Simultaneous Reductive and Oxidative Photocatalytic Nitrogen Fixation in Hydrous Iron(III) Oxide Loaded Nafion Films in Aerated Water

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It is found that Nafion films loaded with quantum sized particles of hydrous iron(iii) oxide, immersed in aerated water at alkaline pH fix nitrogen, reductively and oxidatively at the same time, in a novel photocatalytic reaction which is facilitated by the Nafion polymer matrix.

A method for photocatalytic fixation of N_2 is a demanding invention. An ideal device for this purpose should have the ability to use air and water to generate nitrogeneous fertilizer. In this communication we report our findings on a simple system which gives encouragement for practical photofixation of N_2 . We have found that hydrous iron(III) oxide loaded Nafion films in aerated water at alkaline pH yields both NH₃ and NO₂⁻/NO₃⁻ upon UV irradiation.

In all experiments, extreme precautions were taken to avoid NH₃ and NO₂^{-/NO₃⁻ contamination. Nafion film^{1,2} (Nafion} 117, DuPont) cleaned by refluxing in conc. HCl and repeated washing, and boiling in distilled water was loaded with hydrous iron(III) oxide as follows: The film was immersed in 0.1 mol dm⁻³ aqueous FeCl₃ (pH ca. 1.5) for 30 min, rinsed in water and again immersed in 0.8 mol dm⁻³ NaOH for 45 min, during which quantum particles3 of hydrous iron(III) oxide become embedded in the polymer matrix. The size of the crystallites determined from X-ray diffraction (XRD) using Sherrer's equation was ca. 48 Å. Extraction of Fe from a sample of the film gave the density distribution as $ca. 2 \times 10^{-6}$ Fe^{3+} mol cm⁻². The absorption spectrum of the film compared with that of an aqueous suspension of hydrous iron(III) oxide shows clear evidence for the size quantization blue shift^{3,4} (Fig. 1).

Irradiations were carried out in a 500 ml photochemical reactor with a water cooled (26 °C) cylindrical quartz inner jacket where a 400 W medium pressure Hg lamp was housed. The Nafion film ($10 \times 20 \text{ cm}^2$, thickness = 0.0175 cm) was wrapped around the cylinder and tied by a thin Teflon tape.

Water (350 ml; pH adjusted with NaOH) was continuously purged with purified air at a rate 10 ml min⁻¹. After running the experiment for a given time, the solution was tested for NH₃ by the Indophenol Blue method and NO₂⁻/NO₃⁻ by azo-dye Cd reduction test. As a check on contamination, two blank experiments were conducted: (1) lamp switched-off with a coated film and (2) lamp-on with an uncoated film. NH₃, NO₂⁻/NO₃⁻ levels in these were negligible. In another experiment the solution was purged with N₃ and Ar (99.99%) and the out-going gas examined (Shimadzu GC-9 AM). H₂ and small quantities of O₂ were detected and the yield of the latter in the Ar purged solutions was slightly higher.

Fig. 2 shows the development of the reduced ($N_R = [NH_3]$), oxidised ($N_O = [NO_2^-] + [NO_3^-]$) and total fixed ($N_T = N_R + N_O$) nitrogen concentrations in the air-purged (AP) and N_2 purged (NP) solutions. In both cases N_R increases at a decreasing rate, but quite unexpectedly AP solutions give higher yields in the initial stages of photolysis. Again NP solutions show detectable N_O only at later stages whereas the AP system gives much larger amounts of N_O from the beginning. Clearly N_R is always higher in the AP solution. Under similar conditions N_T from an equivalent quantity of bare hydrous iron(III) oxide reaches a saturation value of *ca*. 0.1 µmol 1⁻¹ in about 3 h.

Absorbance (arbitrary units)

Fig. 1 Absorption spectrum of (a) hydrous iron(III) oxide loaded Nafion, (b) Nafion and (c) aqueous dispersion of hydrous iron(III) oxide



Fig. 2 Yields of reduced (N_R) , oxidised (N_O) and total (N_T) nitrogen in irradiation of the loaded Nafion film at pH 12.0 in (----) air purged $(--) N_2$ purged solutions; (pH = 12.0)

The general belief is that NP semiconductor dispersions photogenerate NH_3 via the reactions (1) and (2).^{5–7} Holes could also be transferred to chemisorbed N₂, as in reaction (3).

$$N_2 + 6H^- + 6e^- \text{ (conduction band)} \rightarrow 2NH_3$$
 (1)

$$2H_2O + 4h^+$$
 (valence hand) $\rightarrow O_2 + 4H^+$ (2)

$$N_2 + 4H_2O + 6h^+ \rightarrow 2NO_2^- + 8H^+$$
 (3)

$$2H_2O + N_2 + O_2 + 2h^+ \rightarrow 4H^+ + 2NO_2^-$$
(4)

In addition to the activation barrier, reaction (3) necessitates transfer of six holes compared to four in the case of reaction (2). Thus, reaction (3) cannot happen to an appreciable extent [small quantities of N_O seen in NP systems⁵⁻⁷ probably originate from photooxidation of NH₃ by O₂ from reaction (2)]. In the presence of O_2 , another hole-consuming process is possible [see reaction (4)]. The reaction between chemisorbed N_2 and O_2 is more probable as it involves transfer of two holes compared to six in the case of reaction (3). Again the hole-transfer to OH⁻ leading to reaction (2) is suppressed as the cation exchange membrane cannot easily accommodate OH- ions. We believe that reactions (1) and (4) are responsible for the photosynthesis of $N_{\rm R}$ and $N_{\rm O}$ in the AP Nafion-hydrous iron(III) oxide system. As O2 readily accepts electrons to form O_2^- , which in turn scavenges holes, the reactions (1) and (4) occur more effectively when electron donation to O_2 is suppressed. Presumably, the microenvironment of the Nafion matrix⁸ is suppressing the formation of O_2^{-} . Hydrated iron(III) oxide-loaded Nafion films remained active for nearly 60 h of irradiation. However, on repeated use, some deterioration which affects N_T as well as the relative proportions of N_R and N_O is noted. The optimum pH for both

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 N_R and N_O yields is *ca.* 12.0. At neutral pH they are reduced by a factor of *ca.* 8. Although low pH is kinetically favourable for the reaction (1), the flat-band potential of hydrous iron(III) oxide shifts in an unfavourable direction with the decrease of pH.⁶ The two opposing effects leads to an optimum pH. Furthermore, with progress of the reaction, pH decreases resulting in a gradual decline of the rate of production of N_R (Fig. 1). The molar ratio $NO_2^-: NO_3^-$ depends on the pH and the rate of purging.

Reactions (1)-(4) indicate the possible overall stoichiometry in fixation of N₂. As multi-electron transfer is highly improbable the above reactions could involve several primary steps.

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