

Photoreduction of dioxygen to hydrogen peroxide at porphyrins and phthalocyanines adsorbed Nafion membrane

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Abstract

The metal porphyrins (MP) and metal phthalocyanines (MPC) adsorbed Nafion membranes are prepared (Nf/MP and Nf/MPC) and used as photocatalysts for the photoreduction of dioxygen (O_2). Photoinduced electron transfer reactions carried out using the MP and MPC adsorbed Nafion membrane. The back electron transfer reaction between h^+ with O_2^- 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 semiconducting nature metal porphyrins and phthalocyanines with dissolved dioxygen. The photosensitized reaction mechanism of the photocatalytic reduction of O_2 to H_2O_2 formation is explained. The turnover number of the photocatalysts are high in the presence of sacrificial electron donor. The surface morphology of the modified photocatalysts are analysed by scanning electron microscope. The detailed mechanism of the dioxygen reduction in the modified systems are presented. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Porphyrins; Phthalocyanines; Oxygen reduction; Nafion

1. Introduction

Interest in the photocatalytic reduction of dioxygen to useful products such as hydrogen peroxide has been increasing in recent years [1–5]. In this context solar energy conversion by artificial photosynthesis is becoming an increasingly important research subject [5–7]. The difficulty in creating non-biological model system for the photoinduced multistep one-electron process lies in the requirement to couple the multielectron reduction of O_2 with the one-electron chemistry of the redox molecules. The light-induced reduction of O_2 in an aqueous solution using semiconductor and metal complex photocatalysts has been attempted [1–5,8–10]. The electrocatalytic reduction of O_2 using metal complexes, metal porphyrins (MP) and metal phthalocyanines (MPC) have been studied. [11–13] Two- and four-electron reduction products such as hydrogen peroxide and water have been reported.

Metalloporphyrins, which include important natural complexes such as chlorophyll and heme and related complexes. A large number of biological system are known in which metalloporphyrins act as

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initiators of a particular biological process. Most investigations have involved chlorophyll, which being part of the protein–lipid system initiates photosynthesis in green plants and in photosynthetic bacteria, that is it initiates the stage of accumulation and transfer of the energy of a light quantum, the stage of electron transfer reaction through the complex photosynthetic system all the way from the reducing to the oxidising agents. In artificial photosynthesis the development of more efficient photocatalyst in solid/membrane is a promising approach for the photoreduction of O_2 . The catalytic molecules immobilized in a Nafion membrane are particularly advantageous due to their separation from the reaction medium by microheterogeneous environment and a small amount of catalyst material necessary for reaction. In an attempt to develop a photocatalytic system in solid phase, we have utilized the MP and MPC adsorbed Nafion membranes for the photocatalytic reduction of O_2 . The utility of immobilized catalysts is drastically evident since they are not leached from the membrane where the immobilized metal phthalocyanines are quite active and stable.

Transition metal complexes (porphyrins and phthalocyanines) are a class of electrocatalyst for the reduction of O_2 that have received extensive study [11,12]. Mechanistic interpretations of the catalytic activity of a variety of complexes have been offered but uncertainties remain, especially about the relationship between the formal potentials of the adsorbed catalyst in the absence of O_2 and the potential where the catalysed reduction of dioxygen proceed. The aim of this research was to examine this point and to assess the effects of major substitution on the phthalocyanine ring on the stability and activity of catalyst-coated electrodes. In this paper, we present the results of the photocatalytic reduction of O_2 using MPs and MPCs adsorbed Nafion membrane.

2. Experimental

The porphyrins (protoporphyrin (PP), hematoporphyrin (HP)) and the phthalocyanines (iron(II)phthalocyanine (FePC), cobalt(II)phthalocyanine (CoPC) and zinc(II)phthalocyanine (ZnPC)) and Nafion membrane (Nf) (type 125, equiv.wt. 1100, thickness 0.13 mm) were purchased from Aldrich Chemical. Tetraphenylporphyrine was purchased from Tokyo Kasei Kogyo, Japan. Cobalt(II)tetraphenylporphyrin (CoTPP) and cobalt(II)porphyrin (CoP) were prepared by reported procedures [14]. Triethanolamine (TEA), dimethyl formamide (DMF) and perchloric acid ($HClO_4$) were purchased from Merck. The Nf membrane was pretreated prior to use by boiling in concentrated nitric acid for about 10–20 min and it became clear and transparent [15]. The MP and MPC adsorbed Nf membrane was prepared by dipping the Nf membrane (1 cm^2) in a known concentration of MP or MPC in DMF at various time intervals. The resulting MP or MPC adsorbed Nf membrane (represented Nf/PP, Nf/HP, Nf/TPP, Nf/CoTPP, Nf/CoP, Nf/FePC, Nf/CoPC and Nf/ZnPC) washed with distilled water and dried at room temperature under dark. The amounts of adsorbed MP and MPC in the Nf membrane were determined by measuring the absorbance of the MP and MPC solutions before and after dipping. The reported molar extinction coefficient values of the MPs and MPCs [16] were used to calculate the concentrations of the complexes. The absorption spectra of MP and MPC in DMF and adsorbed in Nf membrane were recorded using JASCO 7800 spectrophotometer. The MP or MPC adsorbed Nf membrane was dipped in a O_2 saturated solution containing TEA and $HClO_4$ using a glass cell with optical window (volume of the solution was 15 ml) and the membrane was illuminated with visible light using a 500 W tungsten–halogen lamp with pyrex glass and water filters to cut-off ultra-violet and infra-red radiations. The distance from the centre of the halogen lamp to the cell was 45 cm. A procedure typical of kinetic experiment for the formation of H_2O_2 was employed using titrimetry and spectrophotometry methods [17,18]. To a 10 ml of the

sample solution, 5 ml of 0.2 M sulfuric acid and 5 ml of 5% potassium iodide were added and the liberated iodine was titrated against 1 mM of sodium thiosulfate solution [17] and the H_2O_2 concentration was determined. A blank titration was also carried out. The amount of H_2O_2 was also determined by spectrophotometric method [18]. The sample solution (1.5 ml) was taken in a 5 ml standard measuring flask to which 1.5 ml of 0.2 M sulfuric acid was added. Then 5% potassium iodide solution was added into the 5 ml standard measuring flask upto the mark and the absorbance value was quantitatively monitored at 351 nm²⁶ (absorption maximum = 351 nm for I_3^- and molar extinction coefficient at 351 nm = $26400 \text{ M}^{-1} \text{ cm}^{-1}$). The reference cell was filled with the blank oxygen saturated solution treated with acidified potassium iodide solution in a similar way. From the absorbance value, the amount of H_2O_2 produced was calculated. Pure grade nitrogen and oxygen gases were used for deaeration and O_2 saturation purpose. Continuous bubbling of O_2 gas was maintained in the experimental solution throughout the experiment. The surface morphology of the MP and MPC adsorbed Nf membranes was examined by scanning electron microscope (Hitachi S-450). The porphyrins and phthalocyanines adsorbed Nf membranes were stable for weeks and reused. Experiments were repeated several times and reproducible results were obtained.

3. Results and discussion

The MPs and MPCs were irreversibly adsorbed in the Nf membrane. The MPs and MPCs were adsorbed by dipping the Nf membrane in different concentrations of MP or MPC in DMF. The

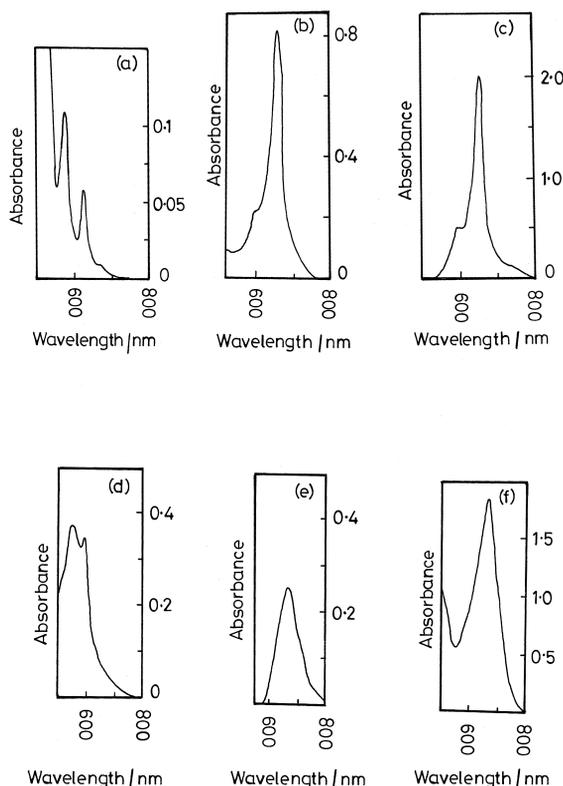


Fig. 1. Absorption spectra of MP and MPC in DMF solution and incorporated into Nf membranes. (a) HP, (b) FePC, (c) CoPC in DMF and (d) Nf/HP, (e) Nf/FePC, (f) Nf/CoPC vs. Nf membrane.

desorption of MP and MPC in the Nf/MP and Nf/MPC membranes was not observed in any rigorous conditions, in acids and in neutral solutions. This has been checked by recording the absorption spectra of the solutions before and after dipping the Nf/MP and Nf/MPC membranes in solutions. The absorption spectra of the MP and MPC adsorbed Nf membranes are recorded and shown in Fig. 1. The absorption spectra observed for the MP and MPC adsorbed Nf membrane are almost similar to the spectra observed in DMF solution (Fig. 1). The Nf membrane consists of hydrophobic fluorocarbon region, hydrophilic- SO_3^- ionic cluster region and interfacial region formed between these two [19]. The MP and MPC molecules mostly will occupy the interfacial and hydrophobic regions of the Nf membrane due to the hydrophobic interaction.

The scanning electron micrographs of the MP and MPC adsorbed Nf membranes are shown in Fig. 2. The SEMs show dark spots on the surface of the MP and MPC adsorbed Nf membrane when

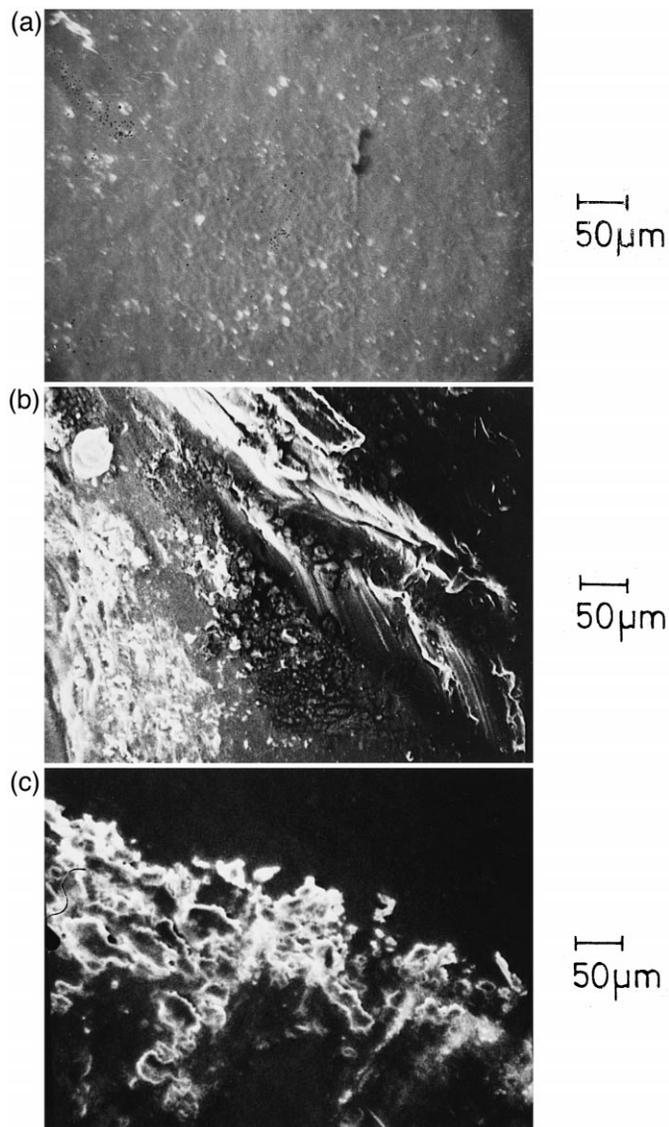


Fig. 2. Scanning electron micrographs of (a) Nf, (b) Nf/CoTPP and (c) Nf/CoPC membranes.

compared to plain Nf membrane. The MP and MPC adsorbed in the Nf membranes agglomerate into larger deposits and are randomly distributed in the Nf membrane. The MPs and MPCs interact with the structural units of the Nf membrane (hydrophobic fluorocarbon and interfacial regions) as well as interact with each other in forming a three dimensional disordered network of chemically reactive molecule.

Photocatalytic O₂ reduction was carried out using the MP and MPC adsorbed Nf membranes. The Nf/MP or Nf/MPC membrane was dipped into a photolysis cell containing O₂ saturated 0.1 M HClO₄ and 0.1 M TEA and then irradiated. After 10–60 min irradiation, the oxygen reduction product hydrogen peroxide was analysed. When the experiments were carried out in dark or under illumination using MP or MPC solution filter to cut off the light in the MP or MPC absorption band region, hydrogen peroxide was not detected with any one of the MP or MPC membrane.

The yield of hydrogen peroxide formed at different light irradiation time using Nf/MP and Nf/MPC membranes were determined and the corresponding turnover numbers (TONs) of MP and MPC are shown in Fig. 3. The TONs of MP and MPC were obtained from the relation 2 (mole of hydrogen peroxide)/(mole of MP or MPC adsorbed). In the Nf/MP and Nf/MPC membrane

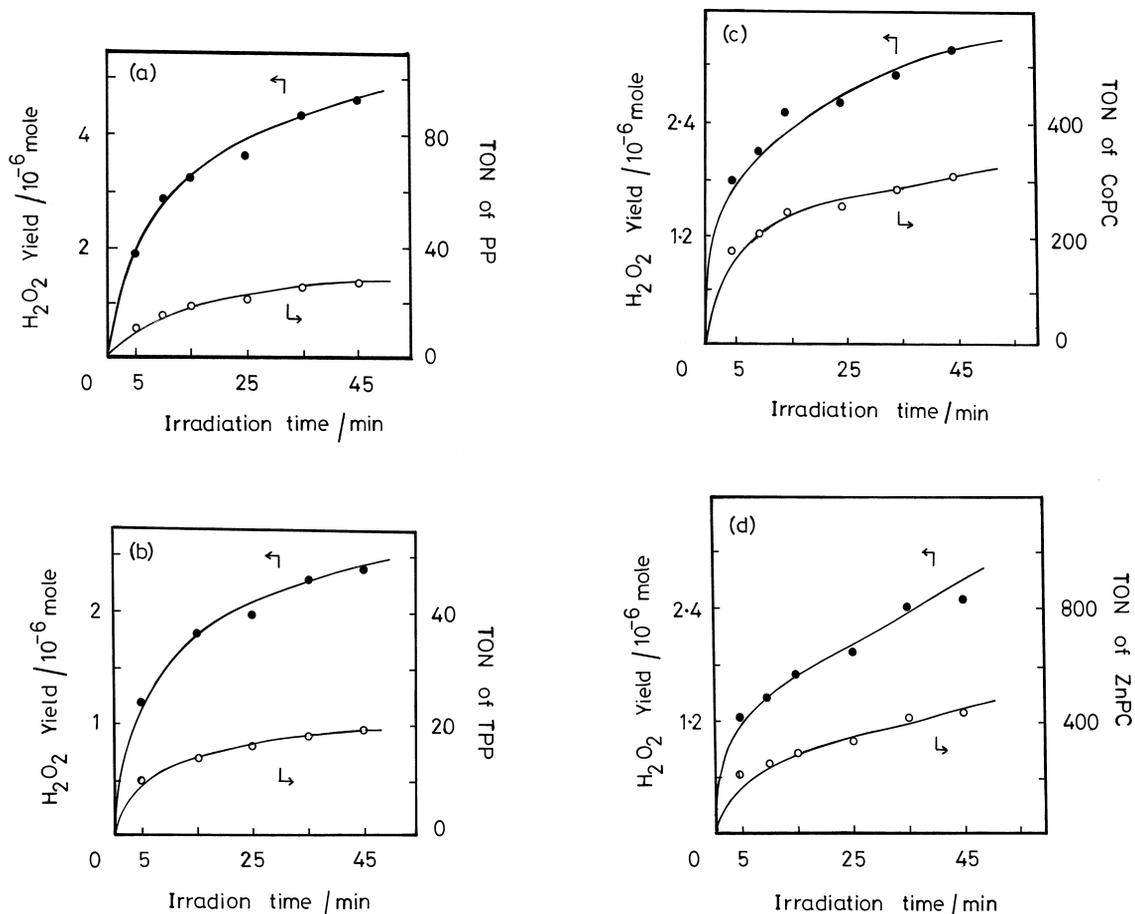
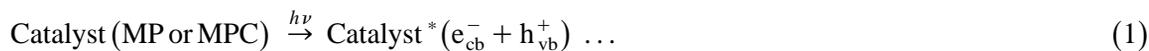


Fig. 3. Yields of H₂O₂ and turnover number (TON) in an oxygen saturated solution containing 0.1 M HClO₄ and 0.1 M TEA of (a) Nf/PP, (b) Nf/TPP, (c) Nf/CoPC and Nf/ZnPC membranes at different light irradiation time. (a) 1.738×10^{-7} mole of HP, (b) 2.386×10^{-8} mole of TPP, (c) 2.046×10^{-8} mole of CoPC and (d) 1.054×10^{-8} mole of ZnPC in Nafion membrane.

systems (Fig. 3) the yield of hydrogen peroxide reached maximum at longer irradiation time. This may due to the decomposition of hydrogen peroxide by the holes [20] of the semiconducting property of MP or MPC molecules. When the same Nf/MP and Nf/MPC membranes were washed and reused in the O₂ reduction experiment similar results (Fig. 3) were obtained. This clearly shows that the membranes are highly stable and active for O₂ reduction. The photocatalytic reactions occurring at MP and MPC adsorbed Nf membranes can be considered as given in Eqs. (1)–(3).



where e_{cb}^- and h_{vb}^+ denote an electron in the conduction band and a positive hole in the valance band of the MP or MPC film, respectively. The TEA acts as a sacrificial electron donor. Porphyrin and phthalocyanine films were relatively well behaved as p-type semiconductors [21,22]. Band edges and interfacial states have been mapped and the nature of the interfacial charge transfer has been discussed in terms of Gerischer's model and modified by inclusion of surface states in the band gap region. Recently, the properties of ZnPC and H₂PC have been illuminated in detail by studying the rectifying properties and photovoltaic effects using phthalocyanine/metal junctions [23]. These materials are p-type semiconductors with a high density of intermediate energy levels. The electrochemical properties of ZnPC and H₂PC electrodes in solution containing different redox couples are therefore predictable, provided the electrode processes are not complicated by additional reactions such as chemisorption.

The p-type character of many MPC films have been taken for granted by several investigators, but the origins of such behavior have not been fully explored. Some reports of the O₂ sensitivity of MPC conductivities and photoconductivities have appeared, as well as the sensitivity of these parameters to the presence of other chemisorbed dopants. The presence of radical oxygen and MPC films have been postulated as the result of the O₂ doping process. For the trivalent-metal MPC's this is confirmed in the studies reported [24]. MPC thin films produced for photoelectrochemical studies as well as for the formation of solid-state photovoltaics are generally deposited in vacuum that are no better than 10⁻⁶ Torr [24]. It is clear from these studies that these conditions can give rise to extensive O₂ incorporation into the MPC film (if substrate temperatures are high enough), which may explain in part the p-type character attributed to these materials.

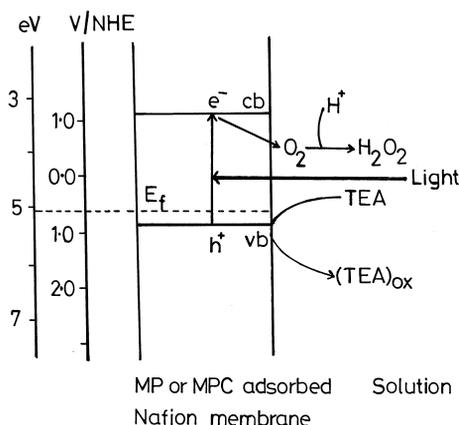
Photoelectrochemical cells in the presence of various redox couples in aqueous solution have been investigated with thin films of metal-free and metal containing phthalocyanines obtained by vapour deposition and spin or drop coating techniques [22]. The interface between the phthalocyanine as molecular semiconductor and the electrolyte forms a junction which is active in photoconversion. Casted film consisting of metal-free phthalocyanine dispersed in a polymer binder exhibits the maximum short-circuit photocurrent with redox couples, whose redox levels are located within the bandgap of the semiconductor. The acceptor O₂ is the most important dopant incorporated into the phthalocyanine films [23]. The presence of the so-formed defect sites is a fundamental prerequisite for a good performance of the phthalocyanines photovoltaic/photoelectrochemical cells and for their electrical conductivity as well as photoconductivity. In the charge carrier generation process (in the bulk of the film), O₂ plays an active role as a dopant of the p-type porphyrin or phthalocyanine film. For MPs and MPCs the width of the band gap in a slip-stack orientation of adjacent molecules is around 2.0 eV [22]. Illumination results in a S₀ → S₁ transition, i.e., formation of MP* and MPC*

located about 0.2 eV below the conduction band edge. The ionized intermediate $MP \cdot^+$ or $MPC \cdot^+$ and O_2^- are formed by electron transfer. In a semiconductor catalyst, the photoexcited electrons in the more negative conduction band have the greater ability to reduce O_2 in solution (Scheme 1).

The TON of ZnPC is higher than the other metal phthalocyanines (Fig. 3). This may be due to the greater interaction of ZnPC with O_2 than the interaction of other MPCs with O_2 . In dioxygen reduction experiment, the ZnPC film coated on ITO (Indium Tin Oxide) electrode showed higher photocurrent for dioxygen reduction than other MPCs in a photoelectrochemical cell [22]. This observation is understood in terms of the axial coordinating capability of ZnPC. The axial coordinating capability of other metals is smaller when compared to Zn. Therefore, the phthalocyanine with Zn as central metal turned out to be the most suitable for the photoreduction of O_2 . The formation of H_2O_2 depends on the intensity of the incident light (I_0). The yields of H_2O_2 obtained at Nf/CoTPP and Nf/ZnPC systems with O_2 saturated solution of 0.1 M $HClO_4$ and 0.1 M TEA using different light intensities at a light irradiation time of 15 min are shown in Fig. 4 and linear plot was obtained.

In photoelectrochemical experiments [22], the metal-free phthalocyanine shows higher dark currents which are slightly enhanced under illumination. The FePC and CoPC are well-known as electrocatalysts for the dioxygen reduction in fuel cell reactions. Their high dark current cannot be improved under illumination. For zinc complex (MP, MPC) yielded a high photocurrent and a high ratio of the current under illumination to that in the dark. This indicates that the influence of the central metal seems to be similar for the studied porphyrin compounds and that the central metal plays an important role in the charge carrier generation and/or in the surface kinetics. Compared to the other ring systems the phthalocyanines exhibited the highest photocurrents.

Nafion membrane provides good regions to the p-conducting porphyrin. The active part for the cathodic photoreduction of O_2 is the porphyrin film in contact with the electrolyte. The strong influence of the central metal on the efficiency of the O_2 photoreduction is explained by the importance of the central metal for the photoelectrical properties in the capability of a porphyrin to O_2 . The reduction of O_2 to H_2O_2 involves two electrons and the redox potential has to be regarded as an average value of two one-step potentials. The O_2 reduction potential is located in the negative region and at higher energy than the MP and MPC valance band edge. No charge transfer seems to be necessary from the MP and MPC films to the solvated species in the bulk solution, but the O_2 reduction product at the Nf membrane would diffuse into the electrolyte solution and will be replaced



Scheme 1. Schematic illustration of photocatalytic reduction of dioxygen at MP or MPC adsorbed Nafion membrane. TEA = triethanolamine, cb = conduction band, vb = valance band and E_f = fermi level.

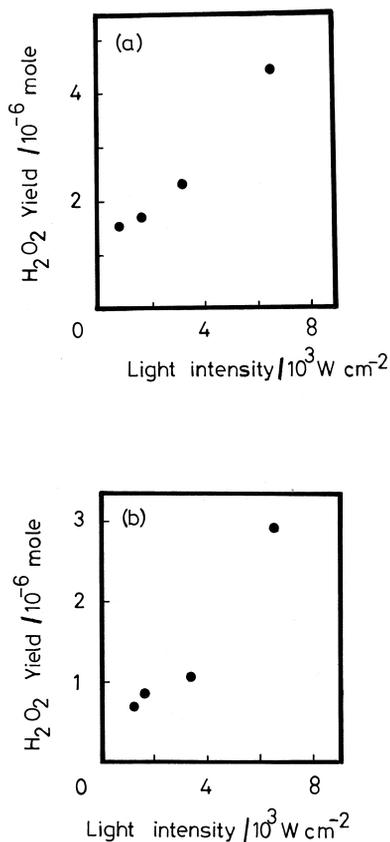
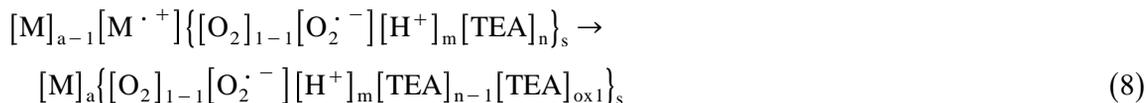
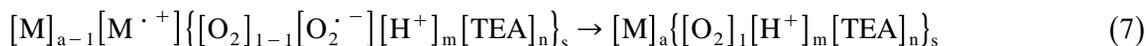
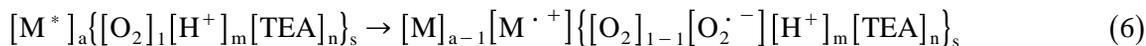
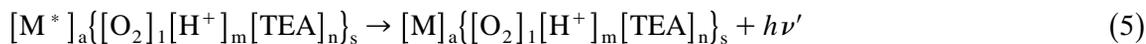
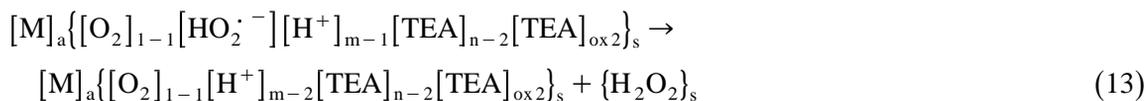
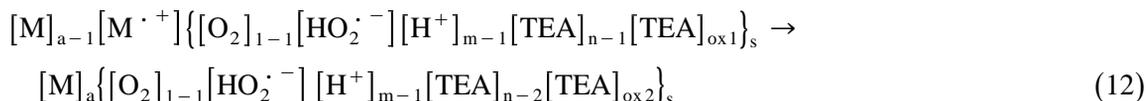
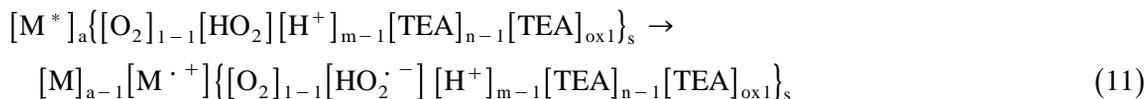
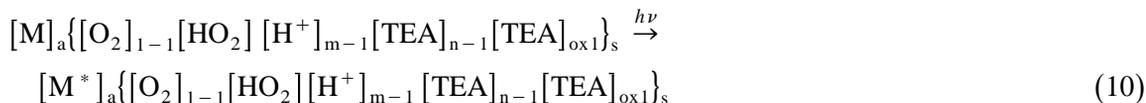
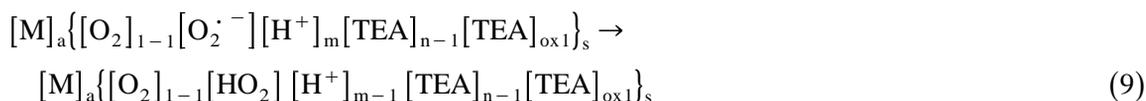


Fig. 4. Yields of H_2O_2 at different light intensity (I_0) in an oxygen saturated solution containing 0.1 M HClO_4 and 0.1 M TEA. (a) Nf/CoTPP and (b) Nf/ZnPC. Light irradiation time = 15 min. Adsorbed amount of CoTPP = 5.631×10^{-8} mole and ZnPC = 1.824×10^{-9} mole.

by O_2 molecules from the solution. The surface states are populated by electrons only under illumination so that the described mechanism works only under illumination of the membrane.

The results are best interpreted by a mechanism in which the reaction of $\text{MP}^{\cdot+}$ or $\text{MPC}^{\cdot+}$ with the electron donor TEA occurs efficiently. Under the conditions employed, the concentration of TEA is sufficiently large and scavenge the holes of $\text{MP}^{\cdot+}$ and $\text{MPC}^{\cdot+}$ efficiently. The main features of the reaction mechanism of the photocatalysed reduction of O_2 are represented by Eqs. (4)–(13).





In these equations, the chemical species written in brackets with subscript ‘a’ represents those adsorbed (MP or MPC) in Nf membrane and ‘s’ represents the species in solution, O_2 , $HClO_4$ and TEA. The subscript ‘1’, ‘m’ and ‘n’ denote the ratios of the average number of O_2 , $HClO_4$ and TEA molecule, respectively in the solution. M, M^* and $M^{\cdot +}$ represents MP or MPC, MP^* or MPC^* and $MP^{\cdot +}$ or $MPC^{\cdot +}$, respectively. $[TEA]_{ox}$ is the oxidised species of triethanolamine. Eqs. (4) and (10) represent the light induced charge separation in the MP or MPC film. Eq. (5) represents the possible process leading to the recombination of e_{cb}^- and h_{vb}^+ . Eqs. (6) and (11) represent the two-step light-induced electron transfer reactions between MP or MPC and O_2 and HO_2 species. Eq. (7) represents the back electron transfer reaction. Eqs. (8) and (12) represent the reduction of h^+ in the MP or MPC film by TEA. Eq. (9) represent the protonation of $O_2^{\cdot -}$ species. Eq. (13) represent the protonation of $HO_2^{\cdot -}$ species and release of H_2O_2 molecules from the reactive site in the membrane. The light induced reaction of O_2 can also be represented as one-step two-electron reduction process.

The Nf membrane plays an important role in the photocatalytic O_2 reduction system. The hydrophobic environment around the MP and MPC imposed by the Nf membrane would allow the molecule to function selectively as catalyst for O_2 reduction and not as catalyst for H^+ reduction which usually takes place predominantly in water. The diffusion of the reacting species (O_2 , H^+ and TEA) from the bulk solution to the membrane is facilitated by the well solvate ionic cluster region of the Nafion membrane. In the present catalytic system, the MPs and MPCs are highly concentrated in the Nf membrane and may form specifically active sites where these complexes are cooperatively involved in the reduction of O_2 molecules. Thus, the photocatalytic reactions occurring at MP and MPC adsorbed Nf membranes appear to take place through the action of the photogenerated carriers i.e., reduction by electrons in the conduction band and oxidation by holes in the valance band. The present work demonstrates the importance of immobilization of the photocatalytic molecules in a solid matrix to realize multielectron transfer process (Scheme 1).

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