Photochemical reduction of nitrite to ammonia at a solid phase photoredox system

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The photoassisted reduction of the nitrite anion to ammonia in alkaline aqueous solution was achieved by illumination with visible light in the presence of $[Ni(teta)]^{2+}$ and $[Ru(bpy)_3]^{2+}$ adsorbed Nafion membrane.

The reduction of nitrogen oxyanions has been one of the most interesting aspects in recent chemistry concerned with the development of new methods for artificial nitrogen fixation and the conversion of pollutants such as NO_x into useful chemicals, and also in bioinorganic chemistry in comparing enzymatic reactions with their model ones.[1–7] In artificial photosynthesis, the aim is to mimic the ability of green plants and other photosynthetic organisms in their use of sunlight to make high energy chemicals.[8] In homogeneous solution, the photoredox products recombine in the dark to regenerate the starting materials or undergo side reactions to deplete the concentration of the high energy products.[8] Attempts to construct artificial solar energy conversion systems have been made in terms of the use of micro- and macro-heterogeneous reaction environments such as micelles, bilayers, *etc.*[8–10] However, the utilization of the solid–solution interface has not been studied extensively except in the context of photogalavanic cells. Tris(2,2′-bipyridine)ruthenium(II), ($[Ru(bpy)_3]^{2+}$) has been established as the best photosensitizer for photoredox reactions both in homogeneous and in microheterogeneous media.[8,11,12] Here we describe the utilization of $[Ru(bpy)_3]^{2+}$ and the macrocyclic nickel(II) complex $[Ni(teta)]^{2+}$, (teta = 5,5,7,12,12,14-hexamethyl-1,4,8,11,-tetraazacyclotetradecane) in the solid phase which can be used efficiently to realize a multistep photoreduction of nitrite to ammonia.

The $[Ru(bpy)_3]^{2+}$ and the macrocyclic $[Ni(teta)]^{2+}$ complex ions were prepared according to literature procedures.[13,14] $[Ni(teta)]^{2+}$ was adsorbed into Nafion membrane (1 cm^2 area, Aldrich) by dipping the membrane into an aqueous solution containing a known concentration of $[Ni(teta)]^{2+}$. The membrane $Nf/[Ni(teta)]^{2+}$ was then washed and dipped in distilled water. The $[Ni(teta)]^{2+}$ complex was adsorbed irreversibly and the amount of $[Ni(teta)]^{2+}$ adsorbed into the Nafion membrane was determined by measuring the decrease in the absorbance of $[Ni(teta)]^{2+}$ (λ_{max} = 460 nm, ε_{460} = 40 $dm^3\ mol^{-1}\ cm^{-1}$) in solution after dipping. The $[Ni(teta)]^{2+}$ adsorbed Nafion membrane was then dipped in an aqueous solution containing a known concentration of $[Ru(bpy)_3]^{2+}$ and then washed with distilled water to give the membrane $Nf/[Ni(teta)]^{2+}/[Ru(bpy)_3]^{2+}$. $[Ru(bpy)_3]^{2+}$ was also adsorbed irreversibly and the amount of $[Ru(bpy)_3]^{2+}$ adsorbed in the $Nf/[Ni(teta)]^{2+}/Ru(bpy)_3]^{2+}$ membrane was determined by measuring the decrease in the absorbance of $[Ru(bpy)_3]^{2+}$ (λ_{max} = 452 nm, ε_{452} = 14 600 $dm^3\ mol^{-1}\ cm^{-1}$) in solution after dipping. The $Nf/[Ni(teta)]^{2+}$ and $Nf/[Ni(teta)]^{2+}/[Ru(bpy)_3]^{2+}$ membranes were characterized by absorption and emission spectra. Fig. 1 shows the absorption spectra of $[Ni(teta)]^{2+}$ in Nafion membrane recorded using JASCO 7800 spectrophotometer. $[Ni(teta)]^{2+}$ adsorbed into Nafion membrane is evident [Fig. 1(*b*)] when compared to $[Ni(teta)]^{2+}$ in water [Fig. 1(*a*)]. A similar result was also obtained for the $Nf/[Ni(teta)]^{2+}/[Ru(bpy)_3]^{2+}$ membrane.

The $Nf/[Ni(teta)]^{2+}/[Ru(bpy)_3]^{2+}$ membrane was dipped into a photolysis cell containing deaerated aqueous 1 mol dm^{-3} sodium nitrite–1 mol dm^{-3} sodium hydroxide 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 30 min irradiation, the cell solution was tested for ammonia, hydroxylamine and hydrazine.[15] Only ammonia was identified as the sole nitrite reduction product. The ammonia concentration was determined using Nessler's reagent and careful spectroscopic analysis in the 400–430 nm wavelength range.[16] 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 reagent[17] 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 as described above.[16]

The yield of $NH_3(aq)$ formed after 30 min irradiation using samples containing different amounts of $[Ru(bpy)_3]^{2+}$ in $Nf/[Ni(teta)]^{2+}$ matrix was determined [Fig. 2(*b*)] and the corresponding turnover numbers (TON) of the adsorbed $[Ru(bpy)_3]^{2+}$ complex based on yields of $NH_3(aq)$ are shown in Fig. 2(*a*). The TON for $[Ru(bpy)_3]^{2+}$ was obtained from the relation: 6 × mol of $NH_3(aq)$ produced/mol of $[Ru(bpy)_3]^{2+}$ adsorbed.

The results were reproducible and the Nafion membrane was stable over months and could be reused in repeated experiments. The absence of any one reaction component (visible light, $[Ni(teta)]^{2+}$, $[Ru(bpy)_3]^{2+}$ or $NaNO_2$) in the solid–solution photoredox system led to no formation of $NH_3(aq)$. When the homogeneous solution containing the photoredox system $[Ni(teta)]^{2+}$–$[Ru(bpy)_3]^{2+}$ was irradiated (*i.e.* in the absence of

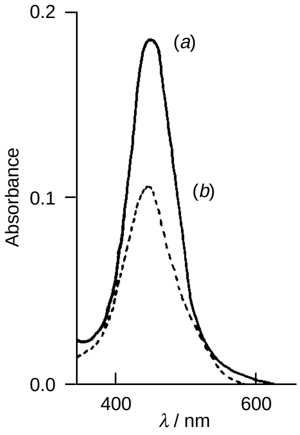


Fig. 1 Absorption spectra of (*a*) $[Ni(teta)]^{2+}$ in water and (*b*) $[Ni(teta)]^{2+}$ adsorbed in Nafion membrane

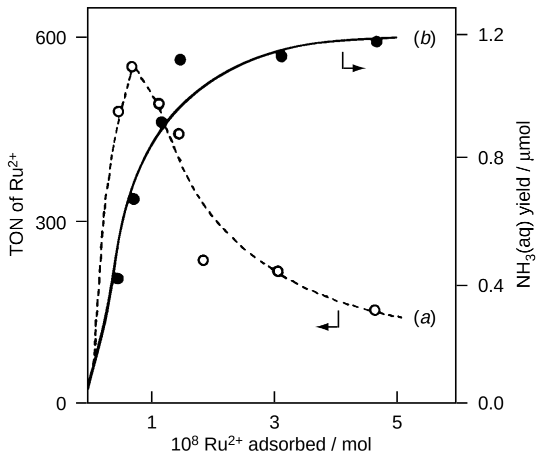


Fig. 2 (*a*) Turnover numbers (TONs) of $[Ru(bpy)_3]^{2+}$ and (*b*) yields of NH_3(aq) observed for the Nf/$[Ni(teta)]^{2+}$/$[Ru(bpy)_3]^{2+}$ matrix (1 cm^2) dipped in deaerated aqueous 1 mol dm^{-3} $NaNO_2$–1 mol dm^{-3} NaOH. Irradiation time 30 min; 3.75×10^{-6} mol of $[Ni(teta)]^{2+}$ was adsorbed.

Nafion) negligible amounts of NH_3(aq) were produced compared with Nf/$[Ni(teta)]^{2+}$/$[Ru)bpy)_3]^{2+}$.

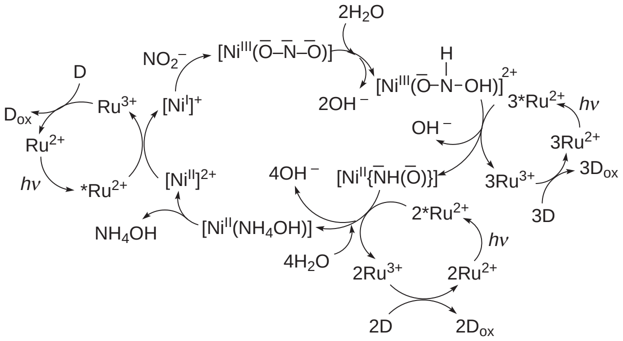
The amount of $[Ru(bpy)_3]^{2+}$ adsorbed into the Nafion matrix was found to influence the yield of NH_3(aq) produced [Fig. 2(*b*)]. An increase of concentration of $[Ru(bpy)_3]^{2+}$ in the Nafion increased the yield of NH_3(aq) and the TON of $[Ru(bpy)_3]^{2+}$ up to a limiting value, above which a decrease in the TON was observed [Fig. 2(*a*)], at higher local concentrations, the self quenching of the excited state $[Ru(bpy)_3]^{2+}$ complex and a light filtering effect were predominant.

In the solid-phase photoredox system, the excited-state electron-transfer quenching between $*[Ru(bpy)_3]^{2+}$ and $[Ni(teta)]^{2+}$ (Ni^{II}) complex produces $[Ru(bpy)_3]^{3+}$ and $[Ni(teta)]^{+}$ (Ni^{I}) complex. The latter (Ni^{I}) reacts[18] with NO_2^- to produce $[Ni(O^-–N^-–O^-)]$ (Ni^{III}). This species undergoes successive reductions and finally produces $[Ni(teta)]^{2+}$ and NH_3(aq) (Scheme 1). The overall reaction is given by eqn. (1). The role

$$NO_2^- + 6e^- + 5H_2O \rightarrow NH_3(aq) + 7OH^- \qquad (1)$$

of Nafion matrix in the photo-induced electron transfer reaction between $[Ru(bpy)_3]^{2+}$ and the $[Ni(teta)]^{2+}$ complexes is (*i*) immobilization of positively charged metal complexes in a dispersed state and (*ii*) provision of a microheterogeneous environment for the reacting molecules.

The present work demonstrates the importance of the immobilization of photoredox molecules in a solid matrix to realize the multistep one-electron transfer process by a series of one-electron transfer reaction (Scheme 1). Investigations into the role of the $[Ru(bpy)_3]^{2+}$ and $[Ni(teta)]^{2+}$ catalyst in Nafion membrane in the production of ammonia by nitrite reduction are under way.



Scheme 1 Schematic illustration of photocatalytic reduction of nitrite at a Nafion matrix containing $[Ni(teta)]^{2+}$ and $[Ru(bpy)_3]^{2+}$. $[Ni^{II}]^{2+}$ = $[Ni(teta)]^{2+}$, Ru^{2+} = $[Ru(bpy)_3]^{2+}$. D = electron donor (H_2O), and D_{ox} = oxidized species of electron donor.

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