Coordination Chemistry Reviews, 64 (1985) 225—245
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

PHOTOSENSITIZATION OF SEMICONDUCTORS WITH TRANSITION METAL COMPLEXES - A ROUTE TO THE PHOTOASSISTED CLEAVAGE OF WATER

N. SERPONE ,[1,2] E. PELIZZETTI,[1,3] and M. GRATZEL[1]
[1]Institut de Chimie Physique, Ecole Polytechnique Fédérale, Lausanne (Suisse)
[2]Department of Chemistry, Concordia University, Montréal, Québec (Canada)
[3]Istituto di Chimica Analitica, Università di Torino, Torino (Italia)

ABSTRACT

Development of artificial (non-biological) devices that achieve fuel generation by visible light is currently an ever growing area of research. Light driven redox reactions on organized assemblies afforded by semiconductor dispersions or colloidal sols provide the impetus. The various strategies used in achieving generation of dihydrogen, H_2, from the photodissociation of water are discussed. One important point that is made is dye sensitization of wide bandgap semiconductors to improve their spectral response to visible light. In practical terms, we present three examples from our recent work, in which the semiconductor particle surface (TiO_2) has been modified by adsorption of various dye molecules and by surface derivatization with ruthenium(II) complexes. In the latter case, we have demonstrated the feasibility of producing both H_2 and O_2 in stoichiometric amounts from the cleavage of water, and this without the need for a sacrificial electron donor.

INTRODUCTION

Research activity in the field of photochemical conversion and storage of solar energy has experienced tremendous growth in recent years as a result of interdisciplinary efforts from many areas such as photochemistry, electrochemistry, catalysis, solid state chemistry, and photobiology. Various teams in many laboratories throughout the world are making great contributions towards achieving a practical device(s) for the generation and storage of chemical fuels from a variety of cheap and readily available non-fossil energy sources (ref.1).

Light driven redox reactions, coupled with redox catalysts, have been and continue to be investigated as a possible route for the generation of fuels by visible light (refs.2-5). Extensive studies with transition metal complexes containing such ligands as bipyridines and phenanthrolines, organic dyes, and metalloporphyrins have shown the potential utility of these materials as "photosensitizers" in the photochemical conversion of solar energy (refs.6-11). These investigations have also revealed an important problem in the utilization of these materials in homogeneous solutions; this is the thermal reverse electron transfer between the redox products, an energy wasting reaction. Results from studies in organized molecular assemblies such as micelles, vesicles, and micro-emuls-

0010-8545/85/$07.35

ions show promise (refs.5,12,13). To some extent, the light-induced charge separation process can be controlled. With the limitations imposed by the near diffusion-controlled rates for the back reactions that follow endergonic (uphill) photoredox reactions with organic, inorganic dye based systems, attention is increasingly being focused towards heterogeneous semiconductor particulates and colloidal systems as light harvesting units.

Heterogeneous photocatalysis with semiconductor particulate systems offers several advantages. Colloidal semiconductors combine a number of desirable properties such as high absorption cross-sections, fast carrier diffusion to the interface and suitable positioning of valence and conduction bands to achieve high efficiencies in light energy conversion processes. Particularly attractive is also the added possibility of modifying the surface of the semiconductor particles by chemisorption, chemical derivatization and/or catalyst deposition that assist the light-induced charge separation and subsequent fuel generating dark reactions. Moreover, it is important to note that photoredox reactions that occur at the semiconductor/solution interface between the excited semiconductor material and the redox species in solution occur in one direction and are, in general, not reversible (ref.14).

In any practical energy conversion device, both energy transfer processes and to a greater extent electron transfer processes play a vital role. Indeed, of primordial importance is the charge separation event. Thus, in photosynthesis antenna chlorophyll molecules perform the task of light harvesting, while the light-induced charge separation is achieved through vectorial electron transfer across the photosynthetic membrane (ref.15). In a similar fashion, the distinct environment present in molecular assemblies (micelles, vesicles,...) affords a kinetic control on the charge transfer events. In the case of small semiconductor particles, it is the rapid movement of charge carriers in their respective band and the presence of local electrostatic fields at the particle/water boundary that renders possible the separation of oxidizing and reducing equivalents, and the subsequent formation of fuel from light. Recent studies in our laboratory in Lausanne has revealed that through coupling of two semiconductor catalysts possessing suitable redox potentials for the respective conduction bands, an efficient vectorial displacement of charges (conduction band electrons, e^-_{cb}, and valence band holes, h^+_{vb}) can be achieved (ref.16).

STRATEGIES USED IN PHOTOCONVERSION

Two major strategies are being considered (ref.17) in the design of potential devices to produce H_2 and O_2 from the photocleavage of water. (i) One approach considers homogeneous systems (or nearly homogeneous systems) in which a photosensitizer is used to promote electron transfer between suitable electron relay species. The oxidized and reduced forms of these relays, in the presence of

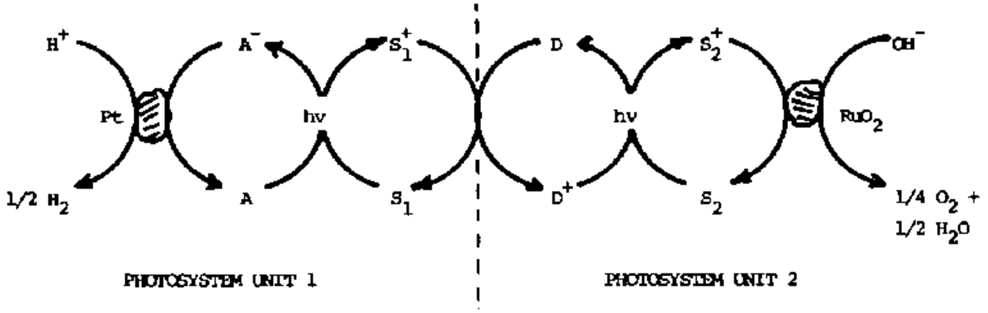


Fig. 1. Perceived coupling of two photosystem units in the photodecomposition of water employing two photosensitizers and two electron relays. From ref.17.

some appropriate catalyst(s), can liberate oxygen and hydrogen, respectively. Fig.1 shows the coupling of two photosystem units in which, in one photosystem, a photosensitizer S_1 (e.g. a water soluble metalloporphyrin) reduces an electron acceptor A (e.g. methylviologen, MV^{2+}). The oxidized form of the sensitizer, S_1^+, is subsequently reduced by an electron donor D thereby recycling S_1; A^- is used to liberate H_2 from water in the presence of a Pt catalyst. In photosystem unit 2, D^+, the oxidized form of the donor, oxidizes another photosensitizer S_2 (e.g. $Ru(bpy)_3^{2+}$, where bpy is 2,2'-bipyridine) to S_2^+ which can oxidize water to O_2 in the presence of RuO_2 or IrO_2 under suitable conditions. While photosystem units 1 and 2 have separately been investigated extensively, coupling of the two units has not been realized, and moreover the D^+/D couple has normally consisted of such sacrificial donors as EDTA, triethanolamine (TEOA),...In Tables 1 and 2 are summarized the nature of the sensitizers, electron acceptors and electron donors as well as the catalysts used in the photosystem units 1 and 2 of Fig.1.

TABLE 1

Hydrogen photosystem unit 1[a]

Sensitizer	Electron Acceptor	Electron Donor	Catalyst	$\Phi_{1/2H_2}$
$Ru(bpy)_3^{2+}$	MV^{2+}	EDTA	Pt colloid	0.26
"	"	cysteine	PtO_2	–
Proflavine	"	EDTA	Pt/asbestos	–
acridine yellow	"	"	Pt colloid	0.32
$ZnTMPyP^{4+}$	"	"	"	0.60
"	none	"	"	0.07
$ZnTSPP^{4-}$	MV^{2+}	"	"	0.02

[a] Ref.17

(ii) The other approach uses inorganic semiconductor materials (TiO_2, $SrTiO_3$, CdS,...) for which irradiation with $h\nu > E_{bg}$ leads to formation of e_{cb}^-/h_{vb}^+ pairs that can separately migrate to the semiconductor surface where water red-

TABLE 2

Oxygen photosystem unit 2[a]

Sensitizer	Electron Acceptor	Catalyst	1/4O_2
$Ru(bpy)_3^{2+}$	$Co(NH_3)_5Cl^{2+}$	RuO_2 powder	0.012
"	"	RuO_2 colloid	0.20
"	"	$CoSO_4$	0.08
"	"	RuO_2/zeolite	0.05
"	"	RuO_2/TiO_2	0.12
"	"	MnO_2	-
"	$S_2O_8^{2-}$	RuO_2/TiO_2	0.24
"		IrO_2	0.14
"	Ti^{3+}"	RuO_2 colloid	0.01

[a] From ref.17

uction and oxidation can occur in the presence of some suitable redox catalyst (cf. Fig.2); alternatively, the e^-_{cb}/h^+_{vb} pair can recombine at the semiconductor particle surface. An alternative approach to the photosystem units 1 and 2 of Fig.1 is illustrated in Fig.3 which utilizes a single sensitizer (S), one electron relay species (R) and two appropriate redox catalysts to effect water cleavage (ref.18).

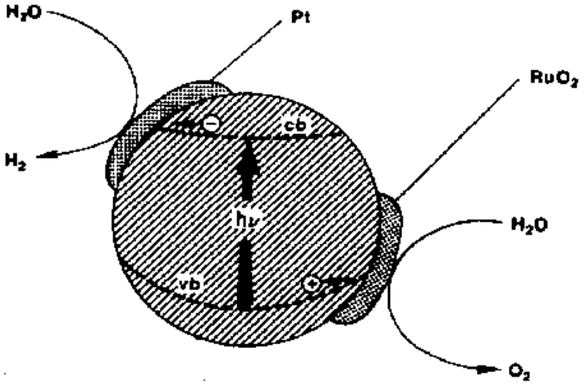


Fig. 2. Schematic illustration of a water cleavage process by a semiconductor particle. From ref.1.

The common denominator in the above approches is that light is first used to generate reduction equivalents (R^- in Fig.3, or A^- in Fig.1, or e^-_{cb} in Fig.2) and oxidation equivalents (D^+ in Fig.1, or h^+_{vb} in Fig.2, or S^+ in Fig.3). This light induced reaction is then coupled to some dark (catalytic) processes producing hydrogen and oxygen from water and regenerating the starting chemicals. Taking the processes in Fig.1, the overall fuel generating steps can be summa-

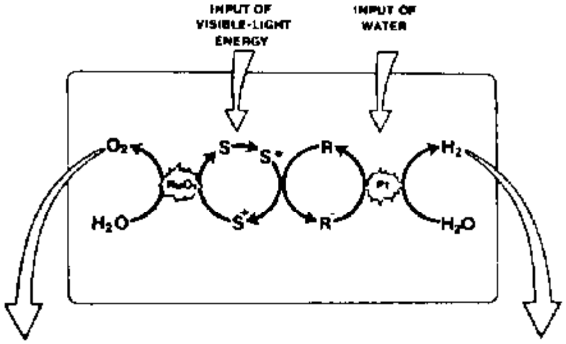


Fig. 3. Schematic illustration of the principle of water cleavage cycles involving sensitizer, electron relay, and two redox catalysts. From ref.1.

rized as in eq.1 and eq.2. Clearly, four oxidation equivalents are needed to produce dioxygen, O_2, and two reduction equivalents are necessary to generate dihydrogen, H_2. Indeed, the formation of oxygen from water by a single electron

$$4D^{+} + 2H_2O \longrightarrow 4D + 4H^{+} + O_2 \qquad (1)$$

$$2A^{-} + 2H_2O \longrightarrow 2A + 2\,OH^{-} + H_2 \qquad (2)$$

oxidant (D^+ or S^+) is a formidable task because it proceeds in four subsequent steps involving high energy intermediates such as OH· radicals, hydrogen peroxide, and superoxide radicals. To avoid formation of these intermediates, electron storage catalysts are required. Some years ago (1978) it was discovered in our laboratory (Lausanne) (ref.19.20) that noble metal oxides such as PtO_2, IrO_2, and RuO_2 in macrodispersed or colloidal form are capable of mediating water oxidation by such reagents as Ce^{4+}, $Ru(bpy)_3{}^{2+}$, and $Fe(bpy)_3{}^{2+}$. Of these three metal oxides, RuO_2 has been the most widely investigated (refs.21-26). However, it should be noted that RuO_2 is not a selective catalyst for oxygen production alone inasmuch as it can also be used for hydrogen generation.

A further comment needs to be made concerning the fuel generating dark reactions (eq.1 and eq.2). They both represent multi-electron transfer reactions connected with high kinetic barrier; in the absence of suitable redox catalysts, reactions 1 and 2 are either not observed at all or are very inefficient. It must also be emphasized here that attempts to design artificial photoconversion devices should not blindly imitate the intricate steps of natural photosynthesis. It would be inconceivable,for example,to accomplish the challenging task of driving endergonic chemical reactions by visible light without suitable engineering on the molecular scale. Simple homogeneous solution systems have little, if any, prospects of being applied in such artificial devices. First, these systems suffer from the fact that the rate of light driven electron transfer processes is limited by the diffusion of the reactants. Secondly, there is no barrier to impair the thermal back electron transfer which degrades light energy into heat. Finally, the solution reaction is almost always a single electron transfer event, while multi-electron redox processes are frequently required in fuel generating reactions such as eqs. 1 and 2. These problems can only be overcome by using microheterogeneous solution systems (as may be the case with semiconductor dispersions).

PHOTOCLEAVAGE OF WATER ON CATALYST-LOADED SEMICONDUCTORS

(a) Metallized Semiconductors

Semiconductor dispersions coated with metals and/or noble metal oxides are finding extensive application in studies of the photoreduction and photooxidation of water. As implied earlier, bandgap excitation of a semiconductor leads to the formation of h^+_{vb} and e^-_{cb} as specifically depicted in Fig.4. In the case of TiO_2, WO_3, and $SrTiO_3$ semiconductors, h^+_{vb} have high oxidizing properties ($E_{vb} \gtrsim 2.0$ eV) that should lead to oxidation of water without the assistance of redox catalysts. The overvoltage requirements to oxidize water as in Fig.4 are not clear at present. Our previous studies (ref.4) have clearly shown the catalytic effects of a noble metal oxide (RuO_2) in this regard. Most naked semiconductors are poor electrocatalysts in the reduction of water by e^-_{cb} and often a metallic deposit such as Pt is necessary to reduce the overvoltage requirements to convert protons to hydrogen. Naked TiO_2 shows no activity towards the photolysis of either liquid- or gas-phase water, but Pt-coated TiO_2 dispersions are active (refs.27-29). Presumably, water photolysis though thermodynamically

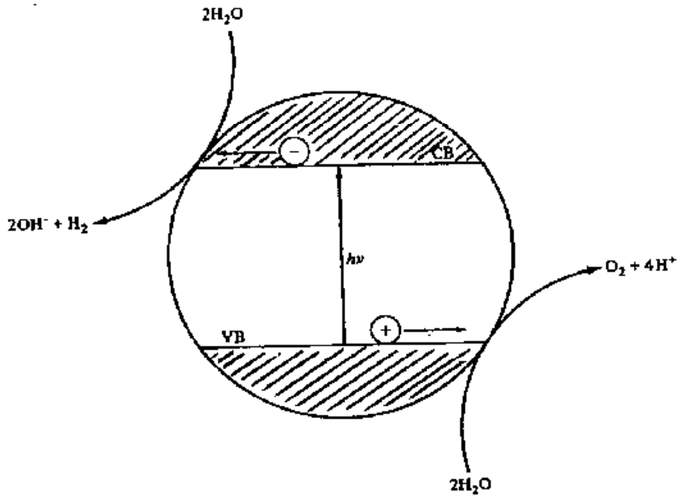


Fig. 4. Principle of water cleavage from naked semiconductors.

favourable does not compete with e^-_{cb}/h^+_{vb} pair recombination in naked semiconductors. Photoadsorption of the photogenerated O_2 on the semiconductor often precludes observation of the concomitant evolution of O_2 with H_2 during photolysis (see below). Sustained generation of H_2 from photolysis of gas-phase water have not been achieved (refs.28,29) because of the thermal back reaction between the photoproducts (eq.3) of the cleavage reaction catalyzed by platinum.

$$H_2 + 1/2\ O_2 \xrightarrow{TiO_2/Pt} H_2O \qquad (3)$$

Early reports of successful uv-induced water cleavage with metallized semiconductor dispersions were those of Bulatov and Khidekel (ref.30) who used platinized TiO_2 in 1N H_2SO_4. Wrighton and co-workers (ref.31) have described simultaneous evolution of H_2 and O_2 from water upon irradiation of platinized single crystals of $SrTiO_3$ and $KTaO_3$. Cleavage of water into H_2 and O_2 has also been reported by us and by others on TiO_2/Pt (refs.28,32-35) and on Rh-coated $SrTiO_3$ (ref.25). Detailed discussions on various features, results, exisiting problems, and possible strategies of the photodecomposition of water with catalyst-loaded semiconductor dispersions have been presented by Pelizzetti and Visca (ref.36), Kiwi (ref.37), Sakata and Kawai (ref.38) and by Kalyanasundaram (ref.14).

Bandgap irradiation of metallized semiconductor dispersions in the presence of "sacrificial" electron donors leads to very efficient production of H_2 from water (ref.14). Platinized CdS and TiO_2 have been the most studied systems with a wide variety of sacrificial substrates such as EDTA, cysteine, TEOA, and alcohols. These substrates scavenge h^+_{vb}, thus reducing e^-_{cb}/h^+_{vb} recombination. The photooxidation of water in aqueous WO_3 dispersions with Fe^{3+} acting as an electron acceptor has been examined by Darwent and Mills (ref.39); the quantum efficiency is low, 0.0031 at 405 nm. Oxygen production is inhibited by Fe^{2+}, O_2, and high concentrations of Fe^{3+}. Deposits of RuO_2 on WO_3 enhance oxygen generation but deposits of Pt, Rh, and Ru only appear to inhibit generation of O_2.

In our laboratory, Pt (ref.40) and Rh or Ru (ref.41) loaded TiO_2 particles have been examined for water cleavage with emphasis being placed on achieving very high dispersions of the metal deposits. $Rh_6(CO)_{16}$ and $Ru_3(CO)_{12}$ clusters were employed in the preparation of the catalysts, and the activity of these in mediating water cleavage through bandgap excitation increases in the order Ru < RuO_2 < Rh $\sim$ Rh_2O_3 $\sim$ Pt.

(b) Bifunctional Catalysts

Studies using noble metal oxide deposits of Ru, Rh, Ni, and Ir on semiconductor powders have shown promising results in the possible catalysis of various oxidation reactions of h^+_{vb}. The oxide layer/semiconductor junction must behave as a Schottky barrier (the height of which determines the oxidizing power of h^+_{vb}) for the metal oxide layer to act as a "hole-transfer catalyst" (ref.14).

If the catalytic redox reaction by these deposits were specific, then a bifunctional redox catalyst would be obtained if both Pt and RuO_2, for example, were deposited on the semiconductor particle surface. Bifunctional catalysis with TiO_2 (amorphous or anatase) and coated with Pt and RuO_2 in the photodecomposition of water has been examined in some detail in our laboratory (refs.4,32,42). Fig.2 schematically depicts the bifunctional redox behaviour of such $TiO_2/RuO_2/$ Pt particles: the e^-_{cb} migrate to Pt (forms a ohmic contact with the semiconductor) sites where H_2 is formed and the h^+_{vb} migrate to RuO_2 which catalyzes evolution of O_2 from water. The initial rate of H_2 evolution is 2-3 mL/h for a 25-mL solution. Similar to the results obtained from experiments with TiO_2/Pt (see eq.3), a photostationary state obtains and if irradiation were stopped, a dark recombination of H_2 and O_2 would occur over the Pt sites. Chromium-doping of TiO_2 particles significantly improves the sensitivity of the photoprocess to visible light (ref.5). Bifunctional Rh/RuO_2 loaded TiO_2 exhibits optimal performance over Rh, Rh/Ru, RuO_2, or Ru doped TiO_2 particles (ref.41); the overall light to chemical energy conversion efficiency was 0.13%. Oxygen was not observed in the gas phase during photolysis in closed systems owing to significant O_2 uptake by the TiO_2 particles. A μ-peroxo bridged titanium species was identified in water cleavage in alkaline solutions where O_2 uptake is surprisingly high. Bifunctional catalysis has been further dealt with in refs.14, 36, and 37.

Redox catalysts can also be supported on "inert" supports. For example, finely dispersed Pt or Rh when deposited on semiconductor particles such as TiO_2 or $SrTiO_3$ ("inert" supports in absence of direct bandgap excitation) exhibit excellent catalytic activity for H_2 formation in the photoredox system comprised of $Ru(bpy)_3^{2+}$, MV^{2+}, and EDTA (ref.43) as well as in the $Ru(bpy)_3^{2+}/Rh(bpy)_3^{3+}/$ TEOA system (ref.44). In these two systems, photogenerated MV^+ and $Rh(bpy)_3^{2+}$ are believed to directly reduce water to H_2 at the catalytic sites afforded by Pt or Rh deposits. (Note that EDTA and TEOA act as the sacrificial donors and MV^{2+} acts as the electron acceptor relay). We have also achieved total water decomposition to H_2 and O_2 with visible light without the sacrificial donor EDTA by utilizing the bifunctional catalyst TiO_2/RuO_2/Pt in the presence of $Ru(bpy)_3^{2+}$ and MV^{2+} (refs.32,43,45). Moreover, employing surfactant derivatives of $Ru(bpy)_3^{2+}$ we have demonstrated that H_2 evolution can be achieved even without methylviologen (refs.32,33).

DYE SENSITIZATION OF SEMICONDUCTORS

The photocleavage of water that uses the systems just considered above can be rationalized by direct charge injection from the excited state of $Ru(bpy)_3^{2+}$ to the conduction band of TiO_2 followed by water reduction at Pt, while water is oxidized by the oxidized dye $Ru(bpy)_3^{3+}$ and catalyzed by RuO_2. Fig.5 depicts the processes and eqs. 4-6 summarize the various steps involved. The sequence

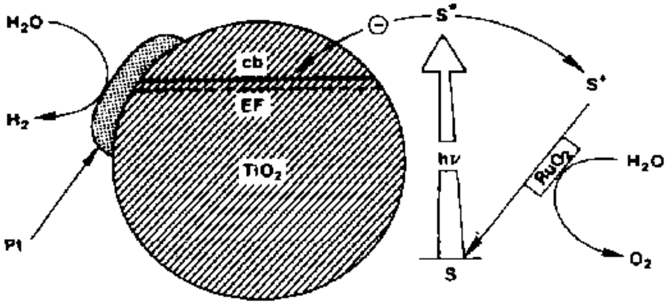


Fig. 5. Schematic illustration of the dye-sensitized photodecomposition of water with a TiO_2 semiconductor dispersion. From ref.1.

$$^{*}Ru(bpy)_3^{2+} + TiO_2 \longrightarrow Ru(bpy)_3^{3+} + e^-_{cb}(TiO_2) \quad (4)$$

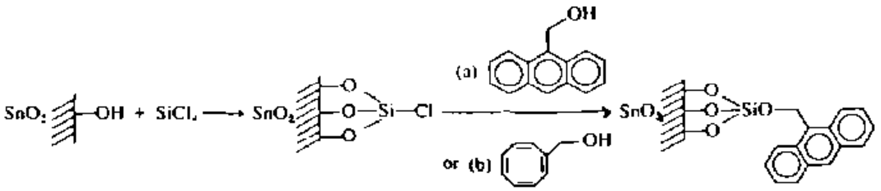
$$4Ru(bpy)_3^{3+} + 2H_2O \longrightarrow 4Ru(bpy)_3^{2+} + 4H^+ + O_2 \quad (5)$$

$$e^-_{cb}(TiO_2) + 2H_2O \longrightarrow H_2 + 2\ OH^- \quad (6)$$

of reactions 4-6 represents "sensitization" of the semiconductor into the visible region by the use of a dye. To make use of a large portion of the solar spectrum (sunlight), extension of the photoresponse of stable wide bandgap materials to visible light has been studied extensively by many workers. This has been made possible through impurity doping with transition metals (refs.46-48), dye sensitization (e.g. organic dyes (ref.49), phthalocyanines (refs.50,51), porphyrins (refs.51-53), and transition metal complexes (refs.33,42,54,55)) and surface complexation (ref.56,57).

Honda and co-workers (refs.58,59) have examined the photochemical behaviour of adsorbed rhodamine B and methylene blue on CdS particles. Surface derivatization via silanation of semiconductor photo-electrodes has received much attention and has been found useful in suppressing corrosion reactions of the electrode, in accelerating the rate of the desired redox process, in measuring rate constants for reactions of surface confined redox reagents, in bringing about changes in the energetics of the semiconductor/electrolyte interface, and in altering the distribution of surface states associated with the semiconductors (ref.60). As well, it has also been demonstrated to be important in improving the visible light response of the semiconductor surface (refs.61-64) and in enhancing the kinetics of the deposition of the n-heptylviologen cation radical HV^+ (ref.61). Furlong and Sasse (refs.65,66) have reported detailed studies of the adsorption and desorption of photosensitizers and redox relay species on metal oxide surfaces; pH, ionic strength, and equilibrium adsorbate concentration are important factors.

Fox and co-workers (ref.67) have discussed four ways of attaching a highly conjugated dye (organic or inorganic) onto a semiconductor surface: (a) silanation with tetrachlorosilane or some related silane compound (refs.60,67-69) appears very common (eq.7); (b) via a linking agent such as cyanuric chloride; (c) via the electropolymerization (ref.68) of functionalized monomers; and (d) via adsorption of dyes (ref.70) or preformed polymers onto the surface. The



(7)

latter method is very much dependent on the nature of the surface charge. Tsubomura and co-workers (ref.70) have suggested a model for the direct adsorption of rose bengal on ZnO, or through Al^{3+} ions (see Fig.6).

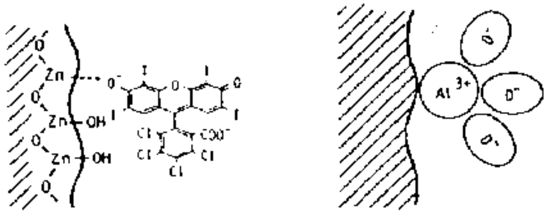


Fig. 6. Models for the adsorption of rose bengal on ZnO. From ref.70.

Of greater importance to us here is the sensitization of metal oxide semiconductors with inorganic dye based systems as with the well known $Ru(bpy)_3^{2+}$ or related derivatives. In 1979, the Oxford-Imperial Energy Group (ref.71,72) reported an interesting method of attaching a derivative of $Ru(bpy)_3^{2+}$, the bis-(2,2'-bipyridyl)(2,2'-bipyridine-4,4'-dicarboxylate)ruthenium(II), $Ru(bpy)_2$-(bpca) on a semiconductor; the mode of attachment, depicted in Fig.7, occurs through two ester linkages using the carboxylate groups to titanium (for n-TiO_2)

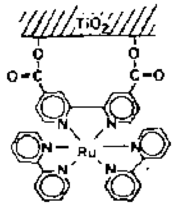


Fig. 7. Chemical attachment of $Ru(bpy)_2$(bpca) to the TiO_2 surface through an ester linkage.

exposed on the particle surface. n-$SrTiO_3$ and n-SnO_2 have likewise been surface modified. A kinetic analysis reveals a surprisingly low quantum efficiency ($\eta_e \sim 0.0025$) for electron injection from the photoexcited dye into the semiconductor and a low rate constant for reoxidation of the dye. Illumination of the sensitized electrode for many hours lead to a deterioration in the performance of the photo-electrode (ref.72).

Attachment of an analogous complex onto the SnO_2 semiconductor surface through silanation with OH groups on the particle surface has been employed by Ghosh and Spiro (ref.69). Though the surface coating was stable to organic solvents as well as to aqueous acids and bases, prolonged irradiation produced extensive hydrolysis of the outer layers of the coating (there were about 1000 layers in the surface coating). Also, only a small fraction of the electroactive molecules (corresponding to a few layers) appeared to participate in the excited state electron transfer process ($\eta_e \sim 0.03$).

CHARGE INJECTION IN DYE SENSITIZATION

Photosensitization of electron transfer across a semiconductor/solution interface can play an important role in light energy conversion as witnessed by the several studies on photoelectrochemical cells (ref.73). The major efforts in this area have been devoted to the improvement of visible light response of wide bandgap semiconductors (e.g. ZnO, TiO_2, $SrTiO_3$,...). As pointed out earlier sensitization can be achieved (other ways have been noted) by adsorption of some suitable dye molecules onto the semiconductor surface which, upon light excitation, injects an electron into the conduction band of the semiconductor. While the overall performance of dye-sensitized semiconductor systems has been reported (ref.74) extensively, details of the electron injection process have been scarce. This is the result of difficulties that are encountered in the application of fast kinetic methods to studies of solid electrodes and powders. However, this is not the case of semiconductor colloidal sols owing to their small dimensions (20-200 Å) that yield transparent solutions, and thus allow for direct application of laser photolysis techniques to unravel interfacial charge transfer processes (refs.4,42,75,76). In this regard, the excellent studies by Kamat and Fox (ref.77) on the erythrosine sensitization of colloidal TiO_2 in CH_3CN, by Kiwi (ref.45) on the electron transfer from the excited $Ru(bpy)_3^{2+}$ to colloidal TiO_2 at elevated temperatures, and the very recent extensive work by Moser and Gratzel (ref.78) on the eosine-Y sensitized electron injection into TiO_2 are worth noting. In the latter study, apart from the initial electron transfer event (refs.78,79) we have also explored the fate of the injected electron with particular emphasis on its back reaction with the eosine cation, EO^+, as well as the competing electron trapping process by noble metals deposited on the surface of the semiconductor colloidal particles.

Coulombic interactions between the TiO_2 surface and eosin dianion play a vital role in the adsorption of EO onto colloidal TiO_2 particles, inasmuch as absorption spectral shifts occur in the pH range (7.5 to 5) where the charge of the colloidal particles changes from negative to positive. Addition of TiO_2 to a EO solution at pH 4 also has a pronounced effect on the luminescence which redshifts upon adsorption of EO to the TiO_2 surface indicating binding to the OH groups at the TiO_2 surface with relatively acidic character. The eosin fluorescence is strongly quenched by TiO_2 particles; the smallest emission intensity was obtained for the highest mean occupancy of TiO_2 particles: 160 molecules of EO per particle (surface eosin concentration $\sim 2 \times 10^{13}$ cm^2; eosin-eosin distance on the surface $\sim$ 22 Å). Thus, efficient dipolar energy transfer is possible. Using a picosecond laser/streak camera system, fluorescence lifetimes (τ_f) in the range of 50-60 psec have been measured for eosin adsorbed on SnO_2 and In_2O_3 surfaces (ref.80). These short lifetimes on the two semiconductors as well as on glass have been interpreted as most likely due to energy transfer followed by trapping at defect sites. Liang et al.,(ref.80) did not consider electron injection for the decrease of τ_f from 1.4 nsec to $\sim$ 60 psec in the adsorbed state.

Addition of TiO_2 to a solution of eosin leads to dramatic changes in the photoredox behaviour of EO. The formation of EO^+ by photoexcitation of the ground state $EO(S_o)$ in colloidal TiO_2 solution has been confirmed by Rossetti and Brus (ref.81) by time-resolved laser Raman spectroscopy. Differences in the Raman spectrum of EO^+ in water and aqueous TiO_2 solutions were attributed to protonation of EO^+ by surface hydroxyl groups. The quantum yield of formation of EO^+, Φ_{EO^+}, increases from 0.27 to 0.35 upon increasing TiO_2 from 0.1 to 0.5 g/L and reaches a plateau at 0.38 at 3 g/L TiO_2 (ref.80). In pure water, the photogeneration of EO^+ is a relatively slow ($4.2 \times 10^4 s^{-1}$) and inefficient process (Φ_{EO^+} $\sim$ 0) arising from dismutation of the triplet states (eq.8). By contrast, in the

$$2\ EO(T_1) \longrightarrow EO^+ + EO^- \qquad (1.3 \times 10^9 M^{-1} s^{-1})\,(ref.82) \tag{8}$$

presence of TiO_2, EO^+ is generated efficiently ($\Phi_{EO^+} \sim 0.4$, pH 3) and at high rate ($k_{inj} \sim 8.5 \times 10^8 s^{-1}$), its formation being completed in < 10 nsec (ref. 78). The mechanism of EO^+ formation is different from that in water and involves electron injection from the lowest singlet excited state of EO, $EO(S_1)$, to the conduction band of colloidal TiO_2 particles (eq.9). It should be noted that

$$EO(S_1) + TiO_2 \xrightarrow{k_{inj}} EO^+ + e^-_{cb}(TiO_2) \tag{9}$$

charge injection is only observed at pH $\lesssim$ 6, under conditions where eosin is associated with TiO_2 particles; close proximity of reactants is required for electron transfer to compete with the other channels of $EO(S_1)$ deactivation, viz., intersystem crossing (eq.10) and radiative and nonradiative decay (eqs.

11a and 11b, respectively). While charge injection from $EO(T_1)$ is thermodynamically possible, it does not occur; τ_{T_1} is the same in water as it is in TiO_2 aqueous solutions (eq.12).

$$EO(S_1) \xrightarrow{k_{isc}} EO(T_1) \qquad (10)$$

$$EO(S_1) \xrightarrow{k_r} EO(S_o) + h\nu' \qquad (11a)$$

$$ \xrightarrow{k_{nr}} EO(S_o) \qquad (11b)$$

$$EO(T_1) + TiO_2 \nrightarrow EO^+ + e^-_{cb}(TiO_2) \qquad (12)$$

Back electron transfer between $e^-_{cb}(TiO_2)$ and EO^+ occurs <u>via</u> a rapid intraparticle reaction between $EO^+ \ldots\ldots e^-_{cb}(TiO_2)$ pairs associated with the same TiO_2 host aggregate and <u>via</u> a slower process involving bulk diffusion (ref.78). The rate constant for intraparticle recombination is $2 \times 10^5 s^{-1}$, about 4000 times slower than that for electron injection. This enables light induced charge separation to be sustained on a colloidal TiO_2 particle for several μsecs, sufficient to trap the electron by a noble metal deposit on TiO_2.

The intimate processes of dye sensitization of a TiO_2 semiconductor particle and photosensitization of electron injection in noble metal loaded TiO_2 particles are illustrated in Fig.8 and Fig.9, respectively (ref.78). In the former process, light excitation of EO to S_1 leads to injection of electrons to the conduction band of TiO_2 leaving a EO^+ at the surface. In the second process, the role of the noble metal catalyst is to trap the photoinjected electron and to intercept the rapid back reaction between $EO^+ \ldots\ldots e^-_{cb}(TiO_2)$ pairs. This allows a larger fraction of all the EO^+ formed during the laser pulse to escape to the bulk of the solution with the subsequent back reaction being relatively slow.

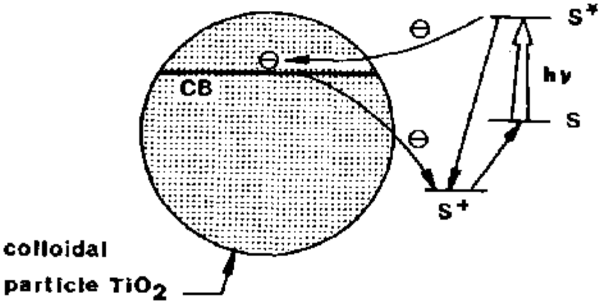


Fig. 8. Schematic illustration of electron injection and intraparticle back electron transfer in the photosensitization of colloidal semiconductor particles, without redox catalyst. From ref.78.

The effect of high pressure (to 10 kbar) on the dye-sensitized photocurrent

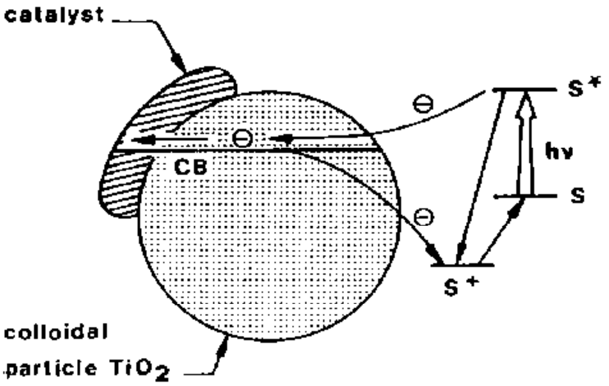


Fig. 9. Schematic illustration of electron injection and intraparticle back electron transfer in the photosensitization of colloidal semiconductor particles, in the presence of a redox catalyst. From ref.78.

spectrum of an n-type TiO_2 photo-anode has also been investigated using the TiO_2 bound ruthenium-bipyridine complex depicted in Fig.7 (ref.83). The complex Ru-$(bpy)_2(bpca)$ is bound to the TiO_2 particle surface (ref.71) *via* a π-bond between a 3*d* titanium orbital and a π* of the $-COO^-$ group (ref.72). With $Ru(bpy)_3^{2+}$ as the sensitizer, light absorption leads first to formation of the lowest'singlet' of *d*π-π* character which relaxes to the MLCT 'triplet' manifold of states from which ensues electron injection into the conduction band of the semiconductor (eq.13). Alternatively, as suggested by Goodenough and co-workers (refs.71,72, 84), the observed lack of structure in the dye sensitized absorption spectrum is

$$S \xrightarrow{h\nu} S^* \xrightarrow{TiO_2} e^-_{cb}(TiO_2) \quad + \quad S^+ \tag{13}$$

due to direct excitation of the electron from the ground state of the dye to the conduction band of TiO_2 (eq.14). The high pressure studies (ref.83) appear to

$$S \xrightarrow{h\nu,\ TiO_2} e^-_{cb}(TiO_2) \quad + \quad S^+ \tag{14}$$

indicate otherwise, however. On the basis of shifts of the absorption-peak locations in the absorption spectrum, the dye sensitization process involves, initially, electron excitation to a dye excited state followed by electron injection into the semiconductor conduction band, rather than initial electron excitation directly into the conduction band.

WATER CLEAVAGE VIA DYE SENSITIZATION

As noted earlier, surface modification of large bandgap semiconductors (TiO_2, SnO_2,...) by adsorbed or covalently linked photo-active dyes is a matter of great interest in view of potential applications to solar energy conversion.

Clark and Sutin (ref.55) were the first to achieve spectral sensitization of TiO_2 with $Ru(bpy)_3^{2+}$ in aqueous solution. One major drawback of this sort of spectral sensitization is that the light absorbed by the dye is inefficiently used. While all the dye molecules will absorb the incoming light, only those excited dye molecules in close enough proximity to the semiconductor particle surface can efficiently inject an electron into the TiO_2 conduction band. One means of overcoming this difficulty is direct attachment of the dye molecule onto the semiconductor surface.

Our laboratory has long been involved in improving the various techniques of dye sensitization of semiconductor colloidal sols and dispersions in an effort of achieving the photocleavage of water (and other photoprocesses) using visible light sources. In this regard, we present below three examples from our recent work: (a) surface modification of anatase TiO_2 by the dye 8-hydroxyquinoline, HOQ, and the ability of such modified TiO_2 powders to generate H_2 in a sacrificial water reduction system using visible light (ref.56); (b) sensitization of Pt-loaded TiO_2 with $M(OQ)_n$ complexes (M = Pt(II), Ir(III), Pb(II), and Bi(III)) which show suitable absorption in the visible spectral region and suitable excited state properties (E_{T_1} = 2 eV and $\tau_{T_1} \sim 2$ µsec) (ref.85); and (c) a recent integrated system for water cleavage by visible light employing sensitized TiO_2 particles which have been surface-derivatized with ruthenium(II) complexes (ref. 86).

(a) Surface Complexation of TiO_2 with 8-Hydroxyquinoline

When powdered TiO_2 is introduced in an aqueous solution of HOQ, a bright yellow orange color develops owing to the formation of surface Ti(IV)-OQ complexes, most likely the result of 'esterification' of surface hydroxyl groups with concomitant loss of water. Emission normally detectable for HOQ and closed shell $M(OQ)_n$ complexes (refs.87,88) was not observed from solid samples of HOQ-modified TiO_2 powder or -modified TiO_2 colloidal sols at room temperature. Even nsec flash photolysis studies of HOQ-modified TiO_2 colloid showed neither emission nor transients. Hence, the excited state lifetime of the surface Ti(IV)-OQ complex is less than the 11-25 nsec typically observed for emissive $M(OQ)_n$ complexes in DMF (ref.88). The HOQ-modified TiO_2 powder proved to be a good photosensitizing agent in the following sacrificial water reduction system comprising in 5-mL samples of 10^{-3}M HOQ equilibrated with 5 mg TiO_2 powder, 2 x 10^{-2}M EDTA (the sacrificial electron donor), and 10 mg/L of Pt(0) sol. For comparison purposes, an analogous sample was studied in which 10^{-4}M of $Ru(bpy)_2(4,4'\text{-tridecyl-}2,2'\text{-bpy})^{2+}$ surfactant was physisorbed onto TiO_2 and HOQ was omitted. Noteworthy is the fact that this surfactant absorbed 2-6 times more light depending on the surface area of the TiO_2 powder. Table 3 summarizes the results of the study (ref.56), which shows that HOQ-modified TiO_2 samples compare favourably with

TABLE 3

Rates of H_2 formation (STP) at $\lambda \gtrsim 435$ nm[a] in different anatase TiO_2 powders containing Pt in sacrificial hydrogen generating systems (ref.56)

HOQ on TiO_2	$r(H_2)$, µL/h	Uptake of HOQ, µequiv/g
Degussa P-25	300 - 420	300
Bayer Sol	800 - 1220	800
TiO_2(U)	750 - 1000	1000
TiO_2(U)/0.2%RuO_2[b]	310 - 350	-
$Ru(bpy)_2(4,4'\text{-tridecyl-}2,2'\text{-bpy})^{2+}$		
Degussa P-25	700 - 840	
Bayer Sol	700 - 800	
TiO_2(U)/0.2%RuO_2[b]	800 - 1080	

[a] 100 - 200 mW/cm^2
[b] No Pt

the surfactant ruthenium-bipyridine modified samples, despite the lower light absorption by the former. Φ_{H_2} were 0.0034 at 458 nm and 0.0014 at 515 nm for the HOQ-modified TiO_2(U) sample. Also, initial $r(H_2)$ were sustained for > 15 hours (turnover > 40 with respect to HOQ) in samples where EDTA was replenished before the concentration dropped below 15 mM and where H_2 was regularly removed through argon purging. Interestingly, HOQ also forms a bright yellow complex with neutral Al_2O_3 chromatographic powder, but the sample was inactive in producing H_2. This establishes the fact that semiconductor properties of TiO_2 particles are involved in the function of the HOQ-modified TiO_2.

The mechanism for H_2 production is one in which light excitation of the surface Ti(IV)-OQ species is followed by charge injection into the TiO_2 particle bulk. Subsequently, EDTA reduces the oxidized surface before decomposition occurs and the e^-_{cb} is channeled to the Pt (or some other suitable catalyst) catalyst island on the surface where reduction of H^+ occurs.

(b) Sensitization of TiO_2 with 8-Quinolinol Complexes

8-Quinolinol metal complexes (M = Pt(II), Ir(III), Pb(II), or Bi(III)) are powerful reductants in the excited states; $E({}^*M(OQ)_n{}^+/M(OQ)_n) \sim -0.83$ to -1.27 V (vs. SCE) (ref.89). When deposited onto Pt-loaded TiO_2, the compounds sensitize H_2 production from water *via* electron injection from the ligand centred excited states of these $M(OQ)_n$ complexes to the conduction band of TiO_2 (driving force $\sim$ −270 mV for the charge injection process from $Pt(OQ)_2$; the activation barrier to charge injection was estimated to be $\sim$ 16 kcal mol^{-1} (ref.85)); $Pb(OQ)_2$ and $Pt(OQ)_2$ were the most efficient.

A typical sample consisted of 500 mg TiO_2(U) (anatase, Montedison) loaded with 0.4% Nb_2O_5, 0.2% RuO_2, and 4% Pt placed in a 2×10^{-4}M solution of $Pt(OQ)_2$ dye. In the presence of 0.1M EDTA (pH 4.7), argon purging and irradiating at $\lambda > 420$ nm gave $r(H_2) = 0.8$ mL/h (30°C), 6 mL/h (50°C), and 20 mL/h (75°C). In the absence of dye, $r(H_2) = 0$. By comparison, substitution of $Pt(OQ)_2$ by $Ru(bpy)_3^{2+}$ gave $r(H_2) = 0.085$ mL/h at 30°C. Turnover numbers of ∿ 200 with respect to $Pt(OQ)_2$ obtained in a long term experiment at 30°C.

(c) Water Cleavage *via* Surface Derivatization of TiO_2 with Ruthenium(II) Complexes

A drawback of the HOQ-modified TiO_2 and the $M(OQ)_n$-sensitized TiO_2 systems, making necessary the use of sacrificial electron donors, is the inability of the oxidized sensitizer to produce oxygen from water. Recently, we (ref.86) discovered a new method for derivatizing the TiO_2 particle surface by a more suitable chromophore which should prove most useful in the design of catalytic systems affording water cleavage by visible light and this *without the assistance from sacrificial electron donors or acceptors*.

A TiO_2 dispersion loaded with Pt and RuO_2 was surface derivatized by photolyzing ($\lambda > 320$ nm) the aqueous mixture in the presence of RuL_3^{2+} (L = 4,4'-diisopropyldicarboxylato-2,2'-bipyridine) under reflux conditions (100°C) to give a pink coloured material after centrifugation or filtration. The reflectance spectrum (Fig.10) of this material and the absorption spectrum of the filtrate show that the pink material is the surface derivatized TiO_2. The dye RuL_2^{2+} is chemically linked to the surface titaniums by two Ru-O-Ti bonds. The

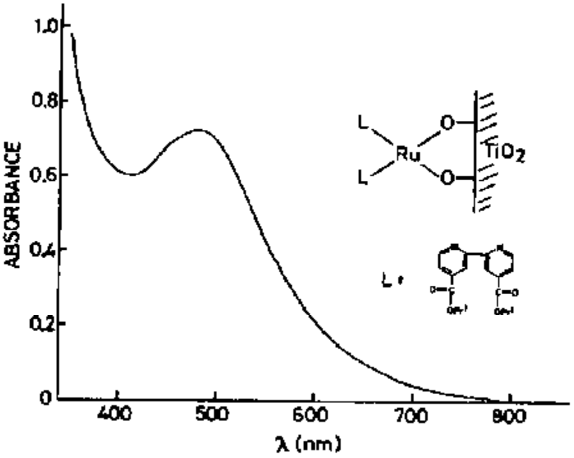


Fig. 10. Reflectance spectrum of RuL_2^{2+}-derivatized TiO_2 particles loaded simultaneously with 0.5% Pt and RuO_2. The absorption maximum in the visible is at 480 nm. From ref.86.

reflectance spectrum of Fig.10 is particularly significant in sensitization of large bandgap semiconductors such as TiO_2 (E_{bg} ∿ 3 eV). Apart from the bandgap transition of TiO_2 below 400 nm, a pronounced absorption in the visible with maximum at 480 nm and a tail extending beyond 600 nm are also observed. The features in the visible are practically identical to those observed for cis-Ru-$(bpy)_2(H_2O)_2^{2+}$ adsorbed onto hectorite (ref.90). Contrary to the behaviour of this hectorite species, RuL_2-derivatized TiO_2 particles proved to be excellent catalysts for H_2 generation from water by visible light, both in the presence and absence of a sacrificial electron donor. For example, irradiation of a 5-mL solution, containing 0.01M TEOA (pH 10) and 10 mg of RuL_2-derivatized $TiO_2/RuO_2/Pt$ particles, with visible light ($\lambda > 405$ nm; 200 mW/cm^2) produced H_2 at a rate of 0.93 mL/h. Even with $\lambda > 590$ nm illumination, H_2 was produced at a rate of 50 μL/h.

Most important is that RuL_2-derivatized TiO_2 particles also produce hydrogen from water by visible light and this in the absence of sacrificial organic donors! In a typical experiment consisting of irradiating at 100°C, 50 mg of the catalyst in 40 mL of H_2O (pH 2, HCl) with light at $\lambda > 420$ nm resulted in the formation of H_2 at an initial rate of 30 μL/h. Typically, 400 μL of H_2 were produced after 20 hours of irradiation. Treatment of the catalyst under various conditions resulted in no loss of its catalytic activity. A turnover number of ∿ 80 was found for the total H_2 produced with respect to RuL_2^{2+}. What is also significant is that concomitant with the formation of H_2, O_2 is also produced in stoichiometric amounts, though oxygen appearance in the gas phase was not consistently observed, especially at lower than boiling temperature where only H_2 was found. The inconsistency in finding O_2 is the result of O_2 uptake by TiO_2 particles. Gratzel and co-workers (ref.91) have presented convincing evidence for the occurrence of such a process in titania-based water cleavage systems.

Introducing the semiconductor surface directly onto the coordination sphere of the transition metal complex allowing the charge injection to occur via an inner sphere mechanism has rendered sensitization of TiO_2 particularly effective.

ACKNOWLEDGEMENTS

We are particularly grateful to our various collaborators without whose efforts much of this work would not have been accomplished. Our work has benefitted from financial support from the Swiss National Fund for Scientific Research (MG) from the "Progetto Finalizzato Chimica Fine e Secondaria", CNR (Rome, EP) , and from the Natural Sciences and Engineering Research Council of Canada (NS). Their continued sponsorship is gratefully appreciated.

REFERENCES

1 See for example, M. Gratzel (Ed.), "Energy Resources through Photochemistry and Catalysis", Academic Press, New York, 1983.
2 N. Sutin and C. Creutz, Pure & Appl.Chem., 52 (1980) 2717.
3 D.G. Whitten, Acc.Chem.Res., 13 (1980) 83.
4 M. Gratzel, Acc.Chem.Res., 14 (1981) 376.
5 J. Kiwi, K. Kalyanasundaram, and M. Gratzel, Struct.& Bonding, 49 (1982) 37.
6 V. Balzani, F. Bolletta, M.T. Gandolfi, and M. Maestri, Topics Curr.Chem., 75 (1978) 1.
7 J.R. Bolton (Ed.), "Solar Power and Fuels", Academic Press, New York, 1977.
8 J.S.Connolly (Ed.), "Photochemical Conversion and Storage of Solar Energy", Academic Press, New York, 1981.
9 K. Kalyanasundaram, Coord.Chem.Rev., 46 (1982) 159.
10 G. Porter and M.D. Archer, Interdisc.Sci.Rev., 1 (1976) 119.
11 K.I. Zamaraev and V.N. Parmon, Catal.Rev., 22 (1980) 261.
12 K. Kalyanasundaram, Chem.Soc.Rev., 7 (1978) 453.
13 N.J. Turro, A.M. Braun, and M. Gratzel, Angew.Chem.Int.Ed.Engl., 19 (1980) 675.
14 K. Kalyanasundaram, in ref. 1, chapter 7, p 217.
15 M. Gratzel, Pure & Appl.Chem., 54 (1982) 2369.
16 N. Serpone, E. Borgarello, and M. Gratzel, J.Chem.Soc.Chem.Commun., (1984) 342.
17 A. Harriman, Platinum Metal Rev., 27 (1983) 102.
18 M. Gratzel, in ref. 1, chapter 3, p 71.
19 M. Gratzel in "Dahlem Conferences on Light Induced Charge Separation", H. Gerischer and J.J. Katz (Eds.), Verlag Chemie, Weinheim, 1978, p 299.
20 J. Kiwi and M. Gratzel, Angew.Chem.Int.Ed.Engl., 17 (1978) 624.
21 K. Kalyanasundaram, O. Micic, E. Pramauro, and M. Gratzel, Helv.Chim.Acta, 62 (1979) 2432.
22 J. Kiwi and M. Gratzel, Chimia, 33 (1979) 284.
23 J. Kiwi and M. Gratzel, Angew.Chem.Int.Ed.Engl., 18 (1979) 624.
24 J.M. Lehn, J.P. Sauvage, and R. Ziessel, Nouv.J.Chim., 3 (1979) 423.
25 J.M. Lehn, J.P. Sauvage, and R. Ziessel, Nouv.J.Chim., 4 (1980) 623.
26 M. Neumann-Spallart, K. Kalyanasundaram, C.K. Gratzel, and M. Gratzel, Helv. Chim.Acta, 63 (1980) 1111.
27 T. Kawai and T. Sakata, Chem.Lett., (1981) 81.
28 S. Sato and J.M. White, Chem.Phys.Lett., 72 (1980) 83.
29 S. Sato and J.M. White, J.Phys.Chem., 85 (1981) 336.
30 A.V. Bulatov and M.L. Khidekel, Izv.Akad.Nauk.SSR Ser.Khim., (1976) 1902.
31 M.S. Wrighton, P.T. Wolczanski, and A.B. Ellis, J.Solid State Chem., 22 (1977) 17.
32 E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca, and M. Gratzel, J.Am.Chem. Soc., 103 (1981) 6324.
33 E. Borgarello, J. Kiwi, M. Visca, and M. Gratzel, Nature (London), 289 (1981) 158.
34 S. Sato and J.M. White, J.Catal., 69 (1981) 128.
35 S. Sato and J.M. White, J.Phys.Chem., 85 (1981) 592.
36 E. Pelizzetti and M. Visca, in ref. 1, chapter 8, p 261.
37 J. Kiwi, in ref. 1, chapter 9, p 297.
38 T. Sakata and T. Kawai, in ref. 1, chapter 10, p 331.
39 J.R. Darwent and A. Mills, J.Chem.Soc.Faraday Trans.II, 78 (1982) 359.
40 J. Kiwi and M. Gratzel, J.Phys.Chem., 88 (1984) 1302; and refs. therein.
41 E. Yesodharan and M. Gratzel, Helv.Chim.Acta, 66 (1983) 2145.
42 D. Duonghong, E. Borgarello, and M. Gratzel, J.Am.Chem.Soc., 103 (1981) 4685.
43 J. Kiwi, E. Borgarello, E. Pelizzetti, M. Visca, and M. Gratzel, Angew.Chem. Int.Ed.Engl., 19 (1980) 646.
44 J.M. Lehn, J.P. Sauvage, and R. Ziessel, Nouv.J.Chim., 5 (1981) 291.
45 J. Kiwi, Chem.Phys.Lett., 83 (1981) 594.
46 H.P. Maruska and A.K.Ghosh, Solar Energy Mat., 1 (1979) 237.

47 G. Campet, M.P. Dare-Edwards, A. Hammet, and J.B. Goodenough, Nouv.J.Chim., 4 (1980) 501.

48 E. Borgarello, J. Kiwi, M. Gratzel, E. Pelizzetti, and M. Visca, J.Am.Chem. Soc., 104 (1982) 2996.

49 H. Gerischer and F. Willing, Topics Curr.Chem., 61 (1976) 31.

50 A. Giraudeau, F-R.F. Fan, and A.J. Bard, J.Am.Chem.Soc., 102 (1980) 5137.

51 J.R. Darwent, P. Douglas, A. Harriman, G. Porter, and M.C. Richoux, Coord. Chem.Rev., 44 (1982) 83.

52 P.A. Breddels and G. Blase, Chem.Phys.Lett., 79 (1981) 209.

53 K. Kalyanasundaram, E. Borgarello, Y. Okuno, and M. Gratzel, Helv.Chim.Acta, 64 (1981) 1937.

54 R. Memming, Electrochim.Acta, 25 (1980) 77.

55 W.D. Clark and N. Sutin, J.Am.Chem.Soc., 99 (1977) 4676.

56 V.H. Houlding and M. Gratzel, J.Am.Chem.Soc., 105 (1983) 5695.

57 K.H. Hauffe, Photographic Sci and Engineering, 20 (1976) 124.

58 T. Takizawa, T. Watanabe, and K. Honda, J.Phys.Chem., 82 (1978) 1391.

59 T. Watanabe, T. Takizawa, and K. Honda, J.Phys.Chem., 81 (1977) 1845.

60 M.S. Wrighton, in "Chemically Modified Surfaces in Catalysis and Electrocatalysis", J.S. Miller (Ed.), A.C.S.Symp.Ser., 192 (1982) 99.

61 N.R. Armstrong, T. Mezza, C.L. Linkous, B. Thacker, T. Kloffa, and R. Cieslinski, in ref. 60, p 205.

62 D. Duonghong, N. Serpone, and M. Gratzel, Helv.Chim.Acta, 67 (1984) 1012.

63 H.D. Abruna, J.M. Calvert, P. Denisevich, C.D. Ellis, T.J. Meyer, W.R. Murphy Jr., R.R. Murray, B.P. Sullivan, and J.L. Walsh, in ref. 60, p 133.

64 H.D. Abruna, T.J. Meyer, and R.R. Murray, Inorg.Chem., 18 (1979) 3233.

65 D.N. Furlong and W.H.F. Sasse, Colloids & Surfaces, 7 (1983) 29.

66 D.N. Furlong and W.H.F. Sasse, Colloids & Surfaces, 7 (1983) 115.

67 M.A. Fox, J.R. Hohman, and P.V. Kamat, Can.J.Chem., 61 (1983) 888.

68 P.K. Ghosh and T.G. Spiro, J.Electrochem.Soc., 128 (1981) 1281.

69 P.K. Ghosh and T.G. Spiro, J.Am.Chem.Soc., 102 (1980) 5543.

70 M. Matsumura, S. Matsudaira, H. Tsubomura, M. Takata, and H. Yanagida, Ind. Eng.Chem.Prod.Res.Dev., 19 (1980) 415.

71 S. Anderson, E.C. Constable, M.P. Dare-Edwards, J.B. Goodenough, A. Hammet, K.R. Seddon, and R.D. Wright, Nature (London), 280 (1979) 571.

72 M.P. Dare-Edwards, J.B. Goodenough, A. Hammet, K.R. Seddon, and R.D. Wright, Faraday Disc., Chem.Soc., 70 (1980) 285.

73 H. Gerischer, M.E. Michel-Beyerle F. Rebentrost, and H. Tributsch, Electrochim.Acta, 13 (1968) 150.
H. Tributsch and H. Gerischer, Ber.Bunsenges.Phys.Chem., 73 (1969) 251.
H. Gerischer and F. Willig, Topics Curr.Chem., 61 (1976) 31.
M. Spitler and M. Calvin, J.Chem.Phys., 67 (1977) 5193.
T. Takizawa, T. Watanabe, and K. Honda, J.Phys.Chem., 84 (1980) 51.
T. Iwasaki, S. Oda, T. Sawada, and K. Honda, Photographic Sci.Eng., 25 (1981) 6.
C.D. Jaeger, F-R.F. Fan, and A.J. Bard, J.Am.Chem.Soc., 102 (1980) 2592.
T. Watanabe, A. Fujishima, and K. Honda, in ref. 1, chapter 11, p 359.

74 R. Memming, Philips Tech.Rev., 38 (1978) 160.
K. Rajeshwar, P. Singh, and J. DuBow, Electrochim.Acta, 23 (1978) 111.
H. Gerischer, Ber.Bunsenges.Phys.Chem., 77 (1973) 771.

75 D. Duonghong, J.J. Ramsden, and M. Gratzel, J.Am.Chem.Soc., 104 (1982) 2977.

76 N. Serpone, D.K. Sharma, M.A. Jamieson, M. Gratzel, and J.J. Ramsden, submitted.

77 P.V. Kamat and M.A. Fox, Chem.Phys.Lett., 102 (1983) 379.

78 J. Moser and M. Gratzel, J.Am.Chem.Soc., 106 (1984) 0000.

79 J. Moser, M. Gratzel, D.K. Sharma, and N. Serpone, work in progress.

80 Y. Liang, A.M. Ponte Gonclaves, and D.K. Negen, J.Phys.Chem., 87 (1983) 1.

81 R. Rossetti and L.E. Brus, J.Am.Chem.Soc., 104 (1982) 7321.

82 V. Kasche and L. Lindquist, Photochem.Photobiol., 4 (1965) 923.

83 D.A. Gulino and H.G. Drickamer, J.Phys.Chem., 88 (1984) 1173.

84 J.B. Goodenough, A. Hammet, M.P. Dare-Edwards, G. Campet, and R.D. Wright, Surf.Sci., 101 (1980) 531.

85 E. Borgarello, E. Pelizzetti, R. Ballardini, and F. Scandola, Nouv.J.Chim., (1984) in press.

86 D. Duonghong, N. Serpone, and M. Gratzel, Helv.Chim.Acta, 67 (1984) 1012.

87 F.E. Lytle, D.R. Storey, and M.E. Juricich, Spectrochim. Acta, 29A (1973) 1357.

88 F. Scandola, R. Ballardini, and M.T. Indelli, in "Photochemical, Photoelectrochemical, and Photobiological Processes", D.O. Hall and W. Palz (Eds.), Reidel, Dorecht, 1982, p 66.

89 M.T. Indelli, R. Ballardini, C. Bignozzi, and F. Scandola, submitted.

90 H. Nijs, M. Cruz, J. Frippiat, and H. Van Damme, J.Chem.Soc.Chem.Commun., (1981) 1026; idem., Nouv.J.Chim., 6 (1982) 551.

91 E. Yesodharan, S. Yesodharan, and M. Gratzel, Solar Energy Mat., (1984), in press.