Photoassisted Electrolysis of Water by Irradiation of a Titanium Dioxide Electrode

(optical energy conversion/hydrogen production/photoelectrolysis/solar energy)

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ABSTRACT   Ultraviolet irradiation (351, 364 nm) of the n-type semiconductor TiO_2 as the single 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 two: one (H_2:O_2) volume ratio. The photoassisted reaction seems to require applied voltages, but values as low as 0.25 V do allow the photoassisted 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 photoassistance agent for the electrolysis of water. Minimum optical storage efficiencies of the order of 1% can be achieved by the production of H_2.

Conversion of light energy to chemical energy is a fundamental problem of scientific interest where solutions may be of practical importance. The photoassisted‡ evolution of H_2 and O_2 from H_2O, reaction [1], represents such an energy

$$H_2O \xrightarrow[\substack{\text{[photoassistance]} \\ \text{agent}}]{h\nu} H_2 + 1/2\ O_2 \qquad [1]$$
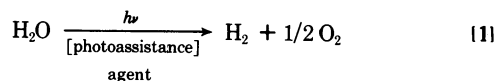
conversion and storage system. The photoassistance agent serves not only as a receptor for the incident light but also must channel the electronic excitation energy into pathways to achieve the desired chemical reactions. It has been pointed out (1–3) that the photoinduced oxidation and reduction of aquo transition metal ions such as Fe^{2+}/Fe^{3+} and Ce^{3+}/Ce^{4+} could be coupled to the reduction and oxidation of H_2O. However, these systems have never been shown to be catalytic with respect to the aquo ions used, and the reactions proceed inefficiently in terms of quantum yield and require high energy ultraviolet light. Heterogeneous photoassistance agents have been proposed and some experimental effort has been directed towards semi-conducting metal oxides (4–6). The results reported (5, 6) concerning n-type TiO_2 as a photoassistance agent for reaction in a wet photoelectric cell similar to that in Fig. 1a were particularly promising. However, several key

points remained to be resolved: (*1*) the chemical identity and the origin of the gas evolved at the TiO_2 electrode was not definitively established, (*2*) the question of whether the reaction could be catalytic with respect to TiO_2 was not answered, (*3*) the role of the diffusion barrier (frit) in the photoelectrochemical cell was not communicated, (*4*) the photoaction spectrum of the TiO_2 was not given, and (*5*) the relationship of current and product yield was not established. In this report we wish to outline our preliminary results which clarify some of these points. The results reported herein show for the first time that reaction [1] can be sustained using an electrode system as the photoassistance agent.

EXPERIMENTAL

First, a description of the preparation of a typical TiO_2 electrode used in our experiments is appropriate. A TiO_2 crystal was grown by the flame fusion technique (7) using a seed crystal oriented along the *c* axis. The crystal was grown until approximately 2.5 cm long. The synthesis yields a gray-black reduced TiO_2 crystal which is too brittle for cutting. Consequently, the crystal was annealed at 1100°C in TiO_2 powder to yield the clear, yellow unreduced TiO_2 single crystal. The crystal was cut into slices from 0.8 to 2.5 mm thick such that the *c* axis was perpendicular to the face (001) to be irradiated§. The orientation was by x-ray diffraction¶. The surface area available for photolysis was varied from 1 mm² to about 1 cm². The slices were then reduced by heating to 700°C for 4 hr in the presence of H_2. However, reduction for as short a period as 0.5 hr under the same conditions does yield suitable crystals. An unreduced crystal exhibited no detectable photoassistance. The resistance of a typical slice was 200 Ω after reduction. The surfaces to be illuminated were polished to variable degrees and etched (9) in concentrated H_2SO_4 in an ultrasonic bath for 40 min. A gallium-indium eutectic was rubbed onto the back side of the slice, and a copper wire was attached to the back surface using conducting silver epoxy. Alternatively, the copper wire can be attached to the crystal using only the silver epoxy. The entire back side (including

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the copper wire) was insulated by coating with a generous amount of epoxy.

An electrode as prepared above was then used in an electro-chemical cell as schemed in Fig. 1a or b. The solutions were not stirred. The Pt electrode was either Pt-black, Pt-gauze, Pt-foil, or Pt-wire. The currents produced by photolysis were measured by determining the potential across a 100 Ω resistor in series with the two electrodes. The voltage across the resistor was monitored continuously with a Varian model A-25 recorder. Where an applied potential was used in an assembly as in Fig. 1b, the power supply used was a Hewlett-Packard model 6241A. The irradiation source used in all experiments (except excitation wavelength response) was the 351.1, 363.8 nm doublet emission of a Spectra-Physics model 164 argon ion laser. The intensity was typically 10^{-5} einstein/min as measured by ferrioxalate actinometry (10). The volumes of gases evolved at the TiO_2 and Pt electrodes were measured by collecting the gas in inverted 25 or 10 ml graduated cylinders initially filled with the solution. The gas analyses by mass spectroscopy were performed with a Hitachi Perkin-Elmer RMU-6 mass spectrometer.

The wavelength response (relative current versus excitation wavelength) of the TiO_2 electrodes was studied using the excitation optics of an Aminco-Bowman spectrophotofluorimeter. The TiO_2 electrode in 1 M NaOH was placed in a Vycor vessel in a circuit as in Fig. 1b. The TiO_2 was positioned in the sample chamber of the spectrometer such that the excitation beam illuminated the TiO_2 surface. The excitation source was a 150 W xenon lamp whose emission was passed through the excitation monochromator of the spectrometer. The relative intensity of the excitation beam versus wavelength at the sample was determined using the standard rhodamine B quantum counter method (11). The relative current output was determined by measuring the potential across a 4000 Ω resistor in series with the TiO_2 and Pt electrodes. The relative response was displayed on a Hewlett-Packard model 7044A X-Y recorder, and the observed curve was corrected for the variation in excitation beam intensity over the wavelength range of interest and for a small amount of absorption by the Vycor glass at the higher excitation energies.

RESULTS AND DISCUSSION

An initial set of experiments was carried out in a cell as shown in Fig. 1a with the TiO_2 electrode in 1 M NaOH and the Pt electrode in 1 N H_2SO_4. Illumination of the TiO_2 resulted in a photocurrent (electrons flow from TiO_2 to Pt) and gas evolution at each electrode. The gas evolution at Pt is not instantaneous, requiring a short induction period. Gas evolution at TiO_2 occurs only at the spot (about 1 mm diameter) where the laser beam strikes the TiO_2 electrode. Sustained currents of about 1.5–2.0 mA could be achieved and consequently the current density is typically of the order of 10^2 mA/cm² of illuminated TiO_2. Generally, the current and gas evolution rate is highest immediately upon exposure to the laser and then falls to a constant level. The initial current can be several times the sustained value and the fall-off time varies with conditions. The identity of the gases evolved at the TiO_2 electrode was determined by irradiation of the TiO_2 in a 1 M NaOH $D_2{}^{18}O/D_2O$ (1/4) solution which had been deaerated with argon. The Pt electrode was immersed in 1 N H_2SO_4. The compartment was equipped with an airless gas collection device, and mass spectroscopic analysis of the
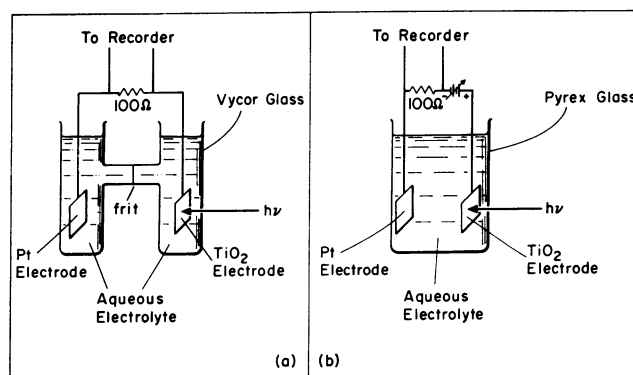

Fig. 1. Photochemical cells used for the photoassisted electrolysis of H_2O. In (a) the two electrode compartments are separated by a fine glass frit to prevent diffusion of the 1 N H_2SO_4 on the Pt side and the 1 M NaOH on the TiO_2 side. In (b) the external power supply indicated is a Hewlett-Packard model 6241A with variable applied potential (0–12 V). The "hν" and heavy arrow indicate the laser beam.

evolved gases showed a mass to charge ratio, m/e = 32 (O_2); m/e = 34 ($^{18}O^{16}O$) and a small increase above background at m/e = 36 ($^{18}O_2$). The ratio of the 32 to the 34 peak was 2.0 ± 0.2 as expected based on the relative amounts of ^{18}O and ^{16}O in the solution. In a similar way, but in a second experiment, the gas evolved at the Pt electrode was found to be D_2 when the Pt electrode was immersed in 1 N H_2SO_4 in D_2O. A very small amount of HD was also observed. Thus, the products are unequivocally identified and the production of $^{18}O^{16}O$ suggests that the reaction is not simply photorelease of oxygen from TiO_2.

In a second series of experiments, very small, pre-weighed (0.004–0.300 g) TiO_2 crystals were fabricated into electrodes to determine whether the reaction is catalytic with respect to TiO_2. Some representative data are given in Table 1. The number of moles of O_2 generated is of the same order of magnitude as the number of moles of TiO_2 initially present,

TABLE 1. *Test for disappearance of TiO_2 upon irradiation*

Crys-tal	TiO_2			μmol O_2[b] evolved
	Initial weight, mg ± 0.1	Final weight[a], mg ± 0.2	Initial μmol	
A	121.0	120.6	1510	240
B	18.7	19.1	238	220
C	Not measured	242.7[c]	Not measured	920
D	65.8	64.0	824	170
E	4.1	3.9	51.3	110

[a] The error in the final weight is larger than in the initial weight because the TiO_2 crystal must be removed from the electrode and epoxy and metallic backing must be cleaned off.

[b] Moles of O_2 evolved by irradiation of the TiO_2 electrode in a cell as in Fig. 1a or b. If used in the one compartment cell (Fig. 1b) the applied voltage was 2.0 V or less. All irradiations are with the 351, 364 nm emission of an argon ion laser, about 8 × 10^{-6} einstein/min.

[c] No obvious deterioration of the crystal occurred during its use. The value of the data rests in the fact that a large absolute amount of O_2 was evolved from this crystal.

TABLE 2.   *Photoassisted electrolysis of H_2O in a two-compartment cell*[a]

Electrolyte at TiO_2	Electrolyte at Pt	Irradiation time, min	μmol of H_2	μmol of O_2	μmol of electrons	Φ[b] for H_2 production
1 M NaOH[c]	1 N H_2SO_4	426	160	80	410	0.04₇
1 M NaClO₄[c] + 0.1 M NaOH	1 M NaClO₄ + 0.1 N H_2SO_4	572	150	76	420	0.03₇
1 M NaOH[d]	1 N H_2SO_4	1280	480	240	840	0.04₇

[a] Cell assembly as in Fig. 1a.

[b] Light intensity striking electrode is 8×10^{-6} einstein/min with the 351, 364 nm emission of an argon ion laser; Φ is quantum efficiency.

[c] TiO_2 electrode from first synthesis of n-type TiO_2 crystal, crystal C in Table 1.

[d] TiO_2 electrode from a second synthesis of n-type TiO_2 crystal.

and the weight of the recovered crystal is unchanged from that of the starting material. Further, we note that no crystal has become defective because of prolonged illumination. The data in Table 1 and the ^{18}O data unequivocally establish that the reaction is catalytic with respect to TiO_2.

Some quantitative measurements involving the cell assembly in Fig. 1a are given in Table 2. The data show that the gases are generally evolved in nearly a 2:1 (H_2/O_2) volume ratio. The integrated current compares favorably with that expected based on the amount of H_2 and O_2 collected; i.e., 2 moles of electrons yield 1 mole of H_2 and 4 moles of electrons yield 1 of O_2. The relationship is not exact in every case and can be due in part to the estimated experimental error which is ±5% in integrated current and ±5% gas volumes. Included in Table 2 are data concerning the quantum efficiency, for hydrogen production, Φ, defined here to be the number of moles of H_2 produced per mole of photons striking the electrode. At the present time the actual fraction of incident light absorbed is not known. The quantum efficiencies are seen to be of the order of 0.05.

Naturally, the photoassisted electrolysis of H_2O, reaction [1], would be most promising if the reaction could be run in a homogeneous solution without the diffusion barrier. Towards this end we have carried out experiments with an electrochemical cell as shown in Fig. 1b. With no applied voltage little or no photocurrent is observed with a Pt electrode of very small surface area (about 1 cm²). However, in the same circuit with an applied potential of 12.0 V with no irradiation, a Pt electrode of this area will carry several milliamperes of current with H_2 and O_2 evolutions (2:1 by volume) at Pt and TiO_2, respectively. Use of a much larger surface area Pt electrode (about 50 cm²) does yield photocurrents of about 1 mA with evolution of gas at TiO_2 at zero applied potential, but we have been frustrated in our attempts to observe H_2 evolution at Pt. These results suggest that some other substrate (impurity) other than H_2O is reduced at Pt at zero applied potential. However, even at applied voltages as small as 0.25 V, gas evolution at TiO_2 *and* Pt can be observed. As expected from current-voltage curves previously reported (5, 6), the photoeffect is much larger as the external voltage

TABLE 3.   *Photoassisted electrolysis of H_2O in a one-compartment cell*[a]

Electrolyte	Applied voltage, V	Irradiation time, min	μmol of H_2	μmol of O_2	μmol of electrons	Φ for H_2[b] production
1 M NaOH[c]	2.0	207	180	85	390	0.11
1 M NaClO₄[c]	2.0	507	220	110	570	0.05₄
1 M NaClO₄[c]	2.0	180	130	63	270	0.09₀
0.1 M NaOH[c]	2.0	252	220	92	420	0.11
0.1 M NaOH[c]	2.0	777	290	120	760	0.04₇
0.1 M NaOH[c] + 4 M NaClO₄	2.0	96	100	54	190	0.13
1 N H_2SO_4[c]	2.0	471	290	89	650	0.07₇
1 N H_2SO_4[d]	2.0	3579	500	160	1200	0.01₇
0.1 N H_2SO_4[c]	2.0	1001	350	120	760	0.04₄
0.1 M NaOH[c]	0.5	1266	170	89	520	0.01₇
1.0 M NaOH[c]	0.5	666	120	58	340	0.02₃
1.0 M NaOH[e]	0.5	1514	310	100	590	0.02₆
1.0 M NaClO₄[e]	2.0	413	170	74	340	0.05₁
2.0 M NaOH[c]	0.25	990	76	36	160	0.01₀
2.0 M NaOH[f]	2.0	801	250	110	480	0.03₉

[a] Cell as in Fig. 1b; no current flows without light.

[b] Light intensity striking electrode is 8×10^{-6} einstein/min using the 351, 364 nm emission of an argon ion laser; Φ is quantum efficiency.

[c] Electrode C in Table 1.

[d] Electrode A in Table 1.

[e] Electrode D in Table 1.

[f] Electrode E in Table 1.

is increased. Quantitative measurements have been carried out at an applied voltage in an assembly as in Fig. 1b using the Hewlett-Packard 6214A power supply as the external voltage source with the positive lead attached to the TiO_2 electrode. As in the cell in Fig. 1a the photocurrent is such that electrons flow from TiO_2 to Pt. Data in Table 3 show typical results for the photoassisted electrolysis using an applied potential of ≤ 2.0 V. Under these conditions no measurable current flows without light. The photoassisted electrolysis data reveal that the reaction occurring is as indicated in reaction [1], the electrolysis is generally efficient, and the light is used at a quantum efficiency (as defined above) of 10^{-2}–10^{-1}. The oxygen imbalance may be due to H_2O_2 formation at TiO_2, which was detected qualitatively after prolonged irradiation. The experiments reported in Table 3 at 0.5 V or 0.25 V applied potential (lower than that required to electrolyze H_2O) show that TiO_2 is indeed a true photoassistance agent for the electrolysis of water.

The results presented thus far do show that the TiO_2 electrode system is, to our knowledge, the first photoassistance agent for the electrolysis of water. But the situation is complicated because of the apparent requirement for the applied voltage from an external power supply. In principle, the electrolysis of water at potentials of less than 1.23 V at standard conditions requires an external energy source which in the present case is the light. In practice the electrolysis of water cannot be sustained at 1.23 V because of overvoltage problems, etc., and for the case at hand (TiO_2 anode and Pt cathode) the current-voltage curves (5, 6) suggest that the O_2 overvoltage on TiO_2 may be substantial. In our photoassisted electrolysis experiments at 0.5 or 0.25 V the data show that the stored energy as H_2 (68 kcal/mol) is greater than the energy put into the system by the power supply. Some data are summarized in Table 4 indicating that the minimum optical storage efficiency is of the order of 1%. These energetic considerations clear any doubts remaining as to the importance of the TiO_2 photoassistance agent. In the two-compartment cell with the diffusion barrier the reaction can proceed without any external power supply at all, but the acid at Pt and base at TiO_2 provide a potential which is apparently enough to allow the electrolysis to proceed. The positive bias likely induces changes in the electronic energy levels of the semiconductor near the surface exposed to the electrolyte which tends to keep the reactive holes near the surface while electrons excited to the conduction band flow into the bulk of the semiconductor (12–14).
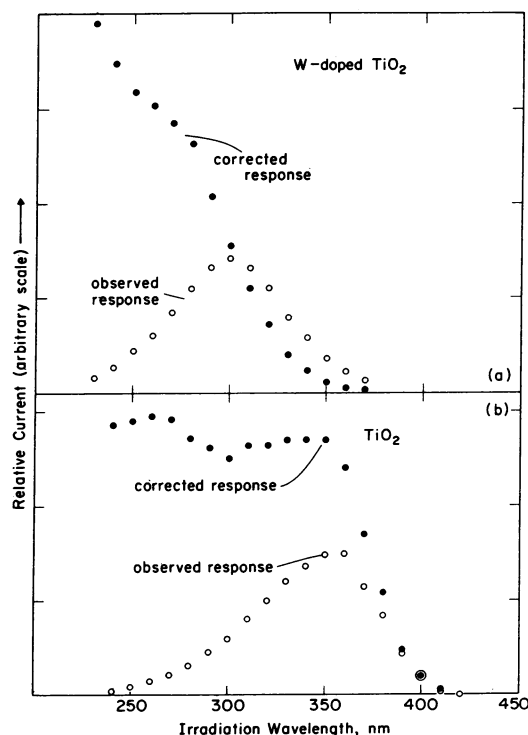

FIG. 2. Relative current versus excitation wavelength for (a) tungsten-doped n-TiO_2 and (b) n-TiO_2 electrode when used in a cell as in Fig. 1b. The open circles (O) show the uncorrected, observed response and the filled circles (●) show the actual, corrected response after correction for variation of the excitation light intensity as a function of 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.

One property governing efficiency of energy conversion is the wavelength of the light which is necessary to run the reaction. A typical TiO_2 electrode has its onset of response near 400 nm which corresponds closely to the band gap of 3.0 eV (15). The wavelength response of a typical TiO_2 electrode is shown in Fig. 2b. The response levels off near 350 nm. Preliminary results using a tungsten-doped n-type TiO_2 electrode, Fig. 2a, reveal that the onset of response can be shifted by nearly 0.5 eV. Unfortunately, the shift is towards the blue, but the fact that the response can be shifted at all is noteworthy and encouraging.

TABLE 4. *Efficiency of storage of optical energy as hydrogen*[a]

Applied potential, V	Irradiation time, ksec	Average current, mA	μmol of H_2	Energy stored[b] as H_2, cal	Energy in from[c] power supply, cal	Energy in[d] from laser, cal	Optical energy[e] storage efficiency, %
0.5	76.0	0.66	170	12.0	6.0	810	0.74
0.5	40.0	0.82	120	8.2	3.9	430	1.0$_0$
0.5	91.0	0.63	310	21.0	6.8	980	1.4$_5$
0.25	59.0	0.26	76	5.2	0.9	640	0.6$_7$

[a] From data given in Table 3; the electrolyte is 0.1, 1.0, 1.0, and 2.0 M NaOH for the four experiments, respectively.
[b] Assuming H_2 can be recovered at 68 kcal/mol, which is the standard heat of formation of H_2O (1).
[c] Energy from power supply = (applied potential) (average current) (irradiation time) (0.239 cal/J).
[d] 8×10^{-6} einstein/min at 351, 364 nm is equivalent to about 0.011 cal/sec.
[e] Optical energy storage efficiency = $\dfrac{\text{(energy stored as } H_2) - \text{(energy in from power supply)}}{\text{(energy in from laser)}} \times 100$.

SUMMARY

The n-type TiO_2 semiconductor electrode has been demonstrated to be a true photoassistance agent for the electrolysis of water. The electrode operates with maximum quantum efficiency upon irradiation with near ultraviolet light; the maximum quantum efficiency for the photoassisted electrolysis of water is obtained when an external potential is applied; and the reaction is catalytic with respect to TiO_2. These results stimulate us to continue study of this and related systems with three goals in mind: (*1*) move the wavelength of maximum response to the red; (*2*) change the current-voltage properties such that maximum efficiency for the photoassisted electrolysis is at zero applied voltage; and (*3*) increase the maximum quantum efficiency.

1. Balzani, V. & Carassiti, V. (1970) in *Photochemistry of Coordination Compounds*, eds. Balzani, V. & Carassiti, V. (Academic Press, New York), pp. 159-161, 174-178, 315–318.
2. Heidt, L. J., & McMillan, A. F. (1953) *Science* 117, 75–76.
3. Marcus, R. J. (1956) *Science*, 123, 399–405.
4. Fujishima, A., Sugiyama, E. S. & Honda, K. (1971) *Bull. Chem. Soc. Jap.* 44, 304.
5. Fujishima, A. & Honda, K. (1971) *Bull. Chem. Soc. Jap.* 44, 1148–1150.
6. Fujishima, A. & Honda, K. (1972) *Nature* 238, 37–38.
7. Merker, L. & Espenschied, E. (1960) U.S. Patent 2,521,392 (Sept. 5, 1960).
8. Wycoff, R. W. G. (1963) *Crystal Structures* (John Wiley & Sons, New York), 2nd ed., Vol. 1.
9. Koffyberg, F. P. (1965) *J. Appl. Phys.* 36, 844–849.
10. Harchard, C. G. & Parker, C. A. (1956) *Proc. Roy. Soc. Ser. A* 235, 518–536.
11. Melhuish, W. H. (1962) *J. Opt. Soc. Amer.* 52, 1256–1258.
12. Gerischer, H. (1972) *Photochem. Photobiol.* 16, 243–260.
13. Freund, T. & Gomes, W. P. (1969) *Catal. Rev.* 3, 1–36.
14. Pettinger, B., Schoppel, H.-R., Yokoyama, T. & Gerischer, H. (1974) *Ber. Bunsenges. Phys. Chem.* 78, 1024–1030, and references therein.
15. Cronemeyer, D. C. (1952) *Phys. Rev.* 87, 876–886.