Photoreduction of carbon dioxide by metal phthalocyanine adsorbed Nafion membrane

J. Rajan Premkumar and Ramasamy Ramaraj*

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

Formic acid is photosynthesised from carbon dioxide upon reduction by metal phthalocyanines adsorbed onto a Nafion membrane (photocatalyst) in acidic aqueous solution containing triethanolamine as a hole scavenger.

The rise of carbon dioxide (CO_2) concentration in the atmosphere because of the 'greenhouse effect' has now become a global environmental issue. In this context, the reduction of CO_2 into other useful chemicals has attracted much attention.[1,2] Electrochemical reduction of CO_2 has been reported using modified electrodes[2–4] while its photochemical reduction has been reported using semiconductor colloids[5] and metal complexes[6] in homogeneous solution. The development of more efficient photocatalysts in the solid phase is desirable for the efficient multielectron photoreduction of CO_2. Catalysts immobilized in Nafion membranes are particularly advantageous due to their spatial separation from the solution phase which normally contains very many species. In the present investigation, we have used metal phthalocyanines (MPCs) adsorbed into a Nafion membrane for the photocatalytic reduction of CO_2. The MPC film behaves as p-type material.[7] The dopant/electron acceptor, CO_2, diffuses into the phthalocyanine matrix which is adsorbed in the Nafion membrane. The presence of such defect sites is a fundamental prerequisite for a good performance of the MPC film in photovoltaic/photoelectrochemical cells and for their electrical conductivity as well as photoconductivity.[7,8]

MPCs [cobalt(ii) phthalocyanine (CoPC), zinc(ii) phthalocyanine (ZnPC)] and Nafion membrane (type 115, 1100 equiv. wt., thickness 0.13 mm) were purchased from Aldrich. The Nafion membrane (1 cm^2) was pretreated by boiling in concentrated HNO_3 followed by washing with distilled water.[9] The MPC-adsorbed Nafion membrane was prepared by immersing the membrane in a solution containing a known concentration of CoPC or ZnPC in dmf. Then the MPC-adsorbed Nafion membrane (represented as Nf/CoPC or Nf/ZnPC) was washed and dipped in distilled water. The CoPC and ZnPC were adsorbed irreversibly and the amounts of CoPC and ZnPC adsorbed into the Nafion membrane were determined by measuring the changes in absorbance of CoPC and ZnPC in solution before and after dipping the Nafion membrane.[10] The Nf/MPC membrane was characterized by absorption and emission spectra. Fig. 1 shows the surface morphology of the

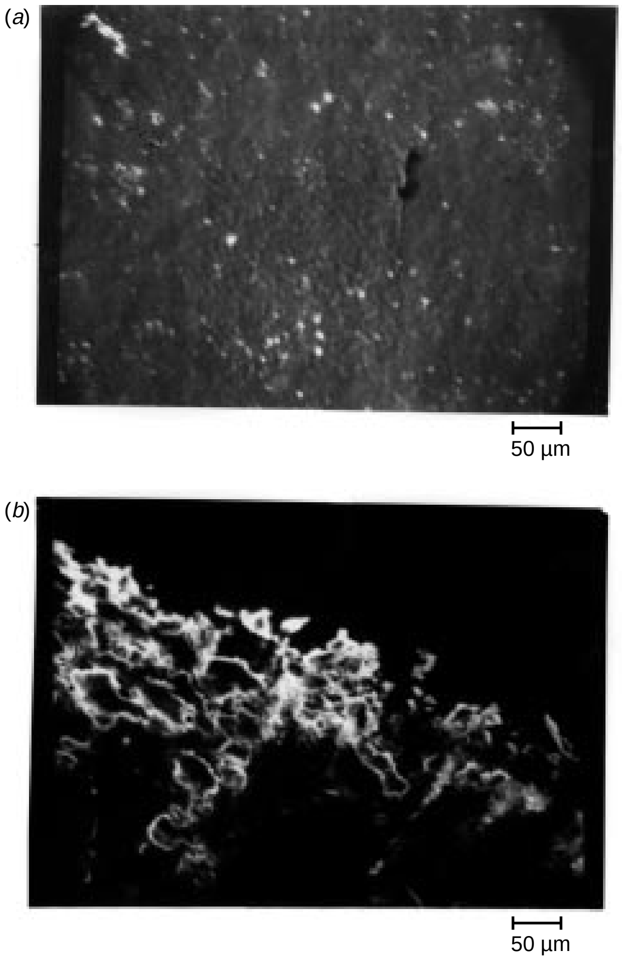


Fig. 1 SEM photographs of (*a*) Nafion and (*b*) Nf/CoPC membranes

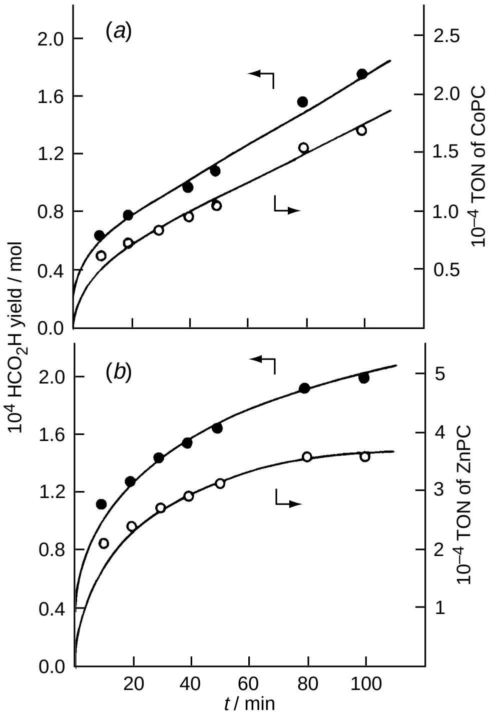


Fig. 2 Yield of formic acid and turnover number (TON) of (*a*) Nf/CoPC and (*b*) Nf/ZnPC (1 cm^2 area Nafion membrane) at different light irradiation times (t). Adsorbed amounts: (*a*) 2.046×10^{-8} mol CoPC and (*b*) 1.057×10^{-8} mol ZnPC.

Nafion and Nf/CoPC membranes recorded using a scanning electron microscope (SEM) (Hitachi S-450). Adsorption of CoPC into the Nafion membrane [Fig. 1(*b*)] is evident when compared to the SEM of a blank Nafion membrane [Fig. 1(*a*)]. The adsorbed CoPC then agglomerates into larger deposits.

The prepared Nf/MPC was used for photocatalytic reduction of CO_2. The Nf/CoPC and Nf/ZnPC were dipped into a photolysis cell containing a CO_2-saturated aqueous solution of triethanolamine (TEA) (0.1 mol dm^{-3}) and $HClO_4$ (0.1 mol dm^{-3}) and then irradiated with visible light. A 500 W tungsten–halogen lamp was used as the light source with a water filter cell (6 cm pathlength with Pyrex glass windows) and a Pyrex-glass filter to cut off IR and UV radiation. The distance between the light source and the Nafion membrane was 40 cm. After 10–100 min of irradiation the cell solution was tested for formic acid, formaldehyde and oxalic acid using HPLC (Shimadzu, LC-8A modular HPLC system, reverse-phase column (ODS), 70% methanol mobile phase) and spectrophotometric methods.[4,11] Formic acid alone was detected as the CO_2 reduction product. The yields of formic acid formed at different light irradiation times at Nf/CoPC and Nf/ZnPC were determined and the corresponding turnover numbers (TONs) of CoPC and ZnPC are shown in Fig. 2. The TONs of MPCs were obtained using the relation 2 × (mol of formic acid produced/mol of MPC in Nafion membrane). The TON of ZnPC was higher than that of CoPC (Fig. 2). This may be due to the greater interaction of ZnPC with CO_2 than that of CoPC with CO_2. The axial coordinating ability of other central metals is relatively lower when compared to ZnPC.[7,12] The experiments were repeated several times and reproducible results were obtained. The Nf/MPC membrane was found to be very stable for weeks and was reused in the experiments.

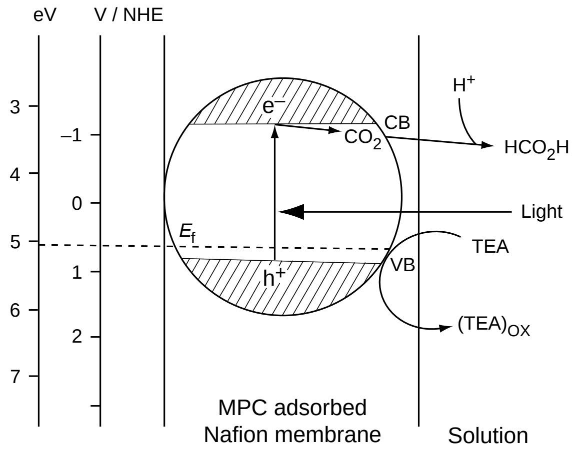
In the absence of any one of the reaction components (visible light, MPC, TEA, H^+ and CO_2) formic acid was not observed. The p-type semiconductor nature of MPC film has already beenreported[7,8] and the probable photocatalytic reactions are given below [eqns. (1)–(3)]:

$$\mathrm{MPC} + h\nu \longrightarrow \mathrm{MPC^*}\ (e^-_{CB} + h^+_{VB}) \tag{1}$$

$$2\ \mathrm{TEA} + 2\ h^+_{VB} \longrightarrow 2\ (\mathrm{TEA})_{ox} \tag{2}$$

$$CO_2 + 2\ e^-_{CB} + 2\ H^+ \longrightarrow HCO_2H \tag{3}$$

where e^-_{CB} and h^+_{VB} denote an electron in the conduction band and a positive hole in the valence band of the Nf/MPC system, respectively.



Scheme 1 Schematic illustration of the photocatalytic reduction of carbon dioxide at MPC adsorbed in a Nafion membrane. The circle describes the semiconducting nature of the adsorbed MPC Nafion membrane. MPC = CoPC or ZnPC, TEA = triethanolamine, CB = conduction band, VB = valence band and E_F = Fermi level.

In the bulk of the Nf/MPC film, CO_2 plays an active role as a dopant of the p-type phthalocyanine. For MPCs, in the intrinsic case, the width of the bandgap in a slip-stack orientation of adjacent molecules is *ca.* 2.0 eV.[8] Light irradiation results in an $S_0 \rightarrow S_1$ transition, *i.e.* the formation of MPC* located about 0.2 eV below the conduction band edge. The ionized intermediates $MPC^{\cdot+}$ and $CO_2^{\cdot-}$ are formed by electron transfer. It is assumed that 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). It is also reasonable to assume that the field in the microenvironmental sites as well as the highly acidic nature of the Nafion membrane[13,14] accelerate further the CO_2 reduction process. Investigations on the role of the MPC catalyst in the Nafion membrane in the selective production of formic acid by CO_2 reduction are under way.

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References

1 P. Braunstein, D. Matt and D. Nobel, *Chem. Rev.*, 1988, **88**, 747.
2 T. Yoshida, K. Kamato, M. Tsukamoto, T. Iida, D. Schlettwein, D. Wohrle and M. Kaneko, *J. Electroanal. Chem.*, 1995, **385**, 209 and references therein.
3 M. N. Mahmood, D. Masheder and C. J. Harty, *J. Appl. Electrochem.*, 1987, **17**, 1159.
4 J. R. Pugh, M. R. M. Bruce, B. P. Sullivan and T. J. Meyer, *Inorg. Chem.*, 1991, **30**, 86.
5 S. Kuwabata, H. Uchida, A. Ogawa, S.Hirao and H. Yoneyama, *J. Chem. Soc., Chem. Commun.*, 1995, 829 and references therein.
6 H. Hori, F. P. A. Johnson, K. Koike, O. Ishitani and T. Ibusuki, *J. Photochem. Photobiol. A: Chem.*, 1996, **96**, 171 and references therein.
7 J. J. Simon and J. J. Andre, *Molecular Semiconductors*, Springer-Verlag, Berlin, 1985.
8 D. Schlettwein, M. Kaneko, A. Yamada, D. Wohrle and N. I. Jeager, *J. Phys. Chem.*, 1991, **95**, 1748.
9 F. R. Fan, H. Y. Liu and A. J. Bard, *J. Phys. Chem.*, 1985, **89**, 4418.
10 B. D. Berezin and V. G. Vopion, *Coordination Compounds of Porphyrins and Phthalocyanines*, Wiley, New York, 1981.
11 T.Yoshida, K. Tsutsumida, S. Teratani, K. Yasufuku and M. Kaneko, *J. Chem. Soc., Chem. Commun.*, 1993, 631.
12 P. Day and R. J. P. Williams, *J. Chem. Phys.*, 1962, **37**, 567.
13 *Perfluorinated Ionomer Membranes*, ed. A. Eisenberg and H. L. Yeager, ACS Symposium Series 180, American Chemical Society, Washington, 1982.
14 G. A. Olah, G. K. Prakash and J. Sommer, *Super Acids*, Wiley-Interscience, New York, 1985.

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