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Photoelectrolysis of Water by Irradiation of Platinized *n*-Type Semiconducting Metal Oxides*

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The basic principles of semiconductor photoelectrochemistry as applied to light to chemical and/or electrical energy conversions are outlined. Special emphasis is on the photoelectrolysis of H_2O to H_2 and O_2. New results are presented which show that platinized *n*-type $SrTiO_3$ and $KTaO_3$ evolve H_2 and O_2 from alkaline aqueous solutions when irradiated with ultraviolet light. The irradiated portions of the metal oxide behave as the photoanode and the dark platinized portions behave as the cathode. The nonplatinized oxides are energetically capable of evolving H_2 and O_2 upon irradiation but the overvoltage for H_2 is too great. The general requirement for the "short-circuit" redox chemistry at the irradiated *n*-type semiconductor surface is that the dark cathodic reaction occur at a potential more positive than the anodic reaction upon irradiation. The role of the Pt coating is to reduce the H_2 overvoltage to meet this requirement. It is demonstrated that polished *n*-type TiO_2 and $SrTiO_3$ are both capable of oxidizing H_2O to evolve O_2 and reducing Cu^{2+} to plate out Cu upon irradiation in 0.5 *M* $CuSO_4$ (pH = 7). We discuss the importance of "short-circuit" redox chemistry and overvoltage in obtaining opencircuit photopotential in photoelectrochemical cells.

Introduction

Sunlight-induced decomposition of H_2O according to reaction (1) represents a potential system for the storage of solar energy. There

$$H_2O \xrightarrow{\text{light}} H_2 + \tfrac{1}{2}O_2 \qquad (1)$$

are a large number of chemical reactions which involve an unfavorable free energy change, and any of these can be used as solar energy storage systems. It is, therefore, probably wholly inappropriate to settle on reaction (1) as the only potentially viable photochemical fuel-forming reaction for the storage of solar energy. Recent laboratory success, though, with reaction (1) has stimulated some considerable interest, and in this paper we will use the work on reaction (1) to illustrate some key principles. We will also use this forum to present some new results for the irradiation of platinized $SrTiO_3$ and $KTaO_3$ exposed to alkaline aqueous solutions.

The decomposition of H_2O according to reaction (1) involves a free energy change of 2.46 eV (*3*). This represents an extremely high energy density, since H_2 is only 2 g per mole. Also, H_2O is very abundant and inexpensive. Finally, only the H_2 need be stored, since it can be recombined with O_2 from the air to recover the energy. These advantages are offset by the fact that H_2O is transparent to visible and ultraviolet light which represents the spectral region usually used in photochemical reactions involving electronic excitation. Approximately 50% of

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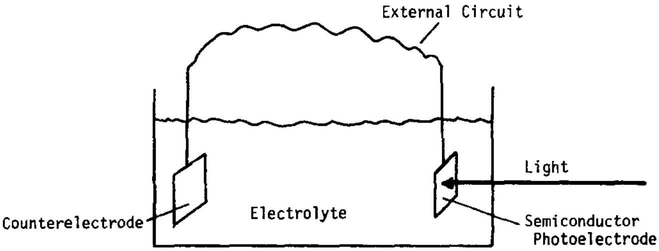


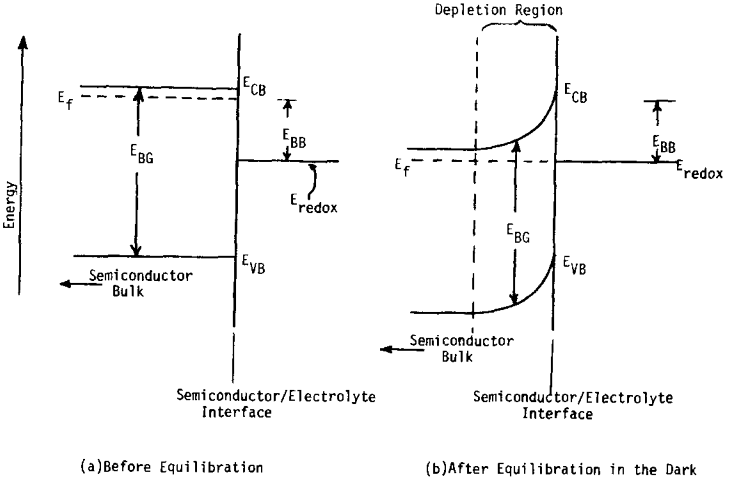
SCHEME I

the sun's energy is in the visible and ultraviolet region. Therefore, fuel-forming reactions like (1) must be "sensitized" to the visible–ultraviolet spectral output of the sun. We have used the term *photoassistance agents* (*4, 5*) to refer to additives that (1) serve to absorb light of longer wavelengths than the substrate, and (2) dissipate the electronic excitation into desirable chemical decay channels. This paper will describe efforts related to the use of electrode systems as photoassistance agents for reaction (1). The principles outlined here are applicable to any energy storage reaction which can be run electrochemically.

Background: Semiconductor Photoelectrodes

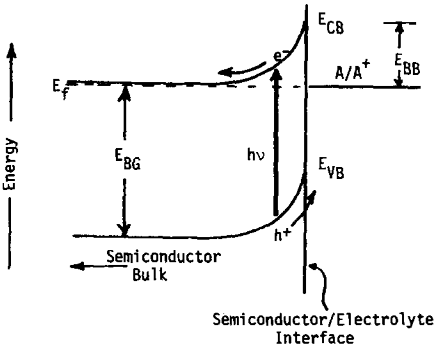
Irradiation of a semiconductor electrode in a cell as sketched in Scheme I can result in the flow of current. The flow of current must be accompanied by redox chemistry, and thus one can conceive of photoelectrochemical cells for the photoelectrolysis of H_2O. Also, since current flows in the external circuit, the direct conversion of light to electricity is possible. The unique aspect of semiconductor photoelectrodes is that the quantum efficiency for electron flow, Φ_e, can be very high, often approaching unity.

Efficient photocurrents and the energetics in photoelectrochemical cells can be appreciated from a consideration of the model outlined by Gerischer (*6*). The crucial feature of this model is that the electrochemical potential in the semiconductor, E_f, and the electrolyte, E_{redox}, must be the same upon equilibration of the dark. The E_{redox} value is taken as the potential of the half-cell reaction occurring at the photoelectrode, and E_f for the semiconductor is the Fermi level. Equivalence of E_f and E_{redox} is achieved by a small amount of charge transfer from one material to the other.



(a)Before Equilibration (b)After Equilibration in the Dark

SCHEME II

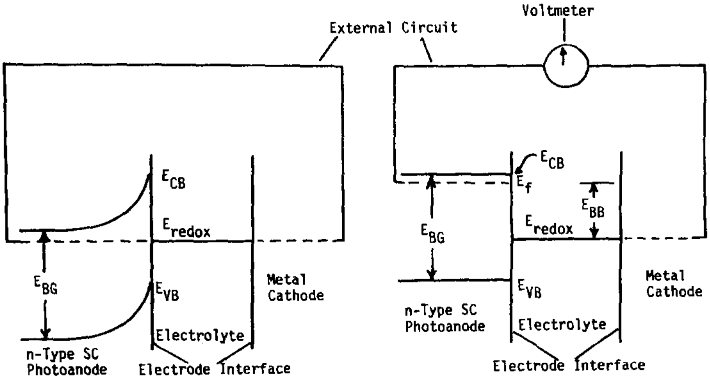


SCHEME III

The consequences of the equilibration on the energy levels in a heavily doped *n*-type semiconductor near the interface are sketched in Scheme II. The initial difference in E_f and E_{redox}, E_{BB}, results in the depletion region (depleted of majority charge carriers) and the bent bands. To a good approximation the potential drop across the interface occurs in the semiconductor and for a given electrolyte, the position of the valence band, E_{VB}, and conduction band, E_{CB}, is fixed at the interface. Excitation of electrons from the valence band to the conduction band can be accomplished using light of wavelengths short enough to equal or exceed the band gap energy, E_{BG}. The bent bands cause the photogenerated electrons and holes in the conduction band and valence band, respectively, to move in opposite directions. This inhibits the recombination of photoseparated charge. Moreover, the barrier E_{BB} inhibits back reaction of the excited electron with the primary photoredox product. For example, as sketched in Scheme III, the oxidation of A to A^+ obtains because the photogenerated hole is at a potential capable of accepting an electron from A. But back reaction of A^+ with the excited electron is inhibited in the ideal case because there is a barrier of height E_{BB} preventing the electron from returning to the electrolyte. Thus, efficient photocurrents are a consequence of the bent bands arising from an initial mismatch of E_f and E_{redox}.

The *n*-type semiconductor is a photoanode, since the minority carriers, holes, must be photogenerated. Generally, *n*-type semiconductors exhibit little or no anodic current flow unless the holes are photogenerated, but since there are a large number of electrons available dark cathodic currents are observed and these are not significantly influenced by illumination. For *p*-type semiconductors the situation is opposite; typically *p*-type electrodes are dark anodes and photocathodes, since the minority carriers are electrons. Band bending for efficient photocathodic currents is opposite to that for *n*-type materials.

The energetics involved in the semiconductor photoassisted redox processes can also be understood in terms of the sketches in Schemes II and III. The maximum photopotential from the photoelectrochemical cell is



(a) Short-circuit in the Dark

(b) Open-circuit under Intense Illumination

SCHEME IV

E_{BB}. That is, in Scheme II, irradiation can raise the Fermi level no higher than E_{BB} above its value when in equilibrium with the half-cell reaction occurring at the photoelectrode. Thus, whether the objective is conversion of light to electricity or to chemical products, the efficiency will be determined, in part, by the value of E_{BB}.

Consider first the objective of producing only electricity. In such a case the desirable electrolyte system would be one where the oxidation product produced at the anode is converted back to the starting substance at the cathode. The chemistry could be as represented in reactions (2) and (3). The maximum photopotential is just E_{BB}

$$A \rightarrow A^+ + e^- \quad \text{(anode)} \qquad (2)$$

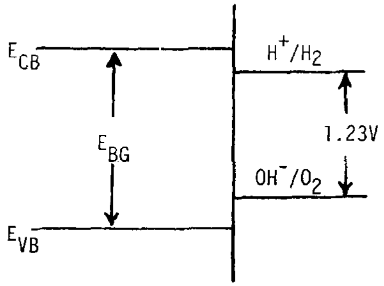
$$A^+ + e^- \rightarrow A \quad \text{(cathode)} \qquad (3)$$

in Scheme IV. The overall energy conversion efficiency for monochromatic light input in such a device additionally depends on Φ_e and E_{BG}. The maximum energy conversion efficiency, η_{max}, is given by Eq. (4) where $E_{h\nu}$ is the excitation energy. Factors contributing

$$\eta_{max} = \Phi_e E_{BB}/E_{h\nu}, \qquad \text{where } E_{h\nu} \geq E_{BG} \qquad (4)$$

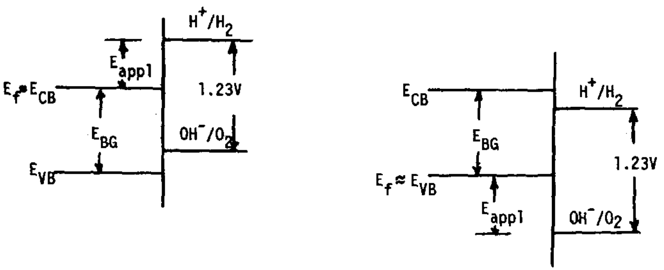
to Φ_e less than 1.0 may include (1) lack of complete light absorption within the depletion region and (2) increased rates of electron–hole recombination as the bands flatten as one raises the level E_f (Scheme IV). Scavenging photogenerated holes at the n-type semiconductor is, in principle, fastest when the position of the hole overlaps the distribution of filled levels in the electrolyte. For the n-type semiconductor, then, we increase E_{BB} by moving E_{redox} close to E_{VB} and at the same time hole capture should be fastest. The ideal electrolyte A/A^+ would have an E_{redox} value just above E_{VB} for n-type photoelectrodes or just below E_{CB} for p-type electrodes. In any case, E_{redox} must be between E_{CB} and E_{VB} or the system will not be thermodynamically stable in the dark!

Now let us turn to energy conversions like the photoelectrolysis of H_2O. The situation differs in that the half-cell reactions are not the reverse of each other. But for the half-cell redox reaction occurring at the photoelectrode we still have the same desires: E_{redox} just above E_{VB} for n-type and just below E_{CB} for p-type semiconductor photoelectrodes. The placement of E_{redox} for the reaction occurring at the dark electrode has no influence on the energetic feasibility of the reaction at the photoelectrode, but will influence the overall operation of the cell. The photoelectrolysis of H_2O is illustrative. The two E_{redox} values for the half-cell reactions differ by 1.23 V. If E_{BB} does not exceed 1.23 V, then one must add potential from another source such as a power supply in series in the external circuit. But naturally, if the photoelectrolysis of H_2O can be accomplished with an applied potential, E_{appl}, of less than 1.23 V from the power supply, one must be converting light energy to chemical energy with some positive efficiency. These considerations lead to the following statement. No applied potential is needed, in principle, to photoelectrolyze H_2O if the valence and conduction bands of a heavily doped semi-conductor photoelectrode straddle the E_{redox} values of the half-cell reactions involved. The ideal situation is sketched in Scheme V. If the H_2/H^+ couple is above E_{CB} for an n-type or if O_2/OH^- is below E_{VB} for a p-type photoelectrode, an applied potential in series with the photoeffect is required (Scheme VI). Similar arguments can be made for any electrolysis.



SCHEME V

The energy conversion efficiency in the fuel-forming photoelectrolytic systems depends on Φ_e, E_{BG}, E_{BB}, and the standard electrolysis po-



(a) n-Type SC (b) p-Type SC

SCHEME VI

tential which we will call E_s. The maximum energy conversion efficiency for monochromatic excitation is given by Eq. (5). The significance of a negative amount

$$\eta_{\max} = \frac{\Phi_e(E_s - E_{\mathrm{appl}})}{E_{h\nu}}, \qquad \text{where } E_{h\nu} \geq E_{\mathrm{BG}} \qquad (5)$$

of E_{appl} is that electricity and fuels can be simultaneously produced (cf. Scheme V) by irradiation of the semiconductor electrode.

This background on semiconductor electrodes is meant to represent a working model. In many respects, the simple features can be illustrated with experiments and new results can be rationalized with the model. The next section will elaborate on the recent successes related to the photoelectrolysis of H_2O, and emphasis will be on illustrating these principles.

Photoelectrolysis of H_2O

The use of *n*-type semiconductor electrodes as photoanodes in cells for the photoelectrolysis of any substance has been limited by one general fact: *n*-type semiconductors are often unstable to photoanodic dissolution as in reaction (6) for *n*-type ZnO (*7*). The half-cell reaction does not involve

$$\mathrm{ZnO} \rightarrow \mathrm{Zn}^{2+} + \tfrac{1}{2}\mathrm{O}_2 + 2\mathrm{e}^- \qquad (6)$$

the electrolyte; rather, the electrode decomposes. But in 1971 and 1972, papers (*8*) were published on the use of *n*-type TiO_2 as a photoanode for the oxidation of H_2O to O_2. Subsequent studies showed that TiO_2 is essentially indestructible (*9*) under the photoelectrolysis conditions but that an applied potential is necessary to achieve photoelectrolysis according to reaction (1). The minimum applied potential was found to be ~0.2 V. Thus, the TiO_2-based cell can be used to photoelectrolyze H_2O with a significant light to chemical energy conversion efficiency (*9*). The TiO_2 results (*8, 9*) have stimulated numerous new studies (*10–20*) on TiO_2-based cells.

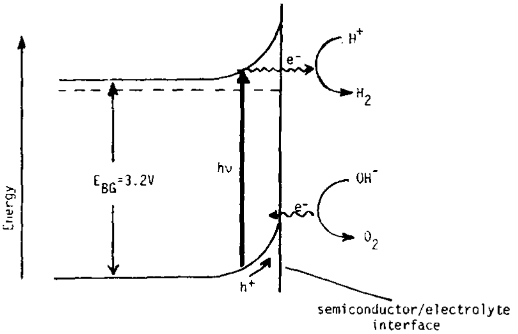
During the past 2 years *n*-type SnO_2 (*21*), $SrTiO_3$ (*22–24*), $KTaO_3$ (*25*), $KTa_{0.77}Nb_{0.23}O_3$ (*25*), WO_3 (*26*), and Fe_2O_3 (*27*) have all been found to be stable to photoanodic dissolution in aqueous electrolytes and can be used as the anode in the photoelectrolysis of H_2O. However, though these systems are stable and do work, they either have rather large values for E_{BG} and/or require a large applied potential. In fact, only $SrTiO_3$-, $KTaO_3$-, and $KTa_{0.77}Nb_{0.23}O_3$-based cells are claimed to be able to photoassist reaction (1) with no other energy input than the light. But these materials have band gaps of ≥3.0 eV, and consequently, respond to only a small portion (~3%) of the sun's energy. For monochromatic ultraviolet light (~330 nm), optical to chemical energy conversion efficiencies were found (*22*) to be of the order of 30% for the $SrTiO_3$-based cells. This system seems to represent the best man-contrived photochemical energy conversion scheme.

Results: Photoelectrolysis Using Platinized Semiconductors

The observation that $SrTiO_3$, $KTaO_3$, and $KTa_{0.77}Nb_{0.23}O_3$ all can be used as photoanodes for the photoelectrolysis of H_2O with no applied potential stimulated the new work to be reported here. This observation suggests that one should be able to run reaction (1) by simply irradiating the semiconductor in the electrolyte. That is, both the oxidation reaction and the reduction reaction should occur on the same surface. The situation for *n*-type $SrTiO_3$ is shown in Scheme VII. The oxidation of H_2O would occur upon band gap irradiation which produces holes, and H_2O would be reduced by electrons excited to the conduction band. The notion of photoassisting redox processes by irradiation of the semiconductor alone is not new, and in fact, some examples of such chemistry do exist (*28*). We think of such processes as short-circuit processes on a semiconductor where the irradiated site is the photoelectrode and the dark portion is the counterelectrode.

a. Qualitative Observations

We first attempted to photoelectrolyze H_2O by irradiating $SrTiO_3$ or $KTaO_3$ in 5.0 *M* NaOH. Intense, ultraviolet light irradiation of a single crystal, *n*-type $SrTiO_3$ or $KTaO_3$ photoanode at *open circuit* results in no obvious gas evolution from the metal oxide surface. However, short-circuiting the $SrTiO_3$ or $KTaO_3$ to a Pt electrode results in gas evolution at both the irradiated metal oxide surface and at Pt. We have previously associated the latter observations with the photoelectrolysis of H_2O, with the gases evolved at Pt and the metal oxide as H_2 and O_2, respectively.



SCHEME VII

The ready evolution of O_2 from the $SrTiO_3$ or $KTaO_3$ upon short-circuiting to Pt and the lack of gas evolution from the metal oxide at open circuit suggest that the difficulty at open circuit is in the relative rate of H_2 evolution. The irradiation should raise the E_f level in the semiconductor above the H_2/H^+ couple to allow the reduction of H_2O. But there may be only slow reduction of H_2O at the semiconductor at the potential achievable with irradiation. This slow rate of reduction may well be the result of the band bending barrier, since the electrons to reduce H_2O would either have to go over the barrier or tunnel through it. Also, there may be a substantial overvoltage of the ordinary sort for H_2 evolution from the semiconductors. Both of these problems should be solved by platinizing the metal oxide surface, since H_2 evolution from Pt occurs with only a small overvoltage (*29*) and the Pt coating should be little different than having the semiconductors short-circuited to a Pt counter electrode. In principle, the Pt coating could also aid in O_2 evolution.

It is important to realize one final fact. When $SrTiO_3$ or $KTaO_3$ is short-circuited to Pt, the semiconductor is at the same potential as the Pt electrode. Upon irradiation of the $SrTiO_3$ or $KTaO_3$, O_2 evolution occurs at the irradiated positions but the potential of the photoelectrode is the H_2/H^+ potential of the Pt electrode. The significant point is that for $SrTiO_3$, $KTaO_3$, and $KTa_{0.77}Nb_{0.23}O_3$ the H_2/H^+ potential is a few tenths of a volt below the conduction band. This means that there is enough band bending to allow efficient current flow at photoequilibrium. The metal oxide band positions (*30*) and H_2/H^+ and O_2/OH^- positions (*31*) are given in Fig. 1. As seen in Fig. 1, the position of the H_2/H^+ and O_2/OH^- couples meets the requirements indicated in Scheme V for the photoelectrolysis of H_2O

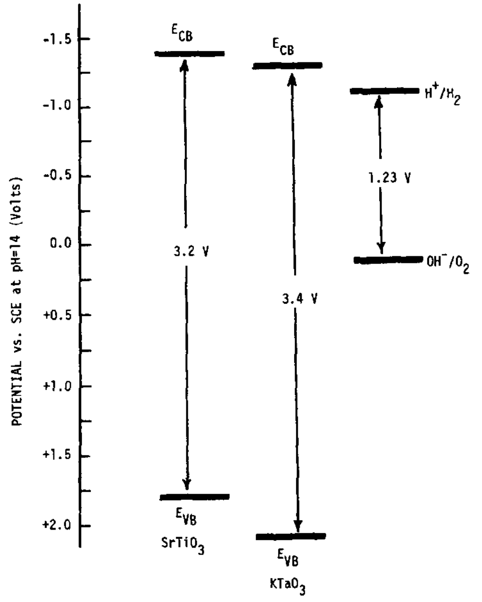


FIG. 1. Metal oxide conduction and valence band positions and H_2/H^+ and O_2/OH^- positions at pH = 14.

with no applied potential. However, if the H_2/H^+ couple was even more below E_{CB} we could obtain more efficient photocurrents and/or introduce a more sizable electrical load in the external circuit. One is tempted to resort to changing the pH of the electrolyte, since the H_2/H^+ and O_2/OH^- couples move more positive with lower pH by 0.059 mV/pH. Unfortunately, the positions of E_{CB} and E_{VB} for the metal oxides move more positive with lower pH by 0.059 mV/pH (*30*) and at any pH the relative position of E_{CB} and H_2/H^+ is the same. The use of pH in other situations, however, might prove useful.

b. Platinized $SrTiO_3$ and $KTaO_3$

n-type semiconducting $SrTiO_3$ and $KTaO_3$ single-crystals were "platinized" electrochemically by using the $SrTiO_3$ or the $KTaO_3$ as a cathode in an aqueous solution of H_2PtCl_6. The Pt-coated oxides were then investigated as possible photoassistance agents for the electrolysis of H_2O.

1. Qualitative observations. Irradiation of Pt-coated $SrTiO_3$ or $KTaO_3$ results in gas evolution from 5.0 *M* NaOH in H_2O. Irradiation of either the Pt-coated or the polished side of the metal oxide yields gas evolution. Irradiation of the polished side of the metal oxide crystal results in gas evolution from both sides of the crystal. That is, gas evolves from the illuminated side where the light strikes the surface and from the platinized dark side. However, irradiation of the Pt-coated side only results in gas evolution on the illuminated side, but gas evolution is observed from portions of the Pt-coated side which are in the dark. These observations are consistent with the bare $SrTiO_3$ or $KTaO_3$ serving as a normal photoanode and the Pt-coated dark portions serving as a normal cathode. Observation of gas evolution at all is in marked contrast to the nonplatinized metal oxides. It is noteworthy that neither polished nor Pt-coated TiO_2 photoelectrodes evolve any gas upon irradiation at open circuit in aqueous electrolytes. The TiO_2 conduction band is slightly positive of the H_2/H^+ couple and no "short-circuit" photoelectrolysis is expected.

Total gas evolution rates of 1–2 cm^3 per hr have been observed for fresh samples, but we invariably find that the evolution rate slows considerably after several hours of irradiation with the full output of a 200 W high pressure Hg lamp. We can regenerate the action by renewing the Pt coating. The lack of sustained, large gas evolution rates seem to be associated in part with the quality of the Pt coating. The platinized metal oxides work no more efficiently than the polished oxide short-circuited to a Pt-wire counter electrode.

One final qualitative point concerns wavelength response. Ultraviolet light excitation is required for gas evolution. This is consistent with the known values of E_{BG} for $SrTiO_3$ and $KTaO_3$ of 3.2 eV (*32*) and 3.4 eV (*33*), respectively. We found that light of visible wavelengths longer than ~400 nm is ineffective in causing gas evolution.

2. Identification of gaseous products. The gaseous products evolved from the irradiated platinized $SrTiO_3$ exposed to a mixture of $D_2{}^{18}O/H_2O/NaOH$ have been analyzed by

TABLE I

MASS SPECTRAL ANALYSES OF ELECTROLYSIS OF $D_2{}^{18}O/H_2O$ MIXTURE[a]

Electrolytic procedure	Observed relative abundance[b]				
	H_2	HD	D_2	$^{16}O_2$	$^{16}O^{18}O$
Conventional[c] (Pt electrodes)	0.7	0.9	0.5	4.9	1.0
Photoelectrolysis[d] (Pt–$SrTiO_3$)	0.7	0.9	0.7	5.0	1.0

[a] Electrolyte is 2 *M* NaOH in $D_2{}^{18}O/H_2O$.

[b] Measured by mass spectral analyses using a Hitachi Perkin–Elmer RMU-6 spectrometer.

[c] Conventional electrolysis: Pt anode and Pt cathode.

[d] Irradiation of platinized $SrTiO_3$ surface.

mass spectroscopy. The same solution was electrolyzed conventionally to presumably evolve H_2, HD, and D_2 at the cathode and O_2, $^{18}O_2$, and $^{16}O^{18}O$ at the anode. The observed mass spectral peaks are given in Table I. The similarity of the photoelectrolysis products and the conventional electrolysis is gratifying and shows that the photoelectrolysis does yield the expected products.

3. *Current-voltage behavior of platinized metal-oxide electrodes.* A comparison of the current-voltage behavior of polished and platinized $SrTiO_3$ and $KTaO_3$ electrodes is shown in Figs. 2 and 3. The noteworthy difference concerns the potential at which H_2 can be evolved (cathodic current flow). For both polished $KTaO_3$ and $SrTiO_3$ the flow of cathodic current corresponding to H_2 evolution is substantially more negative than the thermodynamic potential of ~−1.1 V vs SCE at pH = 14. But for the platinized electrodes the cathodic current onset is near the reversible potential for H_2 evolution. Thus, the partial Pt coating on the metal oxide has significantly improved its performance as a cathode. Other than the obvious effect of partially absorbing the incident light, we note that the photo-behavior of the metal oxide electrode is comparable to the nonplatinized, polished electrode. That is, the anode properties have not been altered dramatically over the potential range of interest.

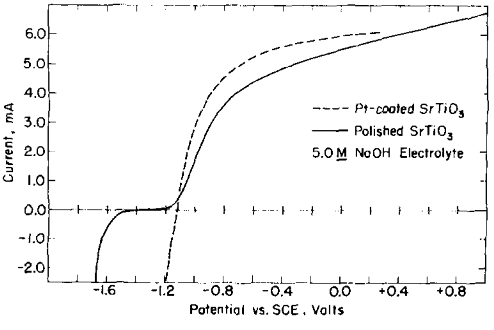


FIG. 2. Current-voltage behavior of polished and platinized $SrTiO_3$ electrodes, The cathodic (negative) currents correspond to H_2 evolution and are not influenced significantly by irradiation. The anodic (positive) currents correspond to O_2 evolution and no anodic current is observed in the dark over the potential range scanned. The electrolyte is 5.0 *M* NaOH.

In order to photoelectrolyze H_2O according to reaction (1) by irradiation of the Pt-coated semiconductor the following operational requirements must be fulfilled: *the cathodic reaction in the dark must occur at a more positive potential than the anodic reaction*

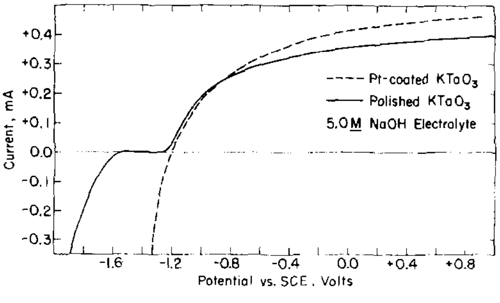


FIG. 3. Same as Fig. 2 except for $KTaO_3$.

upon irradiation. The current-voltage properties for the platinized metal oxide electrodes apparently just barely meet this requirement for reaction (1). We can do no better than evolve the H_2 at the thermodynamic potential, and apparently the Pt coating brings the oxide close to this value.

It is interesting to note that it is just the overvoltage for H_2 evolution from these oxides that allows their use as photoanodes without simultaneous H_2 evolution in the two electrode configuration. The overvoltage is logically a consequence of the band bending–depletion region, and the difference in overvoltage at various oxides should be related to the value of E_{BB} and the depletion depth. Other factors contributing to the overvoltage may be just those associated with overvoltage for gas evolution from other electrodes (*29*).

4. Open-circuit photopotential. One potential important consequence of having the cathodic reaction occur at more positive potentials than the photoanodic reaction is that one may not be able to develop significant open-circuit photopotential with such an electrode. This results from the fact that the chemistry occurring at the one electrode (oxidation *and* reduction) may prevent any significant net change in the value of E_f in the electrode.

Data in Table II show some comparisons of the open-circuit photopotential for platinized vs polished $KTaO_3$ and $SrTiO_3$. The photopotential is the difference in the dark and light potential between the metal oxide electrode and a Pt-gauze electrode. For H_2-purged electrolytes the Pt gauze is close to the H_2/H^+ potential, and the platinized photoelectrodes show little or no photopotential. This likely reflects that fact that the Pt coating allows the photoelectrode to come into equilibrium with the H_2/H^+ couple. Upon irradiation O_2 and H_2 evolution can occur at this potential resulting in little or no change in light vs dark potential compared to the H_2-purged Pt-gauze counterelectrode. The notion is that one can not raise E_f on the platinized material significantly beyond the H_2/H^+ potential. However, for the nonplatinized $KTaO_3$ or $SrTiO_3$ the photopotential is fairly significant. This is likely true for two reasons: (1) in the dark the H_2-purged metal oxide does not approach the H_2/H^+ potential; and (2) the E_f can be rasied more negative than H_2/H^+ without resulting in H_2 evolution.

TABLE II

OPEN-CIRCUIT PHOTOPOTENTIALS FOR PLATINIZED-$SrTiO_3$ AND $KTaO_3$ ELECTRODES

	Photopotential, V[b]	
Photoelectrode[a]	Air purged	H_2 purged
$SrTiO_3$	0.37	0.37
Pt–$SrTiO_3$-1	0.63	0.00
Pt–$SrTiO_3$-2	—	0.04
$KTaO_3$	—	0.72
Pt–$KTaO_3$-1	—	0.09
Pt–$KTaO_3$-2	—	0.03

[a] Single-crystal photoelectrodes with and without Pt coating. Numbers after the Pt-coated samples indicate different samples.

[b] Potential measured between a Pt-gauze counterelectrode and the photoelectrode using a high impedence voltmeter. The photopotential is the difference in the potential in the light and in the dark. The solution is 5.0 *M* NaOH either purged with air or H_2. In all cases the photoelectrode was exposed to the full output of a 200 W superpressure Hg-arc lamp focused onto the electrode. Measurements were made at 298°K.

For air-purged electrolytes both platinized and polished electrodes give open-circuit photopotentials under the experimental conditions. This is understandable, since the Pt-gauze electrode is no longer at the H_2/H^+ potential. When irradiated the Pt-coated electrode at least goes to the H_2/H^+ potential, and the nonplatinized photoelectrode can go even more negative.

The major point here is that the platinized electrode compared to the nonplatinized electrode can do the cathodic reaction at a more positive potential. For the platinized case, irradiation can apparently raise E_f no higher than the H_2/H^+ potential. But for the nonplatinized electrode E_f can be raised higher than the H_2/H^+ level because such an electrode is not a good cathode for H_2 evolution.

Significance

The results outlined above show that it is possible to photoelectrolyze H_2O to H_2 and O_2 by irradiation of a single surface. The important feature with respect to this photoredox chemistry is that a platinized $SrTiO_3$ or $KTaO_3$ surface is capable of evolving H_2 in the dark at a potential more positive than O_2 evolution in the light. Neither $SrTiO_3$ nor $KTaO_3$ alone is capable of evolving H_2 at the thermodynamic potential, and it is the Pt coating that reduces the H_2 overvoltage enough to allow the photoelectrolysis of H_2O. In terms of practical use, we presently attach little significance to these results. The $SrTiO_3$ and $KTaO_3$ both still suffer from having large values of E_{BG}, and actually the position of E_{CB} is still not negative enough to give the optimum photoelectrolysis efficiency.

The significance of these results rests in pointing out the importance of having the overvoltage at the semiconductor to prevent "short-circuit" chemistry in two electrode configurations. Moreover, we have established that it is possible to manipulate these photoelectrode overvoltages. Finally, the results and considerations above show that certain energetic requirements must be met to have "short-circuit" photoredox chemistry on a given electrode. These important aspects of the work can be illustrated further with other examples of photoelectrochemical reactions at semiconductor electrodes. We will consider two additional examples here for which preliminary results are available.

a. Cadmium Chalcogenic Photoelectrodes in Chalcogenide Electrolytes

We have published work on the oxidation of polysulfide species, S_n^{2-}, at Cd*X*(*X* = S, Se) photoelectrodes (*34*). The current-voltage data show, however, that it appears possible to sustain cathodic currents at Cd*X* at potentials more positive than the S_n^{2-} photooxidation. That is, on the same Cd*X* surface it is possible to both oxidize and reduce S_n^{2-} species with the irradiated portion as the anode and the dark portion serving as the cathode. Such effects could be the reason for low output potential and relatively small quantum efficiency at the output potential for maximum energy conversion efficiency. At this point, however, no detailed assessment of this effect has been made in such cells.

b. Photoelectrolysis of Aqueous Solutions of $CuSO_4$

The Cu/Cu^{2+} couple is at 0.08 V vs SCE (*31*). At pH = 7 many of the stable *n*-type metal oxide semiconductors should have E_{CB} positions (*39*) which are more negative than the Cu/Cu^{2+} position. At the same time the E_{VB} position should be below the O_2/OH_2 potential which is at +0.5 V vs SCE (*31*). Therefore, these *n*-type metal oxides should be capable of effecting the half-cell reactions (*7*) and (*8*) since the band and redox levels are as in Fig. 4. Indeed,

$$Cu^{2+} \xrightarrow{2e^-} Cu \qquad \text{(dark cathode)} \qquad (7)$$

$$H_2O \longrightarrow 2H^+ + \tfrac{1}{2}O_2 + 2e^- \qquad \text{(photoanode)} \qquad (8)$$

irradiation of either an *n*-type $SrTiO_3$ or TiO_2 photoelectrode short-circuited to a Cu-metal electrode in a 0.5 *M* $CuSO_4$ aqueous solution at pH = 7 results in an excellent photocurrent. Current flow results in gas evolution at the metal oxide which is presumably O_2, and logically Cu^{2+} is reduced at the Cu electrode. The interesting fact is that irradiation of either of the photoelecrodes at *open circuit* still results in significant gas evolution! Accompanying the gas evolution is obvious Cu^{2+} reduction to form a Cu deposit in dark areas on the photoelectrode.

Current-voltage curves for $SrTiO_3$ and TiO_2 in 0.5 *M* $CuSO_4$ (pH = 7) in the dark and in the light compared to a Cu-wire electrode are

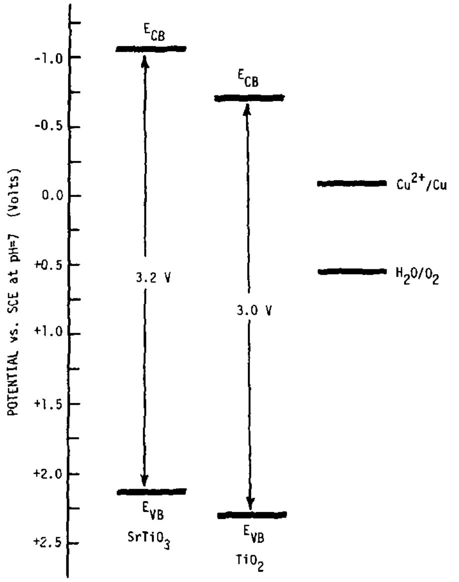


FIG. 4. Band positions and Cu/Cu^{2+} positions at pH = 7.

shown in Fig. 5. Reduction of Cu^{2+} at either $SrTiO_3$ or TiO_2 in the dark is more negative than at the Cu wire which shows nearly reversible behavior. That is, there is an apparent overvoltage for Cu^{2+} reduction at the metal oxides. The crucial point, though, is that Cu^{2+} reduction in the dark obviously occurs at potentials more positive than O_2 evolution upon irradiation. The overvoltage itself and the difference between $SrTiO_3$ and TiO_2 again is likely attributable to the band bending and depletion region which exists in metal oxides when exposed to the electrolyte. For metal ion reductions, though, overvoltage is generally inherently smaller than for gas evolution reactions (*29*). Additionally, as Cu plates out on the metal oxide we have detected a shift of the metal oxide potential toward the Cu-wire potential for Cu^{2+} reduction.

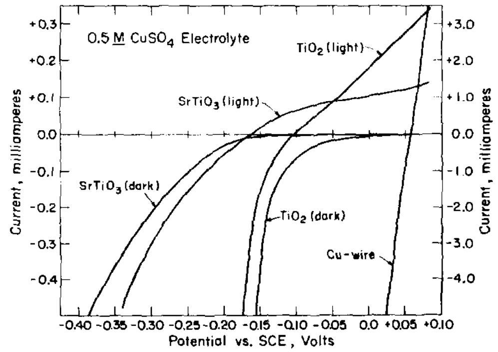


FIG. 5. Current-voltage behavior of TiO_2, $SrTiO_3$, and Cu-wire electrodes in 0.5 *M* $CuSO_4$ (pH = 7). Left scale applies to metal oxide and right scale to Cu wire.

These preliminary results show that other net photoelectrolytic processes can be carried out at an irradiated semiconductor surface. Potentially, significantly energy-storing chemical reactions should be doable at a single surface. In any case it appears important to consider the possibility of "short-circuit" photoelectrochemistry as a contributor to inefficiency. Learning how to manipulate the dark cathodic behavior of *n*-type semiconductors or dark anodic behavior of *p*-type materials should prove fruitful in exploiting photoelectrochemistry.

Appendix: Experimental

Electrodes and electrode materials. The TiO_2, $SrTiO_3$, and $KTaO_3$ are the same reduced, single crystal *n*-type semiconductors used in previous studies (*9, 22, 25, 30*). The exposed areas were 1–2 cm^2 and the thicknesses were ~1 mm. For studies in 0.5 *M* $CuSO_4$ (pH = 7) the TiO_2 and $SrTiO_3$ electrodes were prepared as described previously (*9, 22, 25, 30*). Likewise, in original tests of whether irradiation of nonplatinized $SrTiO_3$, $KTaO_3$, or TiO_2 would result in gas evolution in 5.0 *M* NaOH, the crystals were mounted into a normal electrode configuration.

The reduced metal oxide crystals were platinized on a side by one of two procedures: (1) an aqueous solution of H_2PtCl_6 was painted onto the face of the crystal and the material was heated using a Corning hotplate; or (2) the metal oxide was mounted into an electrode configuration and was used as a cathode in an aqueous H_2PtCl_6 solution.

Current was passed until Pt was visible on the electrode surface. Either of the procedures can result in a $SrTiO_3$ or $KTaO_3$ surface capable of H_2 and O_2 evolution when irradiated with ultraviolet light.

Irradiations. In all cases irradiations were carried out using a Bausch and Lomb 200 W high pressure Hg-arc source. The output was filtered with 18 cm of H_2O to remove infrared light, and was focused onto the metal oxide surface using a quartz lens. All glassware holding electrolytes was made of quartz.

Current-voltage curves. Current-voltage curves were measured using a PAR 174 Polargraphic Analyzer to potentiostat the electrode relative to an SCE reference electrode. The counterelectrode in all cases was a Pt wire.

Open-circuit photopotential. The potential between a photoelectrode and a Pt-gauze electrode was measured in the dark and upon irradiation. The potential was measured with a Data Precision 1450 multimeter.

Gas analyses. Gases evolved in the photoelectrolysis and conventional electrolysis of an aqueous 2.0 *M* NaOH aqueous solution were identified by using an RMU-6 Hitachi Perkin–Elmer mass spectrometer. The same solution was electrolyzed using either a platinized $SrTiO_3$ crystal in the photoelectrolysis or two Pt electrodes in the conventional electrolysis. The electrolysis vessel was either a quartz tube (photoelectrolysis) or a small Pyrex vessel with Pt electrodes cemented into place with epoxy. In both cases the electrolyte was freeze-pump-thaw degassed in at least four cycles prior to electrolysis. Each vessel was equipped with an evacuable stopcock assembly to analyze the gases (O_2, H_2) which are not condensable with a dry-ice/iso-propanol bath. The $D_2{}^{18}O$ enrichment of the electrolyte was provided by addition of a small sample obtained from Stohler Isotopes. The exact D_2-${}^{18}O$ enrichment was not measured, but the important fact is that the same distribution of gases obtains from both the photo- and conventional electrolysis.

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