

Photoreduction of nitrite to ammonia by metal phthalocyanines-adsorbed Nafion membrane

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The metal phthalocyanines (MPCs)-adsorbed Nafion (Nf) membranes (Nf/MPCs) are prepared and used for the photocatalytic reduction of nitrite ion. The selective formation of NH_4OH is observed when the Nf/MPC membrane is dipped in nitrite ion solution and photolysed in the presence of sacrificial electron donor such as triethanolamine (TEA). The Nf/MPC membranes behave as *p*-type semiconductors. The photosensitized reaction mechanism of the photocatalytic reduction of NO_2^- to NH_4^+ formation is explained by the reaction of the e_{cb}^- with nitrite ion and the hole (h_{vb}^+) with TEA.

THE reduction of nitrite ion (NO_2^-) is of broad interest as a means of mimicking reduction processes of nitrogen compounds in nature, and of developing novel nitrogen fixation systems^{1,2}. Reduction of nitrite ion to ammonia (as ammonium ion) is catalysed by the enzyme nitrite ion reductase³. Substantial efforts are directed towards the reduction of nitrite by electrochemical^{4,5} and photochemical methods^{6,7}. However, the metal phthalocyanines (MPCs) are not used as photocatalyst for nitrite ion reduction. Catalysts immobilized in a membrane are particularly advantageous due to their separation from the solution phase (solid–solution interface)⁸. It is important

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to note that the MPC films behave as *p*-type semiconducting material^{9,10}. Recently, we have shown that the MPC-adsorbed Nafion (Nf) membranes (Nf/MPC membranes) act as photocatalysts for the selective reduction of carbon dioxide and oxygen¹¹⁻¹³. In the present investigation, we have succeeded in reducing nitrite ion to ammonia (NH₄OH) using MPCs (cobalt (II) phthalocyanine, CoPC; iron (II) phthalocyanine, FePC; and zinc (II) phthalocyanine, ZnPC)-adsorbed Nf membranes as photocatalyst in aqueous solution.

The Nf membrane (type 115, 1100 eq. wt, thickness 0.13 mm) and MPCs (CoPC, FePC and ZnPC) were purchased from Aldrich. Triethanolamine (TEA) and dimethyl formamide (DMF) were purchased from Merck. The Nf membrane (1 cm²) was pretreated by boiling in concentrated HNO₃ and washing with distilled water¹⁴. The Nf/MPC membrane was prepared by immersing the Nf membrane in a solution containing known concentration of MPC in DMF. The Nf/MPC Nf membranes (i.e. Nf/CoPC, Nf/FePC and Nf/ZnPC) were then washed with distilled water. The MPCs were adsorbed irreversibly and the amount of MPCs adsorbed in the Nf membrane was determined by measuring the change in absorbance of MPCs in solution before and after dipping the Nf membrane. The reported molar extinction coefficient values of the MPCs¹⁵ were used to calculate the concentration of the complexes. The adsorption of MPC into Nf membrane was characterized by UV-visible absorption spectra (JASCO 7800 spectrophotometer). 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 Nf membrane was ca. 40 cm. Pure-grade nitrogen gas was used for deaeration of the cell solutions. The Nf/MPC membranes were stable for weeks, stored in dark and were reused in repeated experiments. All the experiments were carried out at room temperature (25°C).

Figure 1 shows the UV-visible absorption spectrum of ZnPC in Nf membrane. The ZnPC in Nf membrane shows a similar spectrum to that in DMF solution (see Figure 1). This result shows that the absorption spectral properties of MPCs are not significantly influenced by the Nf membrane (see Figure 1). Similar results were also obtained for CoPC and FePC in DMF and in Nf membrane. The Nf membrane consists of hydrophobic fluorocarbon region, hydrophilic-SO₃⁻ ionic cluster region and the interfacial region formed between these two¹⁶. The MPC molecules will mostly occupy the interfacial and hydrophobic regions of the Nf membrane. The Nf/CoPC, Nf/FePC or Nf/ZnPC membrane was used for the photocatalytic reduction of nitrite ion. The membrane was dipped into a photolysis cell with deaerated solution containing sodium nitrite (1 mol dm⁻³), sodium hydroxide (1 mol dm⁻³) and TEA (0.1 mol dm⁻³) and then irradiated with visible light. After irradiation, the cell solution

was tested for ammonia, hydroxylamine and hydrazine¹⁷. Only ammonia was identified as the nitrite-ion reduction product. The concentration of ammonia was determined by adding Nessler's reagent to the test solution and the absorption of the solution was measured in the 400–430 nm wavelength range¹⁸. The samples for analysis were obtained by interrupting the photochemical process at intervals for several seconds and transferring 1 ml of the solution to a 5 ml standard measuring flask (smf). Then 0.5 ml of freshly prepared Nessler's reagent¹⁹ was added to the smf, and the solution was made up to a volume of 5 ml with water. A calibration curve was obtained by dissolving a standard amount of ammonium chloride in water and using Nessler's reagent¹⁸.

In the absence of any one of the reaction components (visible light, MPCs, NaNO₂ and TEA), NH₄OH was not observed in the photocatalytic process using Nf/MPC membranes. In homogeneous solution, the photocatalytic system showed negligible yield of NH₄OH. The amount of ammonia (as NH₄OH) formed at different light irradiation time using Nf/CoPC, Nf/FePC and Nf/ZnPC membranes was determined. The corresponding turnover numbers (TONs) of the CoPC, FePC and ZnPC are shown in Figure 2. The TONs of CoPC, FePC and ZnPC were obtained from the relation: [6 × (mol of NH₄OH produced/mol of CoPC or FePC or ZnPC adsorbed in the Nf membrane)]. The TON of MPC is estimated to be

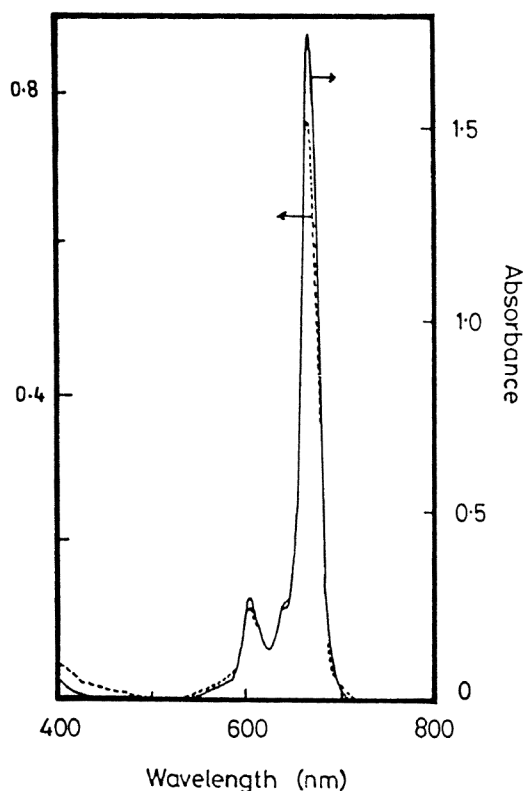


Figure 1. UV-visible absorption spectrum of ZnPC adsorbed in Nf membrane (-----) and ZnPC in DMF (—).

~ 4–8 by assuming that the total amount of MPC present in the whole of the membrane is involved in the photocatalytic reduction of nitrite ion. However, in the photocatalytic process, only the irradiated MPC molecules present in and nearby the interface between the membrane and solution could involve in the reaction efficiently, than the bulk species in the membrane. Hence, the effective TON of MPC for the production of NH_3 should be higher when compared to the directly calculated TON. Experiments were carried out with different

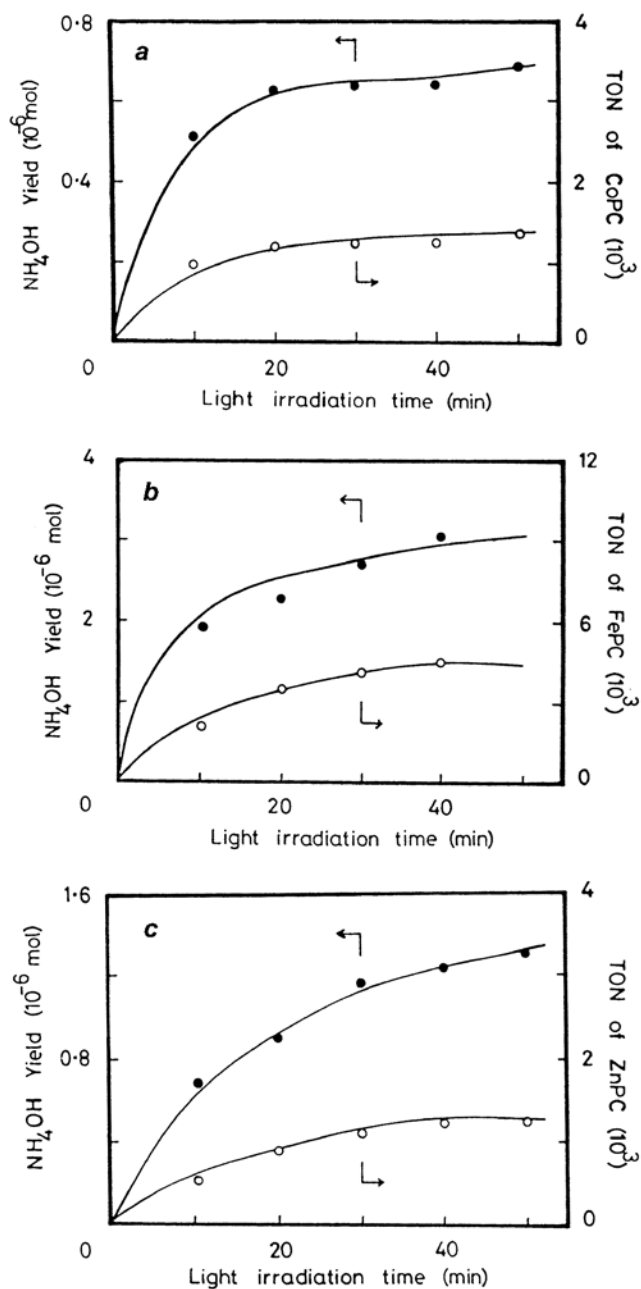
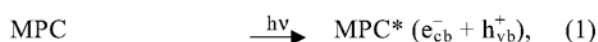


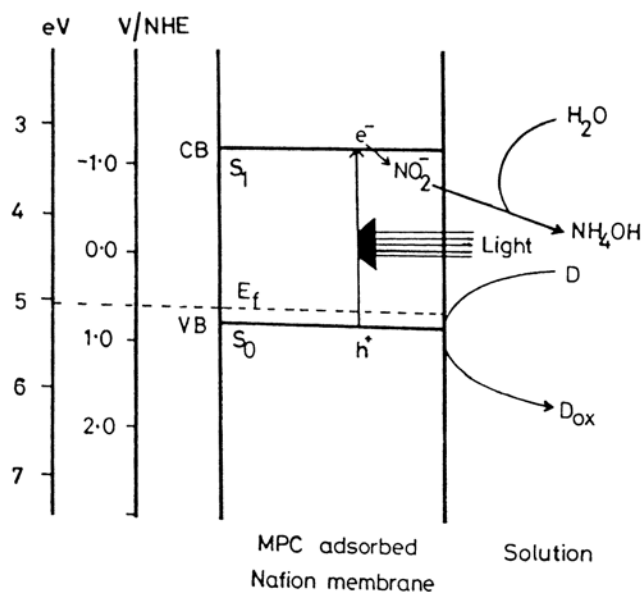
Figure 2. Amount of NH_4OH and turnover number (TON) of (a) Nf/CoPC, (b) Nf/FePC and (c) Nf/ZnPC membranes at different light irradiation time. Adsorbed amount of MPC: a, 3.122×10^{-9} mol of CoPC; b, 4.013×10^{-9} mol of FePC; and c, 6.307×10^{-9} mol of ZnPC.

amounts of adsorbed CoPC, FePC and ZnPC into the Nf membrane, and the Nf/CoPC, Nf/FePC and Nf/ZnPC membranes which showed maximum amount of NH_4OH , were used for detailed studies. In the Nf/MPC membrane system, the amount of NH_4OH reached maximum at longer time of irradiation (Figure 2). This may be due to the build-up of NH_4OH and other secondary reactions of NH_4OH , and the oxidized products of TEA under the experimental conditions, at longer times of irradiation. However, when the same Nf/MPC membranes were washed and reused in the nitrite-ion reduction experiment, similar results were obtained in repeated trials. The experiments were repeated and reproducible results were obtained. The Nf/CoPC, Nf/FePC and Nf/ZnPC membranes were found to be stable for weeks and were reused in the experiments. The *p*-type semiconducting nature of the MPC films has already been reported^{9,10}. The photocatalytic reactions at the heterogeneous photocatalytic system are considered as given in eqs (1–3).



The e_{cb}^- and h_{vb}^+ denote an electron in the conduction band and a positive hole in the valance band of the irradiated Nf/MPC membrane system respectively. TEA acts as a sacrificial electron donor.

Phthalocyanine films are relatively well behaved as *p*-type semiconductors^{9,10}. The band edges and interfacial states have been mapped; the nature of the interfacial



Scheme 1. Photocatalytic reduction of nitrite in Nf/MPC membrane. MPC, CoPC, FePC or ZnPC; CB, Conduction band; VB, Valance band; D, TEA, and E_f , Fermi level.

charge transfer has been discussed in terms of Gerischer's model and modified by inclusion of surface states in the band-gap region. In the bulk of the Nf/MPC film, nitrite ion plays an active role as a dopant of the *p*-type MPC films. For MPC films, in the intrinsic case, the width of the band gap in a slip-stack orientation of adjacent molecules is around 2.0 eV (ref. 10). Light irradiation results in a $S_0 \rightarrow S_1$ transition, i.e. the formation of MPC* located about 0.2 eV below the conduction band-edge. It is assumed that in a semiconductor, the photoexcited electrons in the more negative conduction band have a greater ability to reduce the nitrite ion (Scheme 1). TEA acts as a hole scavenger. It is also reasonable to assume that the field in the microenvironmental site of the Nf membrane¹³ will accelerate the multi-electron nitrite-reduction process.

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