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Sustained Water Cleavage by Visible Light

Enrico Borgarello, J. Kiwi, Ezio Pelizzetti,[1a] Mario Visca,[1b] and Michael Grätzel*

Contribution from the Institut de Chimie Physique, Ecole Polytechnique Fêderale de Lausanne, CH-1015 Lausanne, Switzerland.
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Abstract: Sustained cleavage of water by 4 quanta of visible light is achieved in aqueous solutions by using a bifunctional redox catalyst composed of Pt and RuO_2 cosupported by colloidal TiO_2 particles. A photochemical model system containing $Ru(bpy)_3^{2+}$ as a sensitizer and methyl viologen (MV^{2+}) as an electron relay is used to test the effect of catalyst composition, sensitizer concentration, pH, and temperature on the efficiency of light-induced water decomposition. Electron relay free systems also exhibit high photoactivity. Direct band gap irradiation by UV light leads to efficient water cleavage in the absence of sensitizer and relay.

Our initial discovery[2] of a system capable of decomposing water into its components H_2 and O_2 by 4 quanta of visible light

$$2H_2O \xrightarrow{4h\nu} 2H_2 + O_2 \tag{1}$$

was succeeded by the development of titania based bifunctional redox catalysts.[3] Colloidal TiO_2 particles were loaded with ultrafine deposits of Pt and RuO_2. Such a catalyst is surprisingly efficient in coupling H_2 and O_2 production to a light-driven redox reaction in which an electron relay such as methyl viologen (MV^{2+}) is reduced by the charge transfer excited state[4] of $Ru(bpy)_3^{2+}$. Later is was discovered[5] that such a system can operate even in the absence of methyl viologen. In this case only the part of the sensitizer that adheres to the catalyst particles is photoactive[6] and the conduction band of the TiO_2 serves as an electron relay. In the present paper the $Ru(bpy)_3^{2+}/MV^{2+}$ based model system is used to examine the effect of parameters such as catalyst composition, solution pH, dye concentration, and temperature on the yield of light-induced water cleavage. Experiments with electron relay free solutions and band gap excitation of TiO_2 by UV light in the absence of sensitizer have also been performed. From the results important conclusions concerning the mechanism of water cleavage can be derived.

Experimental Section

i. Catalyst Preparation. TiO_2 was prepared by thermal hydrolysis of titanium sulfate in 4–5 M H_2SO_4 at 98 °C according to the Blumenfeld procedure.[7] Upon dilution a gel-like material is precipitated which after drying was identified by X-ray analysis as amorphous oriented anatase. If Nb^{5+} doping was desired an appropriate amount of Nb_2O_5 was digested together with $TiOSO_4$ in sulfuric acid.

TiO_2 rutile was obtained from the anatase by dissolving the latter in NaOH, precipitation as Na_2TiO_3, and subsequent peptizing in HCl. Upon heating the HCl solution to 70 °C hydrolysis occurs, yielding a precipitate. X-ray diffraction analysis performed with the powder reveals rutile structure with >95% cristallinity. Nb^{5+} doping of rutile was carried out by adding the appropriate amount of Nb_2O_5 to the HCl solution prior to hydrolysis.

RuO_2 loading was carried out after the final hydrolysis step. To the concentrated TiO_2 slurry was added the calculated amount of $RuCl_3$ (1.5 mg of $RuCl_3$/g of TiO_2 for 0.1% loading). After adjusting the pH to 6 with KOH the product was filtered and dried overnight at 100 °C.

The final stage of catalyst preparation consisted of the loading of the TiO_2/RuO_2 particles with Pt. Two different procedures were employed. In the first a solution of H_2PtCl_6 was prepared and reduced with citrate in a separate container as described earlier.[5,8-11] The resultant ultrafine (particle diameter is <30 Å) platinum sol is subsequently mixed with the solution containing the TiO_2/RuO_2 particles and sonicated. The second procedure consisted of photoplatinization:[12,13] H_2PtCl_6 (3 mg) and 1 mL of a 40% aqueous solution of formaldehyde stabilized with methanol were added to a solution containing 25 mL of water and 12 mg of TiO_2/RuO_2. After deaeration with N_2 the dispersion was illuminated by a 450-W Xe lamp through a 305 cut-off filter for 30–45 min. This time suffices for quantitative reduction of the Pt ions by conduction band electrons. The holes created by the band gap irradiation in the TiO_2 valence band are filled by oxidation of formaldehyde (the presence of RuO_2 on the TiO_2 surface is crucial since it catalyzes the latter reaction). HCHO, MeOH, and water were then removed under vacuum at 30 °C. The dried powder has a loading of 80 mg of Pt for 1 g of TiO_2 and is resuspended in solution by sonication. Catalysts with smaller levels of Pt loading were also prepared by adjusting the concentration of H_2PtCl_6 subjected to photoreduction accordingly. The two procedures of Pt loading yield catalysts of almost identical activity. However, photoplatinization is preferred over citrate reduction since it is easier to perform and gives results of excellent reproducibility.[14] In the former case this is better than 10%.

ii. Characterization of the Catalyst. The hydrodynamic radius of the anatase particles had been determined earlier[3] as 470 Å via photon correlation spectroscopy[15] with use of a Chromatix instrument.[16] Application of a more sophisticated light-scattering technique in particular multiangle measurements for the determination of the radius of gyration[17] reveals a prolate structure of the particles, the long and short axis being 1500 and 300 Å, respectively.

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(1) (a) Istituto di Chimica Analitica, Universita di Torino, Italy. (b) Centro Richerche SIBIT (Montedison), Spinetta Marengo, Italy.

(2) Kalyanasundaram, K.; Grätzel, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 701.

(3) Kiwi, J.; Borgarello, E.; Pelizzetti, E.; Visca, M.; Grätzel, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 646.

(4) This reaction was first investigated by Whitten et al. (Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 4710) after Gafney and Adamson discovered that the excited ruthenium complex can serve as a powerful one-electron reductant (Gafney, H. D.; Adamson, A. W. *J. Am. Chem. Soc.* **1972**, *94*, 8238.

(5) Borgarello, E.; Kiwi, J.; Pelizzetti, E.; Visca, M.; Grätzel, M. *Nature (London)* **1980**, *289*, 158.

(6) Sensitization of TiO_2 (or Sr TiO_3) single crystal electrodes by $Ru(bpy)_3^{2+}$ dyes has been described by: (a) Clark, W. D. K.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 4676. (b) Hamnet, A.; Dave-Edwards, M. P.; Wright, R. D.; Seddon, K. R.; Goodenough, J. B. *J. Phys. Chem.* **1979**, *83*, 3280. (c) Mackor, A.; Schoonman, J. *Rec. J. Neth. Chem. Soc.* **1980**, *99*, 71.

(7) Barksdale, J., Ed. "Titanium"; Ronald Press: New York, 1966.

(8) Turkevich, J.; Aika, K.; Ban, L. L.; Okura, I.; Namba, S. *J. Res. Inst. Catal. Hokkaido Univ.* **1976**, *24*, 54.

(9) Turkevich, J. In "Electrocatalysis of Fuel Cell Reactions"; Brookhaven Symposium proceedings, p 123.

(10) Wilenzick, R. M.; Russell, D. C.; Morris, R. H.; Marshall, S. W. *J. Chem. Phys.* **1967**, *47*, 533.

(11) Brugger, P.-A.; Cuendet, P.; Grätzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 2923.

(12) Duonghong, D.; Borgarello, E.; Grätzel, M. *J. Am. Chem. Soc.* 1981 *103*, 4685.

(13) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* 1978, *100*, 4318.

(14) In a few cases Pt loading was carried out by reducing H_2PtCl_6 with hydrogen (Kiwi, J.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7214). This catalyst is about two times less active than those obtained by citrate reduction or photoplatinization. Also, the Pt tends to aggregate during irradiation leading to further loss in activity and repeated sonication is needed to reestablish the ultrafine dispersed state.

(15) Corti, M.; Degiorgio, V. Ann. Phys. (*Paris*) **1978**, *3*, 303.

(16) Chromatix Application Note LS-8 (1978), 560 Oakmed Parkway, Sunnyvale, Calif. 94086.

(17) Corti, M.; Pelizzetti, E., to be published.

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The point of zero ζ potential (ZZP) of the anatase was determined as 4.7 by the electrophoresis technique, using a Rank Bros. II instrument equipped with an He–Ne laser and a cylindrical cell.[12] This value is probably affected by the SO_4^{2-} impurities[18] detected analytically. For anatase particles deprived entirely of anionic impurities ZZP values around 6 have been measured.[19]

Finally, the surface are[20] of both the rutile and anatase support is very high and amounts to 200–240 m^2/g.

iii. Materials. $Ru(bpy)_3^{2+}$ (Strem, dichloride), ruthenium tetroxide (RuO_4, Alpha Inorganics), methyl viologen (BDH), and H_2PtCl_6 (Engelhard) were used as supplied. Deionized water was refluxed over alkaline permanganate and subsequently distilled three times in quartz vessels. All other reagents were at least analytical grade and used as supplied.

iv. Apparatus and Evaluation of Water Cleavage Experiments. Continuous illuminations were carried out with an Osram XBO-450 W Xe lamp equipped with a 15 cm water jacket to remove IR radiation. For visible light experiments a 400 nm cut-off filter was placed in the beam. The optical density of the filter is 3 at 395 nm which suffices to supress entirely any direct band gap excitation of TiO_2. The solution volume was invariably 25 mL and was contained in a Pyrex flask equipped with optically flat entry and exit windows. (The gas volume above the solution is ca. 10 mL.) The filter effect of the Pyrex for UV light is significant. Thus the transmission of the entry window is 50% at 325 nm and practically zero below 300 nm.

For the study of temperature effects a double-wall flask equipped with a 5 mm water jacket was employed which was connected to a thermostate. The light intensity absorbed by the solution in this device is about 10 times smaller than that in the case of the single-wall flask.[21]

The gas evolved under illumination was analyzed by gas chromatography. A 60 W Mac system, carbosieve column (35 °C), and N_2 as a carrier gas were employed for hydrogen detection. Oxygen was determined by gas chromatography, using a Perkin–Elmer 900 GC with a 6 ft × 118 in. molecular sieve (5 Å) column. The carrier gas was He at a column temperature of 40 °C. The filament was set at 225 mA (TCD mode) and attenuation 16. Alternatively, a Teledyne B_1 oxygen specific microfuel cell was employed for oxygen and a hydrogen specific electrode[22] for hydrogen detection, respectively. These electrodes are placed in a small cylindrical glass vessel which is connected through a flow system[12] with the sample cell. Prior to illumination the whole system is freed from oxygen by a stream of N_2. The solution is then exposed to light. The mixture of H_2 and O_2 produced under illumination is transferred by the N_2 carrier gas to the cell where it is readily detected. The N_2 flow through the solution is either continuous or is intercepted during illumination. In the latter case the gas produced by the photolysis is sampled at regular intervals. By using this method the time characteristics of O_2 and H_2 generation could be established.

The following features are typical for the behavior of the system under visible light irradiation in a closed cell: After a short induction period the hydrogen generation rate (rH_2) becomes steady over a period of ca. 20 h. This stationary rate is given in the result section.[23] Pure hydrogen appears in the gas phase during the first hours of irradiation. Only after several milliliters of H_2 have been produced does oxygen manifest itself in the gas phase as shown by the chromatographic analysis. This behavior is due to photoinduced adsorption of O_2 and/or spontaneous adsorption of O_2^- (produced from oxygen and the reduced viologen) onto the surface of the TiO_2 particles. Blank experiments showed that oxygen uptake by deaerated $Pt/RuO_2/TiO_2$ suspensions is very efficient under illumination. The rate of oxygen generation approaches stoichiometric proportion ($rH_2 = 2rO_2$) only after saturation of TiO_2 adsorption sites. (The turnover number of TiO_2 with respect to O_2 formation is greater than 2 showing that oxygen is produced from water and not from the TiO_2 support material.) Thus, apart from supporting the two catalysts TiO_2 plays the role of an oxygen carrier. This aspect is important for practical systems in which separation of H_2 and O_2 is to be achieved. At longer times the rate of water decomposition decreases, a photostationary state being approached after ca. 100 h. When the light is turned off H_2/O_2 recombination occurs and is completed after 10 to 30 h. Upon renewed exposure to light water cleavage resumes at the initial rate. No pH changes are noted even after prolonged irradiation of unbuffered solutions.

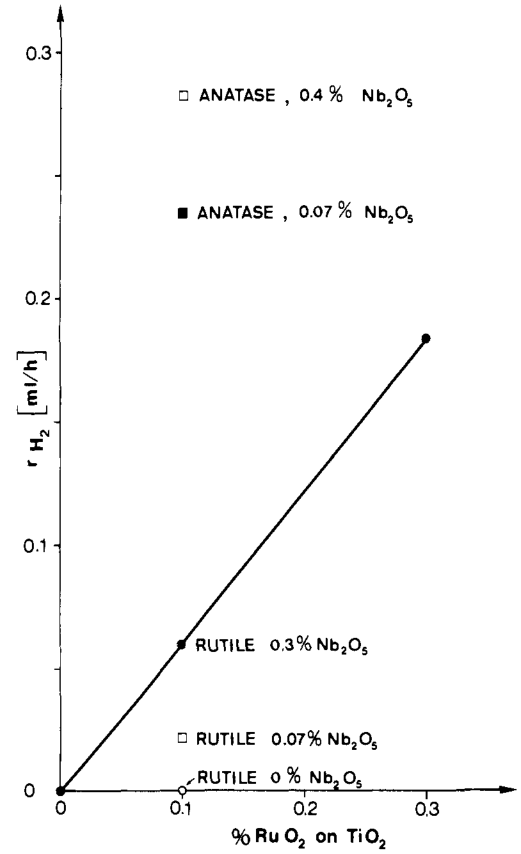

Figure 1. Influence of catalyst structure and composition on the visible light-induced (λ > 400 nm) decomposition of water. Conditions: 500 mg of TiO_2/L loaded with 40 mg of Pt, Nb_2O_5 doping, and RuO_2 loading variable, pH 4.7, $[Ru(bpy)_3^{2+}] = 10^{-4}$ M, $[MV^{2+}] = 5 \times 10^{-3}$ M, $T = 25$ °C.

Results and Discussion

i. Effect of TiO_2 Structure, n-Doping, and RuO_2 Loading. An initial series of experiments was designed to establish the influence of TiO_2 crystal structure, n-doping, and RuO_2 loading on the yield of photoinudced water splitting. The rate of hydrogen and oxygen generation by visible light was measured from 25 mL solutions, always containing $Ru(bpy)_3^{2+}$ (10^{-4} M), MV^{2+} (5×10^{-3} M), and TiO_2 (500 mg/L) loaded with 40 mg/L Pt. Results are shown in Figure 1 where the hydrogen evolution rate (rH_2) is plotted against the percentage of RuO_2 deposited on the TiO_2 particle for various levels of Nb_2O_5 doping.[24] If rutile is used as a support material the efficiency of photoinduced water splitting is relatively small and depends strongly on both RuO_2 loading and Nb_2O_5 doping. At 0.3% Nb_2O_5 the rate increases linearly with RuO_2 concentration within the range investigated. Conversely if the RuO_2 loading is maintained at 0.1% one observes a strong increase of rH_2 upon increasing the level of Nb_2O_5 doping. No hydrogen is obtained in the absence of either RuO_2 or Nb_2O_5.

The activity of anatase is by far superior to that of rutile based redox catalysts. Thus at a loading of 0.1% RuO_2 the rate of hydrogen generation obtained with the former is at least 4 times higher than that observed with the latter modification. A further important feature of anatase supported catalysts is that the degree of Nb_2O_5 doping exerts only a minor influence on its activity: rH_2 values obtained in the presence of Nb_2O_5 are only 10–20% higher than those observed with undoped materials. However, the presence of RuO_2 is also mandatory in anatase based catalysts

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(18) Minute amounts of anions adsorbed at the surface of TiO_2 lower its ZZP, see: (a) Parfitt, G. D.; Ramsbotham, J.; Rochester, C. H. *J. Colloid Interface Sci.* **1972**, *41*, 217; (b) Fukuda, H.; Minra, M. *J. Sci. Hiroshima Univ., Ser. A* **1972**, *A36*, 77.

(19) (a) Parfitt, G. D. *Progr. Surf. Membr. Sci.* **1976**, *11*, 181. (b) Boehm, H. P. *Discuss. Faraday Soc.* **1971**, *52*, 264.

(20) This was derived from BET measurements.

(21) Details concerning actinometry have been given elsewhere, see ref 12 and 14.

(22) This electrode was developed by Dr. Calzaferri and co-workers at the University of Bern, Switzerland.

(23) For clarity of presentation only rH_2 values will be plotted.

(24) Nb^{5+} replaces Ti^{4+} in the TiO_2 lattice and hence acts as an n-dopant. Up to 20 mol % substitution of Ti^{4+} is possible, see: Roth, R. S.; Conghanour, L. V. *J. Res. Natl. Bur. Stand. (U.S.)* **1955**, *55*, 209.

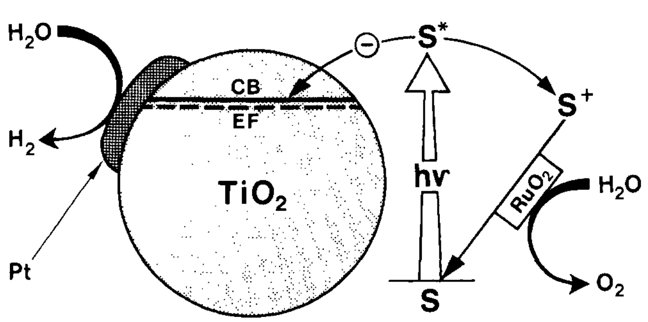

Figure 2. Schematic illustration of the processes involved in the dye-sensitized decomposition of water. S: sensitizer, R: electron relay.

in order to obtain water splitting activity.

A feasible mechanism for the intervention of the bifunctional redox catalyst is pointed out in Figure 2.[25] Light excitation of the sensitizer is followed by electron transfer to the relay (in our case methyl viologen). The latter in turn injects an electron into the conduction band of the TiO_2 from where it is channeled to a Pt site where H_2 evolution occurs. RuO_2, on the other hand, assists the back conversion of S^+ to S under simultaneous oxygen formation from water. This device is reminiscent of the concept of photochemical diodes.[26]

The difference in activity observed between rutile and anatase based catalysts may be accounted for by the location of the conduction band in these semiconductors. The flat band potential of rutile coincides almost exactly with the NHE potential[27] while that of anatase is shifted cathodically by approximately 200 mV.[28] Hence only in the latter case is a driving force for water reduction available.

To explain the effect of Nb_2O_5 we draw attention to the fact that Nb^{5+} has a radius very close to that of Ti^{4+} and therefore replaces isomorphically titanium ions in the TiO_2 lattice. As an n-dopant it produces a Schottky barrier at the particle/solution interface that assists electron injection from the reduced methyl viologen.[29] Moreover, Nb_2O_5 shifts the flat band potential of rutile cathodically.[30] Both effects are likely to contribute to the marked enhancement of hydrogen generation with increasing Nb_2O_5 content observed for the rutile based catalysts.

ii. **Effect of Pt Loading Electron Relay Free Systems.** The following experiments were performed with anatase doped with 0.4% Nb_2O_5 and loaded with 0.1% RuO_2, i.e., the catalyst which according to Figure 1 exhibits optimum activity. $Ru(bpy)_3^{2+}$ was invariably employed as a sensitizer. In order to examine the role of the electron relay (MV^{2+}) in the water splitting process experiments were carried out both with MV^{2+} containing and MV^{2+} free solutions. The first parameter to be checked was the amount of Pt loading of the TiO_2 catalyst. Figure 3 shows that within the range of 10–40 mg of Pt deposited on 500 mg of anatase the rate of H_2 generation increases distinctively with Pt loading. Pt-free catalysts exhibited no activity. The curves obtained in the absence and presence of MV^{2+} are almost parallel with the hydrogen output increasing by a factor of 4–5 through addition of the electron relay.

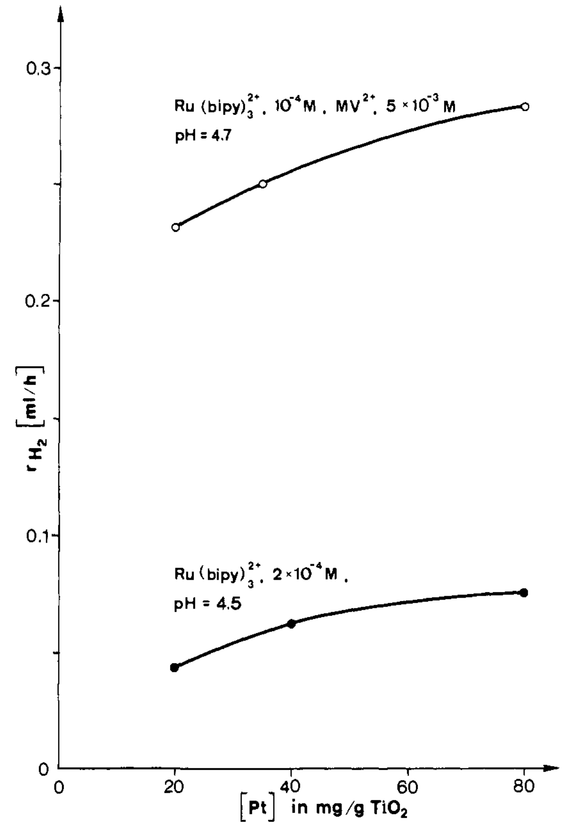

Figure 3. Effect of Pt loading on the efficiency of water splitting. [TiO_2] = 500 mg/L (anatase) doped with 0.4% Nb_2O_5 are loaded with 0.1% RuO_2.

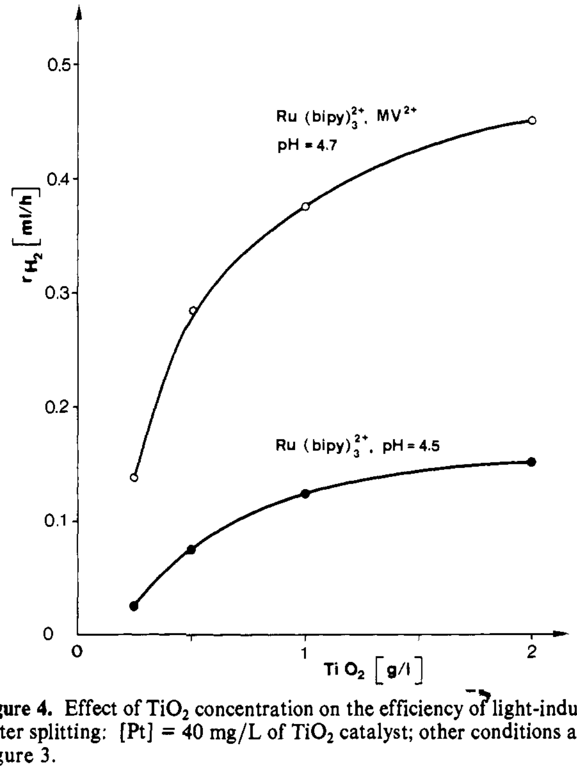

Figure 4. Effect of TiO_2 concentration on the efficiency of light-induced water splitting: [Pt] = 40 mg/L of TiO_2 catalyst; other conditions as in Figure 3.

Next we established for a given Pt concentration (40 mg/L) the effect of TiO_2 concentration on the hydrogen and oxygen yields. Figure 4 shows that upon increasing the TiO_2 content from 0.5 to 2 g/L the augmentation of rH_2 is sixfold in MV^{2+} free and

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(25) Grätzel, M. *Ber. Bunsenges. Phys. Chem.* **1980**, *84*, 981.

(26) (a) Yoneyama, H.; Sakamoto, H.; Tamura, H. *Electrochim. Acta* **1975**, *20*, 341. (b) Nozik, A. J. *Appl. Phys. Lett.* **1976**, *29*, 150; *Ibid.* **1977**, *30*, 567. We are grateful to Dr. A. J. Nozik for valuable suggestions concerning the mechanism of our photocatalytic system and for pointing out the analogies between his concept of photochemical diodes and semiconductor redox catalysis: Nozik, A. J. Discussions of the Faraday Society, Photoelectrochemistry, Oxford, G. B., 1980. (c) Jarret, H. S.; Sleight, A. W.; Kung, H. H.; Gillson, J. L. *J. Appl. Phys.* **1980**, *51*, 3916.

(27) Dutoit, E. C.; Cardon, F.; Gomes, W. P. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 475.

(28) (a) Jaeger, D.; Bard, A. J. *J. Phys. Chem.* **1979**, *23*, 3146. (b) Heller, A., Ed. "Semiconductor Liquid Junction Solar Cells"; The Electrochemical Society: Princeton, N.J., 1977; Chapter VII, p 272. (c) Rao, M. V.; Rajeshwar, K.; Pai Verneker, V. R.; Du Bow, J. *J. Phys. Chem.* **1980**, *84*, 1978.

(29) The calculated carrier density for 0.4% Nb_2O_5 is $^1N = 4.6 \times 10^{19}$ cm^{-3}. The effective Debye length in the depletion layer is $L_D = [\epsilon\epsilon_0 kT/2\,{}^1Ne^2]^{1/2}$. With $\epsilon = 170$ for TiO_2 one obtains $L_D = 6$ Å corresponding to a depletion layer width of ca. 20 Å in the case of anatase. There is evidence, however, that at high doping levels a significant portion of Nb^{5+} is excluded from the TiO_2 lattice, e.g., ref 30.

(30) Salvador, P. *Sol. Energy Mater.* **1980**, *2*, 413.

fourfold in MV^{2+} containing solutions. This increase is not linear, the curves exhibiting a steep ascent at low TiO_2 content and leveling off at higher concentration.

These observations may be rationalized in terms of the scheme shown in Figure 2. In MV^{2+} containing systems the electron transfer reaction[31]

$$^*Ru(bpy)_3^{2+} + MV^{2+} \rightarrow MV^+ + Ru(bpy)_3^{3+} \qquad (2)$$

will be the principal pathway of $^*Ru(bpy)_3^{2+}$ deactivation. As this process occurs in the solution bulk MV^+ has to diffuse subsequently to the surface of a TiO_2 particle where electron injection and hydrogen evolution take place. Competing with this event is the back reaction:

$$Ru(bpy)_3^{3+} + MV^+ \rightarrow Ru(bpy)_3^{2+} + MV^{2+} \qquad (3)$$

as well as oxygen reduction

$$MV^+ + O_2 \rightarrow MV^{2+} + O_2^- \qquad (4)$$

which both occur at a diffusion controlled rate.[32] The competition of the latter reaction will become increasingly important as O_2 accumulates in solution, the mean lifetime of MV^+ at $^1/_3$ atm oxygen pressure being ca. 5 μs. One infers from these considerations that in order to achieve water decomposition the electron injection from MV^+ into the TiO_2 particle must be very fast and occur within only a few microseconds. It is not surprising therefore that the TiO_2 concentration has a decisive influence on the H_2 production rate: electron injection from MV^+ into TiO_2 becomes faster with increasing particle concentration and finally is favored kinetically over back reaction and oxygen reduction.

It is also expected from the model in Figure 2 that the amount of Pt deposited on an individual TiO_2 particle should less critically influence the water photolysis events. Evidently, enough Pt has to be present to assure that an electron once injected is ultimately conducted to a Pt site where H_2 evolution occurs. At 20 mg of Pt/g of TiO_2 this limit appears to be attained and the gain in hydrogen yield achieved with higher loading is small.

Turning now to the MV^{2+} free system one has to take into account the fact that electron injection occurs here directly from the excited $Ru(bpy)_3^{2+}$ complex into the TiO_2 conduction band. We are interested only in those excited state molecules that are capable of electron transfer to the particle, i.e., molecules adsorbed onto the TiO_2 surface or contained within the diffusion layer defined by the thickness $(2D\tau)^{1/2}$, where D is the diffusion coefficient and τ the excited state lifetime (ca. 0.5 μs). The diffusion layer thickness is about 315 Å at room temperature.[33] Both the fraction of $Ru(bpy)_3^{2+}$ adsorbed at the TiO_2 surface and that contained within the diffusion layer increase with particle concentration. This explains the drastic augmentation of rH_2 with TiO_2 concentration observed in the MV^{2+} free system.

iii. Effect of Sensitizer Concentration and pH. Consider first the effect of sensitizer concentration on the rate of water photolysis, Figure 5. This parameter plays an important role in the electron relay free system where rH_2 increases sevenfold upon augmentation of the $Ru(bpy)_3^{2+}$ concentration from 0.5 to 2×10^{-4} M. In the presence of MV^{2+} the increase is relatively small and amounts to only 40% over the same concentration range. Further augmentation of $[Ru(bpy)_3^{2+}]$ leads in both cases to only small improvement in the yield.

To rationalize this behavior we recall that in MV^{2+} free solution essentially the fraction of $Ru(bpy)_3^{2+}$ adhering to the TiO_2 particle surface is photoactive. The latter increases with $Ru(bpy)_3^{2+}$ concentration. Conversely, when MV^{2+} is present sensitizer molecules in the solution bulk can become photoactive as well. Here the effect of sensitizer concentration is related to the total absorbance of the solution which is high already at the lower concentration limit.[34]

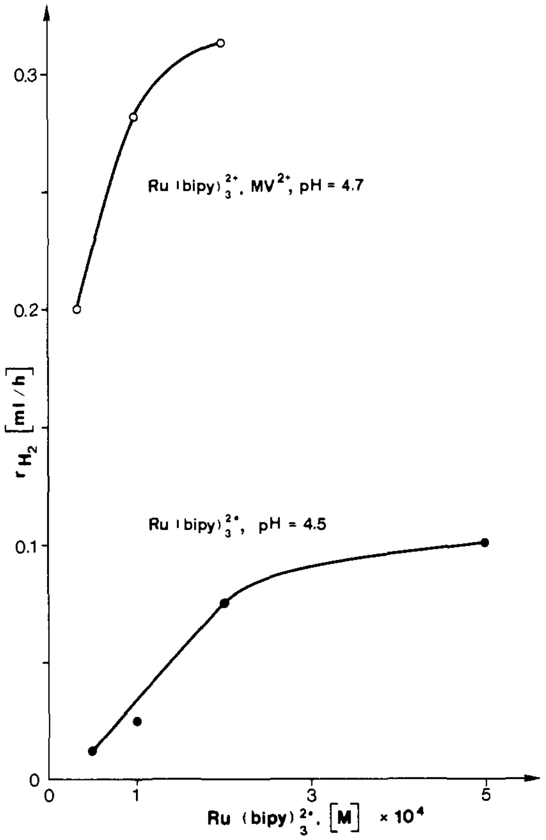

Figure 5. Effect of sensitizer concentration on the efficiency of light-induced was splitting: $[TiO_2]$ = 400 mg/L doped with 0.4% Nb_2O_5 and loaded with 0.1% RuO_2, $[MV^{2+}] = 5 \times 10^{-3}$ M.

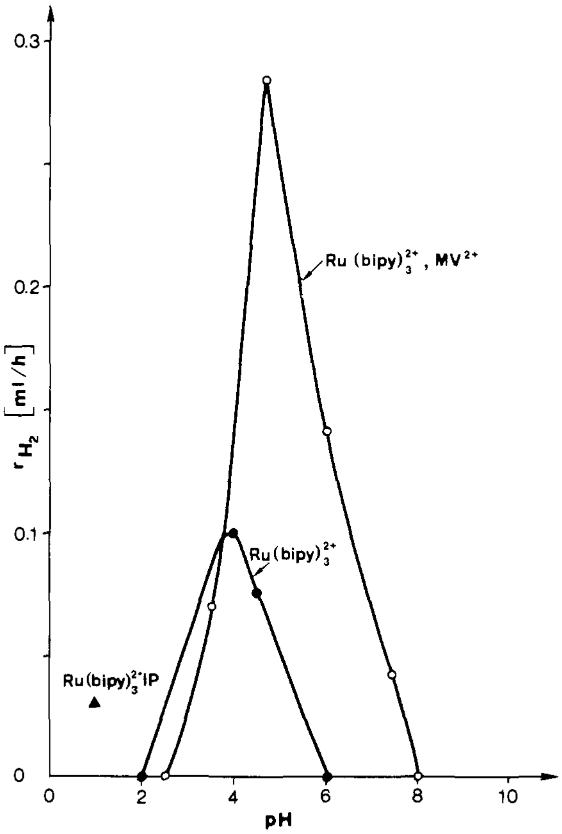

Figure 6. Effect of pH on the efficiency of light-induced water splitting, sensitizer, and relay concentration as in Figure 1.

The solution pH has a decisive influence on the yield of photoinduced water cleavage, Figure 6. $Ru(bpy)_3^{2+}$ alone exhibits

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[31] The rate constant for this reaction is 5×10^8 M^{-1} s^{-1}. Cf. ref 32a and Gaines, G. L. *J. Phys. Chem.* **1979**, *83*, 3088.

[32] (a) Kalyanasundaram, K.; Kiwi, J.; Grätzel, M. *Helv. Chim. Acta* **1978**, *61*, 2720. (b) Farrington, J. A.; Ebert, M.; Land, E. J. *J. Chem. Soc. Faraday Trans. 2* **1978**, *74*, 665.

[33] Gosh, P. K.; Siro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 5543.

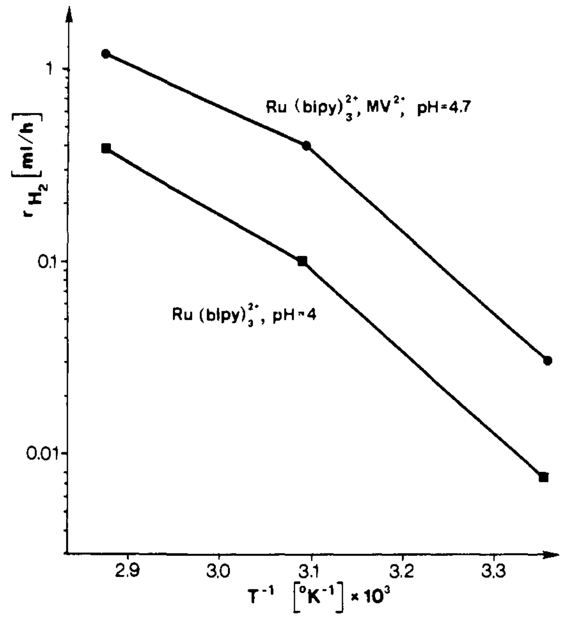

Figure 7. Effect of temperature on the yield of light-induced water splitting; conditions as in Figure 6 except that a double-wall flask was used for irradiations.

a maximum of a pH around 4, no H_2 being formed below pH 2 and above pH 6. The situation is similar in the presence of MV^{2+} where the maximum of the curve is shifted by 0.5 to 1 units to higher pH values. Interestingly, the isopropyl ester derivative[35] of $Ru(bpy)_3^{2+}$ is active even at a pH as low as 1.

While a change in pH does not affect the redox potentials of MV^{2+} and $Ru(bpy)_3^{2+}$ it shifts the flat band potential of TiO_2 and the water oxidation potential by −59 mV/pH. Upon lowering the pH the driving force for the oxygen producing reaction

$$4Ru(bpy)_3^{3+} + 2H_2O \xrightarrow{(RuO_2)} 4Ru(bpy)_3^{2+} + 4H^+ + O_2 \quad (5)$$

diminishes leading to a decrease in the rate of water decomposition.[36] At pH 2 the kinetics of reaction 5 become so slow that water photolysis ceases essentially. However, if a sensitizer with a higher redox potential such as $Ru(bpy)_3^{2+}\cdot 1P$ ($E^\circ = 1.5$ V vs. NHE in water)[37] is employed the rate of oxygen generation is high enough even at pH 1 to afford light-induced water cleavage. Upon increasing the pH, electron injection from MV^+ or $^*Ru(bpy)_3^{2+}$ into the TiO_2 conduction band becomes rate controlling. According to current theories of electron transfer across the semiconductor/electrolyte interface[38] good overlap of donor states in the aqueous phase with the conduction band position is required to render charge injection fast. The maximum in the distribution function for occupied levels of the $^*Ru(bpy)_3^{2+}/Ru(bpy)_3^{3+}$ system (E_{max}^{occ}) is located around −0.4 V (NHE) assuming a reorganization energy of 0.4 eV.[39] Thus E_{max}^{occ} becomes isoenergetic with V_{fb} of anatase at pH ~4. Interestingly, optimum efficiency for water decomposition in the relay free system is found at the same pH.

For the $MV^{2+/+}$ redox couple no data on the reorganization energy are available. Nevertheless, E_{max}^{occ} is certainly located anodic of the standard redox potential, i.e., −0.44 V.[40] It may therefore seem surprising that in the case of MV^+ as electron injecting agent water cleavage is possible at higher pH than in the relay free system. However, since the lifetime of MV^+ is at least a factor of 20 longer than that of $^*Ru(bpy)_3^{2+}$ (even in aerated solution) kinetic requirements are much less stringent in this case. At pH 8 H_2 formation from MV^+ ceases as it becomes thermodynamically unfavorable.

iv. Temperature Effects. The temperature exerts a drastic influence on the yield of photoinduced water cleavage. This is illustrated in Figure 7 where the parameter rH_2 is plotted in a semilogarithmic fashion against the reciprocal temperature. The two curves obtained with and without MV^{2+} are essentially parallel, the former system exhibiting 3 to 4 times higher activity than the latter over the whole temperature range. (We recall here that a double-walled Pyrex flask was employed where the light flux is attenuated 10 times with respect to conditions prevailing in the foregoing experiments.)

Consider first the $Ru(bpy)_3^{2+}$ system in the absence of MV^+. Rates of H_2 evolution are 0.0075, 0.1, and 0.38 mL/h at 25, 50, and 75 °C. Hence over a temperature range of only 50 °C the hydrogen yield has increased 50 times. A similar improvement in the performance of the system is apparent in the presence of MV^+ where the rates are 0.03, 0.4, and 1.2 mL/h.[41]

Attempts were made to determine the quantum yield of water cleavage under these conditions. This is rendered difficult by the fact that the solutions are turbid and scattering of light cannot be neglected. Therefore, a comparison was made with a standard system used under identical experimental conditions and concentration of solutes. The solution contained, apart from $Ru(bpy)_3^{2+}$, MV^{2+} and the catalyst EDTA which functions here as a sacrificial electron donor. Such a system produces hydrogen with a quantum yield $\phi(H_2) = 0.13$ under illumination.[42] Comparison with the cyclic system gives $\phi(H_2) = 0.06$ for an H_2 generation rate of 1.2 mL/h.

The observed temperature effects may be rationalized in terms of the following. (a) Enhancement of the $Ru(bpy)_3^{2+}$ diffusion to the surface of the TiO_2 particle: From the Stokes–Einstein equation one expects the diffusion coefficient to increase 2.8 times over a temperature range from 25–75 °C which expands the diffusion layer from 315–520 Å. (b) Decrease of oxygen concentration in the solution with increasing temperature: It has been shown recently[28c] that oxygen is reduced to O_2^- by TiO_2 conduction band electrons. This process competes with proton reduction and hence lowers the quantum yield of H_2 formation. Upon increasing the temperature from 25–75 °C the saturation limit for O_2 is decreased from 3.16 cm^3/100 mL to 2.38 cm^3/100 mL rendering this process less effective. A further contribution to the yield enhancement may arise from the fact that the temperature coefficient for H^+ reduction is higher than that for O_2 reduction. (c) The diffusional and O_2 concentration arguments appear to be unsatisfactory to account entirely for such a large temperature effect: Note that the activation energy calculated from the lower temperature points in Figure 7 is as high as 20 kcal/mol. In

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(34) Direct charge injection from $^*Ru(bpy)_3^{2+}$ in the conduction band of TiO_2 can also contribute to water cleavage in MV^{2+} containing solutions. This may account for a large part of the observed increase in rH_2.

(35) This compound was synthesized in our laboratory by Dr. Patricia J. De Laive (De Laive, P. J.; Whitten, D. G.; Giannotti, C. In "Inorganic Compounds with Unusual Properties - II"; American Chemical Society: Washington, D.C., 1979; Adv. Chem. Ser. No. 173, p 236).

(36) The redox potential for the couple $Ru(bpy)_3^{2+/3+}$ is located at +1.26 V (Creutz, C.; Sutin, N. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2858); that for the excited state complex has been determined as −0.85 V (cf. Sutin, N.; Creutz, C. *Adv. Chem. Ser.* **1978**, *168*, 1).

(37) Kalyanasundaram, K.; Neumann-Spallart, M., unpublished results.

(38) (a) Memming, R.; *Electrochim. Acta* **1980**, *25*, 77. (b) Harris, L. A.; Wilson, R. H. *Annu. Rev. Mater. Sci.* **1978**, *8*, 99. (c) Gerischer, H. *Pure Appl. Chem.* **1980**, *52*, 2649. (d) Butler, M. A.; Ginley, D. S. *J. Mater. Sci.* **1980**, *15*, 1. (e) Nozik, A. J. *Philos. Trans. R. Soc. London, Ser. A* **1980**, *295*, 453. (f) Horowitz, G.; Bourasse, A. *Rev. Phys. Appl.* **1980**, *15*, 463. (g) Bard, A. J. *Science* **1980**, *207*, 138. (h) Heller, A.; Miller, B. *Electrochim. Acta* **1980**, *25*, 29. (i) Wrighton, M. S. *Acc. Chem. Res.* **1979**, *12*, 303. (j) Rujeshwar, K.; Singh, P.; DuBow, J. *Electrochim. Acta* **1978**, *23*, 1117. (k) Maruska, H. P.; Gosk, A. K. *Sol. Energy* **1978**, *20*, 443. (l) Tomkiwicz, M.; Fay, H. *Appl. Phys.* **1979**, *18*, 1.

(39) Memming has performed a detailed study of electron transfer reactions of excited Ru complexes at semiconductor electrodes. He evaluates the reorganization energy of excited $Ru(bpy)_3^{2+}$ as 0.4 eV (Memming, R. *Surf. Sci.* **1980**, 101).

(40) (a) Michaelis, L.; Hill, E. S. *J. Gen. Physiol.* **1933**, *16*, 859. (b) Elofson, R. M.; Edsberg, R. L. *Can. J. Chem.* **1957**, *35*, 646. (c) Hornbaugh, N. A.; Sundquist, J. E.; Burris, R. H.; Orme-Johnson, W. H. *Biochemistry* **1976**, *15*, 2633.

(41) The presence of acetate buffer does not affect the results. Thus identical rates were obtained in solutions completely free of organic components other than the sensitizer. This rules out that the acetate buffer instead of water can act as an electron source for water reduction.

(42) Kiwi, J.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7214. (References concerning H_2 and O_2 production from water in sacrificial systems are given in ref 25.)

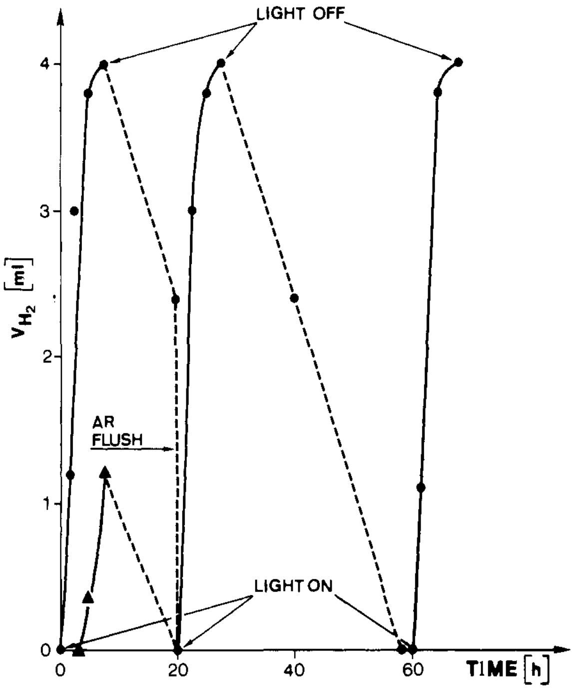

Figure 8. UV irradiation (Pyrex filtered) of the bifunctional TiO_2 (anatase) catalyst: 500 mg of TiO_2/L doped with 0.4% Nb_2O_5, loaded with 0.1% RuO_2 and 40 mg of Pt, pH 4.5, catalyst concentration 500 mg/L, pH adjusted with HCl. Triangles indicate the volume of oxygen in milliliters.

contrast the value is only 6 kcal/mol in a nonregenerating system[42] where diffusional activation may well be of prominent influence. Thus one is led to evoke other factors to rationalize the experimental observations. Recent laser studies with colloidal TiO_2 dispersions indicate that the charge injection from excited $Ru(bpy)_3^{2+}$ into the conduction band of TiO_2 is greatly enhanced by increasing the temperature. Also an increase of the carrier population in the support material and shift of its Fermi level with temperature or simply the enhanced desorption of the product gases H_2 and O_2 from the catalyst may play a role.

v. Near-UV Light Photolysis. The colloidal $Pt/RuO_2/TiO_2$ particles were also irradiated in the absence of sensitizer and relay. If no cut-off filter is used to remove UV irradiation[43] (in this case transmission is restricted by the Pyrex wall of the flask) one observes H_2 and O_2 production through direct band gap excitation of the semiconductor particles. Results are displayed in Figure 8 where the volume of hydrogen produced is plotted against irradiation time. The rate of water cleavage observed initially is very high and amounts to 2–3 mL of H_2/h. It diminishes as pressure builds up and a photostationary state is approached. The illumination was stopped at this point and the solution stirred in the dark which resulted in H_2/O_2 recombination. After completion of the back reaction or removal of the product gas through flushing with Ar, water decomposition resumes at the initial rate. This cycle can be repeated many times.

These results illustrate the capability of the particles to split water into hydrogen and oxygen. The effects observed have been well understood since Honda's[44] work on the light-induced oxygen formation on irradiated TiO_2 macroelectrodes. Band gap excitation leads to formation of an electron/hole pair. The former migrates to Pt sites where H_2 is formed while the latter are channeled to RuO_2 deposits which catalyze water oxidation.[45] The high yields observed indicate efficient electron/hole separation. A crucial role in this process is played by the RuO_2 deposit which greatly enhances the rate of hole transfer from the valence band of TiO_2 to the aqueous solution.[46] Water cleavage on TiO_2 and $SrTiO_3$ powders has been observed before[27c,47] but with significantly lower efficiency.

Conclusions

The present study establishes several basic features concerning the performance of bifunctional TiO_2 based water cleavage catalysts under visible and UV light irradiation. Important is the preparation of the TiO_2 particles during which calcination steps have to be avoided to ensure high surface hydroxyl population. The success of the experiment will also to a large degree depend on the mode of loading of the support with the noble metal catalyst. Deposition of Pt in ultrafine and moreover stable form is not trivial and has to be exercised with care. Visible light-induced water cleavage is based on the concept of light-induced charge injection from either the reduced relay or the excited sensitizer[48] in the semiconductor coupled with RuO_2 catalysis of water oxidation. The influence of fundamental parameters such as catalyst composition, pH, and temperature on the water splitting is now established, opening up the way for further development of these systems.

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(43) For a recent review on UV photosynthesis with TiO_2 powders see: Bard, A. J. *J. Photochem.* **1979**, *10*, 59.

(44) Fujishima, A.; Honda, K. *Nature (London)* **1972**, *238*, 37.

(45) Trasatti, S.; O'Grady, W. E. *Adv. Electrochem. Ser.*, in press. We are grateful to Professor Trasatti for making this manuscript available to us prior to publication.

(46) The important role of RuO_2 as hole transfer catalyst has been illustrated recently also in the water photolysis with use of a CdS based catalyst. Kalyanasundaram, K.; Borgarello, E.; Grätzel, M. *Helv. Chim. Acta* **1981**, *64*, 362.

(47) (a) Bulatov, A. V.; Khidekel, M. L. *Izv. Akad. Nauk SSSR Ser. Khim.* **1902**, 1976. (b) Schrauzer, G. N.; Guth, T. D. *J. Am. Chem. Soc.* **1977**, *99*, 7189. (c) van Damme, H.; Hall, W. K. *Ibid.* **1979**, *101*, 4373. (d) Sato, S.; White, J. M. *Chem. Phys. Lett.* **1980**, *72*, 83. (e) Kawai, T.; Sakata, T. *Chem. Phys. Lett.* **1980**, *72*, 87. (f) Domen, K.; Naito, S.; Sorna, M.; Onishi, T.; Tamaru, K. *J. Chem. Soc., Chem. Commun.* **1980**, 543. (g) Kawai, T.; Sakata, T. *Nature (London)* **1980**, *286*, 474. (h) Jaeger, P. C.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 3146. (i) Wagner, F. T.; Somorjai, G. A. *Nature (London)* **1980**, *285*, 559. (j) Lehn, J. M.; Sauvage, J. P.; Ziessel, R. *Nouv. J. Chim.* **1980**, *4*, 623.

(48) We wish to draw attention to a recent paper on the sensitization of TiO_2 particle catalysts by phthalocyanines. The reaction investigated was oxygen reduction by hydroquinones. Fan, Fu-Ren, F.; Bard, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 6139.