Photocatalytic water oxidation by Nafion-stabilized iridium oxide colloids

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A photosystem composed of colloidal $IrO_2 \cdot xH_2O$ stabilized by soluble Nafion, tris(2,2′-bipyridyl)ruthenium(II), and persulfate efficiently oxidizes water to oxygen under visible light.

Much effort has been applied to the development of photosystems for visible light cleavage of water into H_2 and O_2.[1–3] Although the reaction is thermodynamically possible with light of wavelength ≤1000 nm, efficient water photolysis has not yet been reported. One of the key components of such photolysis systems is the catalyst that converts water into O_2.[4–8] As a four-electron redox process, the evolution of O_2 from water is more difficult than kinetically simpler processes, such as H_2 evolution. Recently, we have reported photocatalytic oxidation of water by a buffered $[Ru(bpy)_3]^{2+}$–colloidal $IrO_2 \cdot xH_2O$ system that uses $S_2O_8^{2-}$ as a sacrificial electron acceptor.[9] In this case, the quantum efficiency for O_2 evolution under optimized conditions is about 50%, and the turnover number with respect to the photosensitizer exceeds 200. The turnover rate is very fast compared with that of other $[Ru(bpy)_3]^{2+}$–catalyst–$S_2O_8^{2-}$ systems, but is still too slow to be coupled with a non-sacrificial hydrogen evolving system[10] for overall water photolysis.

Colloidal catalysts in these photosystems are stabilized by coordinating reagents such as citrate ions and polyethylene glycol. The colloid is negatively charged, and adsorbed cationic sensitizers take part in the water oxidation cycle. Interestingly, there is little or no activity at concentrations below that required to saturate the colloid with sensitizer molecules.[9] This suggests that colloidal catalysts stabilized by polyanions might exhibit a higher activity for O_2 evolution than conventional catalysts. In this paper, we report O_2 evolution from a $[Ru(bpy)_3]^{2+}$–Nafion-stabilized $IrO_2 \cdot xH_2O$–$S_2O_8^{2-}$ photosystem. Very stable colloids form in solutions containing soluble Nafion, and the $[Ru(bpy)_3]^{2+}$ photosystem incorporating these catalytic colloids has an appreciably higher quantum efficiency for water oxidation than conventional systems at moderate to high light intensity.

Nafion-stabilized and citrate-stabilized $IrO_2 \cdot xH_2O$ colloids (Nafion/IrO_2 and citrate/IrO_2) were compared as O_2 evolution catalysts. Citrate/IrO_2 was available from our earlier study, in which hexachloroiridate ions ($IrCl_6^{2-}$) were hydrolyzed in a citrate solution at pH 7.[9] Nafion/IrO_2 was prepared similarly in the presence of soluble Nafion perfluorinated ion-exchange resin.[11] The deep blue colloidal solution was stable over a period of three months. The UV–VIS spectrum of the solution had a broad absorption band in the range of 500–700 nm, signaling the formation of colloidal $IrO_2 \cdot xH_2O$,[7] which is apparently stabilized by interaction with the sulfonate groups of Nafion. A TEM image of Nafion/IrO_2 (0.05 g Nafion/0.030 g K_2IrCl_6) is shown in Fig. 1. Primary particles less than 10 nm in diameter form small aggregates that have diameters of 20–30 nm. The grouping of these aggregates into the micron-size patch shown in Fig. 1 is probably an artifact of TEM sample preparation, since the colloidal solutions are not turbid. Citrate/IrO_2 makes similar colloids, except that larger primary particles (10–15 nm) are observed.[9]

The photolysis reactions were carried out in 5 mL aqueous solutions containing $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$, colloidal IrO_2, $Na_2S_2O_8$, Na_2SO_4 and Na_2SiF_6–$NaHCO_3$ buffer in a Pyrex test tube reactor. The concentrations of $Na_2S_2O_8$, Na_2SO_4 and Na_2SiF_6–$NaHCO_3$ buffer were 1.0×10^{-2}, 5.0×10^{-2} and 2.2×10^{-2}–2.8×10^{-2} M, respectively, and the constantly stirred solutions were irradiated with a Xe lamp of 300 W, equipped with a 450 ± 20 nm interference filter. Except as noted, the intensity of visible light reaching the solution was 18 mW cm^{-2}. The solutions were buffered at pH 5.4–5.7 during photolysis. The details are described elsewhere.[9]

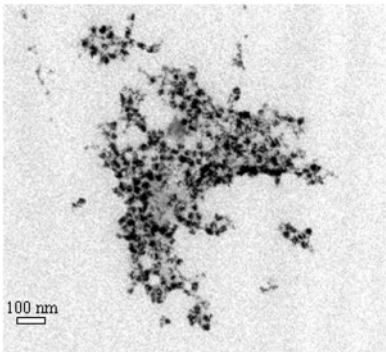

Fig. 1 TEM image of Nafion-stabilized IrO_2 colloid (prepared from 0.05 g Nafion/0.030 g K_2IrCl_6).

Fig. 2 shows the dependence of the sensitizer turnover number and initial O_2 evolution rate on concentration of the sensitizer for $[Ru(bpy)_3]$–Nafion/IrO_2 ([Ir] = 1.0×10^{-4} M) and $[Ru(bpy)_3]$–citrate/IrO_2 ([Ir] = 6.2×10^{-5} M). Nafion/IrO_2 colloids prepared from 0.05 g Nafion/0.030 g K_2IrCl_6 were used for these reactions. The rate of O_2 evolution plotted in this figure is that observed in the early stages of the reaction (5–10

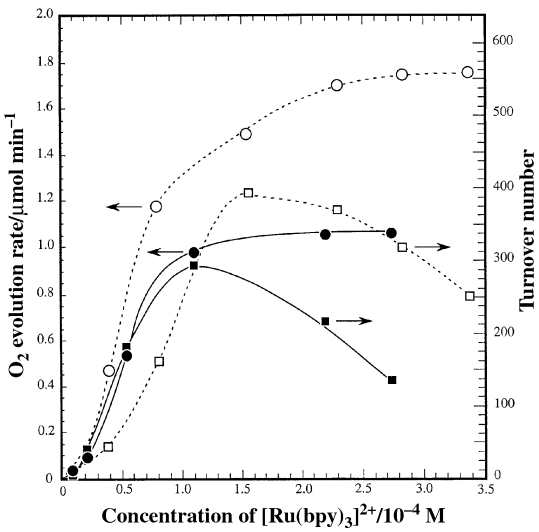

Fig. 2 Dependence of the initial rate of O_2 evolution and turnover number on the concentration of $[Ru(bpy)_3]^{2+}$. For $[Ru(bpy)_3]^{2+}$–Nafion/IrO_2–persulfate, initial rate of O_2 evolution (○), turnover number (□); $[Ru(bpy)_3]^{2+}$–citrate/IrO_2–persulfate, initial rate of O_2 evolution (●), turnover number (■). Nafion/IrO_2: [Ir] = 1.0×10^{-4} M; citrate/IrO_2: [Ir] = 6.2×10^{-5} M.

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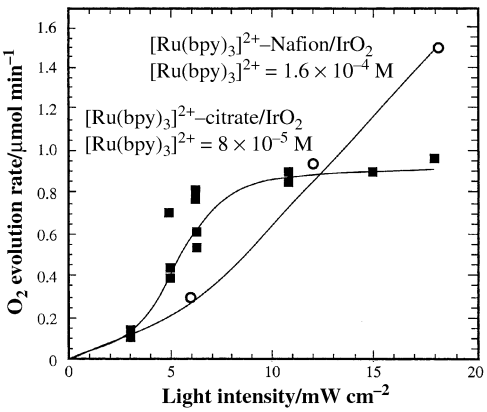

Fig. 3 Light intensity dependence of the initial rate of oxygen evolution for $[Ru(bpy)_3]^{2+}$–Nafion/IrO_2 and $[Ru(bpy)_3{}^{2+}$–citrate/IrO_2.

min) before significant decomposition of the sensitizer occurs. Each photosystem showed the highest O_2 evolution rate at the colloid concentration used in these experiments. Further addition of colloid to either system decreased both the turnover number and the O_2 evolution rate, because at high concentration the colloidal catalyst begins to quench the MLCT excited state of the sensitizer oxidatively.[6] In both systems, the turnover number reaches a maximum and the rate of O_2 evolution reaches a plateau at high sensitizer concentration. Beyond $(1.1–1.5) \times 10^{-4}$ M, the background decomposition rate of $[Ru(bpy)_3]^{3+}$ exceeds the rate of O_2 evolution and the turnover number decreases.[9] At high light intensity, $[Ru(bpy)_3]^{2+}$–Nafion/IrO_2 surpassed $[Ru(bpy)_3]^{2+}$–citrate/IrO_2 in the rate of O_2 evolution at all concentrations, and the difference in rate increased with increasing sensitizer concentration. The turnover number of the former system also exceeded that of the latter at high concentration. The highest quantum efficiencies for O_2 evolution, ϕO_2, with Nafion/IrO_2 and citrate/IrO_2 catalysts were 73% (2.8×10^{-4} M sensitizer) and 45% ($\geqslant 2.2 \times 10^{-4}$ M), respectively.[12] The rate of O_2 evolution in the Nafion/IrO_2 system is light-limited up to the highest light intensity used (18 mW cm^{-2}), whereas that of citrate/IrO_2 is catalyst-limited above about 10 mW cm^{-2} (Fig. 3). This indicates that the turnover rate of the former catalyst is approximately twice that of the latter.

The effects of ionic strength and pH on the time course of O_2 evolution were determined by changing the concentration of buffer and ratio of Na_2SiF_6 to $NaHCO_3$. With buffer concentrations in the range $(3.5–5.7) \times 10^{-2}$ M, there was no noticeable effect of concentration on the time course of O_2 evolution. At lower concentrations, both the rate and turnover number decreased, but in this case the final pH was < 4, so the loss in activity can be attributed to the failure of the dilute buffer to maintain the optimum pH (4–6). At initial pH > 6.5 the rate also decreases, because the driving force for O_2 evolution decreases. An essentially identical pH dependence has been previously noted by Harriman and coworkers.[6–8]

Interestingly, both initial rate curves in Fig. 2 saturate in the manner of an adsorption isotherm, suggesting that O_2 evolution from these catalysts only occurs when sensitizer molecules are adsorbed on to the colloid.[9] In particular, the rate plot for citrate-stabilized IrO_2 resembles a Langmuir adsorption isotherm.[9] This behavior has also been observed in the $[Ru(bpy)_3]^{2+}$–colloidal RuO_2 system.[6] In contrast, the rate–concentration curve of $[Ru(bpy)_3]^{2+}$–Nafion/IrO_2 has a different shape, and appears to be the sum of two different kinds of isotherms. The turnover plot also peaks at higher $[Ru(bpy)_3]^{2+}$ concentration in this case. We tentatively attribute this behavior to the adsorption of more than a single monolayer of sensitizer on the Nafion polyanion-stabilized colloid.

In summary, colloidal IrO_2 can be stabilized using soluble Nafion, which promotes the photocatalytic oxidation of water through adsorption of sensitizer cations. Very high quantum yields and turnover numbers were achieved under optimized conditions. The high activity of these polyanion-stabilized colloids suggests that further rate enhancement may be possible using structured polyanion/polycation films or other organized assemblies. These possibilities are currently under investigation.

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11 20 g Nafion–aliphatic alcohols–water solution (Aldrich, Nafion 5 wt%) was added to 300 mL deionized water. The solution was heated to 70–80 °C on a hot-plate until the total volume was reduced to 50 mL, and was then diluted to 300 mL. This procedure was repeated three times to remove aliphatic alcohols from the solution. The total volume of the final solution was adjusted to 100 mL. 0.030 g K_2IrCl_6 (6.2×10^{-5} mol) was added to 50 mL aqueous solutions containing 0.01–0.25 g dissolved Nafion, which were prepared from the Nafion stock solution described above. The resulting red-brown solution was adjusted to pH 5.0 with 0.25 M NaOH and was heated to 95 °C on the hot-plate with constant stirring. If less than 0.01 g dissolved Nafion was added, or if the pH was above 7, solid IrO_2 precipitated upon heating. After heating for 1 h, the deep blue solution was cooled to room temperature and NaOH solution was added to adjust the pH to the initial value. The solution was transferred to a round bottom flask with a reflux condenser and was kept at 95 °C for 2 h with O_2 bubbling through the solution. The pH was then adjusted to 5.0 with NaOH solution, and the solution was stirred with 10 mL of DOWEX 2X8-50 anion exchange resin to remove excess Nafion. After 30 min, the DOWEX resin was removed by filtration, and the final solution was diluted to 100 mL.
12 Quantum efficiencies (ϕO_2) were calculated using the following equation,[8] in which ϕO_2 (%) = $(2RO_2/I) \times 100$, where RO_2 and I represent the O_2 evolution rate (molecules min^{-1}) and the rate of absorption of incident photons (photons min^{-1}), respectively. The factor of two arises because two photons produce one O_2 molecule when persulfate is used as the sacrificial electron acceptor.