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Yusuke Isaka, Yusuke Yamada, Tomoyoshi Suenobu,
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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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Yusuke Isaka,^a Yusuke Yamada,^{*,b} Tomoyoshi Suenobu,^a Tatsuo Nakagawa^c and Shunichi Fukuzumi^{*,d,e}

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)₂bpy = 4,4'-dimethoxy-2,2'-bipyridine) in the presence of Sc³⁺ in water under visible light irradiation.

Hydrogen peroxide (H₂O₂) 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 H₂O₂ has also merited increasing attention as a green oxidant, because only water is produced as the reduced product.⁸⁻¹⁰

H₂O₂ 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 H₂O₂ from water and dioxygen in the air using solar energy.

We have previously reported that H₂O₂ can be produced by combination of thermal water oxidation using water oxidation catalysts and photocatalytic two-electron reduction of O₂ using Ru complexes as photocatalysts.¹⁴⁻¹⁶ When the water oxidation and O₂ reduction were performed in a one compartment cell, produced H₂O₂ can be decomposed in the presence of water oxidation catalysts to preclude the production of H₂O₂ at higher

concentrations.

We report herein the photocatalytic production of H₂O₂ from H₂O and O₂ 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 Sc³⁺ in an O₂-saturated aqueous solution in the other cell to achieve higher concentrations of H₂O₂ 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 WO₃ or BiVO₄ was used as a photoanode¹⁷ for photooxidation of water and a carbon mesh cathode was used for photoreduction of O₂ by Ru complexes. The two compartments were separated by a Nafion membrane.

When [Ru^{II}((MeO)₂bpy)₃]²⁺ ((MeO)₂bpy = 4,4'-dimethoxy-2,2'-bipyridine, **1**) was employed as a photocatalyst for two-electron reduction of O₂ in the presence of Sc³⁺ (100 mM) in an O₂-saturated aqueous solution, photocurrent generation was observed as shown in Fig. 1a, where no or little photocurrent was observed in the absence of O₂.¹⁸ When [Ru^{II}((MeO)₂bpy)₃]²⁺ was replaced by [Ru^{II}(Me₂phen)₃]²⁺ (Me₂phen = 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 ($\lambda = 450$ nm) was continuously irradiated to acidic aqueous solutions of **1** and **2**, formation of

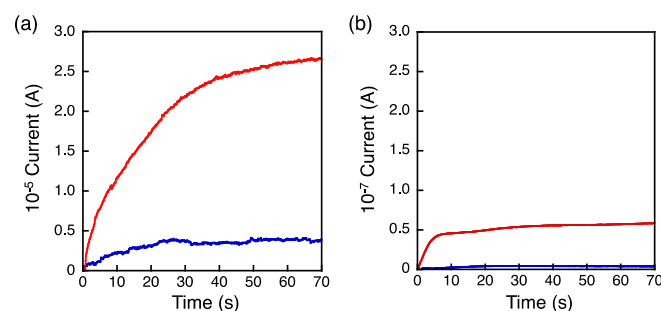


Fig. 1 Photocurrent (at 0.30 V vs. SCE) under photoirradiation by a Xe lamp ($\lambda > 420$ nm) of (a) [Ru^{II}((MeO)₂bpy)₃]²⁺ (160 μM) or (b) [Ru^{II}(Me₂phen)₃]²⁺ (160 μM) in an O₂- (red lines) or N₂-saturated (blue lines) aqueous solution (8.0 mL) of Sc³⁺ (100 mM).

^a Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan. E-mail: fukuzumi@chem.eng.osaka-u.ac.jp

^b Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, Osaka 558-0022, Japan. E-mail: ymd@a-chem.eng.osaka-cu.ac.jp

^c Unisoku Co., Ltd, Kasugano 2-4-3, Hirakata, Osaka 573-0131, Japan

^d Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea

^e Faculty of Science and Technology, Meijo University, ALCA, Japan Science and Technology Agency (JST), Nagoya, Aichi 468-8502, Japan

Electronic Supplementary Information (ESI) available: Experimental details, 5 Figures [UV-Vis absorption spectra of solutions and the electrode, schematic representation of a two-compartment cell, phosphorescence spectrum, time course of photocurrent and oxygen generation], estimation of the O₂ amount, and calculation of the simulated spectrum. See DOI: 10.1039/x0xx00000x

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}(Me₂phen)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

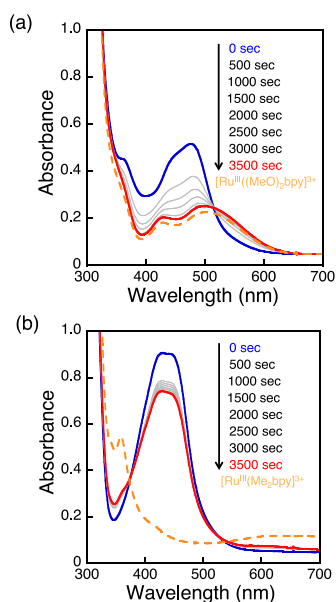


Fig. 2 Changes in the UV-Vis absorption spectrum of an aqueous solution of (a) [Ru^{III}((MeO)₂bpy)₃]²⁺ (40 μM) and (b) [Ru^{III}(Me₂phen)₃]²⁺ (40 μM) containing Sc³⁺ (100 mM) under photoirradiation by monochromatic light ($\lambda = 450$ nm). Absorption spectrum of (a) [Ru^{III}((MeO)₂bpy)₃]³⁺ (40 μM) and (b) [Ru^{III}(Me₂phen)₃]³⁺ in the presence of Sc³⁺ (100 mM) in water are also shown in the figures (orange lines). pH of the aqueous solutions are adjusted to 1.0 by H₂SO₄ for all of the samples.

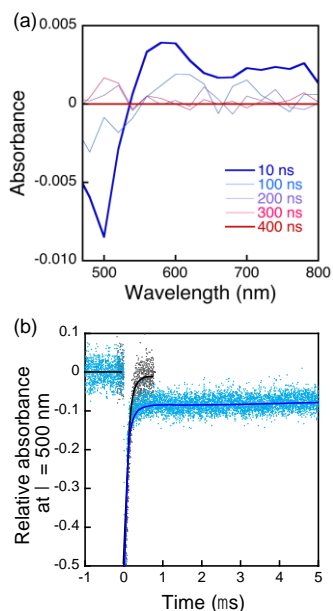


Fig. 3 (a) Transient absorption spectra of [Ru^{III}((MeO)₂bpy)₃]²⁺ (20 μM) in an O₂-saturated H₂O after laser excitation at $\lambda = 355$ nm. (b) Time profiles of bleaching at 500 nm due to [Ru^{III}((MeO)₂bpy)₃]²⁺ in the absence (black line) and presence (blue line) of Sc³⁺ (75 mM).

the electrode to generate photocurrent.

The rate constant of electron transfer from [Ru^{II}((MeO)₂bpy)₃]^{2+*} to O₂ (4.9×10^9 M⁻¹ s⁻¹) was comparable to that from [Ru^{II}(Me₂phen)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 Sc³⁺ (100 mM), back electron transfer from O₂⁻ to [Ru^{III}((MeO)₂bpy)₃]³⁺ examined by nanosecond laser flash photolysis measurements was decelerated significantly due to the strong binding of Sc³⁺ to O₂⁻ as shown in Fig. 3.¹⁸

When BiVO₄ was employed as photocatalyst for the photooxidation of water under visible light irradiation, photocurrent generation as well as O₂ evolution was observed (Fig. 4). When BiVO₄ was replaced by WO₃, the rate of O₂ evolution became significantly reduced (Fig. 4b and Fig. S5).

Formation of the hole in the photoexcited BiVO₄ was detected around $\lambda = 600$ nm as reported previously¹⁹ by a new technique for subnanosecond transient absorption measurement, RIPT (Randomly-Interleaved-Pulse-Train) method (Fig. 5).²⁰

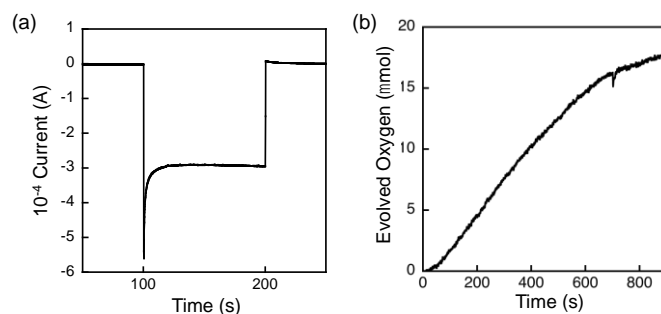


Fig. 4 (a) Photocurrent (at 0.25 V vs. SCE) under photoirradiation of BiVO₄ anode in an aqueous solution of Sc(NO₃)₃ (100 mM) with a Xe lamp ($\lambda > 420$ nm). (b) O₂ evolution during photocurrent generation at an applied potential of 0.52 V vs SCE measured by using an O₂ sensor.

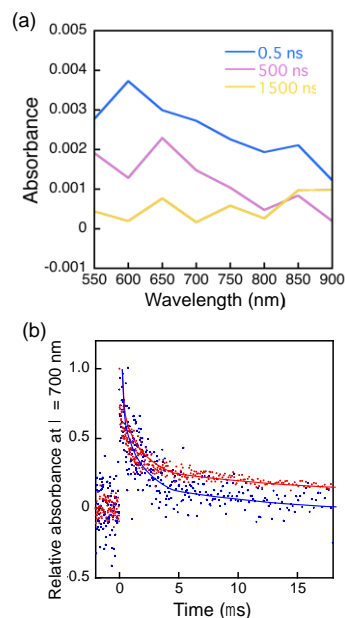


Fig. 5 (a) Transient absorption spectra of photoexcited BiVO₄. (b) Absorbance at $\lambda = 700$ nm relative to absorbance at 0 μ s without bias voltage (blue line) and at 0.5 V vs. SCE (red line).

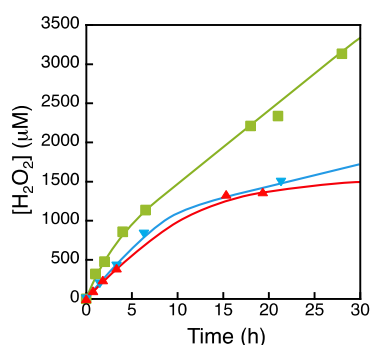
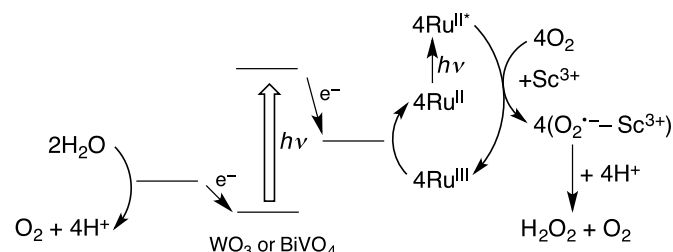


Fig. 6 Production of H_2O_2 under photoirradiation of a two-compartment cell composed of a semiconductor photocatalyst anode (BiVO_4 (green line and blue line) or WO_3 (red line)) in one cell and a carbon cloth cathode in the presence of $[\text{Ru}^{\text{II}}((\text{MeO})_2\text{bpy})_3]^{2+}$ (160 μM , black line) or $[\text{Ru}^{\text{II}}(\text{Me}_2\text{phen})_3]^{2+}$ (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 ($\lambda > 420$ 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. $\text{Ru}^{\text{II}*}$ and $\text{O}_2^{\bullet-}$ 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 $[\text{Ru}^{\text{II}}((\text{MeO})_2\text{bpy})_3]^{2+}$ 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 $[\text{Ru}^{\text{II}}((\text{MeO})_2\text{bpy})_3]^{2+}$ to O_2 occurs to produce $[\text{Ru}^{\text{III}}((\text{MeO})_2\text{bpy})_3]^{3+}$ and $\text{O}_2^{\bullet-}$. Strong binding of Sc^{3+} to $\text{O}_2^{\bullet-}$ to give $\text{O}_2^{\bullet-}-\text{Sc}^{3+}$ complex prohibits back electron transfer from the $\text{O}_2^{\bullet-}-\text{Sc}^{3+}$ complex to $[\text{Ru}^{\text{III}}((\text{MeO})_2\text{bpy})_3]^{3+}$. The $\text{O}_2^{\bullet-}-\text{Sc}^{3+}$ 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 $[\text{Ru}^{\text{III}}((\text{MeO})_2\text{bpy})_3]^{3+}$ to regenerate $[\text{Ru}^{\text{II}}((\text{MeO})_2\text{bpy})_3]^{2+}$.

In conclusion, H_2O_2 was produced from water and dioxygen by combination of BiVO_4 -photoassisted oxidation of water and photocatalytic two-electron reduction of dioxygen with $[\text{Ru}^{\text{II}}((\text{MeO})_2\text{bpy})_3]^{2+}$ 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.

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