

CONVERSION OF LASER ENERGY TO CHEMICAL ENERGY BY THE
PHOTOASSISTED ELECTROLYSIS OF WATER

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ABSTRACT

Ultraviolet irradiation (351, 364 nm) of the n-type semiconductor TiO_2 crystal electrode of an aqueous electrochemical cell evolves O_2 at the TiO_2 electrode and H_2 at the Pt electrode. The gases are typically evolved in a 2:1 ($\text{H}_2:\text{O}_2$) volume ratio. The photo-assisted reaction seems to require applied voltages, but values as low as 0.25 V do allow the photo-assisted electrolysis to proceed. Prolonged irradiation in either acid or base evolves the gaseous products in amounts which clearly demonstrate that the reaction is catalytic with respect to the TiO_2 . The wavelength response of the TiO_2 and the correlation of product yield and current are reported. The results support the claim that TiO_2 is a true photo-assistance agent for the electrolysis of water. Minimum optical storage efficiencies of the order of 1 percent can be achieved by the production of H_2 .

INTRODUCTION

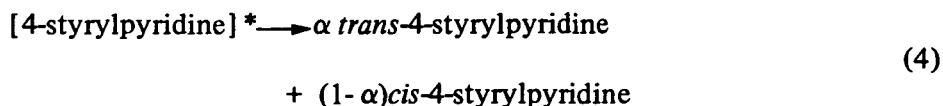
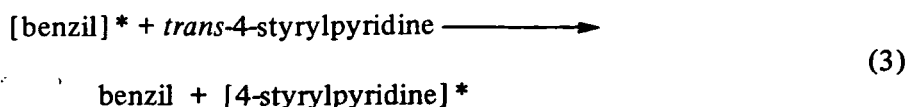
The efficient conversion of optical energy to chemical energy is a problem of great interest. Despite the fact that solid state solar cells have reached a high level of development there is still considerable merit in achieving the direct conversion of optical energy into chemical energy. The reasons for this are severalfold and include the desire to have abundant high energy chemicals for use as fuels and for use in industrial chemical synthesis. Additionally, in view of the rather limited amount of detailed knowledge concerning direct photoproduction of high-energy materials, it is appropriate to undertake fundamental research aimed toward establishing what can be done and how efficiently it can be done. The reaction indicated in (1) is among the many possible chemical reactions of importance in the conversion of optical energy to chemical energy. The standard heat of formation of liquid water is 68.3 kcal/mole



and thus the reaction as written is substantially energetically uphill. The use of optical energy to run reaction (1) is practicable energetically, but H_2O absorbs little in that region of the electromagnetic spectrum commonly regarded as the optical energy region. Thus, irradiation to yield reaction (1) can only occur by an indirect excitation.

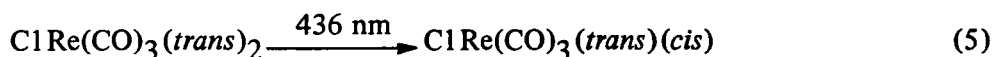
The most common mode of indirect excitation is triplet photosensitization as schemed in reactions (2)-(4) for the benzil sensitized *trans*→*cis* isomerization

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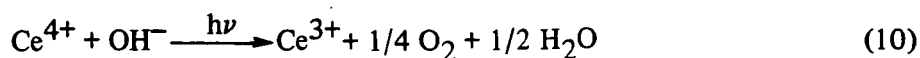
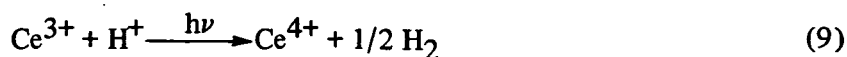
of 4-styrylpyridine. The benzil is the photoreceptor since the 4-styrylpyridine is transparent to 436 nm light, but the benzil excited state can transfer its excitation energy to *trans*-4-styrylpyridine which has a triplet state energetically below the triplet donor level in benzil¹ (ref. 3). Thus, the energetically uphill *trans*→*cis* 4-styrylpyridine isomerization can be achieved with lower energy light than possible without benzil present. The use of a photosensitizer for reaction (1) is conceivable, but in practice H₂O really has no low lying excited states accessible with even the highest energy sensitizers.

A second type of indirect excitation called transition metal photo-assistance (defined in ref. 4) might be more successfully applied to reaction (1). We have recently worked out a model photoassistance situation (ref. 5) and it is schemed in reactions (5) through (8) where *cis* and *trans* refer to *cis* and *trans*-4-styrylpyridine, respectively.

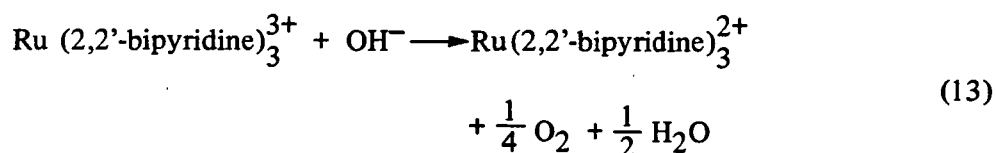
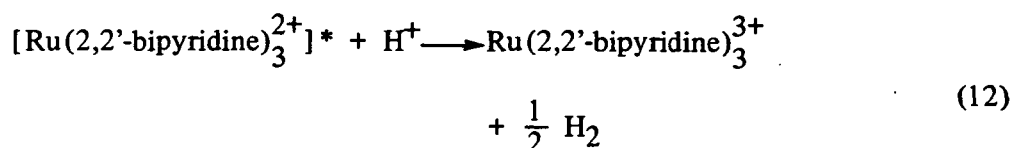
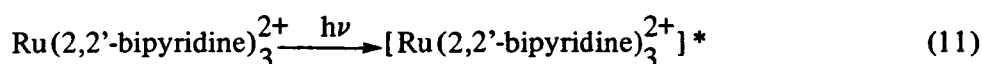


The key points here are that (1) a transition metal complex present in catalytic quantities, serves as the photoreceptor and as the "template" for the desired chemical change; (2) continuous irradiation of the metal complex is required to sustain the uphill *trans*→*cis*-4-styrylpyridine isomerization, but the C1Re(CO)₃L₂ photoassistance agent is not consumed; and (3) the reaction occurs with lower energy light than possible without the photoassistance agent. The use of the transition metal photoassistance technique to run reaction (1) and other valuable uphill chemical reactions merits serious consideration. In fact, it has been pointed out that the photooxidation and photoreduction of aquo transition metal ions can be coupled to the reduction and oxidation of water (ref. 6). The reactions (9) and (10) (ref. 7) together could, in principle, be used to run reaction (1),

¹The triplet energy of *trans*-styrylpyridine is 50 kcal/mole and that of benzil is about 52 kcal/mole (ref. 3).



but actually only extremely small yields (and very low quantum yields of formation) of O_2 and H_2 can be obtained from irradiation of Ce^{3+} , Ce^{4+} aqueous solutions. Such reactions are still good models to demonstrate the principle, however. Another conceivable path for the photoassisted reaction (1) is indicated in the series of reactions (11) through (13) where the metal complex, $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$ becomes an extremely strong reducing agent upon electronic excitation, yielding the products indicated in reaction (12). The oxidized Ru complex is formed in its ground electronic state and may be unstable enough to oxidize OH^- (reaction (13)) and return to the original $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$ complex. Note that in the homogeneous reactions (11) through (13) only one quantum is required for the oxidation and reduction steps whereas in reactions (9) and (10) two quanta are required.



Unfortunately, electronically excited $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$ is unable to reduce H_+ to H^2 (ref. 8). But $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$ has been shown to be an electron donor from its excited state reducing $\text{Fe}(\text{OH}_2)_6^{3+}$ (ref. 9), $\text{Co}(\text{III})$ complexes (ref. 10), and Tl^{3+} (ref. 11). Therefore, continued investigation in this area could prove very fruitful for other chemical transformations besides reaction (1).

Heterogeneous substances have recently shown some promise as photoassistance agents for reaction (1) (refs. 12 and 13). The observation of currents upon photolysis of an electrode in an electrochemical cell has been known for a very long time (ref. 14), but it has not been until recently that it has been claimed that the electrode reactions occurring could actually yield H_2 and O_2 . The photolysis of an n-type TiO_2 single crystal electrode, in a cell like that depicted in figure 1a, was reported to yield current flow such that O_2 is evolved at the TiO_2 and H_2 at the Pt electrode (refs. 12 and 13). We report herein a detailed characterization of this system which shows for the first time that reaction (1) can be sustained with light using an electrode system as the photoassistance agent. Products have been unequivocally identified, and the efficiency of product formation based on current flow and incident optical energy are reported.

RESULTS AND DISCUSSION

Product Identification and Electrode Stability

The use of a metal oxide as a photoelectrode prompts the question of its stability to light in the electrolyte, especially as it may be a source of O_2 . To answer this question two sets of experiments have been carried out in a photoelectrochemical cell, such as that shown in Figure 1a, using the 351.1, 363.8 nm doublet emission of a Spectra Physics Model 164 argon ion laser as the irradiation source. First, mass spectroscopic analyses have been carried out on the gases evolved at both the TiO_2 and the Pt electrode. When the TiO_2 is immersed in 1.0 M NaOH with $D_2^{18}O/D_2O$ (¼) as the solvent and the Pt is in 1 N H_2SO_4 with D_2O as solvent $^{18}O^{16}O$, $^{18}O_2$, and $^{16}O_2$ are evolved at TiO_2 and D_2 and a trace amount of HD is evolved at Pt. The $^{18}O^{16}O$: $^{16}O_2$ ratio is very close to the 1:2 value predicted based on the ratio of ^{18}O to ^{16}O present in the electrolyte. In a second series of experiments, electrodes prepared from pre-weighed crystals of TiO_2 were used in a photoelectrochemical cell and the amount of O_2 evolved was measured volumetrically. The crystal was then recovered and weighed. Typical data (table 1) show that within experimental error no weight loss obtains even when the number of moles of O_2 evolved surpasses the number of moles of TiO_2 initially present. The oxygen labeling experiment and the stability of the TiO_2 electrode under illumination prove that the O_2 comes from the H_2O and show that the reaction is catalytic with respect to TiO_2 .

Stoichiometry and Efficiency of Product Formation

Some quantitative measurements have first been made with a photoelectrochemical cell as shown in figure 1a and the data are summarized in table 2. The data show that (1) the ratio of $H_2:O_2$ is generally close to 2:1, (2) approximately 2 moles of electrons flow per mole of H_2 evolved, and approximately 4 moles of electrons flow per mole of O_2 evolved; and (3) the quantum efficiency of H_2 formation at 351, 364 nm excitation is of the order 10^{-2} to 10^{-1} . Quantum efficiency is defined here to mean the number of moles of H_2 formed per einstein at 351, 364 nm striking the electrode. No correction has been made for losses due to reflection. Sustained currents of the order of 1-2 ma can be typically achieved using the laser (~50 mW) with a beam diameter of ~1 mm; thus, the current density is of the order of 10^2 ma per cm^2 of irradiated surface area. However, little or no hydrogen evolution can be detected in the two compartment cell in figure 1a when the electrolyte at Pt and TiO_2 is the same, although O_2 evolution and current flow is usually observed. Toward the aim of establishing the role of the diffusion barrier in the cell in figure 1a, we have undertaken an investigation of the photoelectrochemical cell depicted in figure 1b.

In the one compartment cell we have been able to observe photo-induced H_2 and O_2 evolution at applied voltages as small as 0.25 V and some quantitative data are given in table 3. Again the stoichiometry is fairly clean and quantum efficiencies are in the range 10^{-2} to 10^{-1} for H_2 evolution. As seen in table 3, the quantum efficiency does seem to depend on the applied voltage, and it is apparent then that the two compartment cell (fig. 1a) works without an external power supply because the acid in the Pt compartment and the base on the TiO_2 side provide the bias necessary for the reaction to occur. However, when the electrolysis of H_2O can be carried out at less than 1.23 V, energy must be supplied from an external source, which in this case is the light. Some indications of the optical storage efficiency are given in table 4. The storage efficiency is calculated with the assumption that H_2 can be used to generate heat and is worth 68 kcal/mole.

These minimum storage efficiencies are seen to be of the order of 1 percent at 351, 364 nm excitation.

Wavelength Response

The n-type TiO_2 has a band gap of ~ 3.0 eV (ref. 15). If the photoassistance activity observed for TiO_2 is associated with an electronic transition from the valence band to the conduction band, we expect that the minimum light energy required will correspond the band-gap energy. The relative current as a function of irradiation wavelength for a cell such as that shown in figure 1b is given in figure 2 for a TiO_2 electrode and a tungsten-doped TiO_2 electrode. The wavelength response is independent of the applied voltage, and, at least for the TiO_2 , the onset of activity does correspond closely to that expected, based on the band gap. The difference in the response for the tungsten-doped TiO_2 electrode is remarkable despite the fact that the shift of the onset is toward higher energy compared to the TiO_2 itself. Understanding of the origin of this effect may make it possible to design tuned response systems.

SUMMARY

These data are the first to show that reaction (1), the conversion of H_2O to H_2 and O_2 , can be sustained using optical energy. The TiO_2 electrode system is a true photoassistance agent serving to absorb light and to dissipate the excitation energy in such a way as to achieve the desired chemical change. Importantly, the electrode system is itself photoinert, and therefore the production of H_2 and O_2 is catalytic with respect to TiO_2 . The merit of the results disclosed here rests in the demonstration that the photoassisted electrolysis of H_2O can be achieved. Further studies are underway and are directed toward more efficient utilization of the optical energy as well as a confident understanding of the mechanism of the processes involved.

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TABLE 1. – TEST FOR DISAPPEARANCE OF TiO₂ UPON IRRADIATION

TiO ₂		Initial TiO ₂ , moles	O ₂ ^b evolved, moles	Crystal
Initial weight, ±0.001, g	Final weight, ^a ±0.002, g			
0.1210	0.1206	1.51 x 10 ⁻³	2.4 x 10 ⁻⁴	A
0.0187	0.0191	2.38 x 10 ⁻⁴	2.2 x 10 ⁻⁴	B
Not measured	0.2427 ^c	Not measured	9.2 x 10 ⁻⁴	C
0.0658	0.0640	8.24 x 10 ⁻⁴	1.7 x 10 ⁻⁴	D
0.0041	0.0039	5.13 x 10 ⁻⁵	1.1 x 10 ⁻⁴	E

^aThe error is larger than initial weight because the TiO₂ crystal must be removed from the electrode and epoxy and metallic backing must be cleaned off.

^bMoles of O₂ evolved by irradiation of the TiO₂ electrode in a cell as in figure 1(a) or 1(b). If used in the one compartment cell (fig. 1(b)) the applied voltage was 2.0 V or less.

^cNo obvious deterioration of the crystal during its use. The value of the data rests in the fact that a large absolute amount of O₂ was evolved from this crystal.

TABLE 2. – PHOTOASSISTED ELECTROLYSIS OF H₂O IN A TWO COMPARTMENT CELL^a

Electrolyte at TiO ₂	Electrolyte at Pt	Irradiation time, min	H ₂ , moles	O ₂ , moles	Electrons, moles	Φ ^b for H ₂ production
1 M NaOH ^c	1 N H ₂ SO ₄	426	1.6 x 10 ⁻⁴	8.0 x 10 ⁻⁵	4.10 x 10 ⁻⁴	0.04 ₇
1 M NaClO ₄ ^c +	1 M NaClO ₄ +	572	1.5 x 10 ⁻⁴	7.6 x 10 ⁻⁵	4.2 x 10 ⁻⁴	0.03 ₇
0.1 M NaOH	0.1 N H ₂ SO ₄					
1 M NaOH ^d	1 N H ₂ SO ₄	1280	4.8 x 10 ⁻⁴	2.4 x 10 ⁻⁴	8.4 x 10 ⁻⁴	0.04 ₇

^aCell assembly as in figure 1(a).

^bLight intensity striking electrode is 8 x 10⁻⁶ ein/min.

^cTiO₂ electrode from first synthesis of n-type TiO₂ crystal C in table 1.

^dTiO₂ electrode from a second synthesis of n-type TiO₂ crystal.

TABLE 3. – PHOTOASSISTED ELECTROLYSIS OF H₂O IN A ONE COMPARTMENT CELL^a

Electrolyte	Applied voltage, V	Irradiation time, min	H ₂ , moles	O ₂ , moles	Electrons, moles	Φ for H ₂ ^b production
1 <u>M</u> NaOH ^c	2.0	207	1.8 x 10 ⁻⁴	8.5 x 10 ⁻⁵	3.9 x 10 ⁻⁴	0.11
1 <u>M</u> NaClO ₄ ^c	2.0	507	2.2 x 10 ⁻⁴	1.1 x 10 ⁻⁴	5.7 x 10 ⁻⁴	0.05 ₄
1 <u>M</u> NaClO ₄ ^c	2.0	180	1.3 x 10 ⁻⁴	6.3 x 10 ⁻⁵	2.7 x 10 ⁻⁴	0.09 ₀
0.1 <u>M</u> NaOH ^c	2.0	252	2.2 x 10 ⁻⁴	9.2 x 10 ⁻⁵	4.2 x 10 ⁻⁴	0.11
0.1 <u>M</u> NaOH ^c	2.0	777	2.9 x 10 ⁻⁴	1.2 x 10 ⁻⁴	7.6 x 10 ⁻⁴	0.04 ₇
0.1 <u>M</u> Na OH ^c +	2.0	96	1.0 x 10 ⁻⁴	5.4 x 10 ⁻⁵	1.9 x 10 ⁻⁴	0.13
4 <u>M</u> NaClO ₄						
1 <u>N</u> H ₂ SO ₄ ^c	2.0	471	2.9 x 10 ⁻⁴	8.9 x 10 ⁻⁵	6.5 x 10 ⁻⁴	0.07 ₇
1 <u>N</u> H ₂ SO ₄ ^d	2.0	3579	5.0 x 10 ⁻⁴	1.6 x 10 ⁻⁴	1.2 x 10 ⁻³	0.01 ₇
0.1 <u>N</u> H ₂ SO ₄ ^c	2.0	1001	3.5 x 10 ⁻⁴	1.2 x 10 ⁻⁴	7.6 x 10 ⁻⁴	0.04 ₄
0.1 <u>M</u> NaOH ^c	0.5	1266	1.7 x 10 ⁻⁴	8.9 x 10 ⁻⁵	5.2 x 10 ⁻⁴	0.01 ₇
1.0 <u>M</u> NaOH ^c	0.5	666	1.2 x 10 ⁻⁴	5.8 x 10 ⁻⁵	3.4 x 10 ⁻⁴	0.02 ₃
1.0 <u>M</u> NaOH ^e	0.5	1514	3.1 x 10 ⁻⁴	1.0 x 10 ⁻⁴	5.9 x 10 ⁻⁴	0.02 ₆
1.0 <u>M</u> NaClO ₄ ^e	2.0	413	1.7 x 10 ⁻⁴	7.4 x 10 ⁻⁵	3.4 x 10 ⁻⁴	0.05 ₁
2.0 <u>M</u> NaOH ^c	0.25	990	7.6 x 10 ⁻⁵	3.6 x 10 ⁻⁵	1.6 x 10 ⁻⁴	0.01 ₀
2.0 <u>M</u> NaOH ^f	2.0	801	2.5 x 10 ⁻⁴	1.1 x 10 ⁻⁴	4.8 x 10 ⁻⁴	0.03 ₉

^aCell as in figure 1(b); no current flows without light.^bLight intensity striking electrode is 8 x 10⁻⁶ ein/min.^cElectrode C in table 1.^dElectrode A in table 1.^eElectrode D in table 1.^fElectrode E in table 1.

TABLE 4. – EFFICIENCY OF STORAGE OF OPTICAL ENERGY AS HYDROGEN^a

Applied potential, V	Irradiation time, sec	Average current, ma	H ₂ , moles	Energy stored ^b as H ₂ , cal	Energy in from ^c power supply, cal	Energy in from ^d laser, cal	Optical energy ^e storage efficiency %
0.5	7.6 x 10 ⁴	0.66	1.7 x 10 ⁻⁴	12.0	6.0	810	0.74
0.5	4.0 x 10 ⁴	0.82	1.2 x 10 ⁻⁴	8.2	3.9	430	1.0 ₀
0.5	9.1 x 10 ⁴	0.63	3.1 x 10 ⁻⁴	21.0	6.8	980	1.4 ₅
0.25	5.9 x 10 ⁴	0.26	7.6 x 10 ⁻⁵	5.2	0.9	640	0.6 ₇

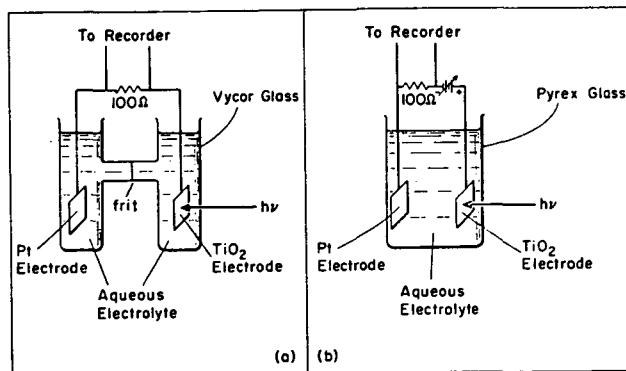
^aFrom data given in table 3.

^bAssuming H₂ can be recovered at 68 kcal/mole which is the standard heat of formation of H₂O, reaction (1).

^cEnergy from power supply = (applied potential)(average current)(irradiation time)(0.239 cal/J).

^d8 x 10⁻⁶ ein/min at 351, 364 nm is equivalent to ~0.011 cal/sec.

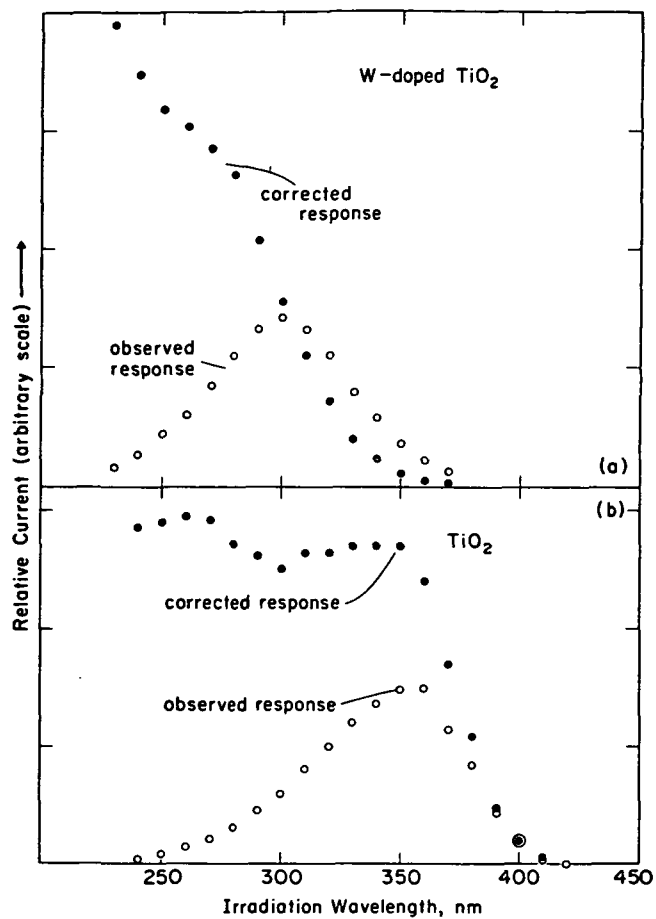
$$^e\text{Optical energy storage efficiency} = \frac{(\text{energy stored as H}_2) - (\text{energy in from power supply})}{(\text{energy in from laser})} \times 100.$$



(a) The two electrode compartments are separated by a fine glass frit to prevent diffusion of the 1 N H₂SO₄ on the Pt side and the 1 M NaOH on the TiO₂ side.

(b) The external power supply indicated is a Hewlett-Packard Model 6241A with variable applied potential (0-12 V). The "hv" and heavy arrow indicate the laser beam.

Figure 1.— Photochemical cells used for the photo-assisted electrolysis of H₂O.



(a) Tungsten doped n-TiO₂.
 (b) n-TiO₂ electrode when used in a cell.

Figure 2.— Relative current vs. excitation wavelength. The open circles (O) show the uncorrected, observed response and the filled circles (●) show the actual, corrected response after correction for variation of the excitation light intensity as a function wavelength. The observed response is given to show the magnitude of the correction factors. Note, however, that even without application of the correction one can see a difference in response of the two crystals.

DISCUSSION

Dick Miles, Princeton University – Did you find that you had to replace the base or the acidic solutions?

Answer: We never reacted enough water that the concentration changed. When you think about what a mole of photons is – it's really a long time at fifty milliwatts. Some of the irradiation times are like a day and to make a mole of photons would take 10,000 days with our laser.

Bill Bottoms, Princeton University – Just to pursue the same question-over the long term just what is going to happen to the pH of those electrolytic solutions? How will you deal with that problem?

Answer: I think the way to go in this system is not to use the two-compartment system. Clearly, we've demonstrated that in a homogenous solution the electrode system serves as a photo-assistance reagent for the reaction and, under those conditons, the only thing that ever needs to be added to that system is water.

Bob Hess, Langley Research Center – Didn't you look at some systems to reduce the applied voltage by using a single cell?

Answer: Well it turns out the current-voltage curves, of course, depend on the electrode reactions which are taking place. Most of our effort has clearly been in trying to make hydrogen at platinum and oxygen at titanium dioxide, but there is no reason why one cannot couple this excitation energy to other electrode processes. For example, if you just toss in iron three at the platinum electrode you can obtain current densities which are as high as in any experiment with iron three going to iron two. So electricity can be the direct result of these systems as well as chemical energy.

Bill Bottoms, Princeton University – It seems to me you are dealing with a wide band gap semiconductor and you could, by doping, shift the inner potential by the one half volt you are applying with a battery. Have you explored the possibility of just using a PN junction in a wide bandgap semiconductor which is effectively what you are doing electrically anyway?

Answer: In fact we are collaborating with some people in Electrical Engineering at M.I.T. and have suggested that they give us some materials which we can put on there which will bias it in a way that is appropriate.

Bill Bottoms, Princeton University: There are some fairly straight-forward ways to establish a one-half volt drop in a wide bandgap semiconductor which will give you a highly reducing surface on one side and highly oxidizing on the other. You will gain back the energy thrown away in the power supply.

Max Garbuny, Westinghouse – You mentioned your laser limitations. Couldn't you use a high pressure mercury arc to obtain higher fluxes? In fact you could obtain an einstein or mole of photons in a relatively short time.

Answer: Yes, in fact with the tin oxide, the band gap is sufficiently high that we really can't get very much out of our system with the argon ion laser. So we've been using a super high pressure mercury arc lamp and under those conditions we can get sustained currents over 0.01 amps and under those conditions you can make quite a bit of hydrogen and oxygen. We have the pleasant problem of not having sufficient volumetric glassware which is large enough to handle the gases!

Katsonori Shimada, J. P. L. – Can you make a comment on the work that is going on at UCLA using rutile? For example, are they getting about the same results as you?

Answer: I guess I don't know about the work at UCLA. Maybe you can tell me about it.

Shimada: As I understand it, JPL has a contract with UCLA to supply the crystal TiO_2 .

Wrighton: I don't know what those results are, but the results that we have show that TiO_2 is inert and all the oxygen which is liberated is coming from the solution. This is determined both by the labeling experiments with O^{18} and by the fact that the crystal doesn't disappear when its illuminated.

Dick Pantell, Stanford University – If the purpose of the light is to generate minority carriers, wouldn't the PN junction then eliminate the necessity of the laser light at all?

Bill Bottoms: Perhaps I can answer that since I'm one of those people from an electrical engineering department such as you mentioned. The difficulty is that you have to put in energy from somewhere. You can do it with a battery and then have copious numbers of minority carriers. You can also do it with light. Its a question of which is preferable.

Mark Wrighton: That is just it. If you just toss something into the water and let it sit there, unless it is a battery itself, it is not going to evolve any high energy products. People talk about photo-catalysis and they really mean they are trying to accelerate thermodynamically favorable reactions. Thats the important problem with respect to energy conversion.

Bill Bottoms, Princeton University –You mentioned the low absorption of laser light. This indicates another reason for going to heavily doped PN junctions since you would enhance this absorption on both sides.

Answer: Yes, some are transparent to visible light. Perhaps I should say the following: Reduced TiO_2 is a black material which is totally opaque to visible light. But even if it were transparent to visible light that doesn't mean that it wouldn't absorb one-hundred percent in the region where its active. For example, the tin oxide is a clear material which looks like a chip of glass but it does absorb quite substantially in the ultraviolet, the relative response at 250 nm and 350 nm being four orders of magnitude.