

Photocatalytic reduction of dioxygen by colloidal semiconductors and macrocyclic cobalt(III) complexes in Nafion and cellulose matrices

J. Premkumar, R. Ramaraj *

School of Chemistry, Madurai Kamaraj University, Madurai-625 021, India

Received 15 February 1997; accepted 28 July 1997

Abstract

The colloidal semiconductors TiO_2 and CdS are used for the photosensitized reduction of MV^{2+} and Co(III) complexes. Photoinduced electron transfer reactions are carried out using the semiconductors in colloidal state, adsorbed and intercalated into Nafion and cellulose matrices. The back electron transfer reaction between $h_{\nu}^+(\text{TiO}_2$ or CdS) and MV^{+} or Co(II) complex is prevented by the reaction of the hole with an electron donor triethanolamine (TEA). Hydrogen peroxide (H_2O_2) is produced by the reaction of the photoproduced MV^{+} or Co(II) complex with dissolved molecular oxygen (O_2). The photosensitized reaction mechanisms of the formation of MV^{+} and Co(II) complex and the photocatalytic reduction of O_2 to yield H_2O_2 in the semiconductor modified systems are explained. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Research activities in the field of photochemical conversion and the storage of solar energy have experienced tremendous growth in recent years as a result of interdisciplinary efforts [1]. In a homogeneous solution, the high energy photoredox products (S^\pm and R^\mp) recombine in dark to produce the starting materials (Eq. (1)) and the efficiency of the energy conversion system is



(where S is the sensitizer and R is the electron relay) found to be very low [1–3]. Unless this

problem is overcome, the energy conversion will not become efficient. One approach to solving this problem is the utilization of a microheterogeneous reaction medium such as micelles, vesicles, monolayer and polyelectrolytes [1–6]. Another promising direction is the use of a macroheterogeneous reaction system such as a solid–solution interface, e.g. the use of chemically modified electrodes or heterogeneous catalyst systems [1,5,7,8].

Light driven redox reactions at semiconductor colloids coupled with redox catalysts continue to be important as a possible route for the generation of high energy chemicals by visible light [9,10]. Colloidal semiconductors combine a number of desirable properties such as high absorption cross-sections, fast carrier diffusion to the interface and suitable positioning of the

* Corresponding author. Tel.: +91-452-85246; fax: +91-452-859139.

valance and conduction bands. The added possibility of modifying the surface of the semiconductor particles by chemisorption, chemical derivatization or catalyst deposition that assist in the light-induced charge separation and subsequent fuel generating dark reactions are particularly attractive [1]. Moreover, it is important to note that the photoredox reaction that occurs at the semiconductor/solution interface (between the excited semiconductor particle and the redox species in solution) is, in general, irreversible [10].

In photosynthesis, antenna chlorophyll molecules perform the task of harvesting light while light-induced charge separation is achieved through vectorial electron transfer across the photosynthetic membrane [11,12]. Recent preliminary studies from our laboratory [13] have revealed that an efficient vectorial displacement of charge can be achieved by coupling a semiconductor photocatalyst and an electron relay in a membrane system.

Titanium dioxide (TiO_2) and cadmium sulfide (CdS) have received much attention in the photosplitting of water and photooxidation of organic compounds [1,7,9]. The utilization of integrated chemical systems to carry out a particular chemical process is of current interest. To carry out photocatalytic and photosynthetic processes, TiO_2 and CdS as colloids and incorporated into a polymer membrane have been used [13–22]. In this paper, we report a photocatalytic system based on TiO_2 and CdS incorporated Nafion (represented as Nf) and cellulose (represented as CL) membranes. For the multi-step one-electron photoreduction of O_2 to H_2O_2 , methyl viologen and macrocyclic cobalt(III) complexes were used as electron relays and as oxygen reduction catalysts.

2. Experimental section

Cadmium chloride, sodium sulfide, triethanolamine (s.d. fine chemicals) and perchloric acid (Merck) were analytical reagents and

used as received. TiCl_4 (Merck) and TiO_2 (5 μm , 99.9%, anatase form from Wako Pure Chemicals Industries, Japan) were used as supplied. Methyl viologen (MV^{2+}) (1,1'-dimethyl-4,4'-bipyridiniumdichloride) (Aldrich) was recrystallized from methanol. Macrocyclic cobalt(III) complex ($[\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2]^{3+}$, cyclam = 1,4,8,11-tetraazacyclotetradecane (represented as Co(III)) was prepared according to reported procedures [23,24]. CdS was prepared by mixing equimolar concentrations of CdCl_2 and Na_2S in distilled water [17]. The deposited CdS particle was used to prepare colloidal CdS. Cellulose paper (Toyo Rosho Chemical Company, Japan), Nafion membrane (Aldrich, type 125, 1100 equiv. wt., 0.13 mm thickness) of 1 cm^2 area were used. The Nafion membrane was pretreated prior to use by boiling in concentrated HNO_3 for about 10 min and the membrane became clear and transparent after washing with distilled water [25].

The incorporation of Ti(IV) peroxo complex (TiO_2) in Nf membrane was carried out using the reported procedure [25]. The Nf membrane was soaked in deionized distilled water. Then it was immersed into a deoxygenated 0.1 M TiCl_4 in methanol for overnight. The light purple Ti(IV) incorporated Nf membrane was then washed thoroughly with deoxygenated methanol. When the Ti(IV)–Nf membrane was immersed in an acidic solution (pH ca. 0.5) containing excess H_2O_2 , it yielded the orange peroxo Ti(IV) complex (represented as $\text{Nf}/(\text{TiO}_2)_{\text{IC}}$). Incorporation of CdS into the Nf and CL matrices was accomplished by soaking the Nf or CL in 0.1 M CdCl_2 for 2 h followed by air drying the membrane and finally submerging the membrane in a 1 M Na_2S solution [26,27] (represented as $\text{Nf}/(\text{CdS})_{\text{IC}}$ and $\text{CL}/(\text{CdS})_{\text{IC}}$). Excess Na_2S was removed by washing the membrane in a waterbath with several water changes in order to ensure the removal of unreacted Na_2S .

Colloidal TiO_2 and CdS were prepared by dispersing a known amount of TiO_2 and CdS powders in water. The colloidal TiO_2 (0.05 ml

of 0.25%) was dispersed onto the Nf or CL matrix and air dried (represented as Nf/(TiO₂)_{ad} and CL/(TiO₂)_{ad}). Similarly the colloidal CdS (0.05 ml of 5%) was dispersed onto the Nf or CL matrix and air dried (represented as Nf/(CdS)_{ad} and CL/(CdS)_{ad}). A 150 W xenon lamp (Photon Technology International) was used as irradiation source (using pyrex glass and water filters). The distance from the centre of the lamp to the sample was 45 cm). The formation of H₂O₂ was estimated using titrimetric and spectrophotometric methods [28,29]. Pure grade nitrogen and oxygen gases were used for deaeration and oxygenation purposes. Continuous bubbling of oxygen was maintained through the experimental solution to maintain the oxygen concentration during the oxygen reduction experiment.

The surface morphology of TiO₂ and CdS coated and intercalated into Nf and CL membranes were examined by a scanning electron microscope (SEM) (Hitachi S-450, Japan). Absorbance studies were carried out using a JASCO 7800 spectrophotometer. Emission spectral studies were carried out using a Hitachi F-4500 spectrofluorometer.

3. Results and discussion

Three major strategies are being considered in the design of potential devices to produce H₂O₂ by O₂ reduction using suitable photocatalysts and electron relays.

(i) One approach considers the colloidal semiconductor systems.

(ii) The second approach considers the colloidal semiconductor coated onto the Nf and CL matrices.

(iii) The third approach considers the semiconductor particles intercalated into the Nf and CL matrices.

3.1. Photophysical properties

The absorption and emission spectral properties of the TiO₂ and CdS coated and interca-

lated into Nf and CL matrices have been checked by recording the absorption and emission spectra of the samples. Fig. 1 shows the absorption spectra of coated TiO₂ into Nf membrane. The modified TiO₂ in the Nf membrane exhibits an absorption below 400 nm corresponding to a bandgap energy of ~ 3.2 eV [30]. The absorption spectra of modified CdS are shown in Fig. 1. The absorption spectra of the CdS systems exhibit an absorption below 600 nm corresponding to a bandgap energy of ~ 2.4 eV [30]. The details of the characterization of the semiconductor colloids can be found elsewhere [30]. The energetics of these semiconductors thermodynamically favour electron injection from the conduction bands of TiO₂ and CdS to MV²⁺ and Co(III) complexes. Fig. 2 shows the emission spectra of intercalated CdS at Nf and CL matrices recorded at an excitation wavelength of 410 nm. A narrow and edge luminescence (often known as green luminescence) [26] at 520 nm

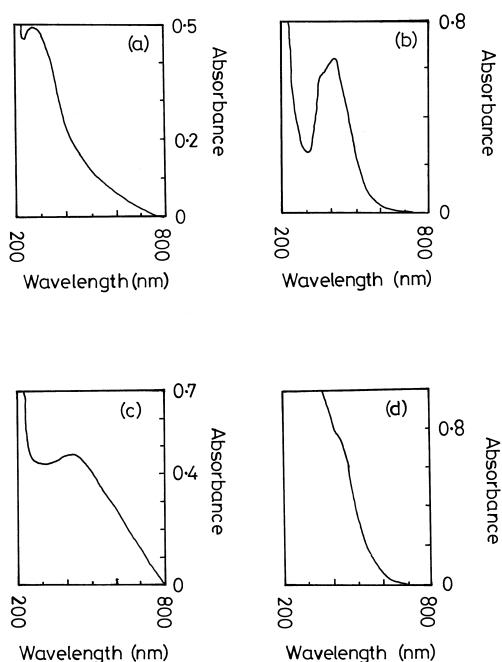


Fig. 1. Absorption spectra of (a) Nf/(TiO₂)_{ad}, (b) Nf/(TiO₂)_{IC}, (c) Nf/(CdS)_{ad} and (d) Nf/(CdS)_{IC} membranes.

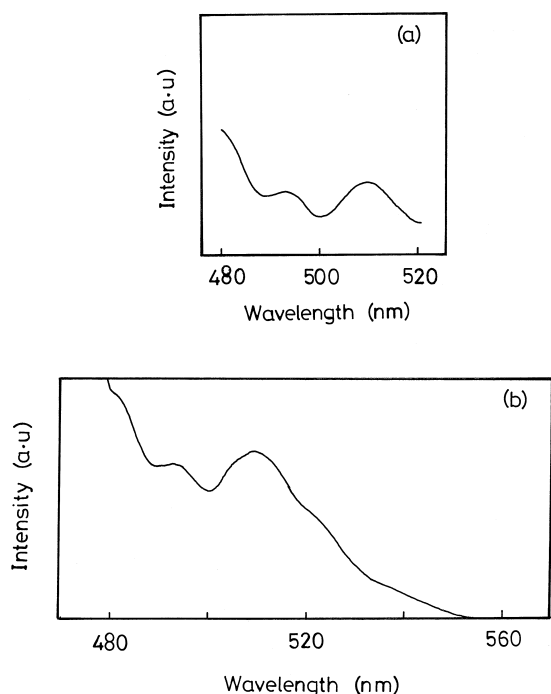


Fig. 2. Emission spectra of (a) Nf/(CdS)_{IC} and (b) CL/(CdS)_{IC} membranes.

was observed (corresponding to a bandgap energy of 2.4 eV).

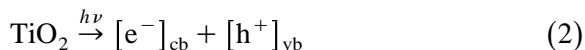
3.2. Surface morphology of TiO₂ and CdS modified Nf and CL membranes

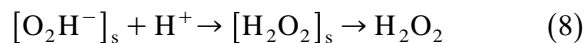
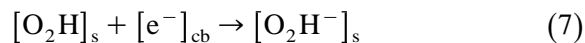
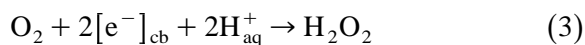
Direct association of semiconductor colloids with membrane is necessary for an efficient photoinduced electron transfer between the semiconductor and the electron relays. The scanning electron micrographs of the semiconductor particles (TiO₂ and CdS) on Nf and CL membranes are shown in Fig. 3. The dispersed semiconductor particles appear as spots in the photographs. These films are less smooth and randomly distributed. The micrographs display a view of the TiO₂ and CdS deposits which are formed well inside the Nf and CL matrices. When the amount of TiO₂ or CdS on the Nf or CL membrane was increased, the number of aggregates increased but the size of the aggre-

gate semiconductors did not change drastically. A similar observation was also observed for TiO₂ and CdS intercalated Nf or CL membrane.

3.3. Photocatalysis

The first approach considers the colloidal semiconductor systems in which the colloidal photocatalyst is used to promote electron transfer to suitable electron relay molecules. The reduced form of these electron relays will reduce O₂ if it possesses the suitable redox potential. The colloidal TiO₂ as photocatalyst and MV²⁺ or Co(III) complex as electron relay were used for O₂ reduction in the colloidal semiconductor solution phase and the yields of H₂O₂ were measured at different irradiation time and the results are shown in Fig. 4. The irradiation of an oxygenated solution containing a mixture of colloidal TiO₂ (5 ml of 0.05%), 0.1 M HClO₄ and 0.1 M TEA produced 0.12 μmol of H₂O₂ in 20 min irradiation (Fig. 4a). The electron acceptor and catalyst MV²⁺ in combination with colloidal TiO₂ did not improve the O₂ reduction process (Fig. 4b) when compared to colloidal TiO₂ (Fig. 4a). When Co(III) complex was used as an electron acceptor and catalyst in combination with colloidal TiO₂ the H₂O₂ yield increased to 0.38 μmol in 20 min irradiation (Fig. 4c). These observations clearly show that the Co(III) complex is a better electron acceptor and catalyst for O₂ reduction to produce H₂O₂ in the presence of colloidal TiO₂. The presence of sacrificial electron donor (TEA) in the solution increased the yield of H₂O₂ by scavenging the holes produced in TiO₂ upon irradiation. The yield of H₂O₂ increased with time and reached a maximum. Different concentrations of colloidal TiO₂ were used for O₂ reduction and a maximum yield was obtained at 0.05% TiO₂ colloid. Using this concentration, we have carried out detailed investigation. The formation of H₂O₂ at colloidal TiO₂ is suggested [31,32] as given in Eqs. (2)–(8).





In the absence of an electron acceptor and catalyst, such as MV^{2+} or a Co(III) complex, a

lower amount of H_2O_2 was obtained. When Co(III) complex was used as an electron relay and catalyst the Co(III) complex was reduced to Co(II) complex by irradiated colloidal TiO_2 and the photoproduced Co(II) complex reacted with O_2 to produce the Co(III)– O_2H complex. The Co(II) complex is known to react with O_2 to form a Co(III)– O_2H complex [24,33]. This Co(III)– O_2H complex further reduced by irradiated colloidal TiO_2 to produce Co(II) and H_2O_2 . When MV^{2+} was used as an electron acceptor

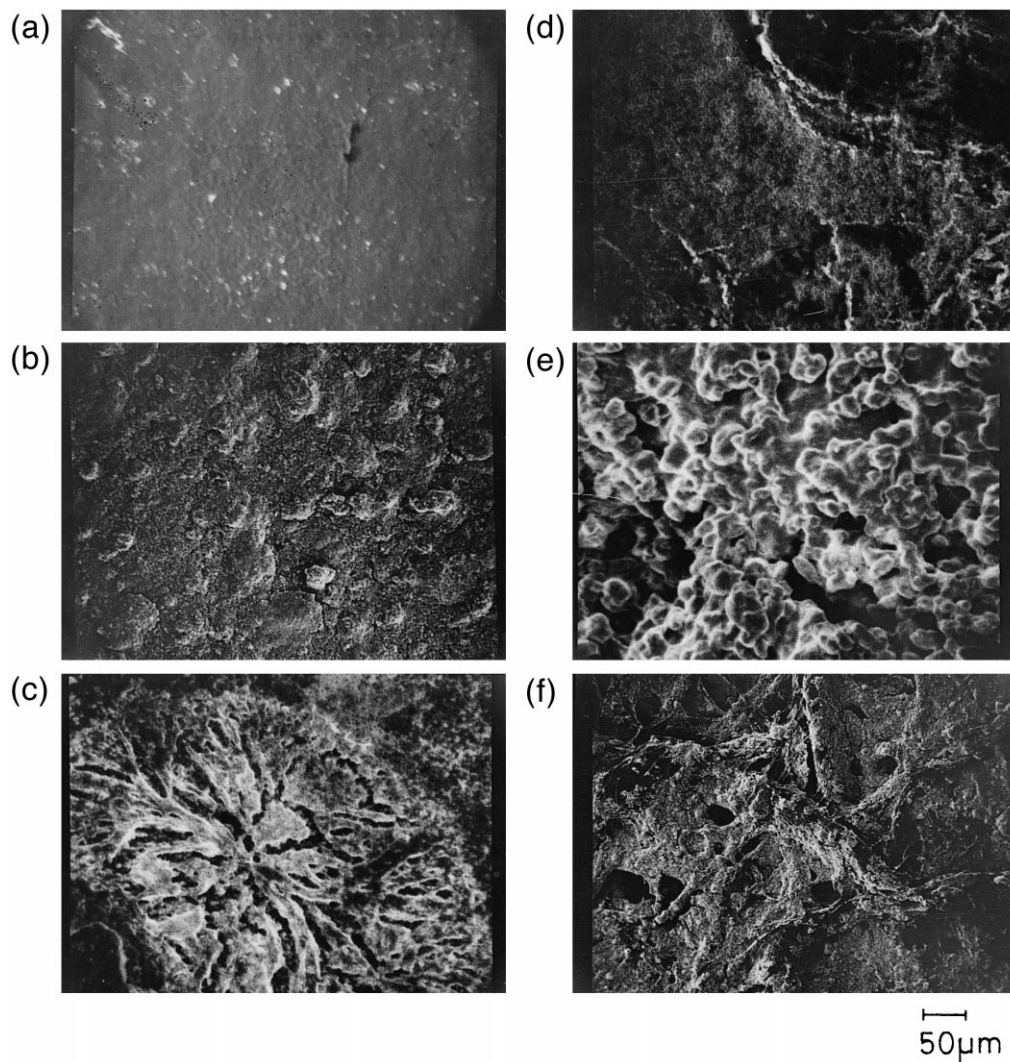


Fig. 3. Scanning electron micrographs of (a) Nf membrane, (b) $\text{Nf}/(\text{TiO}_2)_{\text{ad}}$ (c) $\text{Nf}/(\text{CdS})_{\text{ad}}$, (d) $\text{Nf}/(\text{CdS})_{\text{IC}}$ (e) $\text{CL}/(\text{CdS})_{\text{ad}}$ and (f) $\text{CL}/(\text{TiO}_2)_{\text{ad}}$ membranes.

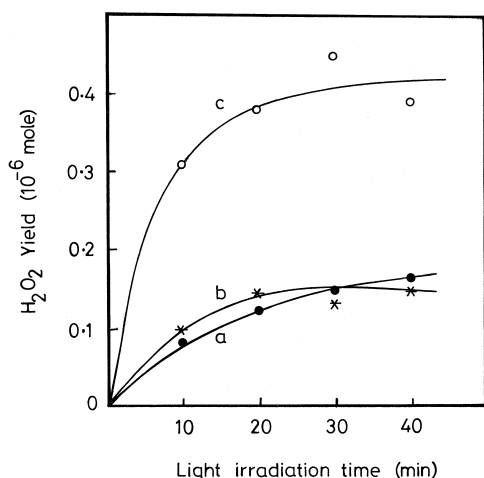
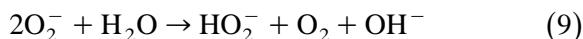


Fig. 4. Yields of H_2O_2 observed with different irradiation time at an oxygenated colloidal TiO_2 suspension (5 ml of 0.05%). (a) 0.1 M HClO_4 and 0.1 M TEA, (b) 1 mM MV^{2+} , 0.1 M HClO_4 and 0.1 M TEA and (c) 1 mM Co(III) complex, 0.1 M HClO_4 and 0.1 M TEA.

and catalyst the MV^{2+} was reduced to $\text{MV}^{+\cdot}$ by irradiated colloidal TiO_2 and the $\text{MV}^{+\cdot}$ reacted with O_2 to produce H_2O_2 .

A higher amount of H_2O_2 was observed in the case of a Co(III) complex when compared to MV^{2+} (Fig. 4). The one-electron reduction of O_2 produces superoxide species (O_2^-). The O_2^- species undergoes disproportionation reaction in aqueous solution [34] (Eq. (9)). In the case of MV^{2+} , the photoproduct $\text{MV}^{+\cdot}$ reduces



O_2 to O_2^- and the O_2^- undergoes disproportionation reaction (Eq. (9)). In addition, the $\text{MV}^{+\cdot}$ species undergoes dimerization to produce the inactive dimer $(\text{MV}^{+\cdot})_2$ [35,36]. When the Co(III) complex was used as catalyst the photoproduct Co(II) complex reacts with O_2 and produces Co(III)– O_2H complex and hinders the disproportionation reaction of O_2^- and enhances the yield of H_2O_2 .

In the second approach, the colloidal semiconductors (TiO_2 and CdS) were spread on Nf and CL matrices ($\text{Nf}/(\text{TiO}_2)_{\text{ad}}$, $\text{Nf}/(\text{CdS})_{\text{ad}}$, $\text{CL}/(\text{TiO}_2)_{\text{ad}}$ and $\text{CL}/(\text{CdS})_{\text{ad}}$) and used for O_2 reduction. The irradiation of TiO_2 or CdS in Nf

Table 1

Photocatalyst	Electron relay	Matrix for the photocatalyst
TiO_2	—	cellulose and Nafion
TiO_2	MV^{2+}	cellulose and Nafion
TiO_2	$[\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2]^{3+}$	cellulose and Nafion
CdS	—	cellulose and Nafion
CdS	MV^{2+}	cellulose and Nafion
CdS	$[\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2]^{3+}$	cellulose and Nafion

or CL with $h\nu > E_{\text{bg}}$ leads to the formation of a $e_{\text{cb}}^-/h_{\text{vb}}^+$ pair that can separately migrate to the semiconductor surface where O_2 reduction will occur in the presence of suitable catalyst. Different amounts of TiO_2 or CdS colloids coated on the surfaces of Nf and CL membranes were used for O_2 reduction experiments. A maximum

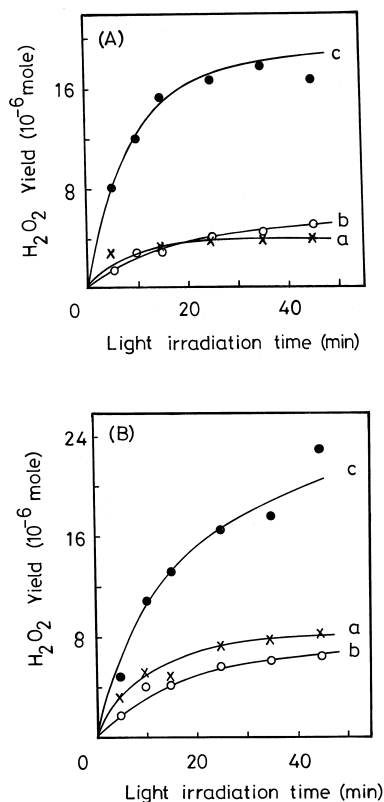
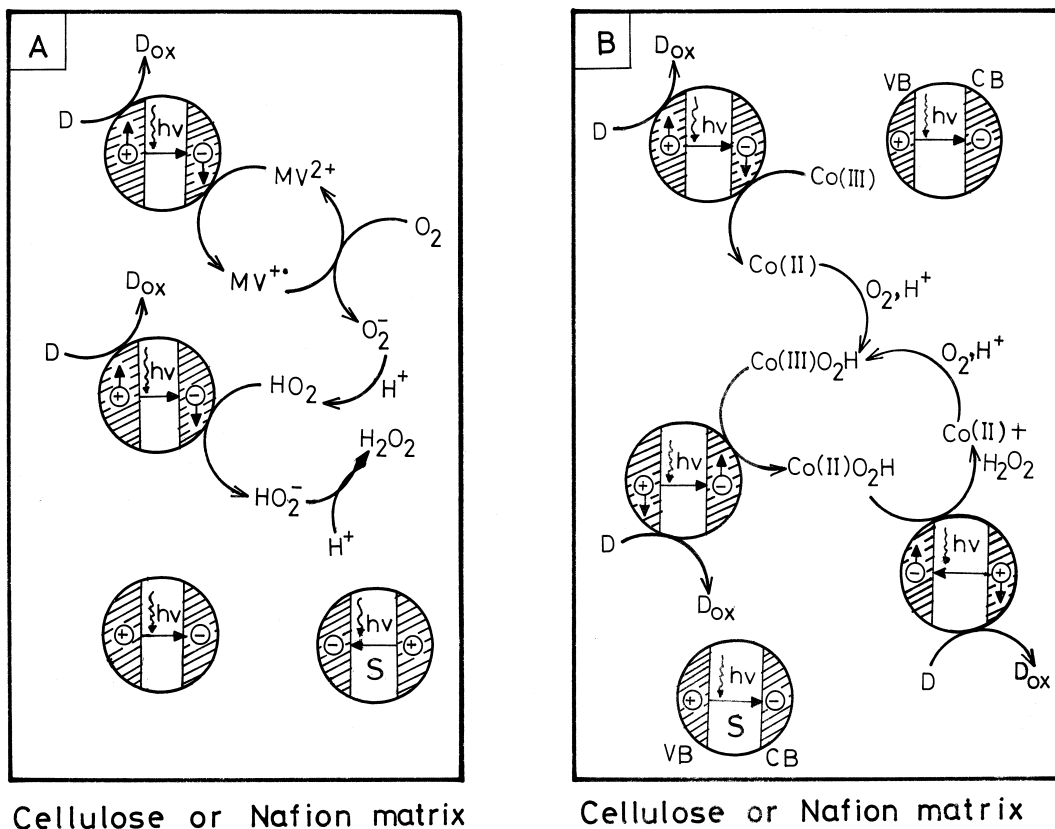


Fig. 5. Yields of H_2O_2 observed with different irradiation time at (A) $\text{Nf}/(\text{TiO}_2)_{\text{ad}}$ and (B) $\text{CL}/(\text{CdS})_{\text{ad}}$ membrane dipped in an oxygenated solution containing (a) 0.1 M HClO_4 and 0.1 M TEA, (b) 1 mM MV^{2+} , 0.1 M HClO_4 and 0.1 M TEA and (c) 1 mM Co(III) complex, 0.1 M HClO_4 and 0.1 M TEA.

yield of H_2O_2 was obtained at 0.25% of 0.05 ml of TiO_2 and 5% of 0.05 ml of CdS on the membranes. Using these concentration ranges we have carried out detailed investigations. The different electron relays and various modified semiconductor systems used for the photocatalytic reduction of O_2 are given in Table 1.

The yield of H_2O_2 observed at $\text{Nf}/(\text{TiO}_2)_{\text{ad}}$ and $\text{CL}/(\text{CdS})_{\text{ad}}$ membranes dipped in an oxygenated solution of a 1 mM Co(III) complex or MV^{2+} at different irradiation times are shown in Fig. 5. A similar observation was also observed for $\text{Nf}/(\text{CdS})_{\text{ad}}$ and $\text{CL}/(\text{TiO}_2)_{\text{ad}}$ membranes. In all the systems, a higher amount of H_2O_2 was observed only in the case of an oxygenated solution containing the Co(III) com-

plex and TEA. The mechanism of photo-reduction of O_2 by Co(III) and MV^{2+} catalysts are the same as discussed earlier for colloidal semiconductor systems. The TiO_2 and CdS coated on Nf and CL matrices are found to yield a higher amount of H_2O_2 (Fig. 5) when compared to colloidal TiO_2 (Fig. 4). The adsorbed TiO_2 and CdS occupy mostly the surface of the membrane and partly the interfacial region formed between the hydrophilic cluster and heterogeneous hydrophobic regions of the Nf and CL membranes. The water soluble Co(III) complex and MV^{2+} electron relays reversibly occupy the cluster regions of the Nf and CL membranes and efficient photoinduced electron transfer occurs at the solid–solution interface.



Scheme 1. Mechanism of dioxygen reduction at the semiconductors (S = TiO_2 and CdS) adsorbed and intercalated into Nafion and cellulose membranes. (A) MV^{2+} and (B) Co(III) complex. D = TEA.

In the absence of an electron donor (TEA), a very low amount of H_2O_2 was observed for the modified semiconductor systems. The mechanism of O_2 reduction using the modified TiO_2 or CdS membrane system is shown in Scheme 1.

In the third approach, the colloidal semiconductors, TiO_2 and CdS were intercalated into the Nf and CL matrices. The electron relays (MV^{2+} and Co(III) complex) and the intercalated semiconductor systems (TiO_2 and CdS) used for the photocatalytic reduction of O_2 are given in Table 2. The yields of H_2O_2 observed at $\text{Nf}/(\text{CdS})_{\text{IC}}$ and $\text{CL}/(\text{CdS})_{\text{IC}}$ dipped in an oxygenated solution containing 1 mM $[\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2]^{3+}$ or MV^{2+} at different irradiation times are shown in Fig. 6. A similar observation was also observed at $\text{Nf}/(\text{TiO}_2)_{\text{IC}}$. A very similar trend was observed for the colloidal semiconductors and semiconductors adsorbed or intercalated in Nf and CL membranes. A higher yield of H_2O_2 was observed for the intercalated TiO_2 and CdS membrane systems when compared to TiO_2 and CdS in the colloid and adsorbed state. In an intercalated system, the particles were homogeneously distributed among the interfacial and cluster regions of the membranes and the active surface area of the semiconductors would be high. The diffusion of Co(III) complex in the hydrophilic cluster region of the semiconductor intercalated membranes will be smooth unlike in the adsorbed TiO_2 and CdS in the membranes. In the adsorbed films, the distribution of TiO_2 and CdS particles inside the membrane was not homogeneous.

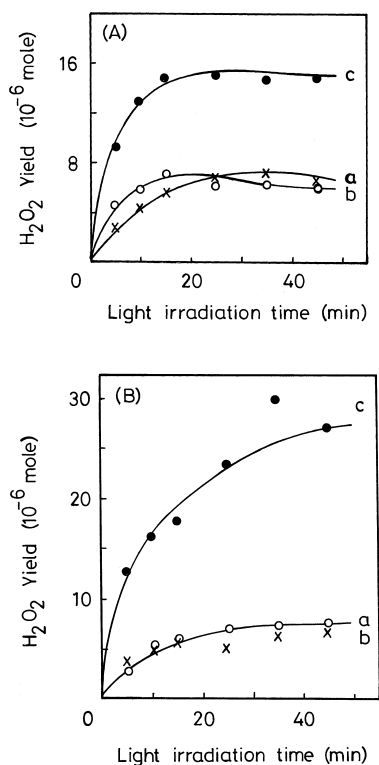


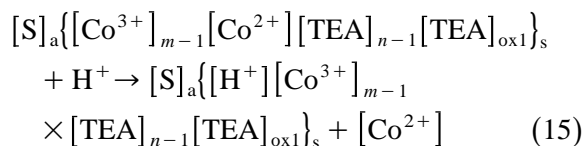
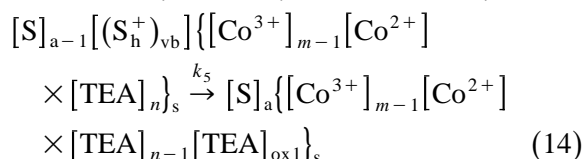
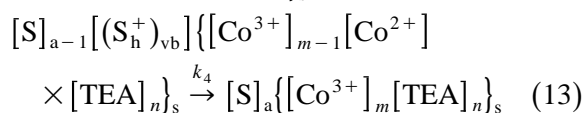
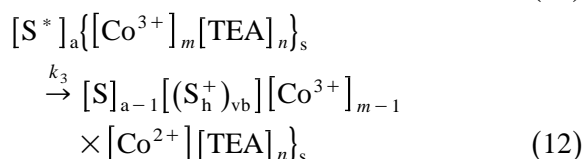
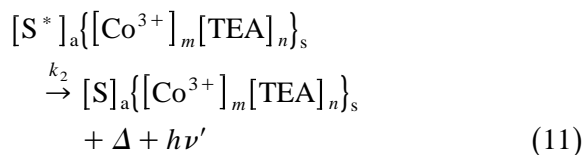
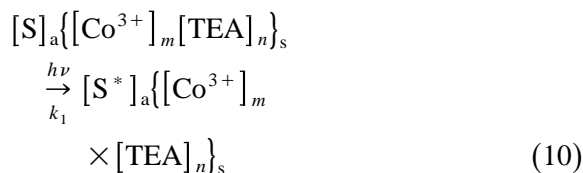
Fig. 6. Yields of H_2O_2 observed with different irradiation time observed at (A) $\text{Nf}/(\text{CdS})_{\text{IC}}$ and (B) $\text{CL}/(\text{CdS})_{\text{IC}}$ membranes dipped in an oxygenated solution containing (a) 0.1 M HClO_4 and 0.1 M TEA, (b) 1 mM MV^{2+} , 0.1 M HClO_4 and 0.1 M TEA and (c) 1 mM Co(III) complex, 0.1 M HClO_4 and 0.1 M TEA.

The results are best understood by a mechanism in which the back reaction of h_{vb}^+ with the Co(II) complex is eliminated by the efficient scavenging of h_{vb}^+ by the electron donor TEA under the conditions employed. The reaction scheme of the photoinduced electron transfer

Table 2

Intercalated photocatalyst	Electron acceptor	Matrix for the photocatalyst
TiO_2	—	Nafion
TiO_2	MV^{2+}	Nafion
TiO_2	$[\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2]^{3+}$	Nafion
CdS	—	Nafion and cellulose
CdS	MV^{2+}	Nafion and cellulose
CdS	$[\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2]^{3+}$	Nafion and cellulose

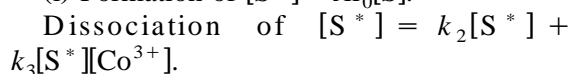
reaction of the Co(III) complex with TiO₂ or CdS are given in Eqs. (10)–(15).



In Eqs. (10)–(15) the chemical species are given in square brackets and subscript ‘a’ represents the adsorbed or intercalated TiO₂ or CdS in Nf or CL matrix and ‘s’ represents the Co(III) complex and TEA present in solution and in contact with TiO₂ or CdS. The subscripts ‘m’ and ‘n’ represent the number of Co(III) complex and TEA and ‘S’ represents the photocatalyst TiO₂ or CdS particle in the Nf or CL matrix. S, S*, [h_{vb}⁺] and Co³⁺ represent the unirradiated TiO₂ or CdS and irradiated TiO₂ or CdS*, holes produced at irradiated TiO₂ or CdS and [Co(cyclam)(H₂O)₂]³⁺ complex, respectively, and (TEA)_{ox} is the oxidised species of TEA. The hole (h_{vb}⁺) scavenging reaction by TEA, Eq. (14), competes with the back electron transfer reaction, Eq. (13). Eq. (15) represents

the ion-exchange equilibrium of Co(II) with H⁺ present in the solution. A semiquantitative analysis of the reaction kinetics of the formation of Co(II) complex at TiO₂ or CdS adsorbed Nf or CL membrane dipped in an aqueous solution could be carried out with the assumption that the rates of the ion-exchange adsorption equilibrium reactions of TiO₂ or CdS, Co(III) and Co(II) complexes in the interior of the membrane would be fast and thus the reactive species would be always distributed homogeneously, so the reactions occurring in the membrane are regarded as well as those occurring in the homogeneous solution [26,27]. On the basis of this assumption and the reaction mechanism represented in Eqs. (10)–(14) and a steady state approximation could be applied to calculate the rate of formation of Co(II) complex (Eqs. (16)–(18)).

(i) Formation of [S*] = AI₀[S].

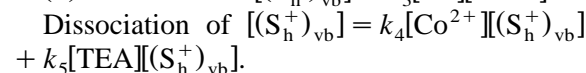


At steady state, AI₀[S] = k₂[S*] + k₃[S*][Co³⁺] = [S*]{k₂ + k₃[Co³⁺]},

$$[S^*] = \frac{AI_0[S]}{k_2 + k_3[Co^{3+}]} \quad (16)$$

Only the species involved in the reaction is used for calculating [S*] and [(S_h⁺)_{vb}].

(ii) Formation of [(S_h⁺)_{vb}] = k₃[S*][Co³⁺].



At steady state, k₄[Co²⁺][(S_h⁺)_{vb}] + k₅[TEA][(S_h⁺)_{vb}] = k₃[S*][Co³⁺]. Rearranging we get [(S_h⁺)_{vb}]{k₄[Co²⁺] + k₅[TEA]} = k₃[S*][Co³⁺],

$$[(S_h^+)_{vb}] = \frac{k_3[S^*][Co^{3+}]}{k_4[Co^{2+}] + K_5[TEA]} \quad (17)$$

The rate of formation of [Co²⁺] is

$$\frac{d[Co^{2+}]}{dt} = k_3[S^*][Co^{3+}] - k_4[Co^{2+}][(S_h^+)_{vb}] \quad (18)$$

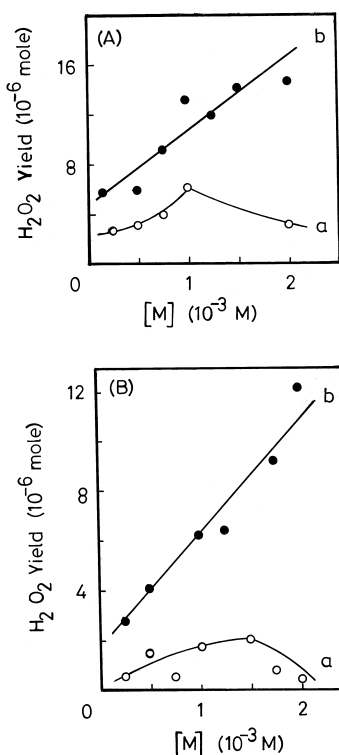


Fig. 7. Yields of H₂O₂ observed at different concentrations of (a) MV²⁺, (b) Co(III) complex in an oxygenated solution containing 0.1 M HClO₄ and 0.1 M TEA. (A) Nf/(CdS)_{ad} and (B) CL/(TiO₂)_{ad}. Light irradiation time = 15 min. [M] = [MV²⁺] (a) and [Co³⁺] (b).

In Eqs. (16) and (17), *A* is a constant which is determined by the experimental conditions, *I*₀ is the light intensity and *k*₁ to *k*₅ are the rate constants of the corresponding reactions. The rate of formation of the Co(II) complex is defined by the moles of Co(II) complex, i.e. [Co²⁺] formed per unit time, and is given by Eq. (18). Substituting [S*] and [(S_n⁺)_{vb}] (Eqs. (16) and (17)) in Eq. (18), we get Eq. (19):

$$\frac{d[\text{Co}^{2+}]}{dt} = \left\{ \frac{k_3 A I_0 [S] [\text{Co}^{3+}]}{k_2 + k_3 [\text{Co}^{3+}]} \right\} - \left\{ \frac{k_3 k_4 [\text{Co}^{2+}] [S^*] [\text{Co}^{3+}]}{k_4 [\text{Co}^{2+}] + k_5 [\text{TEA}]} \right\} \quad (19)$$

When $k_4[\text{Co}^{2+}] < k_5[\text{TEA}]$, $d[\text{Co}^{2+}]/dt$ is given by Eqs. (20) and (21):

$$\frac{d[\text{Co}^{2+}]}{dt} = \frac{k_3 A I_0 [S] [\text{Co}^{3+}]}{k_2 + k_3 [\text{Co}^{3+}]} \quad (20)$$

$$\frac{1}{d[\text{Co}^{2+}]/dt} = 1/(A I_0 [S]) \left\{ \frac{k_2}{k_3 [\text{Co}^{3+}]} + 1 \right\} \quad (21)$$

The relative rate of formation of the [Co²⁺] complex is proportional to the [Co³⁺] complex concentration (Eq. (21)). The photoproduced [Co²⁺] complex reduces O₂ to H₂O₂. Each [Co²⁺] complex reduces one molecule of O₂ and then forms a Co(III)–O₂H complex. The formation of H₂O₂ is proportional to the [Co(III)] complex used in all the modified systems (Figs. 7 and 8).

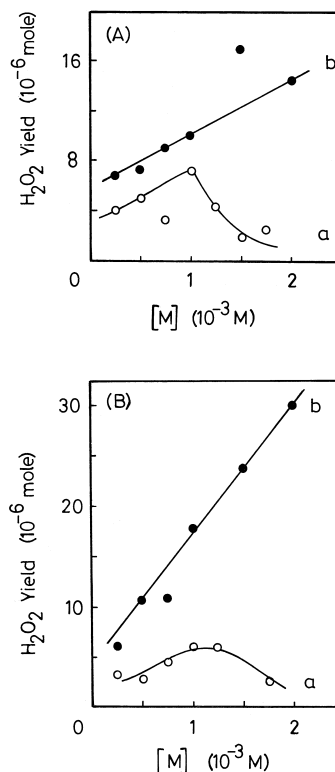


Fig. 8. Dependence of H₂O₂ yield on the concentration of (a) MV²⁺ and (b) Co(III) complex in an oxygenated solution containing 0.1 M HClO₄ and 0.1 M TEA. (A) Nf/(CdS)_{ic} and (B) CL/(CdS)_{ic}. Light irradiation time = 15 min. [M] = [MV²⁺] (a) and [Co³⁺] (b).

The formation of H_2O_2 depends on the concentration of Co(III) complex and MV^{2+} . The yield of H_2O_2 obtained for the various systems, $Nf/(CdS)_{ad}$, $CL/(TiO_2)_{ad}$, $Nf/(TiO_2)_{IC}$ and $CL/(CdS)_{IC}$ at various concentrations of $[Co(cyclam)(H_2O)_2]^{3+}$ and MV^{2+} in 0.1 M $HClO_4$ and 0.1 M TEA at a light irradiation time of 15 min are shown in Figs. 7 and 8. A similar observation was also observed for $Nf/(TiO_2)_{ad}$ and $CL/(CdS)_{ad}$ membrane. For all the systems, linear plots were obtained for the Co(III) complex as an electron relay (Figs. 7 and 8). When MV^{2+} was used as an electron relay, there was a gradual increase of yield of H_2O_2 and it reached a maximum at 1 mM MV^{2+} and then the yield of H_2O_2 decreased (Figs. 7 and 8). The decrease in H_2O_2 yield at higher concentrations of MV^{2+} may be due to the dimerization of photoproducted $MV^{\cdot+}$ cation radical to $(MV^{\cdot+})_2$ [34,35]. These results suggest that the photocatalytic O_2 reduction reac-

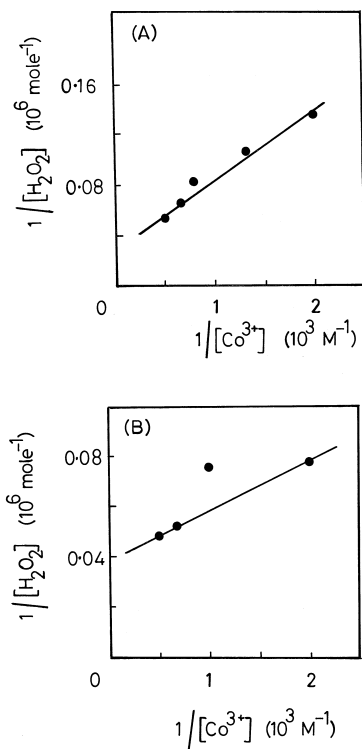


Fig. 9. Plots of $1/[H_2O_2]$ versus $1/[Co^{3+}]$ for (A) $Nf/(TiO_2)_{ad}$ and (B) $CL/(CdS)_{ad}$.

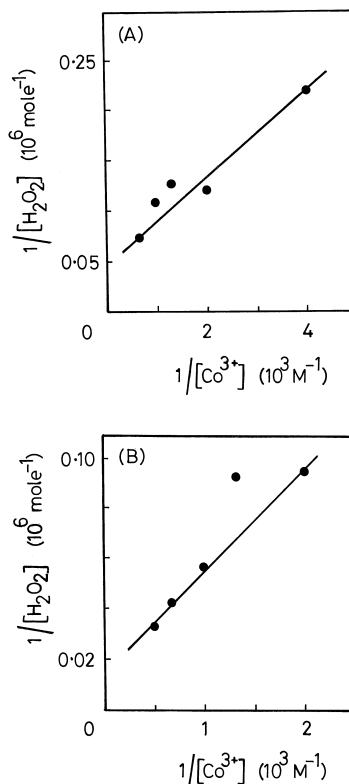


Fig. 10. Plots of $1/[H_2O_2]$ versus $1/[Co^{3+}]$ for (A) $Nf/(TiO_2)_{IC}$ and (B) $CL/(CdS)_{IC}$.

tion depends on the Co(III) complex concentration. Eq. (21) can be written as given in Eq. (22) and it can be modified to Eq. (23).

$$\frac{1}{[H_2O_2]} = (1/(AI_0[S])) \left\{ \frac{k_2}{k_3[Co^{3+}]} + 1 \right\} \quad (22)$$

$$\frac{1}{[H_2O_2]} = (\alpha/(I_0[S])) \left\{ \frac{k_2}{k_3[Co^{3+}]} + 1 \right\} \quad (23)$$

where α is a constant at a given experimental condition. At a given $[S]$ and I_0 , the plot of $1/[H_2O_2]$ versus $1/[Co^{3+}]$ should be linear if the reaction mechanism represented by Eqs. (10)–(15) and the assumption are correct. In all the modified systems ($Nf/(TiO_2)_{ad}$, $CL/(CdS)_{ad}$, $Nf/(TiO_2)_{IC}$ and $CL/(CdS)_{IC}$), the plots of $1/[H_2O_2]$ versus $1/[Co^{3+}]$ were linear (Figs. 9 and 10) (when I_0 and $[S]$ are

constants). These observations indicate that the mechanism proposed for the photoinduced electron transfer reactions of semiconductors in Nf and CL membranes and Co(III) complex (Eqs. (10)–(15)) are correct.

In all the modified semiconductor systems, the Co(III) complex showed a higher yield of H_2O_2 . The presence of TEA in the solution increased the yield of H_2O_2 by scavenging the holes created at the irradiated TiO_2 or CdS. The yield of H_2O_2 increased with time and reached a maximum in all the systems (Figs. 4–6). When the H_2O_2 concentration increases in solution the H_2O_2 may be oxidised by the photo-generated holes of TiO_2 or CdS or may decompose at the surface of the solid phase [32].

Acknowledgements

The financial support from the Department of Science and Technology (DST) and the Council of Scientific and Industrial Research (CSIR) is gratefully acknowledged. J.P. thanks CSIR for the Senior Research Fellowship. We thank Professor G. Kulandaivelu for his help in recording SEM.

References

- [1] V. Krishnan (Ed.), Proceedings of Eleventh International Conference on Photochemical Conversion and Storage of Solar Energy, Bangalore, India, 1996.
- [2] M. Graetzel, Energy Resources through Photochemistry and Catalysis, Academic Press, London, 1983.
- [3] E. Pelizzetti, M. Schiavello, Photochemical Conversion and Storage of Solar Energy, Kluwer Academic Press, Dordrecht, 1991.
- [4] K. Kalyanasundaram, M. Graetzel, Kinetics and Catalysis in Microheterogeneous System, Mercel Dekker, New York, 1991.
- [5] K. Kalyanasundaram, M. Graetzel, Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds, Kluwer Academic Press, Dordrecht, 1993.
- [6] J.R. Norris, D. Meisel, Photochemical Energy Conversion, Elsevier, New York, 1989.
- [7] E. Pelizzetti, N. Serpone, Homogeneous and Heterogeneous Photocatalysis, NATO ASI Series, Reidel, Dordrecht, 1986.
- [8] R.J. Lin, M. Kaneko, in: Molecular Electronics and Molecular Electronic Devices, CRC Press, London, 1992, p. 208.
- [9] A.L. Linsebigler, G. Lu, Y.T. Yates, Chem. Rev. 95 (1995) 735.
- [10] A. Hegfeldt, M. Graetzel, Chem. Rev. 95 (1995) 49.
- [11] M. Graetzel, Heterogeneous Photochemical Electron Transfer, CRC Press, London, 1989.
- [12] J. Biggins, Progress in Photosynthetic Research, Martinus Nijhoff, Dordrecht, 1987.
- [13] J. Premkumar, R. Ramaraj, Radiat. Phys. Chem. 49 (1996) 115.
- [14] D. Meissner, R. Memming, B. Kastening, Chem. Phys. Lett. 96 (1983) 34.
- [15] M. Krishnan, J.R. White, M.A. Fox, A.J. Bard, J. Am. Chem. Soc. 105 (1983) 7002.
- [16] A.W.H. Mau, C.B. Huang, N. Kakuta, A.J. Bard, J. Am. Chem. Soc. 106 (1984) 6537.
- [17] K. Rajeshwar, M. Kaneko, Langmuir 5 (1989) 255.
- [18] S.N. Frank, A.J. Bard, J. Phys. Chem. 81 (1977) 1484.
- [19] J. Kiwi, E. Borgarello, E. Pelizzetti, M. Visca, M. Graetzel, Angew. Chem. Int. Ed. Engl. 19 (1980) 646.
- [20] R. Cai, R. Baba, K. Hashimoto, A. Fujishima, J. Electroanal. Chem. 360 (1993) 237.
- [21] H. Sakai, R. Baba, K. Hashimoto, A. Fujishima, A. Heller, J. Phys. Chem. 99 (1995) 237.
- [22] S. Kuwabata, H. Uchida, A. Ogawa, S. Hirao, H. Yoneyama, J. Chem. Soc. Chem. Commun. (1995) 329.
- [23] B. Bosnich, C.K. Poon, M.L. Tobe, Inorg. Chem. 4 (1965) 1102.
- [24] T. Geigar, F.C. Anson, J. Am. Chem. Soc. 103 (1981) 7489.
- [25] F.R. Fan, H.Y. Liu, A.J. Bard, J. Phys. Chem. 89 (1985) 4418.
- [26] J.P. Kuczynski, B.H. Milosavljevic, J.K. Thomas, J. Phys. Chem. 88 (1984) 980.
- [27] J.P. Kuczynski, J.K. Thomas, J. Phys. Chem. 89 (1985) 2720.
- [28] D.J. Savage, Analyst 76 (1951) 224.
- [29] R.A. Heckman, J.H. Espenson, Inorg. Chem. 18 (1979) 37.
- [30] J.R. Ufford, N. Serpone, Coord. Chem. Rev. 57 (1984) 301.
- [31] J.R. Harbour, J. Tromp, M.L. Hair, Can. J. Chem. 63 (1985) 204.
- [32] R. Cai, K. Hashimoto, A. Fujishima, J. Electroanal. Chem. 326 (1992) 345, and references cited therein.
- [33] J. Premkumar, R. Ramaraj, J. Chem. Soc. Chem. Commun. (1996) 761.
- [34] J.L. Roberts, J.M. Morrison, D.T. Sawyer, J. Am. Chem. Soc. 104 (1978) 329.
- [35] A.G. Evans, N.K. Dodson, N.S. Rees, J. Chem. Soc. Perkin II (1976) 859.
- [36] M. Kaneko, A. Yamada, J. Photochem. Photobiol. A: Chem. 33 (1981) 793.