

Photocatalytic reduction of dioxygen to hydrogen peroxide in a solid-phase photoredox system

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Multistep one-electron photoreduction of dioxygen to hydrogen peroxide is achieved using a solid-phase photoredox system.

Solar energy conversion has become an increasingly important research subject as an alternative renewable energy resource in recent years since the increase in atmospheric carbon dioxide has been recognised to be very serious. 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.^{1,2} The difficulty in creating non-biological model systems to realize the multistep one-electron transfer processes lies in the requirement of coupling the single-step one-electron process of the photoredox molecules. 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.^{1,2} 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.*¹⁻⁶ However, the utilization of the solid-solution interface has not been studied extensively except in the context of photogalvanic cells. Tris(2,2'-bipyridine)ruthenium(II) [Ru(bpy)₃]²⁺ has been established to be the best photosensitizer for photoredox reactions both in homogeneous and micro-heterogeneous media.^{1,2,7-9} Here we describe the utilization of [Ru(bpy)₃]²⁺ and the macrocyclic cobalt(III) complexes [Co(cyclam)(H₂O)₂][ClO₄]₃ and [Co(teta)(H₂O)₂][ClO₄]₃ (cyclam = 1,4,8,11-tetraazacyclotetradecane, 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 dioxygen to hydrogen peroxide.

[Ru(bpy)₃]²⁺ and the macrocyclic cobalt(III) complexes were prepared according to literature procedures.¹⁰⁻¹² The photosensitizer, [Ru(bpy)₃]²⁺, was adsorbed into cellulose paper (1 cm² area, Toyo Roshi Co., Japan) by dipping the paper into a solution containing a known concentration of [Ru(bpy)₃]²⁺. The paper {represented as cellulose/[Ru(bpy)₃]²⁺} was then washed and dipped in distilled water. The [Ru(bpy)₃]²⁺ complex was adsorbed irreversibly and the amount of [Ru(bpy)₃]²⁺ adsorbed into the cellulose paper was determined by measuring the decrease in the absorbance of [Ru(bpy)₃]²⁺ ($\lambda_{\text{max}} = 452 \text{ nm}$, $\epsilon_{452} = 14600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)¹⁰ in solution after dipping. The cellulose/[Ru(bpy)₃]²⁺ paper was then dipped into a photolysis cell containing oxygenated [Co(cyclam)(H₂O)₂]³⁺ (0.15 mmol dm⁻³), triethanolamine (TEA) (0.1 mol dm⁻³) and HClO₄ (0.1 mol dm⁻³) and then irradiated with visible light (500 W tungsten-halogen lamp with suitable UV and IR filters). After 10–30 min, the cell solution was tested for hydrogen peroxide by titrimetry and spectrophotometric methods.¹³ The yield of hydrogen peroxide formed after 10 min irradiation using samples containing different amounts of [Ru(bpy)₃]²⁺ in the cellulose matrix was determined and the corresponding turnover numbers of the adsorbed [Ru(bpy)₃]²⁺ complex based on H₂O₂ yield are shown in Fig. 1(a). The turnover number for [Ru(bpy)₃]²⁺ was obtained from the relation 2 (mol of H₂O₂ produced/mol of [Ru(bpy)₃]²⁺ adsorbed).

After constructing the solid {[Ru(bpy)₃]²⁺}-solution(Co^{III}, O₂) interface system, the solid {[Ru(bpy)₃]²⁺, Co^{III}}-solution (O₂) system using [Co(teta)(H₂O)₂]³⁺ as an electron relay was constructed for dioxygen reduction. The cellulose paper was first dipped in an acetonitrile solution containing a known concentration of [Co(teta)(H₂O)₂]³⁺ and then washed. The [Co(teta)(H₂O)₂]³⁺ treated cellulose paper was dipped in an aqueous solution containing a known concentration of [Ru(bpy)₃]²⁺ and then washed. The water-insoluble [Co(teta)(H₂O)₂]³⁺ was not desorbed from the cellulose matrix whereas the water-soluble [Co(cyclam)(H₂O)₂]³⁺ was slowly desorbed from the cellulose matrix. Since [Co(teta)(H₂O)₂]³⁺ occupies part of the space available in the cellulose matrix, the amount of [Ru(bpy)₃]²⁺ adsorbed into the cellulose/[Co(teta)(H₂O)₂]³⁺ sample was almost 10 times lower when compared to untreated cellulose matrix. In this system, the advantage is that both sensitizer and catalyst molecules are immobilized in the solid phase. The cellulose/[Ru(bpy)₃]²⁺/[Co(teta)(H₂O)₂]³⁺ paper was dipped in an aqueous acidic solution containing 0.1 mol dm⁻³ HClO₄ and 0.1 mol dm⁻³ TEA and then irradiated with visible light. The formation of hydrogen peroxide after 10 min of irradiation with different amounts of adsorbed [Ru(bpy)₃]²⁺ was determined and the corresponding turnover numbers are shown in Fig. 1(b). A very high turnover number of 15550 was observed for the cellulose/[Ru(bpy)₃]²⁺/[Co(teta)(H₂O)₂]³⁺ system. This observation clearly shows that the photoinduced electron-transfer quenching between excited-state [Ru(bpy)₃]²⁺ and [Co(teta)(H₂O)₂]³⁺ in the cellulose matrix is very efficient and that the reduction of dioxygen to hydrogen peroxide by the photoproduct cobalt(II) complex and [Ru(bpy)₃]³⁺ by TEA occurs efficiently in the cellulose matrix (Scheme 1). The results were reproducible and the system was very stable over extended periods. The absence of any one reaction component in the solid-solution photoredox

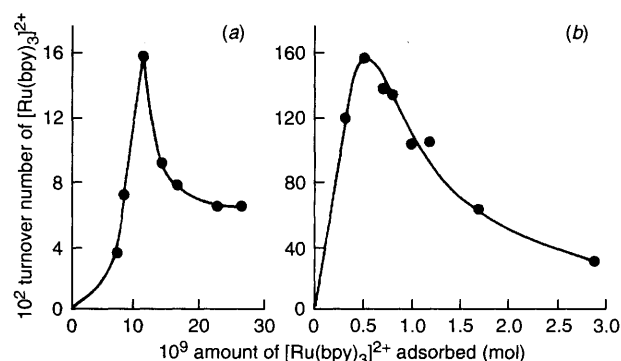
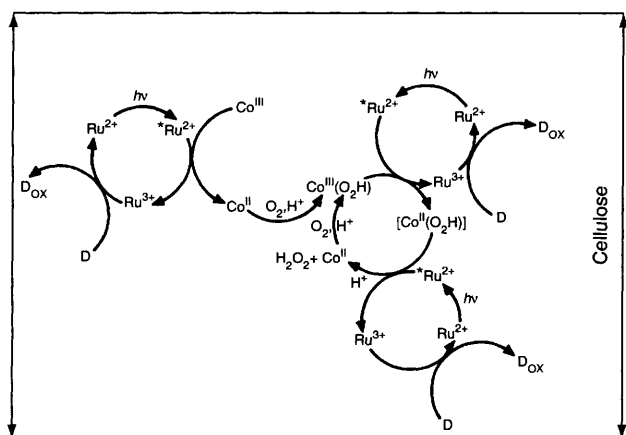


Fig. 1 (a) Turnover number of [Ru(bpy)₃]²⁺ observed for the cellulose/[Ru(bpy)₃]²⁺ matrix (1 cm²) dipped in oxygen-saturated solution containing 0.15 mmol dm⁻³ [Co(cyclam)(H₂O)₂]³⁺, 0.1 mol dm⁻³ TEA and 0.1 mol dm⁻³ HClO₄. Irradiation time 10 min. (b) Turnover number of [Ru(bpy)₃]²⁺, observed for the cellulose/[Ru(bpy)₃]²⁺/[Co(teta)(H₂O)₂]³⁺ system dipped in oxygen saturated solution containing 0.1 mol dm⁻³ TEA and 0.1 mol dm⁻³ HClO₄. Irradiation time 10 min; 7.375 × 10⁻⁸ mol of [Co(teta)(H₂O)₂]³⁺ was adsorbed.

system led to no formation of hydrogen peroxide. When the homogeneous solution containing the photoredox system $[\text{Ru}(\text{bpy})_3]^{2+}\text{-Co}^{\text{III}}$ was irradiated (*i.e.* in the absence of cellulose) negligible amounts of hydrogen peroxide were produced when compared to cellulose/ $[\text{Ru}(\text{bpy})_3]^{2+}/\text{Co}^{\text{III}}$.

The amount of $[\text{Ru}(\text{bpy})_3]^{2+}$ adsorbed into the cellulose matrix was found to influence the yield of hydrogen peroxide produced (Fig. 1). An increase of concentration of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the cellulose increased the yield of hydrogen peroxide and the turnover number of $[\text{Ru}(\text{bpy})_3]^{2+}$ up to a limiting value, above which a decrease in the turnover number was observed; at higher local concentrations, the self quenching of the excited-state $[\text{Ru}(\text{bpy})_3]^{2+}$ complex and the light filtering effect were predominant.

In the solid-phase photoredox system, the excited-state electron-transfer quenching between $[\text{Ru}(\text{bpy})_3]^{2+}$ and a Co^{III} complex produces $[\text{Ru}(\text{bpy})_3]^{3+}$ and a Co^{II} complex. The latter reacts with O_2 ^{14,15} to produce $\text{Co}^{\text{III}}\text{-O}_2\text{H}$ at pH 1. This species also quenches excited-state $[\text{Ru}(\text{bpy})_3]^{2+}$ and produces a Co^{II} complex and H_2O_2 (Scheme 1). The excited-state electron-transfer quenching rate constants for $[\text{Ru}(\text{bpy})_3]^{2+}\text{-Co}^{\text{III}}$ and $[\text{Ru}(\text{bpy})_2]^{2+}\text{-Co}^{\text{III}}\text{-O}_2\text{H}$ were determined using a photoelectrochemical method¹⁶ and were found to be *ca.* $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in each case. In the presence of TEA, the photoproduced $[\text{Ru}(\text{bpy})_3]^{3+}$ complex is efficiently converted into $[\text{Ru}(\text{bpy})_3]^{2+}$ and the Co^{II} complex reacts with oxygen. The photoproduced $[\text{Ru}(\text{bpy})_3]^{3+}$ complex was also reduced by



Scheme 1 Photocatalytic reduction of dioxygen at cellulose matrix containing $[\text{Ru}(\text{bpy})_3]^{2+}$ and a macrocyclic cobalt(III) complex; $\text{Co}^{\text{III}} = [\text{Co}(\text{cyclam})(\text{H}_2\text{O})_2]^{3+}$ or $[\text{Co}(\text{teta})(\text{H}_2\text{O})_2]^{3+}$, $\text{Ru}^{2+} = [\text{Ru}(\text{bpy})_3]^{2+}$, $\text{D} = \text{TEA}$ or H_2O

water¹⁷ and the reduction was found to be efficient in the adsorbed state.

The role of the cellulose matrix on the photoinduced electron-transfer reaction between $[\text{Ru}(\text{bpy})_3]^{2+}$ and the Co^{III} complexes are: (*i*) immobilization of positively charged metal complexes in a dispersed state and (*ii*) provision of a microheterogeneous environment for the reacting molecules. The advantage of the solid-phase $[\text{Ru}(\text{bpy})_3]^{2+}\text{-Co}^{\text{III}}$ photoredox system is that the reactivity or disproportionation¹⁸ of O_2^- was suppressed by formation of the $\text{Co}^{\text{III}}\text{-O}_2\text{H}$ complex.

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 reactions (Scheme 1).

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