

Photocatalytic reduction of carbon dioxide by immobilized nickel(II) and ruthenium(II) complexes into a Nafion membrane

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Identifying suitable catalysts for selective reduction of molecules to form useful chemical compounds is very interesting. A very stable and reproducible catalytic system was prepared by immobilizing macrocyclic nickel(II) and tris(2,2'-bipyridine)ruthenium(II) complexes into a Nafion membrane and was used to achieve selective reduction of carbon dioxide to formic acid.

THE development of photocatalytic systems based on molecular systems for photochemical reduction of carbon dioxide has attracted much attention in recent years¹⁻⁴. Reports on the photoreduction of carbon dioxide catalysed by semiconductors and transition metal complexes have provided an outlook into the photochemical fixation of carbon dioxide in the solution system¹⁻⁶. The search for more selective and probably more sophisticated catalysts is a challenging task. For efficient charge separation of the high energy photoproducts in homogeneous solution, the energy wasting back reaction in a photoredox system should be prevented. To overcome this problem, micro-/macro-heterogeneous reaction environments (micelles, vesicles, micro-emulsion, liposome, Nafion, clay and zeolites) have been used⁷⁻¹¹. Here we describe the utilization of tris(2,2'-bipyridine)ruthenium(II) ion, ($[\text{Ru}(\text{bpy})_3]^{2+}$) and macrocyclic nickel(II) complex, ($[\text{Ni}(\text{teta})]^{2+}$, teta = 5, 5, 7, 12, 12, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradecane) incorporated in a Nafion membrane to realize efficient two-step one-electron transfer photoreduction of carbon dioxide to formic acid.

The $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ni}(\text{teta})]^{2+}$ complexes were prepared according to literature procedures^{12,13}. The Nafion membrane obtained from Aldrich (Nafion 117, perfluorinated membrane, equiv. wt. 1100 and 0.07 inch thickness) was pretreated¹⁴ prior to use by boiling in concentrated nitric acid for about 10 to 20 min and after washing it became clear and transparent. The $[\text{Ni}(\text{teta})]^{2+}$ complex was incorporated into a 1 cm² Nafion membrane by dipping the membrane in an aqueous solution containing a known concentration of $[\text{Ni}(\text{teta})]^{2+}$. The membrane (represented as Nf/ $[\text{Ni}(\text{teta})]^{2+}$) was washed and dipped in distilled water. The $[\text{Ni}(\text{teta})]^{2+}$ complex was adsorbed irreversibly

and the amount of $[\text{Ni}(\text{teta})]^{2+}$ complex adsorbed into the Nafion membrane was determined by measuring the decrease in the absorbance of $[\text{Ni}(\text{teta})]^{2+}$ ($\lambda_{\text{max}} = 460 \text{ nm}$, $\epsilon_{460} = 40 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in the solution after dipping. The $[\text{Ni}(\text{teta})]^{2+}$ complex-adsorbed Nafion membrane was then dipped in an aqueous solution containing a known concentration of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex and then washed with distilled water (represented as Nf/ $[\text{Ni}(\text{teta})]^{2+}$ / $[\text{Ru}(\text{bpy})_3]^{2+}$). The $[\text{Ru}(\text{bpy})_3]^{2+}$ complex was also adsorbed irreversibly and the amount of $[\text{Ru}(\text{bpy})_3]^{2+}$ adsorbed in the Nf/ $[\text{Ni}(\text{teta})]^{2+}$ / $[\text{Ru}(\text{bpy})_3]^{2+}$ membrane was determined by measuring the decrease in the absorbance of $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\lambda_{\text{max}} = 452 \text{ nm}$, $\epsilon_{452} = 14600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in solution after dipping. The absorption spectra recorded for the Nf/ $[\text{Ni}(\text{teta})]^{2+}$ and Nf/ $[\text{Ru}(\text{bpy})_3]^{2+}$ membranes are shown in Figure 1. To measure the absorption spectra of metal complex-incorporated Nafion membrane, the transparent naked Nafion membrane was used as reference. The absorption spectra recorded for Nf/ $[\text{Ni}(\text{teta})]^{2+}$ (Figure 1 b) and Nf/ $[\text{Ru}(\text{bpy})_3]^{2+}$ (Figure 1 a) are very similar to the reported spectra of $[\text{Ni}(\text{teta})]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes in aqueous solution. The concentrations of $[\text{Ni}(\text{teta})]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes were checked before and after dipping the Nf/ $[\text{Ni}(\text{teta})]^{2+}$ membrane in the $[\text{Ru}(\text{bpy})_3]^{2+}$ solution. In the concentration range em-

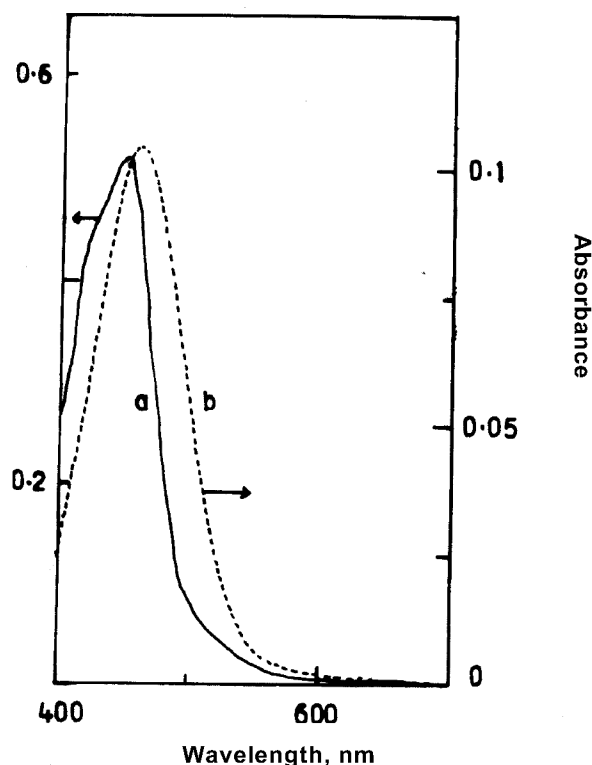


Figure 1. Absorption spectra of Nf/ $[\text{Ru}(\text{bpy})_3]^{2+}$ (a) and Nf/ $[\text{Ni}(\text{teta})]^{2+}$ (b) in the membrane state.

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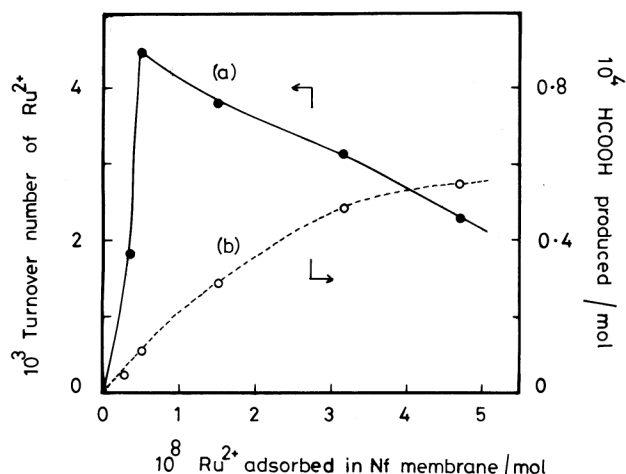


Figure 2. (a) Turnover numbers of $[\text{Ru}(\text{bpy})_3]^{2+}$ and (b) amounts of HCOOH observed for the Nf/ $[\text{Ni}(\text{teta})]^{2+}/[\text{Ru}(\text{bpy})_3]^{2+}$ membrane (1 cm^2) dipped in carbon dioxide saturated $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ and $0.1 \text{ mol dm}^{-3} \text{ TEA}$. pH of the experimental solution = 1.5. Irradiation time = 15 min. Amount of $[\text{Ni}(\text{teta})]^{2+}$ in the Nafion membrane = $3.75 \times 10^{-6} \text{ mol}$.

ployed, the sum of absorbances of adsorbed $[\text{Ni}(\text{teta})]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes measured from the respective solutions was equal to the additive absorbances of $[\text{Ni}(\text{teta})]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes in the Nafion membrane (absorption spectra not shown). Yeager and Steck¹⁵ proposed a three-phase structure for the Nafion membrane comprising a hydrophobic fluorocarbon phase, a $-\text{SO}_3^-$ ionic cluster region and an interfacial region formed between these two. It has been shown^{16,17} that the cationic molecules have not only ion-exchanged into the $-\text{SO}_3^-$ ionic cluster region by electrostatic interaction but also hydrophobic interaction with the Nafion film. The electrostatic and hydrophobic interactions of the metal complexes with the Nafion membrane are responsible for the irreversible binding of the metal complexes.

The Nf/ $[\text{Ni}(\text{teta})]^{2+}/[\text{Ru}(\text{bpy})_3]^{2+}$ membrane was used for the photocatalytic reduction of carbon dioxide. The Nf/ $[\text{Ni}(\text{teta})]^{2+}/[\text{Ru}(\text{bpy})_3]^{2+}$ was dipped into a photolysis cell containing carbon dioxide saturated 0.1 mol dm^{-3} perchloric acid (HClO_4) and 0.1 mol dm^{-3} triethanolamine (TEA) 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 radiations. The distance between the light source and the Nafion membrane was 40 cm. After 15 min of irradiation, the cell solution was tested^{18,19} for formaldehyde, formic acid and oxalic acid using the HPLC method (Shimadzu, LC-8A modular HPLC system, reverse phase). Only formic acid (HCOOH) was identified as the carbon dioxide reduction product. After irradiation, the chromatogram was obtained by injecting a known amount of the cell solution into the HPLC. At

a retention time of 2 min, the formic acid signal was obtained. It was confirmed by injecting standard formic acid solution.

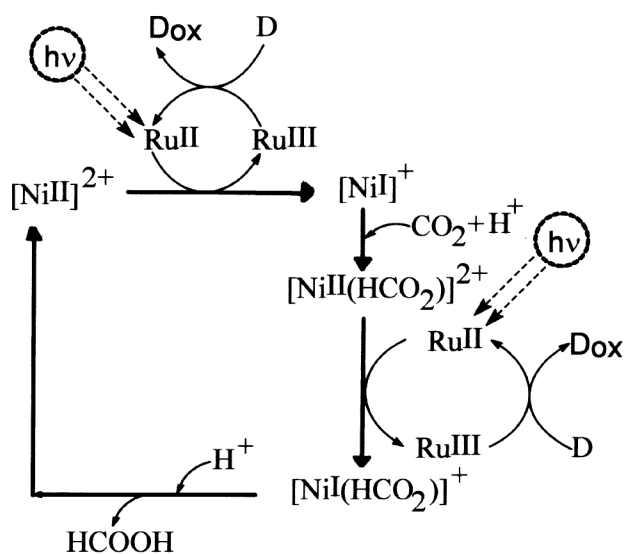
The amounts of HCOOH formed after 15 min of irradiation using the membrane containing different amounts of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the Nf/ $[\text{Ni}(\text{teta})]^{2+}/[\text{Ru}(\text{bpy})_3]^{2+}$ membrane were determined (Figure 2b) and the corresponding turnover numbers (TON) of the adsorbed $[\text{Ru}(\text{bpy})_3]^{2+}$ complex based on the HCOOH amounts are shown in Figure 2a. The TON of $[\text{Ru}(\text{bpy})_3]^{2+}$ was calculated by $2 \times (\text{mol of HCOOH produced})/\text{mol of } [\text{Ru}(\text{bpy})_3]^{2+}$ adsorbed. The results were reproducible and the Nafion membrane was stable for a month time and reused in repeated experiments. In the absence of any one component (visible light, carbon dioxide, Nafion, $[\text{Ni}(\text{teta})]^{2+}$, $[\text{Ru}(\text{bpy})_3]^{2+}$ and the sacrificial electron donor (TEA or EDTA)) in the solid-solution photoredox system, HCOOH was not observed. When the homogeneous solution containing the photoredox system $[\text{Ni}(\text{teta})]^{2+}-[\text{Ru}(\text{bpy})_3]^{2+}$ was irradiated, negligible amount of HCOOH was observed when compared to Nf/ $[\text{Ni}(\text{teta})]^{2+}/[\text{Ru}(\text{bpy})_3]^{2+}$. The amount of $[\text{Ru}(\text{bpy})_3]^{2+}$ adsorbed into the Nafion matrix was found to influence the amount of formation of HCOOH (Figure 2b). The increase in concentration of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the Nafion membrane increased the yield of HCOOH and the TON of $[\text{Ru}(\text{bpy})_3]^{2+}$ above which a decrease in the TON was observed (Figure 2a). At higher local concentration of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the Nf membrane, the self-quenching of the excited state $[\text{Ru}(\text{bpy})_3]^{2+}$ and the light-filtering effect will affect the photo-induced electron transfer reactions.

In the solid phase photoredox system, the excited state electron transfer quenching between $*[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ni}(\text{teta})]^{2+}$ (Ni^{II}) produces $[\text{Ru}(\text{bpy})_3]^{3+}$ and $[\text{Ni}(\text{teta})]^+$ (Ni^{I}) complex. The Ni^{I} complex reacts with CO_2 to produce $[\text{Ni}^{\text{II}}(\text{HCO}_2)]$ (ref. 20). This intermediate species undergoes successive electron transfer reaction coupled with protonation and finally produces $[\text{Ni}(\text{teta})]^{2+}$ and HCOOH (Scheme 1). The overall reaction is given by eq. (1).



The thermodynamic potential of the reduction of CO_2 to formate is $-0.66 \text{ V}(\text{SCE})$ ²¹. The role of Nafion matrix on the photoinduced electron transfer reaction between the $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ni}(\text{teta})]^{2+}$ complexes is (i) the immobilization of the positively-charged metal complex in a dispersed state and (ii) the micro-heterogeneous environment provided to the reacting molecules and the intermediates.

The present work demonstrates the importance of the immobilization of photoredox molecules in a solid matrix to realize the two-step one-electron transfer process



Scheme 1. Illustration of photocatalytic reduction of carbon dioxide in the Nafion membrane containing $[\text{Ni}(\text{teta})]^{2+}$ ($[\text{Ni}^{II}]^{2+}$) and $[\text{Ru}(\text{bpy})_3]^{2+}$ (Ru^{II}) complexes. D, is the sacrificial electron donor (TEA) and D_{ox} , is the oxidized species of electron donor.

by two one-electron transfer reactions (Scheme 1). The novel aspect of the present system is that both the sensitizer molecule and the electron relay/catalytic molecule are incorporated into the Nafion membrane. This membrane is simply dipped in the carbon dioxide saturated solution and is irradiated. It is hoped that this novel photocatalytic system will lead to further work in a new direction to utilize the membrane system in many applications.

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