between the conduction band (CB) and FL decreases upon adsorption of BH₄⁻ ion which caused a lowering of reduction potential in the metal. As the reduction potential becomes lower and lower, the metal system increasingly becomes vulnerable to oxidation. If the reduction potential value crosses that of the O₂/O₂⁻ (E° = + 0.4 V vs NHE) system (this happens in the case of silver in NaBH₄), then the metal could easily be oxidized by O₂.

Under the experimental condition the added NaBH₄ has two-fold action: it reduces silver ion and it lowers the reduction potential of the metal (if produced in situ or already present in the system), upon adsorption onto the metal surface. The redox reaction for silver dissolution can be written as 4Ag⁺ + O₂ + 2H₂O = 4Ag^- + 4OH⁻.

On the same ground, gold wire (0.2 cm dia and 6 cm in length) is oxidized by I₂/SCN⁻ or I₂/I⁻ (E° = + 0.54 V vs NHE) system in a beaker containing 50 ml saturated aqueous solution of I₂ along with 0.2 g KSCN or KI. A comparative kinetic study showed that I₂/I⁻ or I₂/SCN⁻ system dissolves gold more rapidly than the frequently used O₂/CN⁻ system. The micelle does not only the scavenging job, i.e. removes the oxidized metal layer (produced by the oxidant in the presence of a nucleophile) from the metal surface. In doing so, the micelle always freshens the metal surface and the clean metal surface is corroded by the oxidants O₂ or I₂. Thus the dissolution of silver or gold is observed in aqueous micellar phase in the presence of a suitable nucleophile. The reversible generation of silver and gold nanoparticles may be exploited for the study of catalysis⁶,⁷.

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

Malaichamy Ilanachelian, J. Rajan Premkumar and Ramasamy Ramaraj*
School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India

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 NH₄OH is observed when the NF/MPC membrane is dipped in nitrite ion solution and photolyzed 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 NO₂⁻ to NH₄⁺ formation is explained by the reaction of the e⁻, with nitrite ion and the hole (h⁺) with TEA.

The reduction of nitrite ion (NO₂⁻) is of broad interest as a means of mimicking reduction processes of nitrogen compounds in nature, and of developing novel nitrogen fixation systems³. Reduction of nitrite ion to ammonia (as ammonium ion) is catalysed by the enzyme nitrite ion reductase⁵. Substantial efforts are directed towards the reduction of nitrite by electrochemical⁴ and photochemical methods⁵. 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)⁶. It is important

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*For correspondence. (e-mail: ramaraj@yahoo.com)
to note that the MPC films behave as p-type semiconducting material\(^{10}\). 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 oxygen\(^{11-13}\). In the present investigation, we have succeeded in reducing nitrite ion to ammonia (NH\(_2\)OH) using MPCs (cobalt (II) phthalocyanine, CoPC; iron (II) phthalocyanin, 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 cm\(^2\)) was pretreated by boiling in concentrated HNO\(_3\) and washing with distilled water\(^{14}\). The NF/DMF 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 MPCs\(^{15}\) 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–SO\(_2\) ionic cluster region and the interfacial region formed between these two\(^{16}\). 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 hydrazine\(^{17}\). 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 range\(^{18}\). The samples for analysis were obtained by interrupting the photocatalytic 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 reagent\(^{19}\) 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 reagent\(^{18}\).

In the absence of any one of the reaction components (visible light, MPCs, NaNO\(_2\) and TEA), NH\(_2\)OH was not observed in the photocatalytic process using NF/MPC membranes. In homogeneous solution, the photocatalytic system showed negligible yield of NH\(_2\)OH. The amount of ammonia (as NH\(_2\)OH) 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 NH\(_2\)OH produced/mol of CoPC or FePC or ZnPC adsorbed in the NF membrane)]. The TON of MPC is estimated to be

\[ \text{Figure 1. UV–visible absorption spectrum of ZnPC adsorbed in NF membrane (-----) and ZnPC in DMF (-----).} \]

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~ 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 NH₃ should be higher when compared to the directly calculated TON. Experiments were carried out with different 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 NH₄OH, were used for detailed studies. In the NF/MPC membrane system, the amount of NH₄OH reached maximum at longer time of irradiation (Figure 2). This may be due to the build-up of NH₄OH and other secondary reactions of NH₄OH, 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.¹⁰ The photocatalytic reactions at the heterogeneous photocatalytic system are considered as given in eqs (1–3).

\[
\text{MPC} \xrightarrow{\text{hv}} \text{MPC}^* \left( e_{cb}^+ + h_{vb}^- \right), \quad (1)
\]

\[
\text{NO}_2^- + 6e_{cb}^+ + 5\text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH} + 6\text{OH}^- \quad (2)
\]

\[
\text{TEA} + h_{vb}^- \rightarrow (\text{TEA})_{ox}, \quad (3)
\]

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.¹⁰ The band edges and interfacial states have been mapped; the nature of the interfacial

**Figure 2.** Amount of NH₄OH 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, \(3.122 \times 10^{-7}\) mol of CoPC; b, \(4.013 \times 10^{-7}\) mol of FePC; and c, \(6.307 \times 10^{-7}\) mol of ZnPC.

**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.
Study on pinocytosis by monocytes from visceral leishmaniasis patients

Promod Kumar†, Kalpana Paî, Haushila P. Pandey† and Shyam Sundar†,**
†Department of Biochemistry, Faculty of Science, and ‡Department of Medicine, Institute of Medical Sciences, Banaras Hindu University, Varanasi 221 005, India

In the present study, we report that monocytes obtained from active visceral leishmaniasis (VL) patients show low rate of pinocytosis compared to that of healthy controls. Several studies have suggested that any change in pinocytic activity reflects changes in the functional state of the cell. In the present study we have evaluated pinocytosis by monocytes obtained from patients with VL. A reduced pinocytic activity by monocytes from active VL patients was observed in comparison to healthy controls. Our study suggests that reduced pinocytic rate by monocytes in active VL infection reflects down-regulation of macrophage activation or functional state.

*LEISHMANIA* parasites infect exclusively macrophages of the mammalian hosts and subsequently live in the phagolysosomes of these cells. In view of such myriad immune evasion mechanisms of parasites, one might wonder how it is possible for host immunity to contain and resolve parasitic infections. Resolution of infection requires that the host generate an immune response with a cellular (T-cell) component such that activation of macrophages occurs. Analysis of the development of activation was facilitated when the operationally defined stage of activation was characterized using a library of objective markers.

Among the most characteristic properties of monocytes and macrophages is the capacity of these cells to take up large volumes by fluid-phase pinocytosis, and to ingest microbes and other particles by phagocytosis. Phagocytosis and pinocytosis require similar changes in the actin cytoskeleton, and both processes are sensitive to certain dominant negative mutants of the small ras-like GTPase of the Rho family, and are blocked by inhibitor phospho-phosphatase-30-kinase activity. Fluid-phase pinocytosis by macrophage is a constitutive process.

Our earlier studies on state of macrophage activation in active visceral leishmaniasis (VL) patients showed reduced arginase, S'-nucleotidase, lysozyme, NADH-oxidase, NADPH-oxidase and myeloperoxidase levels (unpublished observations) in monocytes. This prompted us to study pinocytic activity of monocytes from active VL patients and healthy controls. Though the importance of internalization is still unclear, immunological experi-

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