctene molecules are incorporated into the trimer. However, *cis*-cycloheptene exerts an accelerating effect on this reaction by replacing the reacted *trans*-cycloheptene at copper(I). The most likely explanation of these results is a concerted "template" cyclotrimerization process of either three (*R*)- or three (*S*)-*trans*-cycloheptene molecules around copper. Another possibility would be a two-step mechanism, involving a cupracyclopentane intermediate, irreversibly formed from two *trans*-cycloheptene molecules. No evidence for such an intermediate has been found so far.

Salomon and Kochi et al.[2] have reported on the photochemical formation of a cycloheptene dimer, catalyzed by copper(I) trifluoromethanesulfonate (triflate). Reinvestigation of this reaction by Evers and Mackor[1] showed that dimerization is only a minor reaction and that a cyclic trimer is formed in over 80% yield. This is essentially a two-step process. First, a photochemical cis → trans isomerization of cycloheptene coordinated to copper takes place. A copper(I) triflate–*trans*-cycloheptene complex, having a 1/1 Cu/olefin ratio, has been isolated as a stable colorless crystalline solid, and it has been characterized.[3] Then, under the conditions of the photocatalytic process or in the dark at

slightly elevated temperatures (50–60 °C), a cyclotrimerization occurs to give the trimer **1** with an all-trans structure,[4] in essentially a quantitative yield.

1
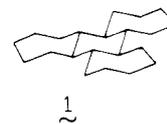
Transition-metal-catalyzed cyclotrimerization reactions, common for alkynes, are very rare for alkenes. To our knowledge,

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(4) According to IUPAC nomenclature, **1** is *trans-anti-trans-anti-trans*-tetracyclo[14.5.0.0²·⁸,0⁹·¹⁵]heneicosane or perhydrocyclohexa[1,2:3,4:5,6]tricycloheptene.