Production of hydrogen peroxide by combination of semiconductor-photocatalysed oxidation of water and photocatalytic two-electron reduction of dioxygen

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Production of hydrogen peroxide by combination of semiconductor-photocatalysed oxidation of water and photocatalytic two-electron reduction of dioxygen†

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Production of hydrogen peroxide from water and dioxygen was achieved by combination of semiconductor-photocatalysed oxidation of water and photocatalytic two-electron reduction of dioxygen with $[Ru^{II}((MeO)_2bpy)_3]^{2+}$ ((MeO)$_2$bpy = 4,4'-dimethoxy-2,2'-bipyridine) in the presence of Sc^{3+} in water under visible light irradiation.

Hydrogen peroxide (H_2O_2) has attracted considerable interest as a green fuel that can be used in one-compartment fuel cells free of expensive membranes with theoretical maximum output potential of 1.09 V, which is comparable to that of a hydrogen fuel cell (1.23 V).[1-7] H_2O_2 has also merited increasing attention as a green oxidant, because only water is produced as the reduced product.[8-10]

H_2O_2 is currently produced by an industrial process composed of sequential hydrogenation and oxidation of an alkyl anthraquinone, which is not environmentally benign because of many reasons, such as utilisation of toxic solvents, consumption of large amount of energy, and requirement for multiple reaction steps.[12,13] It is highly desired to produce H_2O_2 from water and dioxygen in the air using solar energy.

We have previously reported that H_2O_2 can be produced by combination of thermal water oxidation using water oxidation catalysts and photocatalytic two-electron reduction of O_2 using Ru complexes as photocatalysts.[14-16] When the water oxidation and O_2 reduction were performed in a one compartment cell, produced H_2O_2 can be decomposed in the presence of water oxidation catalysts to preclude the production of H_2O_2 at higher concentrations.

We report herein the photocatalytic production of H_2O_2 from H_2O and O_2 using a two-compartment cell composed of a semiconductor photocatalyst anode in one cell and a carbon cloth cathode in the presence of Ru complexes and Sc^{3+} in an O_2-saturated aqueous solution in the other cell to achieve higher concentrations of H_2O_2 as compared with those with a one-compartment cell.

A schematic representation of the two-compartment cell employed in this study is shown in Fig. S2, where WO_3 or $BiVO_4$ was used as a photoanode[17] for photooxidation of water and a carbon mesh cathode was used for photoreduction of O_2 by Ru complexes. The two compartments were separated by a Nafion membrane.

When $[Ru^{II}((MeO)_2bpy)_3]^{2+}$ ((MeO)$_2$bpy = 4,4'-dimethoxy-2,2'-bipyridine, **1**) was employed as a photocatalyst for two-electron reduction of O_2 in the presence of Sc^{3+} (100 mM) in an O_2-saturated aqueous solution, photocurrent generation was observed as shown in Fig. 1a, where no or little photocurrent was observed in the absence of O_2.[18] When $[Ru^{II}((MeO)_2bpy)_3]^{2+}$ was replaced by $[Ru^{II}(Me_2phen)_3]^{2+}$ (Me$_2$phen = 4,7-dimethyl-1,10-phenanthroline, **2**) under otherwise the same conditions, the photocurrent was significantly smaller by two orders of magnitude (Fig. 1b).

When monochromic light (λ = 450 nm) was continuously irradiated to acidic aqueous solutions of **1** and **2**, formation of
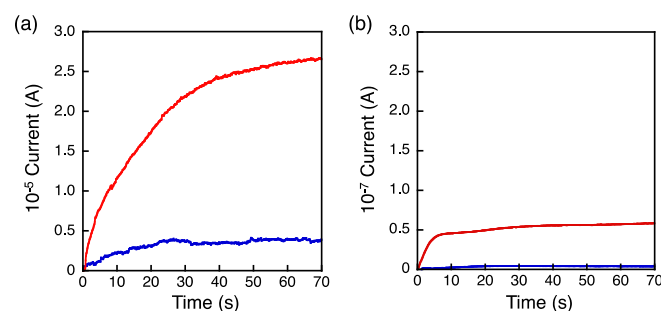
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Fig. 1 Photocurrent (at 0.30 V vs. SCE) under photoirradiation by a Xe lamp (λ > 420 nm) of (a) $[Ru^{II}((MeO)_2bpy)_3]^{2+}$ (160 μM) or (b) $[Ru^{II}(Me_2phen)_3]^{2+}$ (160 μM) in an O_2- (red lines) or N_2-saturated (blue lines) aqueous solution (8.0 mL) of Sc^{3+} (100 mM).

corresponding Ru^{III} complexes was confirmed for both solutions by UV-Vis measurements (Fig. 2). While over 90% of **1** originally present in the solution existed as $[Ru^{III}((MeO)_2bpy)_3]^{3+}$ after 3500 s of photoirradiation, only 22% of **2** was observed as $[Ru^{III}(Me_2phen)_3]^{3+}$ after light irradiation (Fig. S3). Thus the increased photocurrent observed for **1** as compared to **2** was due to increased concentration of Ru^{III} species *in situ* that can oxidise

the electrode to generate photocurrent.

The rate constant of electron transfer from $[Ru^{II}((MeO)_2bpy)_3]^{2+*}$ to O_2 (4.9×10^9 M^{-1} s^{-1}) was comparable to that from $[Ru^{II}(Me_2phen)_3]^{2+*}$ (6.1×10^9 M^{-1} s^{-1}) where asterisk indicating the photoexcited states of the complexes (Fig. S4).[14] In the presence of Sc^{3+} (100 mM), back electron transfer from $O_2^{\bullet-}$ to $[Ru^{III}((MeO)_2bpy)_3]^{3+}$ examined by nanosecond laser flash photolysis measurements was decelerated significantly due to the strong binding of Sc^{3+} to $O_2^{\bullet-}$ as shown in Fig. 3.[18]

When $BiVO_4$ was employed as photocatalyst for the photooxidation of water under visible light irradiation, photocurrent generation as well as O_2 evolution was observed (Fig. 4). When $BiVO_4$ was replaced by WO_3, the rate of O_2 evolution became significantly reduced (Fig. 4b and Fig. S5).

Formation of the hole in the photoexcited $BiVO_4$ was detected around $\lambda = 600$ nm as reported previously[19] by a new technique for subnanosecond transient absorption measurement, RIPT (Randomly-Interleaved-Pulse-Train) method (Fig. 5).[20]
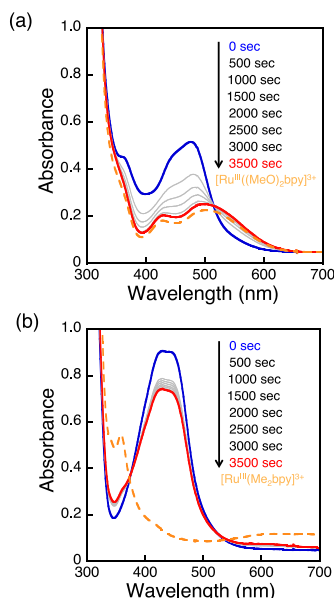

Fig. 2 Changes in the UV-Vis absorption spectrum of an aqueous solution of (a) $[Ru^{II}((MeO)_2bpy)_3]^{2+}$ (40 μM) and (b) $[Ru^{II}(Me_2phen)_3]^{2+}$ (40 μM) containing Sc^{3+} (100 mM) under photoirradiation by monochromic light (λ = 450 nm). Absorption spectrum of (a) $[Ru^{III}((MeO)_2bpy)_3]^{3+}$ (40 μM) and (b) $[Ru^{III}(Me_2phen)_3]^{3+}$ in the presence of Sc^{3+} (100 mM) in water are also shown in the figures (orange lines). pH of the aqueous solutions are adjusted to 1.0 by H_2SO_4 for all of the samples.
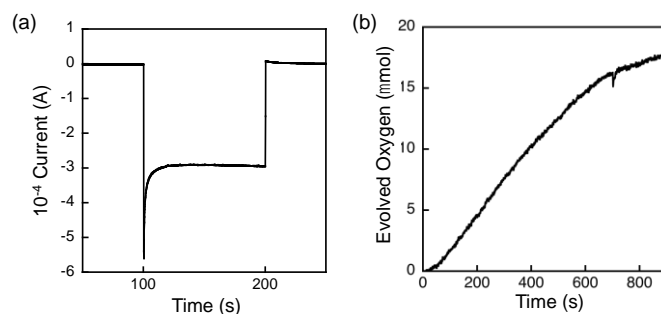

Fig. 4 (a) Photocurrent (at 0.25 V vs. SCE) under photoirradiation of $BiVO_4$ anode in an aqueous solution of $Sc(NO_3)_3$ (100 mM) with a Xe lamp (λ > 420 nm). (b) O_2 evolution during photocurrent generation at an applied potential of 0.52 V vs SCE measured by using an O_2 sensor.
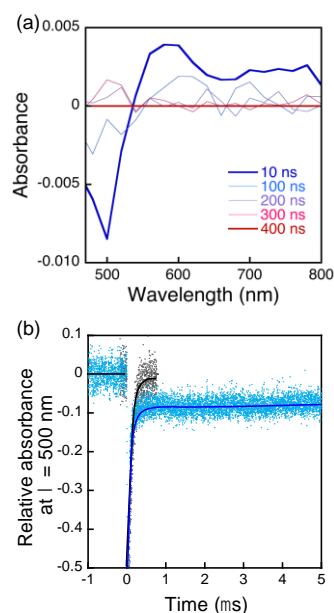

Fig. 3 (a) Transient absorption spectra of $[Ru^{II}((MeO)_2bpy)_3]^{2+}$ (20 μM) in an O_2-saturated H_2O after laser excitation at λ = 355 nm. (b) Time profiles of bleaching at 500 nm due to $[Ru^{III}((MeO)_2bpy)_3]^{3+}$ in the absence (black line) and presence (blue line) of Sc^{3+} (75 mM).
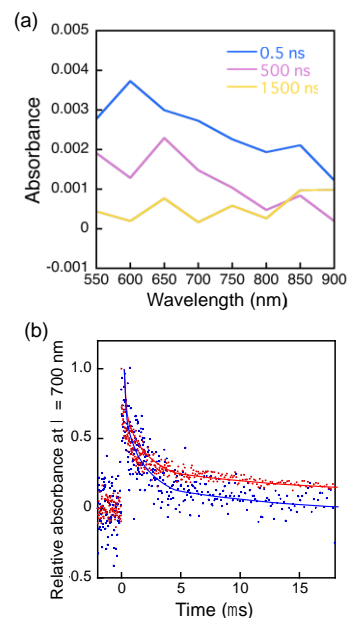

Fig. 5 (a) Transient absorption spectra of photoexcited $BiVO_4$. (b) Absorbance at λ = 700 nm relative to absorbance at 0 μs without bias voltage (blue line) and at 0.5 V vs. SCE (red line).
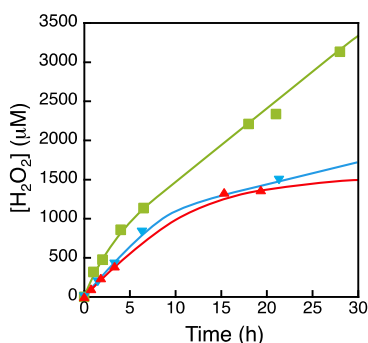
Fig. 6 Production of H_2O_2 under photoirradiation of a two-compartment cell composed of a semiconductor photocatalyst anode (BiVO$_4$ (green line and blue line) or WO$_3$ (red line)) in one cell and a carbon cloth cathode in the presence of [Ru^{II}((MeO)$_2$bpy)$_3$]$^{2+}$ (160 μM, black line) or [Ru^{II}(Me$_2$phen)$_3$]$^{2+}$ (160 μM, blue line and green line) in the other cell. Both cells were filled with aqueous solution of Sc^{3+} (100 mM, 8.0 mL for each cell). A Xe lamp (λ > 420 nm) and a solar simulator were used to irradiate Ru complex and semiconductor photocatalyst, respectively.
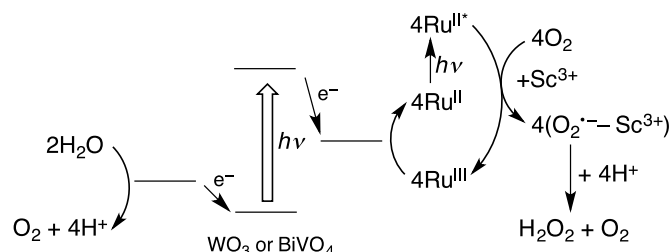
Scheme 1. Catalytic cycle of the photocatalytic production of H_2O_2 from H_2O and O_2 using a Ru photocatalyst and a semiconductor photocatalyst. Ru^{II*} and $O_2^{\bullet-}$ indicate photoexcited state of Ru^{II} complex and superoxide radical anion, respectively.

The lifetime of the observed hole was elongated when a positive voltage was applied to the electrode possibly because recombination of electrons and holes was retarded by accelerated consumption of electrons at electrode (Fig. 5b).

The combination of the BiVO$_4$ photoanode and carbon mesh cathode in the presence of [Ru^{II}((MeO)$_2$bpy)$_3$]$^{2+}$ and Sc^{3+} gave the best performance in terms of the photocatalytic production of H_2O_2 from H_2O and O_2 as shown in Fig. 6.

Based on above-mentioned results, the photocatalytic production of H_2O_2 from H_2O and O_2 is summarised in Scheme 1. Electron transfer from [Ru^{II}((MeO)$_2$bpy)$_3$]$^{2+*}$ to O_2 occurs to produce [Ru^{III}((MeO)$_2$bpy)$_3$]$^{3+}$ and $O_2^{\bullet-}$. Strong biding of Sc^{3+} to $O_2^{\bullet-}$ to give $O_2^{\bullet-}$–Sc^{3+} complex prohibits back electron transfer from the $O_2^{\bullet-}$–Sc^{3+} complex to [Ru^{III}((MeO)$_2$bpy)$_3$]$^{3+}$. The $O_2^{\bullet-}$–Sc^{3+} complex disproportionates in the presence of H$^+$ to produce H_2O_2. On the other hand, the photoexcitation of BiVO$_4$ results in formation of holes that oxidise water to O_2. Electrons in conduction band of BiVO$_4$ reduce [Ru^{III}((MeO)$_2$bpy)$_3$]$^{3+}$ to regenerate [Ru^{II}((MeO)$_2$bpy)$_3$]$^{2+}$.

In conclusion, H_2O_2 was produced from water and dioxygen by combination of BiVO$_4$-phoocatalysed oxidation of water and photocatalytic two-electron reduction of dioxygen with [Ru^{II}((MeO)$_2$bpy)$_3$]$^{2+}$ in the presence of Sc^{3+} in water using a two-compartment cell under visible light irradiation. This study provides a promising way for production of H_2O_2 as a solar fuel.

The further improvement of the catalytic activity and stability is now in progress.

Acknowledgements

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