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Use of Chemically Derivatized n-Type Silicon Photoelectrodes in Aqueous Media. Photooxidation of Iodide, Hexacyanoiron(II), and Hexaammineruthenium(II) at Ferrocene-Derivatized Photoanodes

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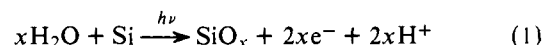
Abstract: n-Type Si can be derivatized using (1,1'-ferrocenediyl)dichlorosilane yielding a photoanode that can be used in aqueous electrolyte solutions under conditions where the naked (nonderivatized) n-type Si undergoes photoanodic corrosion yielding an insulating SiO_x surface layer. Derivatized electrodes in aqueous electrolyte solution exhibit chemically reversible oxidation of the surface-confined, ferrocene-centered redox reagent when the electrode is illuminated. Oxidation is not detectable in the dark, consistent with the fact that n-type semiconductors are blocking to oxidation in the dark. At sufficiently high light intensity, the surface-confined material can be oxidized at more negative potentials than when the same material is confined to the surface of a reversible electrode material such as Pt or Au. Light intensity of ~40 mW/cm² at 632.8 nm is typically sufficient to effect oxidation 200–400 mV thermodynamically uphill for electrodes exhibiting coverages of 10⁻¹⁰–10⁻⁹ mol/cm² of electrochemically active material. Such electrodes can be used to effect the persistent oxidation of I⁻, [Fe(CN)₆]⁴⁻, and [Ru(NH₃)₆]²⁺. The current efficiency for 3I⁻ → I₃⁻ and [Fe(CN)₆]⁴⁻ → [Fe(CN)₆]³⁻ is measured to be >90% and these oxidations can be effected thermodynamically uphill, but with low efficiency. The formal potential of [Ru(NH₃)₆]³⁺/[Ru(NH₃)₆]²⁺ is sufficiently negative, -0.2 V vs. SCE, that oxidation cannot be effected thermodynamically uphill with n-type Si. Oxidation of H₂O using derivatized n-type Si does not occur under any conditions used. The oxidation of the three reductants used occurs by (1) photogeneration of electron-hole pairs by absorption of band-gap irradiation by n-type Si (band gap = 1.1 eV); (2) oxidation of the surface-confined ferrocene-centered redox reagent by the photogenerated holes; (3) oxidation of the solution reductant (I⁻, [Fe(CN)₆]⁴⁻, [Ru(NH₃)₆]²⁺) by the surface-confined ferricenium oxidizing reagent. This mechanism is established by cyclic voltammetry. Current-time plots show that ferrocene-ferricenium turnover numbers exceed 10⁵ and constant (within 10%) photocurrents can be obtained for >5 h, whereas naked electrodes give photocurrents which decay by >90% within 5 min. Energy conversion efficiency for [Fe(CN)₆]⁴⁻ oxidation or I⁻ oxidation at 632.8 nm is of the order of 1%.

Substantial improvement in n-type semiconductor-based cells for light to electricity energy conversion has been possible through judicious choice of aqueous and nonaqueous electrolyte/redox systems.¹⁻⁸ We have recently adopted a strategy involving chemical derivatization of the surface of n-type semiconductor photoanodes in order to design photosensitive interfaces for use in a large number of thermodynamically uphill oxidation processes. The essence of our strategy is to bind redox reagents to the surface of the n-type semiconductor. The bound reagents can be oxidized in a thermodynamically uphill fashion by irradiation of the semiconductor and the oxidized form can then oxidize solution species. The point is that the surface-confined material serves two functions: (1) photogenerated holes are transferred to the attached redox reagent to preclude semiconductor decomposition and (2) the photooxidized, surface-confined material oxidizes solution species that may or may not be directly competitively oxidized at the naked electrode. Just what species in solution can be oxidized does not depend on the kinetics of hole transfer from semiconductor to the solution species, but rather on the nature of the surface-confined material. Thus, electrodes can be "designed" to oxidize certain species selectively. In energy conversion applications what can be oxidized, overall efficiency, and durability are parameters of central importance. Our

earlier articles have been concerned with the preliminary aspects of derivatized n-type Si,⁹ Ge,¹⁰ and GaAs¹¹ characterized in nonaqueous media by electrochemical techniques. In this article we wish to amplify our results^{9c} on the use of derivatized n-type Si in aqueous electrolyte solutions. These are important measurements inasmuch as naked Si is useless in aqueous electrolytes and yet has a band gap, *E*_{BG}, of 1.1 eV¹² that is nearly optimal from the point of view of solar energy conversion. Our new results show that the uphill oxidation of I⁻ to I₃⁻ can be sustained using an n-type Si photoelectrode derivatized with (1,1'-ferrocenediyl)dichlorosilane.

Results and Discussion

A. Characterization of Naked and Derivatized n-Type Si Electrodes in Aqueous Electrodes. Freshly HF-etched, single-crystal, n-type Si photoanodes in aqueous 0.1 M NaClO₄ (pH 0–6) are not durable, and we have been unable to observe any sustained photoanodic reaction other than that represented by the equation



Note that the surfaces of Si used here are not pure Si; the surfaces invariably have a thin air oxide.¹³ Irradiation of the

Table I. Passivation of Naked n-Type Si by Illumination in Aqueous Media^a

passivation potential, V vs. SCE ^b	electrode	coulombs passed, $\times 10^4 \text{ cm}^{-2}$ ^c	fraction of remaining photocurrent ^d
0.0	A	2.0	0.96
0.0	A	6.0	0.91
0.0	A	15.0	0.84
0.0	A	20.0	0.67
0.0	A	27.5	0.33
+0.1	A	10.0	0.89
+0.1	A	30.0	0.80
+0.1	A	55.0	0.36
+0.1	A	57.6	0.33
+0.2	A	30.0	0.91
+0.2	A	70.0	0.65
+0.2	A	100	0.39
+0.5	B	30.0	0.29
+0.5	B	30.0	0.16
+0.5	B	40.0	0.06
+0.5	B	45.0	0.02
+0.5	B	7.0	0.76
+0.5	B	30.0	0.05
+0.5	B	50.5	0.01

^a Electrolyte consists of 0.1 M NaClO₄(aq) adjusted to pH 1.3 with concentrated HClO₄. Illumination is from a 632.8-nm He-Ne laser beam expanded to illuminate total crystal face (0.1 cm²). Input power is 40 mW/cm². ^b Electrode is potentiostated at given potential under illumination. ^c Data indicates number of coulombs passed at the passivation potential. Note that the time necessary to pass a given amount of electrons is a function of the potential. ^d Photocurrent is measured at short-circuit in an EtOH solution of ferrocene/ferricenium with 0.1 M [*n*-Bu₄N]ClO₄ as the supporting electrolyte solution, $E_{\text{redox}} = 0.27 \text{ V vs. SCE}$. Illumination is provided by a 5.2-mW He-Ne laser at 632.8 nm with a beam diameter of 1.0 mm. Fractions given are ratio of photocurrent before and after passivation.

photoelectrode at given potentials leads to rapid growth of the oxide to thicknesses that preclude the flow of current. Figure 1 compares the result of repetitive cyclic voltammograms for irradiated n-type Si in 0.1 M NaClO₄ and in 0.1 M NaClO₄ plus 5 mM K₄[Fe(CN)₆]; additionally plots of photocurrent against time at a fixed potential in the two solutions are in accord with the cyclic voltammetry (vide infra). These data are representative; naked n-type Si in any aqueous electrolyte solution that we have investigated is not stable under illumination. The presence of redox-active material such as I⁻, [Fe(CN)₆]⁴⁻, or [Ru(NH₃)₆]²⁺ gives little, if any, qualitative improvement in the constancy of the photocurrent at potentials where efficient photocurrents can initially be observed. The lack of constant photocurrents in the presence of the reductants evidences the inability of irradiated n-type Si to effect the efficient oxidation of the solution species. The photoanodic decomposition represented by eq 1 dominates the oxidation processes.

The amount of oxide needed to suppress the flow of photocurrent can be measured from integration of current-time plots in aqueous media. However, it is well known that the nature of the oxide is very dependent on the rate at which it is grown and the solution (or other medium) from which it is grown.¹³ Table I lists some quantitative data, under specified conditions, relating the number of coulombs corresponding to SiO_x growth in H₂O/0.1 M NaClO₄ and the suppression of photocurrent for that electrode when used in a standard EtOH electrolyte solution of ferricenium/ferrocene. The experiment for a given electrode would be as follows: (1) the freshly HF-etched electrode is examined in the EtOH/ferricenium/ferrocene solution, $E_{\text{redox}} \approx +0.3 \text{ V vs. SCE}$, and the steady-state pho-

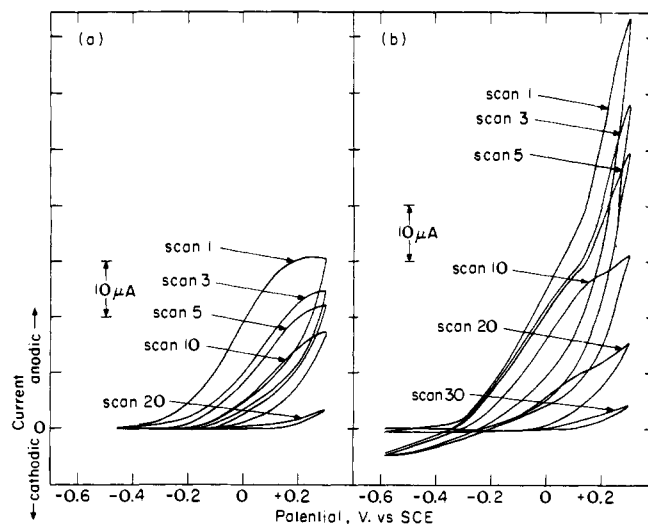
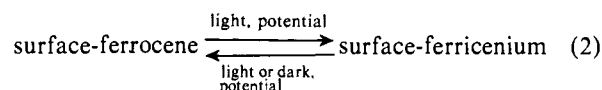


Figure 1. (a) Repetitive cyclic voltammograms (100 mV/s) of illuminated, freshly etched, n-type Si in 0.1 M NaClO₄, pH 1.3. The scans were initiated at -0.6 V vs. SCE and swept to +0.3 V vs. SCE. (b) As in (a) except with 5 mM K₄Fe(CN)₆ added to the electrolyte.

tocurrent is recorded at +0.3 V vs. SCE; (2) the electrode is then put in the H₂O/0.1 M NaClO₄ solution and illuminated at a given potential while current is integrated; (3) the electrode is then reexamined (after rinsing and drying with EtOH) in the EtOH/ferricenium/ferrocene solution to determine the extent to which the photocurrent was attenuated. The procedure was repeated until the photocurrent in the EtOH/ferricenium/ferrocene solution was significantly attenuated. Several electrodes were studied and different potentials were used in the H₂O/0.1 M NaClO₄ solution. Approximately 40 mW/cm² of 632.8-nm irradiation was used in all cases. The essence of the results can be summarized by the observation that $\sim 10^{-7} \text{ mol of electrons/cm}^2$ is more than sufficient to form an SiO_x layer thick enough to significantly attenuate photocurrent under the conditions routinely employed in this experimentation.

n-Type Si can be derivatized with (1,1'-ferrocenediyl)dichlorosilane according to the procedure detailed in the Experimental Section.⁹⁻¹¹ The resulting surface can be characterized by cyclic voltammetry in an aqueous electrolyte solution. Figure 2 shows data for derivatized Si like that shown in Figure 1 for the naked Si. The derivatized n-type Si exhibits a persistent oxidation wave and a reduction wave of equal area in the cyclic voltammogram when the electrode is illuminated with $\geq E_{\text{BG}}$ light. In the dark there is no anodic current, but the reduction of the photogenerated, surface-confined oxidation product can be effected in the dark as evidenced by the cathodic wave when scanning from the anodic limit with the light off. The oxidation/reduction waves correspond to the chemistry represented by the equation



These characteristics are qualitatively the same as reported previously⁹ in nonaqueous media. The data in Figure 2 illustrate that the surface-confined material can be oxidized and reduced a large number of times without substantial deterioration.

The position of the photoanodic peak for the derivatized electrode depends on light intensity.⁹ At low light intensity there is not necessarily even a peak; the photocurrent corresponding to oxidation of the material on the surface is controlled by the hole generation rate. When a peak is observed, the photocurrent becomes limited by the amount of reduced

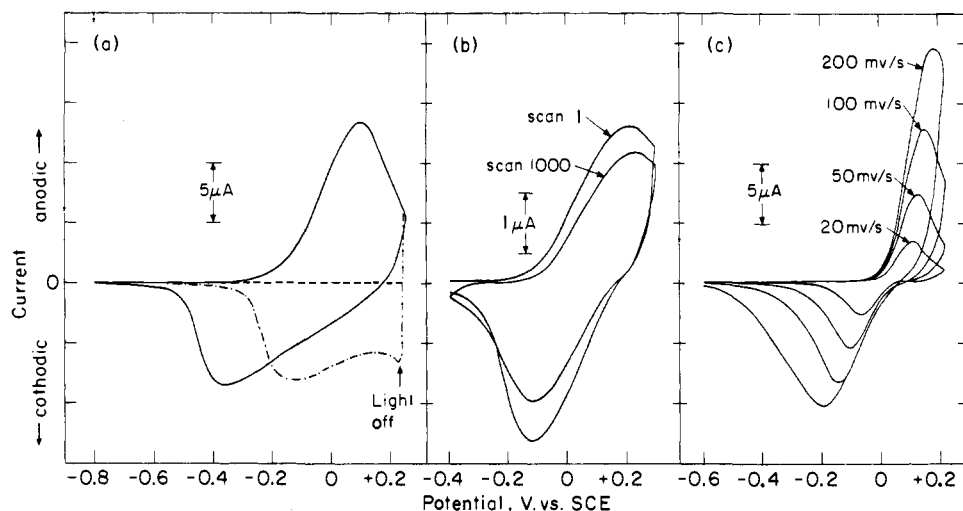


Figure 2. Cyclic voltammetric characterization of three different derivatized n-type Si electrodes in 0.1 M NaClO₄, pH 1.3. Scans are initiated at the negative limit. Illumination is from a He-Ne laser at 632.8 nm, ~4.5 mW over the entire electrode surface (0.1 cm²). (a) Cyclic voltammogram (100 mV/s) in the dark (---), under illumination (—), and an illuminated anodic scan followed by a dark cathodic return (---). (b) The electrode is scanned (200 mV/s) under illumination 1000 times between -0.5 and +0.3 V vs. SCE indicating durability of surface. (c) Scan rate dependence of an illuminated electrode.

material on the surface. The most negative photoanodic peak is observed at the highest light intensity. The most negative peak observed so far from n-type Si in aqueous solution is at ~-0.05 V vs. SCE; more typically, we observe peaks in the range 0.1–0.2 V vs. SCE at the light intensity routinely employed, ~40 mW/cm² at 632.8 nm. By comparison to derivatized Pt or Au using (1,1'-ferrocenediyl)dichlorosilane as the derivatizing reagent,¹⁴ the derivatized n-type Si exhibits waves that are more negative at sufficiently high light intensity. Derivatized Pt or Au exhibits cyclic voltammetric waves centered at ~+0.5 V vs. SCE, which, as expected, is very close to the formal potential of the ferricenium/ferrocene system in solution.^{14,15} That waves on Si can be more negative indicates that the surface-confined ferrocene can be oxidized in an uphill manner by up to ~0.5 V when using a high light intensity. Assuming that the photoanodic wave is symmetrical the peak potential represents the potential at which the ferricenium/ferrocene ratio is unity. We take this potential to be the potential at which the derivatizing layer is at the formal potential of the ferricenium/ferrocene system.^{9b} From the results for Pt and Au we take $E^0(\text{ferricenium/ferrocene}) = +0.45$ V vs. SCE for aqueous electrolyte solutions contacting the surface-confined redox-active material. Thus, the position of the photoanodic peak defines what solution species are energetically capable of oxidation at that electrode potential, assuming that oxidation of solution species occurs exclusively by what we have termed *mediated* oxidation,⁹ i.e., the direct oxidation of solution reductant by the bound redox reagent.

The data show that for electrode potentials of 0.0–0.2 V vs. SCE the oxidizing power of the surface can be ~+0.45 V vs. SCE when the irradiation is sufficiently intense. The cyclic voltammograms generally are not taken to positive excursions that would bring the ferricenium/ferrocene ratio any higher than ~10. Thus, if the potential of the derivatizing reagent layer obeys the Nernst equation, the oxidizing power does not significantly exceed +0.5 V vs. SCE.

The formal potential for O₂/H₂O is ~+1.00 to +0.6 V vs. SCE for a pH range 0–7. Accordingly, the derivatized photoelectrode does not have the oxidizing power to evolve O₂ from H₂O when the O₂ is at unit activity and pH < 7. We find that there is no sustained photocurrent in aqueous solution containing no added reductant. For example, stepping the potential of a derivatized photoelectrode from -0.6 V vs. SCE to +0.1 V vs. SCE in the dark followed by switching on the light (40 mW/cm²) results in a photocurrent spike having an integrated

area corresponding to ~50% oxidation of the surface-confined ferrocene. At a given potential and light intensity a photostationary state ratio of surface-confined ferricenium/ferrocene is achieved, and no current for O₂ evolution is observed.

The oxidizing power of the surface-confined material obviously increases as the ferricenium/ferrocene ratio is increased. At a given light intensity, the ratio theoretically increases without limit as the electrode potential is moved more positive. Accordingly, very difficult oxidations would be thermodynamically possible. However, chemical reality precludes an infinite ferricenium/ferrocene ratio; >9999/1 would be optimistic giving a ~+0.7 V vs. SCE oxidizing power. But *mediated* oxidation rates would likely be very low for species whose formal potential is so positive. Further, there is no special reason to expect a ferricenium-centered reagent to be able to effect the multielectron oxidation of H₂O without being irreversibly hydroxylated or otherwise destroyed. Finally, we find that significantly positive excursions with derivatized n-type Si appear to result in irreversible oxide growth undermining the derivatizing layer. Positive excursions to +0.6 V have been carried out without ill effects, but more routinely we avoid potentials which are >0.2 V more positive than the photoanodic peak.

With respect to durability, we have encountered no difficulty with the cathodic excursion. In the pH range 0–7 the H₂/H₂O potential is -0.23 to -0.63 V vs. SCE. But in this potential range we observe no cathodic current; very negative potentials (~-1.5 V vs. SCE) are needed to effect H₂ evolution at either the naked or derivatized n-type Si in aqueous solutions (pH 0–7). Derivatized electrodes have been routinely scanned to -1.0 V vs. SCE without deleterious effects on electrochemical behavior of the confined material. The lack of efficient H₂ evolution is not a particularly surprising result, since very few materials are good H₂ electrodes. But we find additionally that naked (or derivatized) n-type Si is a poor cathode for either the reduction of [Fe(CN)₆]³⁻ or [Ru(NH₃)₆]³⁺; very negative potentials are needed to reduce either of these ions compared to what obtains for Pt or for the ferricenium → ferrocene system on n-type Si, Figures 3 and 4. The extent to which the reduction peak is more negative seems to depend significantly on the oxide layer thickness. But in no case does the reduction of [Fe(CN)₆]³⁻, [Ru(NH₃)₆]³⁺, or I₃⁻ occur with good kinetics. Cyclic voltammetry shows broad peaks with a more negative cathodic current peak at faster scan rates. Finally, we have been unable to establish any clear-cut, systematic effects

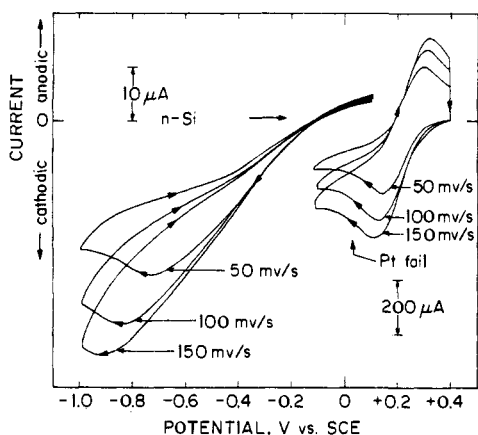


Figure 3. Comparison of cyclic voltammetry of 1.0 mM $K_3[Fe(CN)_6]$ in 0.1 M $NaClO_4$, pH 5, aqueous solution at naked, n-type Si (nonilluminated) and at a Pt-foil electrode.

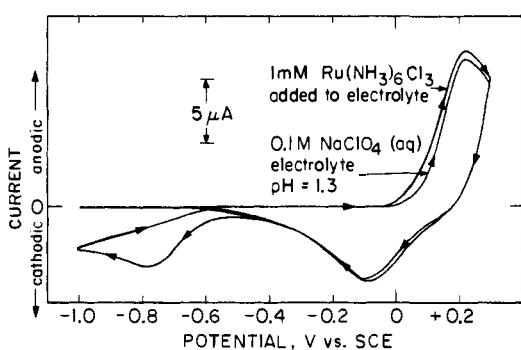


Figure 4. Cyclic voltammogram (50 mV/s) of illuminated, chemically derivatized n-type Si with and without $[Ru(NH_3)_6]Cl_3$. The reduction peak at -0.75 V vs. SCE is associated with the $[Ru(NH_3)_6]^{3+} \rightarrow [Ru(NH_3)_6]^{2+}$ reduction. After the $[Ru(NH_3)_6]^{2+}$ is generated by the excursion to -1.0 V vs. SCE, there is a slightly larger photoanodic current associated with ferrocene \rightarrow ferricenium plus regeneration of $[Ru(NH_3)_6]^{3+}$. The ferricenium \rightarrow ferrocene return peak is slightly attenuated when the $[Ru(NH_3)_6]^{2+}$ is generated, evidencing a mediated oxidation mechanism.

on the cathodic behavior of n-type Si upon derivatization with the (1,1'-ferrocenediyl)dichlorosilane.

One characteristic of the derivatized electrodes remains to be mentioned: coverage and kinetics. The oxidation of surface-confined material in the $H_2O/0.1$ M $NaClO_4$ occurs rapidly at sufficiently high light intensity. Generally, the kinetics for the photooxidation are good as evidenced by the linear plot of peak photocurrent against scan rate, at sufficiently high hole generation rates from appropriate light intensity. But the range of scan rates where linear plots are found does seem to depend on coverage. At coverages which are in the range of $\sim 10^{-10}$ mol/cm² of projected area the fastest kinetics obtain and linear plots at scan rates up to 300 mV/s obtain. But oligomeric coverages, up to 10^{-8} mol/cm² of projected area, using (1,1'-ferrocenediyl)dichlorosilane can be obtained and plots of peak current vs. scan rate fall from linearity even at <200 mV/s. Reduction of the photogenerated ferricenium has irreproducible and complicated kinetics. It would appear that reduction of oxidized material should occur only at potentials more negative than the flat-band potential, E_{FB} , of the semiconductor. E_{FB} is at ~ -0.2 V vs. SCE from the onset of the photoanodic current, but the ferricenium \rightarrow ferrocene reduction peak is at a potential some 0.2–0.4 V more positive than E_{FB} . Such is generally taken to reflect an important role for "surface states"—electronic levels situated between the E_{CB} and E_{VB} positions which facilitate the reduction process.^{4,6,9b} The density and position of surface states

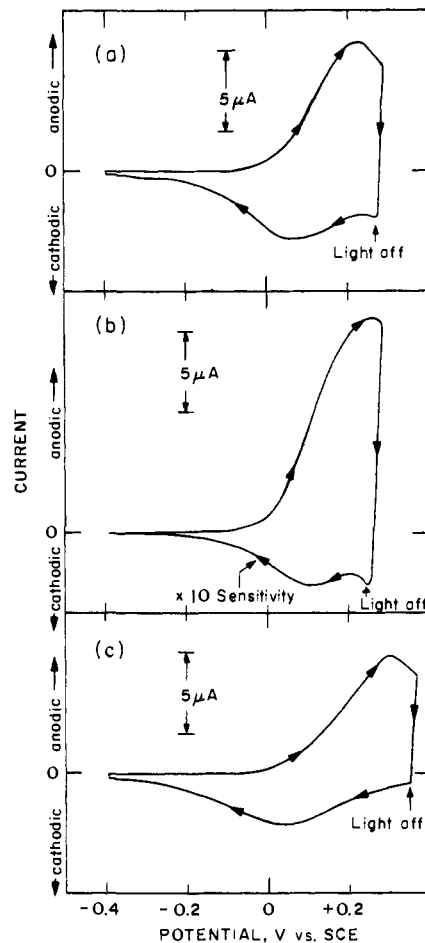


Figure 5. (a) Cyclic voltammogram (100 mV/s) of illuminated (~ 40 mW/cm², 632.8 nm), derivatized n-type Si electrode in quiet 0.1 M $Na[CF_3CO_2]$, pH 1.6. Note that the light is switched off at the anodic limit. (b) Same as in (a) except in the presence of 2 mM $[Ru(NH_3)_6]^{2+}$. (c) Repeat of (a) after doing experiment in (b) ~ 30 times.

presumably control the kinetics for the reduction of ferricenium at potentials more positive than E_{FB} .

B. Mediated Oxidation of Aqueous $[Ru(NH_3)_6]^{2+}$ at Derivatized Si. The $[Ru(NH_3)_6]^{3+}/[Ru(NH_3)_6]^{2+}$ formal potential is at -0.2 V vs. SCE.¹⁶ Accordingly, the oxidation of $[Ru(NH_3)_6]^{2+}$ is not a process which can be effected significantly uphill, since the E_{FB} is at about the same position as the formal potential of the couple. However, the $[Ru(NH_3)_6]^{2+/3+}$ system has a fairly high self-exchange rate, and being a negative couple would allow us to maintain the derivatized n-type Si at potentials where we have established (vide supra) that the derivatized surface is durable.

The $[Ru(NH_3)_6]^{2+}$ is not commercially available but is easily accessible by electrochemical reduction of $[Ru(NH_3)_6]^{3+}$ which is available as the Cl^- salt. We first attempted the in situ reduction¹⁶ of 1 mM $[Ru(NH_3)_6]^{3+}$, Figure 4. But clear evidence for mediated oxidation was not obtained, since only a slightly enhanced photoanodic current and slightly attenuated ferricenium \rightarrow ferrocene wave were observed. Consequently, a 1 mM $[Ru(NH_3)_6]^{2+}$ solution was generated by reduction of $[Ru(NH_3)_6]^{3+}$ at a Hg-pool electrode. Such solutions were used promptly owing to the known acid-accelerated aquation of $[Ru(NH_3)_6]^{2+}$.¹⁷ Figure 5 shows compelling electroanalytical evidence that photogenerated, surface-confined ferricenium is capable of oxidizing $[Ru(NH_3)_6]^{2+}$. The crucial results are that (1) the photoanodic current in the presence of $[Ru(NH_3)_6]^{2+}$ is larger than without it and (2) the ferricenium \rightarrow ferrocene return wave is significantly attenuated. The latter result, particularly,

Table II. Representative Output Characteristics for Aqueous Derivatized n-Type Si Photoelectrochemical Cells^a

electrode coverage	input, μW^b	$\Phi_{e, \text{redox}}^c$	$\Phi_{e, \text{max}}^d$	max power output, μW	V_{onset}^e (SCE)	V at η_{max} , mV	η_{max} , % ^f
A. 0.1 M Na[CF ₃ CO ₂], 4.3 × 10 ⁻² M [Ru(NH ₃) ₆]Cl ₃ , pH 1.6 ($E_{\text{redox}} = -0.26$ V vs. SCE) ^g							
1.3 × 10 ⁻⁹ mol/cm ²	5.1		0.23		0.0		
	140		0.24		-0.08		
	440		0.22		-0.12		
	1280		0.21		-0.18		
	5620		0.084		-0.20		
B. 0.1 M NaClO ₄ , 0.1 M KI, 5.2 × 10 ⁻³ M I ₂ , pH 1.3 with HClO ₄ ($E_{\text{redox}} = +0.32$ V vs. SCE)							
2.0 × 10 ⁻⁸ mol/cm ²	47	0.44	0.58	0.63	+0.16	140	1.3
	150	0.33	0.65	1.33	+0.02	140	0.89
	510	0.15	0.59	2.00	0.00	140	0.39
	1310	0.067	0.34	2.40	0.00	120	0.18
	4900	0.028	0.14	3.6	-0.02	120	0.074

^a Data taken from Figures 6 and 11. ^b Irradiation from a 632.8-nm He-Ne laser. For power density multiply by 10 cm⁻². ^c Quantum yield for electron flow at E_{redox} (the short-circuit potential), measured as electrons in external circuit per photon incident on cell. ^d Quantum yield for electron flow at potential where current is maximized. ^e V_{onset} is the open-circuit photopotential referenced to a SCE. ^f Efficiency for conversion of 632.8-nm light to electricity. ^g The working electrolyte was obtained by electrolyzing this solution at a Hg pool electrode until enough current was passed to reduce 40 mM [Ru(NH₃)₆]Cl₃ to the 2+ salt.

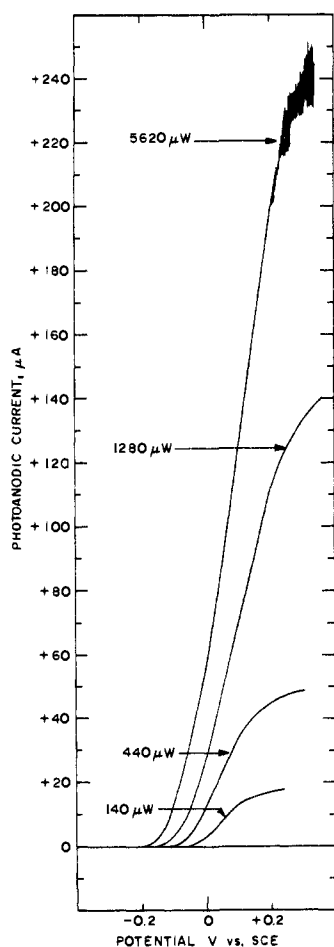
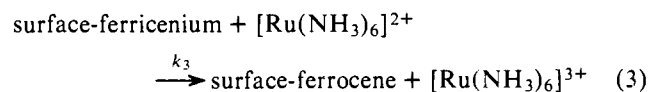


Figure 6. Equilibrium photocurrent-voltage curves (10 mV/s, stirred solution) for derivatized, n-type Si as a function of light intensity (indicated in μW) at 632.8 nm. For current density or power density multiply current or optical power by 10 cm⁻²; see also Table I. The solution is stirred 0.1 M Na[CF₃CO₂], 40 mM [Ru(NH₃)₆]²⁺ at pH 1.6.

establishes that the photogenerated ferricenium can oxidize the solution reductant, [Ru(NH₃)₆]²⁺. Note, however, that there appears to be a residual amount of ferricenium → ferrocene current. This result is a routine finding in our aqueous solution mediated electron transfer experiments.

Qualitatively, the [Ru(NH₃)₆]^{2+/3+} system is more difficult to study than the I₃⁻/I⁻ and [Fe(CN)₆]^{4-/3-} systems to be

described below. The [Ru(NH₃)₆]²⁺ is very air sensitive and the experiments are carried out under Ar. Further, the formal potential of the Ru system is so negative that equilibration with the surface-confined ferricenium/ferrocene system involves a sufficiently large driving force that it is difficult to observe the ferricenium → ferrocene return wave at any scan rate used when [Ru(NH₃)₆]²⁺ is present. But fast scan rates and very low [Ru(NH₃)₆]²⁺ concentration can be used to obtain data which indicate that it may be possible to measure the rate constant associated with the heterogeneous redox reaction represented by the equation



We conclude that k_3 is larger than for any other system that we have investigated to date. Also, we reiterate the point that the naked n-type Si electrode gives no detectable [Ru(NH₃)₆]²⁺ → [Ru(NH₃)₆]³⁺ at the concentrations employed here; only chemistry represented by eq 1 obtains for the naked electrode. Thus, this negative evidence and the electroanalytical data in Figures 4 and 5 prove that eq 2 and 3 represent the *only* mechanism for effecting the oxidation of the solution reductant. In particular, for the derivatized electrode, any areas of the surface not derivatized will be rapidly passivated by SiO_x growth precluding any efficiency for a direct hole transfer to the solution reductant.

Figure 6 shows the steady-state photocurrent-voltage curves as a function of light intensity for a derivatized n-type Si photoanode-based cell in an aqueous solution of [Ru(NH₃)₆]²⁺. Some quantitative facts culled from these curves are included in Table II. The main findings are as follows: (1) the [Ru(NH₃)₆]²⁺ cannot be oxidized in an uphill sense, consistent with the fact that E_{FB} is near the formal potential of the Ru system; (2) the onset of photocurrent is more cathodic with increasing light intensity, consistent with a more powerful oxidizing surface at the higher light intensities; (3) the maximum quantum yield for electron flow is respectable and is not attenuated significantly up to ~20 mW/cm². The lower quantum yield at the highest intensity may be due to the low concentration of [Ru(NH₃)₆]²⁺; note the pen "chatter" at the positive limit due to irregularity in the stirring which indicates that too little reductant is available at the photoanode. The curves in Figure 6 are reproducible and Figure 5c shows that the derivative is still in place after the experiment. With a naked electrode not even a single scan can be reproduced.

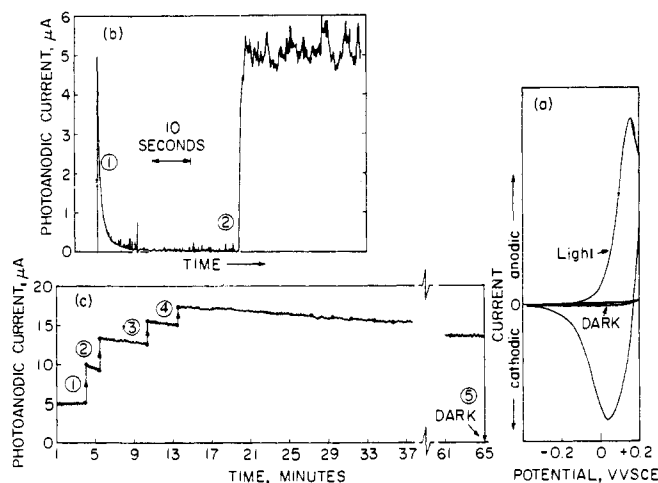


Figure 7. (a) Cyclic voltammogram (50 mV/s) for illuminated, derivatized n-type Si photoelectrode in 0.1 M NaClO₄, pH 1.6. (b) Electrode in (a) is stepped to +0.075 V vs. SCE in the dark from -0.6 V and the light is turned on at ① and then [Ru(NH₃)₆]²⁺ to 0.1 mM is added at ② while current is monitored in the stirred electrolyte solution. (c) Continuation of photocurrent time plot of (b) at a potential of 0.075 V vs. SCE; at ①, ②, ③, and ④ additional [Ru(NH₃)₆]²⁺ is added to bring the concentration to 0.2, 0.45, 0.88, and 1.9 mM, respectively.

The data in Figure 7 provide a direct measure of the durability of a derivatized n-type Si photoanode under these conditions. First, in Figure 7a a cyclic voltammogram for the illuminated derivatized photoelectrode is shown. The electrode has modest coverage, 7×10^{-10} mol/cm² of projected area from integration of a cyclic voltammogram. In Figure 7b the electrode is scanned in the dark to +0.075 V vs. SCE and then held there while the light is switched on to give a photocurrent spike rising instantly to $\sim 5 \mu\text{A}$ and decaying to zero current in < 10 s. This corresponds to photooxidation of some fraction of the surface-confined ferrocene giving some photostationary state ratio of ferricenium/ferrocene. In Figure 7b the result of then adding [Ru(NH₃)₆]²⁺ to a concentration of 0.1 mM is shown; a photocurrent instantly begins and remains constant at $\sim 5 \mu\text{A}$. The plot of photocurrent against time is continued in Figure 7c.

Figure 7c shows the additional effect of adding more [Ru(NH₃)₆]²⁺. The photocurrent is observed to be approximately proportional to the concentration of added reductant only at the lowest concentration levels. At concentrations above 0.2 mM, a significant deviation from linearity is observed. This indicates a light intensity limited current, which is in accord with the data given in Figure 6. At the given potential, light intensity, and solution reductant concentration, production of surface ferricenium is slower than the rate of heterogeneous electron transfer; thus the surface is mainly in its reduced form. Addition of more solution species under these conditions will have little effect on the current observed. The concentration at which this effect is observed will depend on the electron transfer rate constant. The low concentration at which the [Ru(NH₃)₆]²⁺ deviates from linearity indicates that k_3 is large.

Between $t = 13$ min and $t = 65$ min, the photocurrent diminishes somewhat from 17.5 to 14 μA . But during the interval of the irradiation 6.6×10^{-7} mol of electrons passed through the derivatized photoelectrode/liquid interface. Assuming that the mechanism of oxidation is as in eq 2 and 3, this reveals that each surface-confined redox center is oxidized and reduced over 1000 times; after the experiment the derivatized electrode shows the same cyclic voltammogram as before the start of the experiment, Figure 7a. These data confirm that the derivatized electrode is fairly rugged in aqueous solution, and at least such photosensitive interfaces can be used to do reproducible elec-

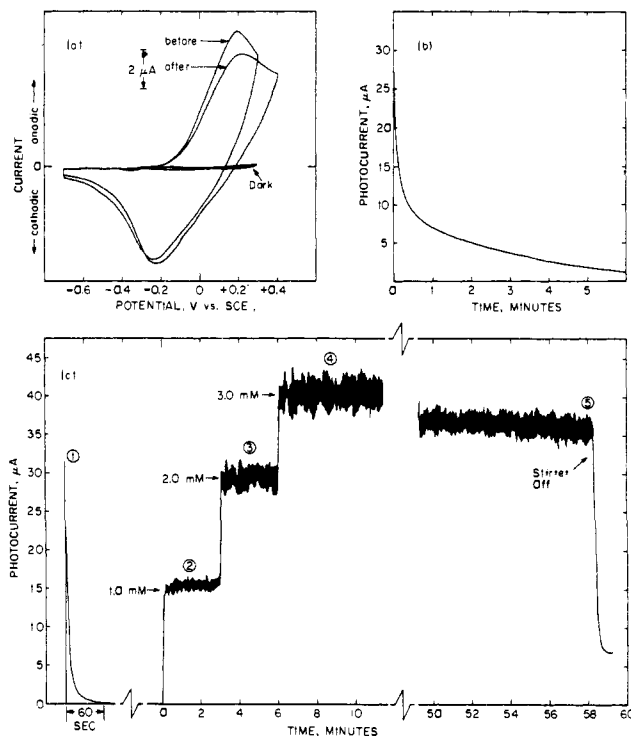
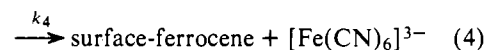
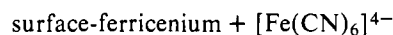


Figure 8. (a) Cyclic voltammogram (20 mV/s) of an irradiated, derivatized n-type Si electrode. "Before" refers to before experiment in (c) and "after" refers to characterization after the experiment in (c). The electrolyte solution is 0.1 M NaClO₄, pH 3.0. (b) Photocurrent vs. time for a naked, n-type Si electrode at +0.10 V vs. SCE in 3.0 mM K₄[Fe(CN)₆], 0.1 M NaClO₄, pH 3.0. (c) Electrode in (a) stepped from -0.6 to +0.10 V vs. SCE in the dark; at ① the light is switched on and at ②, ③, and ④ K₄[Fe(CN)₆] is added to the concentrations indicated.

trochemistry under conditions where the naked electrode is incapable of doing so.

C. Mediated Oxidation of Aqueous [Fe(CN)₆]⁴⁻ at Derivatized Si. Our earlier, preliminary article^{9c} provided evidence that irradiated, derivatized n-type Si is capable of effecting the uphill oxidation of [Fe(CN)₆]⁴⁻. We have repeated and amplified our earlier findings. Figure 8 shows the results of a typical experiment. Under conditions where the naked n-type Si is useless, Figure 8b, the derivatized n-type Si is capable of sustaining the flow of photocurrent corresponding to the process represented by the equation



The oxidation to form [Fe(CN)₆]³⁻ was monitored spectrophotometrically and the data show $> 90\%$ current efficiency for the process. From the experiment detailed in Figure 8c it is apparent that the concentration of reductant is current limiting up to a concentration of 2 mM [Fe(CN)₆]⁴⁻. The photocurrent appears to be approximately proportional to [Fe(CN)₆]⁴⁻ in this range. Saturation begins to set in at a concentration of 3 mM indicating light intensity limited behavior at this concentration. As for the [Ru(NH₃)₆]²⁺ system, the derivatized photoelectrode is not significantly altered by the experiment in Figure 8c; cf. "before" and "after" in Figure 8a. In the experiment shown, each redox center on the surface of the photoelectrode turned over 1000 times. Note that the photocurrent declines from 40 to 36 μA in 60 min—a decline of only 10%, whereas the naked electrode declines $> 90\%$ in < 5 min. In other experiments we have demonstrated > 5000 turnovers of each redox center for the derivatized surface without serious decline in photocurrent.

The formal potential for the [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻

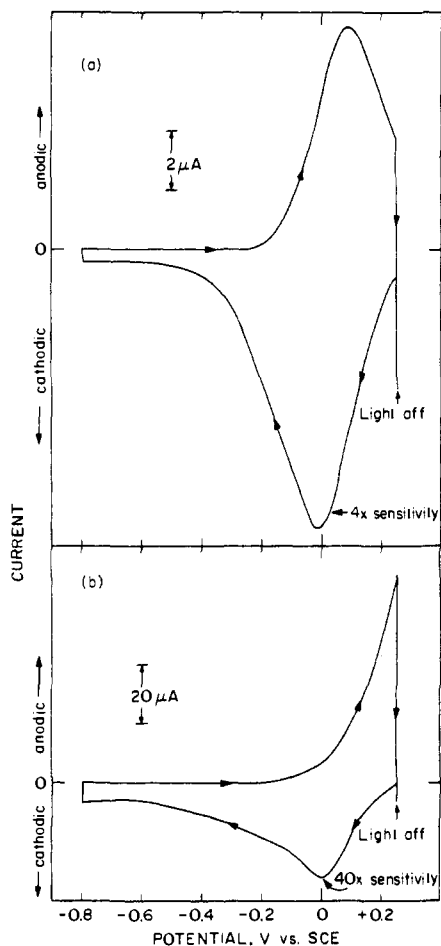
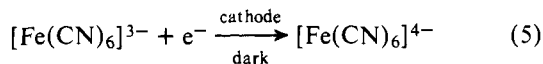


Figure 9. (a) Cyclic voltammetry for derivatized Si photoanode in stirred 0.1 M NaClO₄, pH 1.3, solution. Scan are run at 100 mV/s with a 15-s delay in the dark at the most positive potential. (b) Same as in (a) except 0.2 M KI added. Note that in (a) the reduction peak is on a scale four times more sensitive than for the anodic peak, whereas the cathodic peak is 40 times more sensitive than the anodic current.

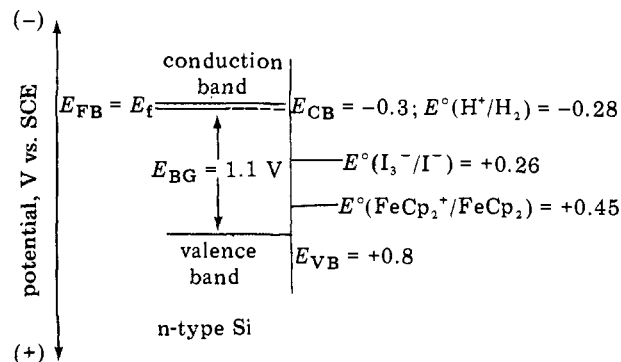
couple is +0.2 V vs. SCE,¹⁸ and it may be that the rate constant k_4 is somewhat less than k_3 , owing to the smaller driving force for the [Fe(CN)₆]⁴⁻ oxidation. The self-exchange rate for [Fe(CN)₆]^{3-/4-} is about the same as that for the [Ru(NH₃)₆]^{3+/4+} system.^{19,20} For now, our comparison of k_4 and k_3 is qualitative; quantitative measurements of such rate constants are in progress and will be reported subsequently.²¹

The formal potential of the [Fe(CN)₆]^{3-/4-} and the value of E_{FB} indicate that the thermodynamically uphill oxidation of [Fe(CN)₆]⁴⁻ should be possible by illumination of the derivatized photoanode. And since the reduction of [Fe(CN)₆]³⁻ at the counterelectrode is possible



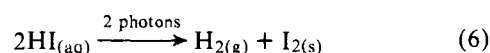
eq 2, 4, and 5 represent the chemistry of a cell for the conversion of light to electricity without chemical change. In this connection it is interesting to point out that the reduction of [Fe(CN)₆]³⁻ at the derivatized Si photoelectrode is very sluggish; cf. Figure 3. This indicates that there should be little back electron transfer to the photoanode when the uphill oxidation of [Fe(CN)₆]⁴⁻ is effected. This contrasts with the EtOH/electrolyte/ferricenium/ferrocene, naked, n-type Si-based cell where ferricenium reduction is observable at potentials where ferrocene can be oxidized in an uphill manner. Despite the apparently optimal conditions for an efficient cell for the sustained conversion of light to electricity, we note two

Scheme I. Interface Energetics for Derivatized n-Type Si against an Aqueous HI Solution



serious drawbacks: (1) both [Fe(CN)₆]⁴⁻ and [Fe(CN)₆]³⁻ absorb to some extent in the blue end of the visible spectrum and each is photosensitive²² and (2) in our hands the [Fe(CN)₆]^{4-/3-} is sufficiently thermally labile in acidic solution that the chemical integrity of the redox couple cannot be taken for granted. Thus, a durable photoelectrochemical cell is not a likely prospect. Our data show, however, that the conversion of 632.8-nm light to electricity can be sustained for periods of the order of several hours. Efficiencies for conversion of 632.8-nm light to electricity are in the range of 0.5–2% at voltages of 200 mV with photocurrent densities of 5 mA/cm². It would appear that the quantum yield at high intensities is low and that the rectangularity of the photocurrent–voltage curves is poor resulting in low fill factors. The main point now, though, is that the Si is useless in the aqueous electrolyte without the derivatization procedure.

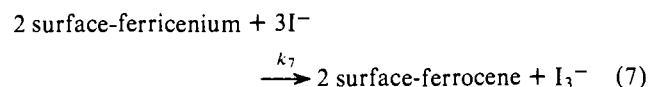
D. Thermodynamically Uphill Iodide Oxidation at Irradiated Derivatized Photoanodes. One of the aims of using derivatized photoanodes is that the derivative allows the oxidation of a large number of reductants. We have amply demonstrated that complexes of Ru(II) and Fe(II) can be efficiently oxidized at the derivatized photoanode, whereas no such reaction can be effected by the naked electrode. But the formation of Ru(III) or Fe(III) complexes does not appear to be a viable approach to light to chemical energy conversion. We now describe our studies concerning the uphill oxidation of aqueous iodide, an ultimate objective being the net chemistry represented by the equation



$$\Delta G^\circ = 24.7 \text{ kcal/mol (HI)}$$

The minimum decomposition voltage for HI is 0.54 V; the I₂/I⁻; I₃⁻/I⁻ formal potential is at +0.26 V vs. SCE.²³ This would indicate that the derivatized n-type Si would be capable of effecting the uphill oxidation of I⁻, but the E_{CB} is at approximately the position of the H⁺/H₂ couple, Scheme I. This indicates that little, or no, efficiency would be obtained by irradiating the photoelectrode short-circuited to the counterelectrode (H₂ electrode). Nonetheless, it would appear that the evolution of I₂ can be effected in a significantly uphill sense, and the reaction is sufficiently interesting that we undertook an attempt to do it.

Figure 9 shows cyclic voltammetry for a derivatized photoanode with and without KI. In the presence of I⁻ the ferricenium → ferrocene reduction peak in the dark is substantially attenuated, consistent with mediated redox reaction according to the equation



As usual, the reduction wave cannot be completely suppressed;

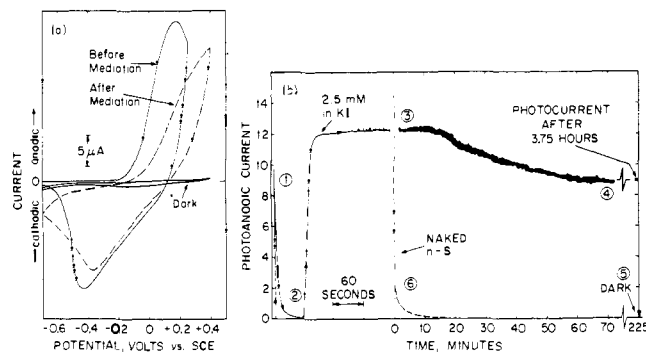


Figure 10. (a) Cyclic voltammetry (100 mV/s) of illuminated derivatized Si before and after the experiment in (b) in 0.1 M NaClO₄, pH 1.3. (b) Plot of photocurrent against time for electrode in (a) after stepping from -0.6 to 0.00 V vs. SCE in the dark and then switching on the light, ①; followed by adding KI, ②; a plot of photocurrent vs. time for a naked Si photoanode in the 2.5 mM KI ③. Note time breaks in the axis at ③ and ④; ⑤ marks the "dark" current (none) showing that all current is due to illumination.

under the conditions shown it is attenuated by $\sim 75\%$. Larger I^- concentrations do attenuate the cathodic return peak more. These data establish the fact that photooxidation of the I^- can be mediated.

Data in Figure 10 establish that a derivatized photoanode is fairly rugged. The derivatized electrode can be used to sustain the uphill oxidation of 2.5 mM I^- . Note that between $t = 70$ and 225 min operation the photocurrent is steady after declining by $\sim 25\%$ in the first 70 min of operation. Integration of the photocurrent and monitoring the I_3^- spectrophotometrically using a two-compartment photoelectrochemical cell show that the photocurrent efficiency exceeds 90% for the $I^- \rightarrow I_3^-$ process. Electrodes have been prepared which exhibit $>10^5$ turnovers for each redox center confined to the surface. In such an experiment photocurrent does generally decline; $<50\%$ decline in photocurrents for such turnover numbers is not atypical. The decline in photocurrent appears to be due mainly to a positive shift in the position of the photoanodic peak; cf. "before" and "after" in Figure 10a. The total coverage of electroactive material does not seem to be substantively affected, as measured by cyclic voltammetry in an innocent electrolyte solution. These data suggest that there is slow SiO_x growth undermining the derivatized layer. But turnover numbers of the order of 10^5 would appear easily accessible with coverages of electroactive material in the monolayer range. Experiments are in progress to assess uniformity of coverage, but the photocurrent density for these electrodes would suggest that there is not a significant area which is not derivatized.

The disappointing find is that the photocurrent-voltage curves, Figure 11, reveal relatively poor overall efficiency for I_3^- generation with respect to the extent to which this can be done thermodynamically uphill. The solution potential is $+0.3$ V and the onset of photoanodic current is -0.05 to $+0.05$ V vs. SCE depending on light intensity, indicating output voltages no greater than 350 mV. But the rectangularity of the current-voltage curves is such that the maximum photocurrent is not reached until a potential somewhat positive of the solution potential. Overall efficiency, culled from the data in Figure 11, is detailed in Table II. For monochromatic 632.8-nm light, the generation of I_3^- at an energy conversion efficiency of $\sim 1\%$ can be maintained.

Summary

Derivatized n-type Si can be used as a photoanode in aqueous electrolyte solution. Uphill oxidation of I^- to I_3^- and $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ can be effected by illumination of the photoanode but the overall efficiency is low, even for monochromatic light ($\sim 1\%$). Problems with durability and

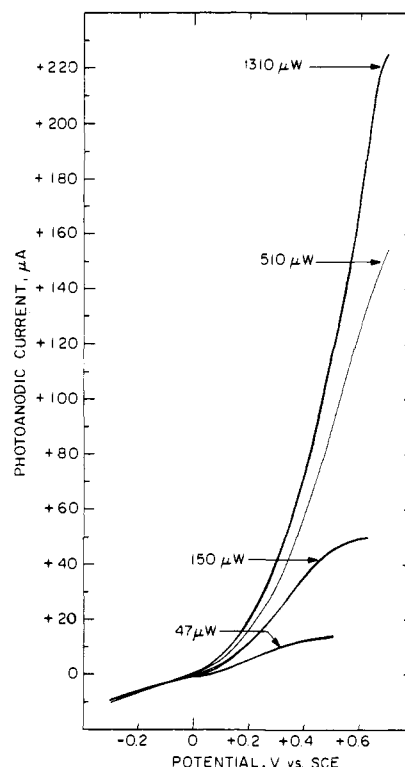


Figure 11. Equilibrium photocurrent-voltage curves (10 mV/s) as a function of 632.8-nm light intensity (indicated in μW) for derivatized n-type Si in a I_3^-/I^- solution where the total I concentration is 0.1 M and the solution potential is $+0.3$ V vs. SCE. For current or optical power density multiply values shown by 10 cm^{-2} . See also Table II.

reproducibility of derivatized n-type Si surfaces remain, but turnover numbers of $>10^5$ can be realized at current densities of several mA/cm^2 , and there is a clear improvement in photocurrent stability compared to naked n-type Si.

Experimental Section

Preparation of Electrodes. Single-crystal, Sb-doped, n-type Si wafers (111 face exposed) were obtained from General Diode Co., Framingham, Mass. The polished wafers were 0.25 mm thick with resistivities between 4 and 5 Ω/cm . Electrodes were made by cutting the Si into pieces $\sim 0.2 \text{ cm}^2$ and mounting as previously reported.^{7,9} The back surface was rubbed with Ga-In eutectic and attached with conducting Ag epoxy to a coiled Cu wire. The Cu wire was passed through a glass tube. The electrode surface was defined by insulating all other surfaces with ordinary epoxy. An electrode area of $\sim 0.1 \text{ cm}^2$ was generally used.

Just prior to use "naked" electrodes were etched in concentrated HF and rinsed in distilled H₂O. Electrodes to be derivatized were treated in 10 M NaOH for 60 s after the HF etch process, then washed with H₂O followed by acetone and air dried. Derivatization was carried out by exposing the pretreated electrodes under an Ar atmosphere for 1–12 h to a $\sim 10^{-2}$ M solution of (1,1'-ferrocenediyl)dichlorosilane in Ar-purged isooctane at 298 K.⁹ The process was completed by rinsing the electrode first with isooctane and then with absolute EtOH.

Chemicals. All chemicals were reagent grade: $K_3[Fe(CN)_6] \cdot 3H_2O$ (Mallinckrodt), $K_4[Fe(CN)_6] \cdot 3H_2O$ (Mallinckrodt), KI (Mallinckrodt), $[Ru(NH_3)_6]Cl_3$ (Alfa), anhydrous NaClO₄ (G. Frederick Smith), and CF₃CO₂H (Aldrich) were used as received. Polarographic grade $[n\text{-Bu}_4N]ClO_4$ (Southwestern Analytical Chemicals) was dried under vacuum (353 K) for 12 h. Absolute EtOH and spectroquality isooctane were used as received. Ferrocene was purified by sublimation before use. Double-distilled, deionized H₂O was used as solvent for aqueous electrolytes.

Preparation of $[Ru(NH_3)_6]^{2+}$. $[Ru(NH_3)_6]_{(aq)}^{2+}$ was formed by exhaustive reduction of $[Ru(NH_3)_6]Cl_3$ at a Hg-pool electrode (-0.3 V vs. SCE) in a two-compartment cell.¹⁶ The reduction was carried out under an Ar purge in a 0.1 M Na[CF₃CO₂] pH 5 electrolyte just prior to use in a photoelectrochemical cell. The product was monitored

by its UV-visible spectrum (ϵ 640, λ 275 nm)¹⁷ using a Cary 17 spectrometer. The formation of $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$ as a side product was monitored by adding an excess of pyridine to an aliquot of the catholyte and observing spectroscopically the formation of $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+}$ (ϵ 7770, λ 407 nm).¹⁷ Over the time scale of the experiments carried out no detectable $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$ was formed.

Electrochemistry. Electrodes were characterized electrochemically using a PAR 173 potentiostat equipped with a PAR 179 coulometer and a PAR 175 universal programmer. Traces were recorded on a Houston Instruments X-Y recorder. All experiments employed a standard three-electrode setup. A saturated calomel (SCE) reference electrode was used. Irradiation was supplied by a He-Ne laser emitting ~ 5.6 mW at 632.8 nm. Laser intensity was measured using a Tektronix J16 digital radiometer equipped with a J6502 probe. A beam split fraction of the beam was monitored.

In order to obtain stable results in aqueous media from derivatized electrodes the following "break-in" procedure was used. The derivatized electrodes were scanned under illumination by cyclic voltammetry in 0.1 M $[\text{n-Bu}_4\text{N}]\text{ClO}_4/\text{EtOH}$ until stable cyclic voltammograms were obtained. The electrodes were then washed in EtOH followed by H_2O and transferred to a cell containing 0.1 M $\text{NaClO}_{4(\text{aq})}$ electrolyte adjusted to pH 1.3 with HClO_4 . Starting with a cyclic scan from -0.5 to -0.2 V vs. SCE the electrodes were repetitively scanned increasing the positive limit on each consecutive scan by ~ 50 mV until a stable cyclic voltammogram was established. The final positive limit ranged between $+0.1$ and $+0.6$ V vs. SCE.

Experiments involving the photooxidation of $\text{K}_4[\text{Fe}(\text{CN})_6]$ or KI employed 0.1 M NaClO_4 as the supporting electrolyte; $[\text{Ru}(\text{NH}_3)_6]^{2+}$ oxidation was carried out in 0.1 M $\text{Na}[\text{CF}_3\text{CO}_2]$ under an Ar purge. Electrode stability was increased by maintaining the solutions at as low as pH as possible (~ 1.0) without affecting the integrity of the electrolyte.

Current-time profiles and equilibrium current potential scans were taken in stirred solutions. Cyclic voltammograms were in quiet solutions. A one-compartment cell was used. Photocurrent efficiencies were obtained for the oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ and I^- in a two-compartment cell. Efficiency was determined by monitoring the UV-visible spectrum of the products ($[\text{Fe}(\text{CN})_6]^{3-}$, I_3^-) as a function of coulombs passed. Spectral changes were monitored against control samples of the electrolyte which were not photoelectrolyzed.

Passivation Study. The short-circuit current from freshly etched, illuminated electrodes in 0.1 M ferrocene, 10^{-4} M ferricenium, 0.1 M $[\text{n-Bu}_4\text{N}]\text{ClO}_4/\text{EtOH}$ electrolyte ($E_{\text{redox}} = +0.27$ V vs. SCE) was obtained in a one-compartment cell. The electrodes were removed from the cell, washed in EtOH and then with H_2O , and replaced in the cell for another short-circuit reading. Only electrodes showing reproducibility under the above conditions were used. Washed electrodes were then transferred to a one-compartment cell containing 0.1 M NaClO_4 adjusted to pH 1.3 with HClO_4 . The electrodes were potentiostated at a given potential under illumination in the stirred electrolyte. After a predetermined amount of coulombs passed, the

electrode was removed from the cell washed with H_2O followed by EtOH and another short-circuit current observed in the ferrocene electrolyte. The cell configuration in both electrolytes was kept unchanged. This process was repeated, each time using a freshly etched electrode, for a variety of potentials and photoanodization time periods. As a control this process was carried out under conditions where no anodization current was passed in the H_2O electrolyte. Under such conditions no change in the short-circuit current in the ferrocene electrolyte was observed. Results are given in Table I.

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