PHOTOCHEMICAL ENERGY STORAGE:
STUDIES OF INORGANIC PHOTOASSISTANCE AGENTS

MASTER

Progress Report

December 17, 1979 - March 31, 1981

Mark S. Wrighton

Massachusetts Institute of Technology

Cambridge, Massachusetts 02139

December, 1980

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Prepared for

The United States Department of Energy

Under Contract No. DE-AC02-77ER04178.A003

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

TABLE OF CONTENTS

	<u>Page</u>
A. Abstract-----	1
B. Research Accomplishments, 12-11-79 to 12-16-80-----	2
C. References-----	25
D. Time Commitment of Principal Investigator-----	26
E. Contract Compliance-----	26
F. Publications-----	27
G. Activities in Remainder of Contract Term-----	28

(Copies of publications #1-5 and #11-12 are attached.)

A. Abstract

Research progress has been made in the study of p-type semiconductor (photocathode) electrode materials. A number of small band gap ($E_g \approx 1.1-1.4$ eV) p-type semiconductors have been demonstrated to have poor H_2 evolution kinetics despite the fact that a reasonable output photovoltage (E_V) compared to E_g could be expected. Special emphasis has been on p-type Si ($E_g = 1.1$ eV) and p-type InP ($E_g = 1.35$ eV). Both of these materials give poor kinetics for H_2 evolution from H_2O , while the kinetics for N,N'-dimethyl-4,4'-bipyridinium, MV^{2+} , reduction to MV^+ are good at a pH where $E^\circ(H_2O/H_2)$ is the same as $E^\circ(MV^{2+}/^+)$. A surface derivatizing reagent from diquarternizing 4,4'-bipyridine with 1-bromo-3-trimethyloxysilylpropane can be used to functionalize p-type Si with polymeric quantities of redox reagent. The surface-confined bipyridinium reagent, $(PQ^{2+})_{surf.}$, can be photoreduced to $(PQ^+)_{surf.}$ and this reduced species can be used to effect H_2 evolution if a Pt catalyst is incorporated into the polymer. Efficiency for conversion of monochromatic 632.8 nm light to H_2 exceeds 6%, compared to <<1% for the "naked" p-type Si without the surface catalyst system.

Studies of n-type semiconductor (photoanode) electrode materials modified with biferrocene-based redox mediators for $I^- \rightarrow I_3^-$ oxidation have been undertaken for comparison to ferrocene-based reagents for the same reaction; a five- to ten-fold overall improvement in heterogeneous $I^- \rightarrow I_3^-$ rate can be achieved using the two-electron mediator compared to the one-electron transfer system.

B. Research Accomplishments, 12-17-79 - 12-16-80

I. Fermi Level Pinning of P-Type InP and Behavior of Platinized InP for H₂ Generation

P-type InP has an optimum band gap, $E_g = 1.35$ eV, for solar energy conversion. We have established by cyclic voltammetry, Figure 1 and Table I, that the term "Fermi level pinning"¹⁻³ applies to p-type InP/liquid electrolyte interfaces. By this we mean that for a large number of redox couples the output photovoltage, E_V , is independent of the potential of the redox couple, E° . Indeed, for InP it would appear that for E° more negative than ~ -0.5 V vs. SCE, $E_V = 0.8 \text{ V} \pm 0.1 \text{ V}$. This value of E_V gives the highest E_V/E_g ratio ever observed for a semiconductor/liquid interface. This is an especially pleasing result, since E_g for InP is so closely matched to the optimum value for solar energy conversion. Our results⁴ are consistent with the findings recently reported for a p-type InP-based photoelectrochemical cell for conversion of solar energy to electricity ($\sim 9.3\%$ efficiency).⁵

Data in Table I are included for aqueous and non-aqueous (CH_3CN) solutions. The $\text{MV}^{2+}/^+$ couple, soluble in both media with a nearly constant E° , was used to establish that the Fermi level pinning applies in CH_3CN , $\text{CH}_3\text{CN}/\text{CH}_3\text{COOH}$; and H_2O at pH = 7.5, 6.0, 4.0, and 2.0. However, the ability to study the $\text{MV}^{2+} \rightarrow \text{MV}^+$ reduction at pH ≈ 6 signals that H_2 evolution kinetics for the InP are poor, since MV^+ is thermodynamically capable of reducing H_2O to H_2 for pH < 6. Figure 2 shows the photocurrent-voltage curves for H_2 generation from naked p-type InP compared to the same electrode that has been modified by directly plating a small amount of Pt onto the surface.⁶ The dramatic improvement is reflected in the significantly more positive onset for photocurrent. For the naked electrode we observe a photovoltage (relative to $E^\circ(\text{H}_2\text{O}/\text{H}_2)$) that is only a fraction of the ~ 0.8 V expected, since the InP

Table I. Photovoltage from Illuminated P-Type InP with Respect to Various Redox Couples.

Electrolyte System	Redox Couple	Pt		p-InP	E_V , mV ^b $\pm$ 50 m
		E_p^a cath.	E_p^a anod.	E_p^a cath.	
CH ₃ CN, 0.1 M TBAP ^c	Anthracene ^{0/-1}	-2.05	-1.96	-1.28	770
"	Ru(bpy) ₃ ^{0/-1^d}	-1.81	-1.72	-0.99	820
"	AQ ^{-1/-2^e}	-1.67	-1.55	-0.88	790
"	Ru(bpy) ₃ ^{+1/0}	-1.62	-1.47	-0.80	820
"	Ru(bpy) ₃ ^{+2/+1}	-1.37	-1.30	-0.55	820
"	AQ ^{0/-1}	-1.00	-0.92	-0.28	720
"	MV ^{+1/0^f}	-0.88	-0.81	-0.06	820
"	MV ^{+2/+1}	-0.47	-0.39	+0.33	800
"	[PtS ₄ C ₄ (CF ₃) ₄] ^{+1/0}	-0.19	-0.10	+0.45	640
"	[Fe(C ₅ Me ₅) ₂] ^{+1/0}	-0.16	-0.07	+0.44	600
"	TMPD ^{+1/0^g}	-0.05	+0.15	+0.30	350
"	[Fe(C ₅ H ₅) ₂] ^{+1/0^h}	+0.35	+0.43	+0.70	350
CH ₃ CN, 0.1 M TBAP	MV ^{+2/+1}	-0.48	-0.41	+0.26	740
CH ₃ CN, 0.1 M TBAP 0.1 M HOAc	MV ^{+2/+1}	-0.48	-0.41	+0.26	740
CH ₃ CN, 0.1 M TBAP 0.5 M HOAc	MV ^{+2/+1}	-0.48	-0.41	+0.26	740
pH 7.5 Phosphate Buffer	MV ^{+2/+1}	-0.72	-0.63	+0.05	770
pH 6.0 Phosphate Buffer	MV ^{+2/+1}	-0.72	-0.63	+0.00	720
pH 4.0 Acetate Buffer	MV ^{+2/+1}	-0.72	-0.63	+0.06	780
pH 2.0 10 ⁻² M HClO ₄	MV ^{+2/+1}	-0.72	-0.63	+0.08	800

^a $E_p^{\text{cath.}}$ and $E_p^{\text{anod.}}$ refer to cathodic and anodic current peaks, respectively, in the cyclic voltammetry. The $E_p^{\text{cath.}}$ for p-InP is for an illumination intensity of $\sim 50 \text{ mW/cm}^2$ at 632.8 nm. Potentials are V vs. SCE; ^b E_V is the photovoltage taken to be the difference in $E_p^{\text{cath.}}$ at Pt and at illuminated p-InP; ^c TBAP = [n-Bu₄N]ClO₄; ^d bpy = 2,2'-bipyridyl; ^e AQ = anthraquinone; ^f MV = N,N'-dimethyl-4,4'-bipyridinium; ^g TMPD = N,N,N',N'-tetramethyl-1,4-benzenediamine; ^h Couples having E° more positive cannot be studied owing to dark anodic decomposition of the p-type InP.

Figure 1. Cyclic voltammetry of a CH_3CN solution containing 0.1 M TBAP, ~1 mM MV^{+2} and ~1 mM $\text{Ru}(\text{bpy})_3^{+2}$ at (a) Pt; and (b) p-InP in the dark and under irradiation with 632.8 nm light. Scan rate employed is 100 mV/s. Light intensity was ~50 mW/cm².

CURRENT

Figure 2. Comparison of photocurrent-voltage curves for a p-type InP before (a) and after (b) platinization to improve H_2 evolution kinetics. At $pH = 7$ $E^\circ(H_2O/H_2) = -0.66$ V vs. SCE and photocurrent positive of this value represents power from the light being converted to chemical energy.

is Fermi level pinned to this value. Poor kinetics allow $e^- - h^+$ recombination, lowering the output performance. However, with Pt on the surface the E_V for H_2 evolution is approximately ~ 0.8 V as expected. From data such as that given in Figure 2 we determine output efficiencies for conversion of monochromatic light to exceed 10%.

The question that arises concerning the platinized semiconductor surface is whether the role of Pt is to just catalyze the reaction of the photoexcited e^- 's with H_2O to produce H_2 or does Pt form a Schottky barrier. If a Schottky barrier results, we would expect that the output performance would be independent of the pH of the solution. This follows from the fact that the Schottky barrier should be unaffected by the solution pH; it would be analogous to having a Schottky barrier solar cell in the external circuit assisting the electrolytic process. Variation in output performance for the Schottky device could result if the kinetics from H_2 evolution from Pt vary with pH. For Pt, acid solutions are better than neutral solutions but at solar intensities it is not likely that a large effect would be observed in any event. We have examined the efficiency of platinized p-type InP-based cells for H_2 evolution as a function of pH. Figure 3 shows the potential onset for photocurrent against pH for the same light intensity. A straight line reflecting a variation of 59 mV/pH unit would be expected for the ideal Schottky barrier. We do not obtain a straight line, and the slope is least in the low pH (best Pt kinetics) regime. This result, and similar results for platinized p-type Si, lead us to conclude that the amounts of Pt that give optimized photoelectrochemical generation of H_2 from H_2O do not give a simple Schottky barrier. The Pt appears to be catalyzing the evolution of H_2 in the true sense: the reaction $2H_2O + 2e^- \rightarrow 2OH^- + H_2$ is accelerated by the surface-confined catalyst.

The platinized p-type InP is a good photocathode for H_2 evolution. However, in our hands durability of such surfaces is a problem. Constant

Figure 3. Onset of photocurrent for H_2 evolution from an illuminated, platinized, p-type InP photocathode as a function of pH. The non-linear plot establishes that the role of Pt is not simply to form a Schottky barrier on InP.

output parameters are difficult to maintain beyond ~1 h of time at ~5 mA/cm². However, the data do establish that (i) catalysis is possible; (ii) high efficiency can be realized; (iii) and the mechanism of improving efficiency has been identified.

II. Surface-Confined Redox Polymers and H₂ Evolution.

Stemming from the hypothesis⁷ that H₂ evolution kinetics from p-type semiconductors limit their efficiency and the finding that MV²⁺ can be efficiently photoreduced to MV⁺ at a pH where MV⁺ is thermodynamically capable of reducing H₂O to H₂,^{3,7,8} we were prompted to synthesize a surface-derivatizing reagent based on MV²⁺. We prepared the reagent shown in I and showed that it

I
could be used to functionalize metallic (e.g. Pt, Au) and semiconductor (e.g. Si, InP) electrode materials.⁹ Polymeric quantities of reversibly electroactive material can be very persistently attached to the surface, equation (1). The surface-confined redox active material, (PQ²⁺)_{surf.}, is

reversibly reducible to both $(PQ^{\cdot+})_{\text{surf.}}$ and $(PQ^0)_{\text{surf.}}$ in CH_3CN solutions but only the first reduction is routinely reversible in aqueous solution. The $E^\circ(PQ^{2+/\cdot+})_{\text{surf.}} \approx -0.5 \text{ V} \pm 0.05 \text{ V}$ vs. SCE is close to that expected for an N,N'-dialkyl-4,4'-bipyridinium reagent; see Table I for $E^\circ(MV^{2+/\cdot+})$ [$E^\circ = \text{av. of } E_{\text{PA}} \text{ and } E_{\text{PC}} \text{ at Pt}$] in various media. The $E^\circ(PQ^{2+/\cdot+})_{\text{surf.}}$ is not found to be as sensitive to solvent variation as is $E^\circ(MV^{2+/\cdot+})$. The $E^\circ(PQ^{\cdot+}/0)_{\text{surf.}}$ is near -0.9 V vs. SCE in CH_3CN solution, again close to the value associated with the $MV^{\cdot+}/0$ couple. Close correspondence of E° 's for surface species and solution analogues is now expected.¹⁰

Photoelectrochemical reduction of $(PQ^{2+})_{\text{surf.}}$ on p-type Si is as expected: both reductions occur at $\sim 0.5 \text{ V}$ more positive potential than on Pt,⁹ reflecting a value of E_V associated with Fermi level pinning of p-type Si.³ For $\text{pH} < 5$, $(PQ^{\cdot+})_{\text{surf.}}$ is thermodynamically capable of reducing H_2O to H_2 . However, reaction does not occur because the kinetics are poor; likewise $MV^{\cdot+}$ does not react, in the absence of catalyst, with H_2O at a measurable rate to give H_2 . Thus, if the $(PQ^{2+/\cdot+})_{\text{surf.}}$ system is to be useful in H_2 production the catalyst must be introduced.

Auger spectroscopy and depth profile analysis by Auger spectroscopy has been used to characterize the essential view of p-type Si functionalized with $\sim 10^{-8} \text{ mol/cm}^2$ of $(PQ^{2+})_{\text{surf.}}$, Figure 4. The redox polymer consists of monomer units, I, each having a 2+ charge. As prepared the derivatized electrode has Br^- counterions to balance charge. These counterions are rapidly exchangeable with other anions, including PtCl_6^{2-} . Indeed, depth profile analysis by Auger spectroscopy establishes rather uniform incorporation of PtCl_6^{2-} when an electrode has first been exchanged with Cl^- to prepare the $(PQ^{2+}2\text{Cl}^-)_{\text{surf.}}$ system, Figure 5.

Figure 4. Interface structure from Auger/depth profile analysis of p-type Si treated with I. Thicknesses are very approximate.

Figure 5. Auger/depth profile analysis of three different p-type Si surfaces functionalized with I ($\sim 10^{-8}$ mol/cm²) and then treated such that (a) Br⁻ is replaced by Cl⁻; (b) Br⁻ is replaced by PtCl₆²⁻ and (c) Br⁻ is replaced by PtCl₆²⁻ and the PtCl₆²⁻ is then photoelectrochemically reduced. Elements (Auger electron energies) monitored were: C (272 eV); N (379 eV); O (503 eV); Si (1619 eV); Br (1396 eV); Cl (181 eV); and Pt (1967 eV).

The interesting finding with respect to H_2 evolution is that the $PtCl_6^{2-}$ can be photoelectrochemically reduced to elemental Pt and after reduction, Figure 5a, the Pt(0) is dispersed throughout the polymer. Such an electrode is then capable of relatively efficient generation of H_2 . P-type Si functionalized first with $(PQ^{2+})_{surf.}$ and then with $PtCl_6^{2-}$ effects photoelectrochemical H_2 evolution with an efficiency of ~6% using monochromatic (632.8 nm) light.¹¹ The mechanism would appear to involve the photoreduction of $(PQ^{2+})_{surf.}$ to $(PQ^+)_{surf.}$ that then equilibrates with Pt(0) and H_2 is liberated from H_2O . Thus, Pt(0) catalyzes the reaction represented by equation (2). The efficiency from H_2 evolution is pH dependent in a manner

consistent with the mechanism where $(PQ^{2+})_{surf.}$ must be the actual reductant. At pH's higher than ~5.5 the $(PQ^+)_{surf.}$ is not a sufficiently strong reductant that H_2O reduction to H_2 can occur at a useful rate. Thus, in contrast to direct platinization, Figures 2 and 3, the efficiency from H_2 evolution decreases as pH is raised. Efficiency decreases again at the lower pH's for the same reason as in the direct platinization procedure. Thus, for the $(PQ^{2+}/^+)_{surf.}/Pt(0)$ system there is an optimum pH for the photoelectrolysis of ~4.7

The $(PQ^{2+}/^+)_{surf.}/Pt(0)$ catalysis of H_2 evolution from p-type semiconductor photocathodes should be general and applicable to either single-crystal or polycrystalline electrode materials. The ideal theoretical efficiency for this approach compared to the direct platinization is the same; however, durability of the $(PQ^{2+}/^+)_{surf.}/Pt(0)$ may be better. And the durability of the $(PQ^{2+}/^+)_{surf.}$ system may be greater than for solution $MV^{2+}/^+$ catalyzed by Pt(0) suspensions.¹² However, this potential advantage of durability remains to be demonstrated. New surface reagents, other semiconductors, and studies of

durability deserve attention in order to assess the importance of the $(PQ^{2+/+})_{\text{surf.}}/Pt(0)$ surface catalyst system for H_2 generation.

III. Surface-Derivatized N-Type Si Photoanodes.

Several articles have appeared during the contract period describing our work on the modification of n-type semiconducting Si with the ultimate aim of improving its durability in H_2O .¹³⁻¹⁶ In two articles we described^{15,16} the techniques for measuring the rate of reduction of a surface-confined, photo-generated oxidant, A^+ , equation (3). We found that for A^+ = ferricenium and

$B = I^-$ that k_{et} is too small to give a good efficiency for the photogeneration of I_3^- . We thus applied our efforts in the preparation of dinuclear ferrocene systems to preparing two-electron mediators for the $3I^- \xrightarrow{-2e^-} I_3^-$ process. Complex II was synthesized according to the procedure given in Figure 6. The

II

two-electron reagent was coupled to the surface of Au or Si electrodes, according to the procedure given in Figure 7. On a reversible electrode, II exhibits two, closely spaced, one-electron oxidations, Figure 8, and the hope was that the close proximity of the two oxidized Fe centers would lead to an enhanced rate for the two-electron oxidation of I^- when II was confined to the surface of

Figure 6. Outline of synthetic procedures for the synthesis of derivatizing reagent II.

Synthesis of Derivatizing Reagent

Figure 7. Schematic representation of procedure used to functionalize electrode surfaces with II.

Derivatization Procedure

Fischer, 1980

Figure 8. Comparison of the cyclic voltammetry for reagent II on a Au electrode and a monoferrrocene reagent on a Au electrode. Note that II on Au exhibits two, one-electron oxidations compared to the one-electron process for the monoferrrocene. The first oxidation is a little easier and the second a little more difficult compared to the monoferrrocene.

n-type Si. The procedure does lead to an improvement of 5 to 10 but this is not sufficiently large that a change in mechanism can be inferred. The rate limiting step is still likely a one-electron transfer that is accelerated when II is used because it is a 2+ species (rather than 1+) in its oxidized state and because the $E^\circ(\text{II}^{2+}/+)$ is somewhat (~50 mV) more positive (more oxidizing) than $E^\circ(\text{ferricenium/ferrocene})$. Studies of this system are continuing.

C. References

1. Bard, A.J.; Bocarsly, A.B.; Fan, F.-R. F.; Walton, E.G.; Wrighton, M.S. J. Am. Chem. Soc., 1980, 102, 3671.
2. Fan, F.-R. F.; Bard, A.J. J. Am. Chem. Soc., 1980, 102, 3677.
3. Bocarsly, A.B.; Bookbinder, D.C.; Dominey, R.N.; Lewis, N.S.; Wrighton, M.S. J. Am. Chem. Soc., 1980, 102, 3683.
4. Dominey, R.N.; Lewis, N.S.; Wrighton, M.S. J. Am. Chem. Soc., 1981, 103, 0000. [In press]
5. Heller, A.; Miller, B.; Lewerenz, H.J.; Bachman, K.J. J. Am. Chem. Soc., 1980, 102, 6555.
6. Cf. similar results for p-type Si and GaP: Nakato, Y.; Ohnishi, T.; Tsubomura, H. Chem. Lett., 1975, 883 and Nakato, Y.; Abe, K.; Tsubomura, H. Ber. Bunsenges. Phys. Chem., 1976, 80, 1002.
7. Bookbinder, D.C.; Lewis, N.S.; Bradley, M.G.; Bocarsly, A.B.; Wrighton, M.S. J. Am. Chem. Soc., 1979, 101, 7721.
8. Fan, F.-R. F.; Reichman, B.; Bard, A.J. J. Am. Chem. Soc., 1980, 102, 1488.
9. Bookbinder, D.C.; Wrighton, M.S. J. Am. Chem. Soc., 1980, 102, 5123.
10. Murray, R.W. Acc. Chem. Res., 1980, 13, 135 and references therein.
11. Bookbinder, D.C.; Bruce, J.A.; Dominey, R.N.; Lewis, N.S.; Wrighton, M.S. Proc. Natl. Acad. Sci., U.S.A., 1980, 77, 6280.
12. Keller, P.; Moradpour, A. J. Am. Chem. Soc., 1980, 102, 7193 and references therein.
13. Bocarsly, A.B.; Walton, E.G.; Wrighton, M.S. J. Am. Chem. Soc., 1980, 102, 3390.
14. Wrighton, M.S.; Bocarsly, A.B.; Bolts, J.M.; Bradley, M.G.; Fischer, A.B.; Lewis, N.S.; Palazzotto, M.C.; Walton, E.G. Adv. Chem. Ser., 1980, 184, 269.
15. Lewis, N.S.; Bocarsly, A.B.; Wrighton, M.S. J. Phys. Chem., 1980, 84, 2033.
16. Lewis, N.S.; Wrighton, M.S. ACS Symposium Series, 1981, 00, 0000.

D. Time Commitment of Principal Investigator

The principal investigator has spent approximately 20% of his time during the academic year on the research. For one summer month he spent 100% of his time on this research. He expects to continue to spend 20% of his time on DOE supported research during the final three months of the present contract.

E. Contract Compliance

The research performed under Contract No. DE-AC02-77ER04178.A003 has been in full compliance with the contract requirements, to the best of the principal investigator's knowledge.

F. Publications Citing DOE Support (Appeared or submitted 12-17-79 - 12-16-80)

1. "Use of Chemically Derivatized n-Type Silicon Photoelectrodes in Aqueous Media. Photooxidation of Iodide, Hexacyanoiron(II), and Hexaammine ruthenium(II) at Ferrocene-Derivatized Photoanodes", Bocarsly, A.B.; Walton, E.G.; Wrighton, M.S. J. Am. Chem. Soc., 1980, 102, 3390.
2. "The Concept of Fermi Level Pinning at Semiconductor/Liquid Junctions. Consequences for Energy Conversion Efficiency and Selection of Useful Solution Redox Couples in Solar Devices", Bard, A.J.; Bocarsly, A.B.; Fan, F.-R. F.; Walton, E.G.; Wrighton, M.S. J. Am. Chem. Soc., 1980, 102, 3671.
3. "Photoreduction at Illuminated p-Type Semiconducting Silicon Photoelectrodes. Evidence for Fermi Level Pinning", Bocarsly, A.B.; Bookbinder, D.C.; Dominey, R.N.; Lewis, N.S.; Wrighton, M.S. J. Am. Chem. Soc., 1980, 102, 3683.
4. "Thermodynamically Uphill Reduction of a Surface-Confined N,N'-Dialkyl-4,4'-bipyridinium Derivative on Illuminated p-Type Silicon Surfaces", J. Am. Chem. Soc., 1980, 102, 5123.
5. "Heterogeneous Electron Transfer at Designed Semiconductor/Liquid Interfaces. Rate of Reduction of Surface-Confined Ferricenium Centers by Solution Reagents", Lewis, N.S.; Bocarsly, A.B.; Wrighton, M.S. J. Phys. Chem., 1980, 84, 2033.
6. "Fermi Level Pinning of P-Type Semiconducting Indium Phosphide Contacting Liquid Electrolyte Solutions: The Rationale for Efficient Photoelectrochemical Energy Conversion", Dominey, R.N.; Lewis, N.S.; Wrighton, M.S. J. Am. Chem. Soc., 1981, 103, 0000 (in press).
7. "Electrochemical Reduction of Horse Heart Ferricytochrome c at Chemically Derivatized Electrodes", Lewis, N.S.; Wrighton, M.S. Science, 1981, 000, 0000 (in press).
8. "Synthesis and Characterization of a Photosensitive Interface for Hydrogen Generation: Chemically Modified P-Type Semiconducting Silicon Photocathodes", Bookbinder, D.C.; Bruce, J.A.; Dominey, R.N.; Lewis, N.S.; Wrighton, M.S. Proc. Natl. Acad. Sci., U.S.A., 1980, 77, 6280.
9. "Rate of Reduction of Photogenerated, Surface-Confined Ferricenium by Solution Reductants: Derivatized N-Type Si Photoanode-Based Photoelectrochemical Cells", Lewis, N.S.; Wrighton, M.S. ACS Symposium Series, 1981, 000, 0000 (in press).
10. "Photoelectrochemical Cells for Solar Energy Conversion", Wrighton, M.S. ACS Symposium Series, 1981, 000, 0000 (in press).
11. "A Comparison of the Interface Energetics for N-Type Cadmium Sulfide/ and Cadmium Telluride/Nonaqueous Electrolyte Junctions", Aruchamy, A.; Wrighton, M.S. J. Phys. Chem., 1980, 84, 2848.
12. "Chemically Derivatized Semiconductor Photoelectrodes. A Technique for the Stabilization of n-Type Semiconductors", Wrighton, M.S.; Bocarsly, A.B.; Bolts, J.M.; Bradley, M.G.; Fischer, A.B.; Lewis, N.S.; Palazzotto, M.C.; Walton, E.G. Adv. Chem. Ser., 1980, 184, 269.

G. Activities in Remainder of Contract Term

The time remaining in the present contract term will be devoted to completion of the studies of p-type semiconducting InP photocathodes for H_2 evolution. Emphasis will be on the demonstration of various procedures for catalyzing the evolution of H_2 from the illuminated surface. In particular, we hope to demonstrate that the combination of a redox active polymer and elemental Pt can be an effective and durable surface catalyst system for the generation of H_2 from photocathodes. Additionally, we hope to be able to complete the synthesis and characterization of two new surface derivatizing reagents from diquarternization of trans-1,2-bis-4-pyridylethylene and 3,5,3',5'-tetramethyl-4,4'-bipyridine. Finally, we expect to complete a study of the mediated photooxidation of I^- to I_3^- using n-type Si photoanodes modified with a biferrocene-based electron transfer mediator.

Reprints Removed