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Photocatalytic reduction of carbon dioxide to formic acid at porphyrin and phthalocyanine adsorbed Nafion membranes

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Abstract

The metal porphyrin (MP) and phthalocyanine (MPC) adsorbed Nafion membranes are prepared (Nf/MP and Nf/MPC) and used as photocatalysts for the photoreduction of carbon dioxide (CO_2). The formation of formic acid (HCOOH) is observed when the Nf/MP and Nf/MPC membranes are dipped in CO_2 saturated solution and irradiated in the presence of a sacrificial electron donor such as triethanolamine (TEA). The turnover number of the photocatalysts are very high in the presence of a sacrificial electron donor. The Nf/MP and Nf/MPC membranes behave as a p-type semiconductor. The irradiation of these membranes leads to the formation of holes ($MP^{\cdot +}$ or $MPC^{\cdot +}$) and HCOOH by electron transfer. The TEA acts as sacrificial electron donor and scavenges the holes. © 1997 Elsevier Science S.A.

Keywords: Photocatalysis; Carbon dioxide reduction; Nafion; Porphyrin; Phthalocyanine

1. Introduction

In recent years, the increase of carbon dioxide (CO_2) in the atmosphere has become a global environmental issue because of the serious problems, such as the 'greenhouse effect'. In this context, solar energy conversion by artificial photosynthesis is becoming an increasingly important research subject. The difficulty in creating a non-biological model system for the photoinduced multistep one-electron process lies in the requirement to couple the multielectron reduction of CO_2 with the one-electron chemistry of the redox molecules. The light-induced reduction of CO_2 in an aqueous solution using semiconductor and metal complex photocatalysts has been attempted [1–4]. The electrocatalytic reduction of CO_2 using metal complexes [5–11], metal porphyrins (MPs) and phthalocyanines (MPCs) [12–16] have been studied. Two-electron reduction products, such as carbon monoxide and formate and four- and six-electron reduction products such as formaldehyde and methanol have been reported.

Chlorophyll, being a part of the protein–lipid system, initiates photosynthesis in green plants by accumulating and transferring light energy and electron transfer through the complex photosynthetic system. In artificial photosynthesis, the development of a more efficient photocatalyst in the solid phase/membrane is a promising approach for the photoreduction of CO_2. The catalytic molecules immobilized in a Nafion membrane are particularly advantageous due to their separation from the reaction medium by a microheterogeneous environment and the small amount of catalyst material necessary for reaction. In this paper, we present the results of the photocatalytic reduction of CO_2 using the MP and MPC adsorbed Nf membrane systems.

2. Experimental section

The porphyrins (protoporphyrin (PP), hematoporphyrin (HP), and the phthalocyanines (iron(II)phthalocyanine (FePC), cobalt(II)phthalocyanine (CoPC), Zinc(II)-phthalocyanine (ZnPC)) and Nafion membrane (Nf) (type 125, equiv. wt. 1100, thickness 0.13 mm) were purchased from Aldrich chemical company. The tetraphenylporphyrin (TPP) was purchased from Kokyo Kasei Kogyo Co., Ltd, Japan The cobalt(II)tetraphenylporphyrin (CoTPP) and cobalt(II)porphyrin (CoP) were prepared using reported procedures [17]. 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 [18]. The MP or MPC adsorbed Nf membrane was prepared [19] by dipping

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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 as Nf/PP, Nf/HP, Nf/TPP, Nf/CoTPP, Nf/CoP, Nf/FePC, Nf/CoPC and Nf/ZnPC) was 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 equilibrium [20]. The absorption spectra of MP and MPC in DMF and adsorbed in Nf membrane were recorded using a JASCO 7800 spectrophotometer. The MP or MPC adsorbed Nf membrane was dipped in a CO_2 saturated solution containing TEA and $HClO_4$ using a glass cell with an optical window (volume of the solution was 15 ml) and the membrane was illuminated with a 500 W tungsten–halogen lamp with pyrex glass and water filters to cut-off ultraviolet and infrared radiations. The distance from the centre of the halogen lamp to the surface of the cell was 45 cm. A procedure typical of the kinetic experiment for the formation of HCOOH was employed using the HPLC method [16,21] (Shimadzu, LC-8A modular HPLC system, reverse phase column (ODS), 70% methanol mobile phase) for analysing HCOOH. After irradiation, the chromatograms were obtained by injecting a known amount of the cell solution into the HPLC. At a retention time of 2 min, a formic acid signal was obtained. It was confirmed by injecting the standard formic acid. Pure grade nitrogen and CO_2 gases were used for deaeration and CO_2 saturation purposes. Continuous bubbling of CO_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 microscopy (Hitachi S-450). The porphyrin and phthalocyanine 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. After adsorption, the Nf/MP and Nf/MPC membranes were washed and dried in the dark at room temperature (25°C). The desorption of MP and MPC from the Nf/MP and Nf/MPC membranes was not observed in any rigorous condition, in acid and in neutral solution. 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 the absorption spectra observed for the MP and MPC adsorbed Nf membrane are almost similar to the spectra observed in DMF solution. The Nf membrane consists of a hydrophobic fluorocarbon region, a hydrophillic $-SO_3^-$ ionic cluster region and an inter-

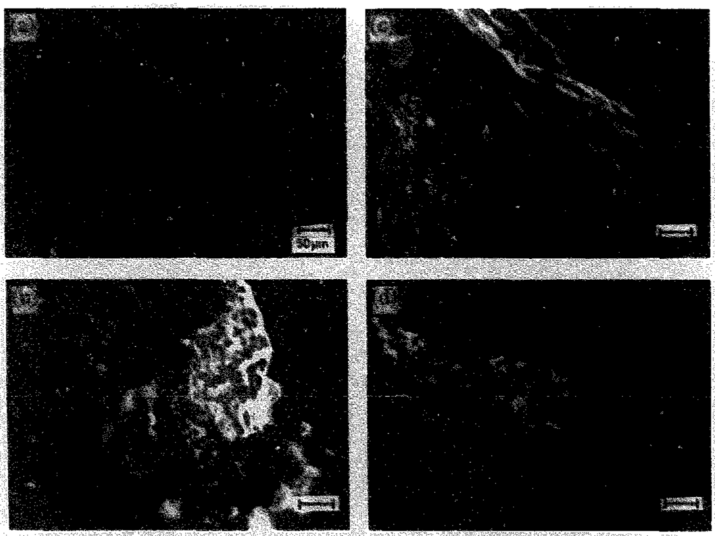


Fig. 1. Scanning electron micrographs of (a) Nf, (b) Nf/PP, (c) Nf/CoTPP and (d) Nf/CoPC.

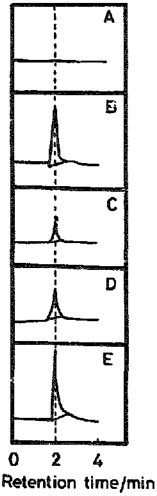


Fig. 2. HPLC detection of formic acid upon irradiation. The membranes dipped in CO_2 saturated solution containing 0.1 M $HClO_4$ and 0.1 M TEA. (A) Nf, (B) Nf/CoTPP, (C) Nf/FePC, (D) Nf/CoPC and (E) standard formic acid.

facial region formed between these two [22]. 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 (SEMs) of the MP and MPC adsorbed Nf membranes are shown in Fig. 1. The SEMs show dark spots on the surface of the MP and MPC adsorbed Nf membranes when compared to a 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) [22] as well as interact with each other in forming a three-dimensional disordered network of a chemically reactive molecule.

Photocatalytic CO_2 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 CO_2 saturated 0.1 M $HClO_4$ and 0.1 M TEA and then irradiated. After 10–100 min irradiation, the cell solution was tested for HCOOH, HCHO and HOOC–COOH by HPLC. HCOOH alone was detected as the CO_2 reduction product. The chromatograms (obtained by HPLC) of HCOOH observed for different MP and MPC adsorbed Nf membranes are shown in Fig. 2. Very similar chromatograms were also observed for Nf/PP, Nf/HP, Nf/TPP and Nf/ZnPC. The retention time of the standard HCOOH was analysed for comparison. The observed retention time of the standard HCOOH (~2

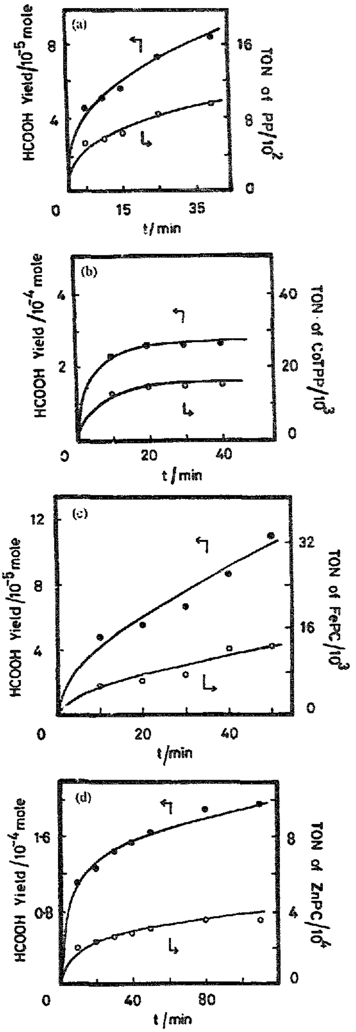


Fig. 3. Yields of formic acid and the corresponding turnover numbers (TONs) of MPs and MPCs in Nf membrane dipped in CO_2 saturated solution containing 0.1 M $HClO_4$ and 0.1 M TEA at different irradiation times. (a) Nf/PP, (b) Nf/CoTPP, (c) Nf/FePC and (d) Nf/ZnPC. Adsorbed amount of porphyrins and phthalocyanines: PP = 1.738×10^{-7}, CoTPP = 3.54×10^{-8}, FePC = 1.774×10^{-8} and ZnPC = 1.054×10^{-8} moles.

min) was the same as observed for the experimental solution showing the formation of HCOOH. When the experiments were carried out in the dark or under illumination using a MP or MPC solution filter to cut off the light in the MP or MPC absorption band region, HCOOH was not detected with any one of the MP or MPC membranes.

The yield of formic acid formed at different light irradiation times using Nf/MP and Nf/MPC membranes were determined and the corresponding turnover numbers (TONs) of MP and MPC are shown in Fig. 3. Very similar results were also observed for Nf/HP, Nf/TPP, Nf/CoP, Nf/CoPC. The TONs of MP and MPC were obtained from the relation 2(mole of formic acid produced)/(mole of MP or MPC adsorbed). In the Nf/MP and Nf/MPC membrane systems (Fig. 3) the yield of formic acid reached a maximum at a longer irradiation time. This may be due to the build up of HCOOH and oxidised TEA species and other secondary reactions. When the same Nf/MP and Nf/MPC membranes were washed and reused in the CO_2 reduction experiment similar results (Fig. 3) were obtained. This clearly shows that the membranes are highly stable and active for CO_2 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.

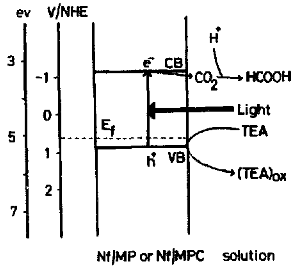
$$\text{Catalyst (MP or MPC)} + h\nu \rightarrow \text{Catalyst}^* \, (e_{cb}^- + h_{vb}^+) \qquad (1)$$

$$\text{oxidation: } 2\,\text{TEA} + 2\,h_{vb}^+ \rightarrow 2\,(\text{TEA})_{ox} \qquad (2)$$

$$\text{reduction: } CO_2 + 2\,e^- + 2\,H^+ \rightarrow HCOOH \qquad (3)$$

The TEA acts as a sacrificial electron donor. Porphyrin and phthalocynaine films were relatively well behaved as p-type semiconductors [23–26]. 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 bandgap region [24]. Recently, the properties of ZnPC and H_2PC have been illuminated in detail by studying the rectifying properties and photovoltaic effects using phthalocynaine/metal junctions [23,27]. These materials are p-type semiconductors with a high density of intermediate energy levels. The electrochemical properties of ZnPC and H_2PC electrodes in solution containing different redox couples are therefore predictable, provided the electrode processes are not complicated by additional reactions such as chemisorption.

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 [28]. The interface between the phthalocynaine as molecular semiconductor and the electrolyte forms a junction which is active in photoconversion. The 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 [28]. The acceptor CO_2 is the most important dopant incorporated into the phthalocyanine films. 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 [29]. In the charge carrier generation process (in the bulk of the film), CO_2 plays an active role as a dopant of the p-type porphyrin or phthalocyanine film. For MPs and MPCs the width of the bandgap in a slip-stack orientation of adjacent molecules is around 2.0 eV. Illumination results in a $S_0 \rightarrow S_1$ transition, i.e. formation of MP* and MPC* located about 0.2 eV below the conduction band edge [23,30]. The ionized intermediates $MP\cdot^+$ or $MPC\cdot^+$ and $CO_2\cdot^-$ are formed by electron transfer. In a semiconductor catalyst, the photoexcited electrons in the more negative conduction band have the greater ability to reduce CO_2 in solution (Scheme 1).



Scheme 1. Schematic illustration of photocatalytic reduction of CO_2 at MP or MPC adsorbed Nafion membrane. MP = PP, HP, TPP, CoTPP, CoP and MPC = FePC, CoPC, ZnPC. TEA = triethanolamine, CB = conduction band, VB = valance band and E_f = Fermi level.

The TON of ZnPC is higher than the other metal phthalocyanines (Fig. 3). This may due to the greater interaction of ZnPC with CO_2 than the interaction of other MPCs with CO_2. In the dioxygen reduction experiment, the ZnPC film coated on an ITO (indium tin oxide) electrode showed a higher photocurrent for dioxygen reduction than other MPCs in a photoelectrochemical cell [23]. 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 [23]. Therefore, the phthalocynaine with Zn as the central metal turned out to be the most suitable for the photoreduction of CO_2.

The reduction of CO_2 to HCOOH involves two electrons and the redox potential has to be regarded as an average value of two one-step potentials. The CO_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 CO_2 reduction product at the Nf membrane would diffuse into the electrolyte solution and will be replaced by CO_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 $MP^{\cdot+}$ or $MPC^{\cdot+}$ with the electron donor TEA occurs efficiently. Under the conditions employed, the concentration of TEA is sufficiently large and scavenges the holes of $MP^{\cdot+}$ and $MPC^{\cdot+}$ efficiently. The main features of the reaction mechanism of the photocatalysed reduction of CO_2 are represented by Eqs. (4)–(8).

$$\begin{aligned}&[\mathrm{M}]_a\{[\mathrm{CO_2}]_l[\mathrm{H^+}]_m[\mathrm{TEA}]_n\}_s\\&\quad\xrightarrow{h\nu}[\mathrm{M^*}]_a\{[\mathrm{CO_2}]_l[\mathrm{H^+}]_m[\mathrm{TEA}]_n\}_s\end{aligned}\qquad(4)$$

$$\begin{aligned}&[\mathrm{M^*}]_a\{[\mathrm{CO_2}]_l[\mathrm{H^+}]_m[\mathrm{TEA}]_n\}_s\rightarrow[\mathrm{M}]_{a-1}[\mathrm{M^{\cdot+}}]\\&\quad\times\{[\mathrm{CO_2}]_{l-1}[\mathrm{CO_2^{\cdot-}}][\mathrm{H^+}]_m[\mathrm{TEA}]_n\}_s\end{aligned}\qquad(5)$$

$$\begin{aligned}&[\mathrm{M}]_{a-1}[\mathrm{M^{\cdot+}}]\{[\mathrm{CO_2}]_{l-1}[\mathrm{CO_2^{\cdot-}}][\mathrm{H^+}]_m[\mathrm{TEA}]_n\}_s\\&\quad\rightarrow[\mathrm{M}]_a\{[\mathrm{CO_2}]_{l-1}[\mathrm{HCO_2}][\mathrm{H^+}]_{m-1}\\&\quad\times[\mathrm{TEA}]_{n-1}[\mathrm{TEA}]_{\mathrm{ox}1}\}_s\end{aligned}\qquad(6)$$

$$\begin{aligned}&[\mathrm{M}]_a\{[\mathrm{CO_2}]_{l-1}[\mathrm{HCO_2}][\mathrm{H^+}]_{m-1}[\mathrm{TEA}]_{n-1}[\mathrm{TEA}]_{\mathrm{ox}1}\}_s\\&\quad\xrightarrow{h\nu}[\mathrm{M}]_{a-1}[\mathrm{M^{\cdot+}}]\{[\mathrm{CO_2}]_{l-1}[\mathrm{HCO_2^{\cdot-}}]\\&\quad\times[\mathrm{H^+}]_{m-1}[\mathrm{TEA}]_{n-1}[\mathrm{TEA}]_{\mathrm{ox}1}\}_s\end{aligned}\qquad(7)$$

$$\begin{aligned}&[\mathrm{M}]_{a-1}[\mathrm{M^{\cdot+}}]\{[\mathrm{CO_2}]_{l-1}[\mathrm{HCO_2^{\cdot-}}]\\&\quad\times[\mathrm{H^+}]_{m-1}[\mathrm{TEA}]_{n-1}[\mathrm{TEA}]_{\mathrm{ox}1}\}_s\\&\quad\rightarrow[\mathrm{M}]_a\{[\mathrm{CO_2}]_{l-1}[\mathrm{H^+}]_{m-2}[\mathrm{TEA}]_{n-2}[\mathrm{TEA}]_{\mathrm{ox}2}\}_s\\&\quad+\{\mathrm{HCOOH}\}_s\end{aligned}\qquad(8)$$

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, CO_2, $HClO_4$ and TEA. The subscript '*l*', '*m*' and '*n*' denote the ratios of the average number of CO_2, $HClO_4$ and TEA molecules, respectively, in the solution. M, M* and $M^{\cdot+}$ represents MP or MPC, MP* or MPC* and $MP^{\cdot+}$ or $MPC^{\cdot+}$ respectively. $[\mathrm{TEA}]_{\mathrm{ox}}$ is the oxidised species of triethanolamine. The light induced reaction of CO_2 can also be represented as a one-step two-electron reduction process. The Nf membrane plays an important role in the photocatalytic CO_2 reduction system. The hydrophobic environment around the MP and MPC imposed by the Nf membrane would allow the molecule to function selectively as a catalyst for CO_2 reduction and not as a catalyst for H^+ reduction which usually takes place predominantly in water. The diffusion of the reacting species (CO_2, H^+ and TEA) from the bulk solution to the membrane is facilitated by the well solvated ionic cluster region of the Nafion membrane [22]. 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 CO_2 molecule. 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 the immobilization of the photocatalytic molecules in a solid matrix to realize a selective multielectron transfer process (Scheme 1).

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