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Photocatalytic reduction of CO₂ and H₂O to CO and H₂ with a cobalt chlorin complex adsorbed on multi-walled carbon nanotubes[†]

Shoko Aoi,^a Kentaro Mase,^a Kei Ohkubo^{*ab} and Shunichi Fukuzumi^{*bc}

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The photocatalytic reduction of CO₂ and H₂O with triethylamine occurred efficiently using a cobalt(II) chlorin complex adsorbed on multi-walled carbon nanotubes as a CO₂ reduction catalyst and $[Ru^{II}(Me_2phen)_3]^{2+}$ (Me₂phen = 4,7-dimethyl-1,10-phenanthroline) as a photocatalyst to yield CO and H_2 with a ratio of 2.4:1 and a high turnover number of 710.

Photocatalytic reduction of carbon dioxide (CO₂) and water (H_2O) to produce synthesis gas, which is a fuel gas mixture consisting primarily of hydrogen (H₂) and carbon monoxide (CO), has merited significant interest, because synthetic gas can be converted to liquid hydrocarbon fuels by Fischer-Tropsch processes.^{1–6} The 2nd and 3rd row transition metal complexes such as Re and Ir complexes have been used as effective photocatalysts for CO2 reduction.7-13 The much more earth abundant metal complexes such as Co complexes have also been used as catalysts for photocatalytic CO2 reduction.¹⁴⁻²¹ However, the turnover number has yet to be much improved for the photocatalytic reduction of CO2 and H₂O to produce synthetic gas with earth-abundant metal complexes.

We report herein the efficient photocatalytic reduction of CO_2 and H_2O using triethylamine (TEA) as a reductant, a cobalt(II) chlorin complex adsorbed on multi-walled carbon nanotubes (MWCNTs) as a CO₂ reduction catalyst and $[Ru^{II}(Me_2phen)_3]^{2+}$ $(Me_2phen = 4,7-dimethyl-1,10-phenanthroline)$ as a photocatalyst in acetonitrile (MeCN) containing 5% (v/v) water to yield CO and H₂ with a 2.4 to 1.0 ratio and a high turnover

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

^b Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea. E-mail: fukuzumi@chem.eng.osaka-u.ac.jp

number. The photocatalytic mechanism is clarified by examining each step of the catalytic cycle.

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Visible light irradiation of a CO₂-saturated MeCN solution of $[Ru^{II}(Me_2phen)_3]^{2+}$, cobalt(II) chlorin complex Co^{II}(Ch) (the chemical structure is shown in Scheme 1) and TEA containing 5% (v/v) H₂O resulted in the formation of CO and H₂ as shown in Fig. 1. The optimised concentration of Co^{II}(Ch) was 40 µM and the higher concentration of $Co^{II}(Ch)$ absorbed more light than $[Ru^{II}(Me_2phen)_3]^{2+}$ to retard the photocatalytic reaction (Fig. S1 in the ESI[†]). When Co^{II}(Ch) was adsorbed on MWCNTs by adding MWCNTs to the reaction solution and then stirring it (Fig. S2 in the ESI⁺), the yield of CO was much improved as compared with that without MWCNTs (Fig. 2). The turnover number (TON) was determined to be 710 with Co^{II}(Ch) (5.0 µM) and MWCNTs (1.0 mg) at 20 h.²⁵ The π - π interaction between MWCNTs and Co^{II}(Ch) may provide a suitable hydrophobic environment for the binding of CO₂ instead of proton, because the binding of CO₂ to the Co(1) complex is required for the formation of CO.14

The emission of [Ru^{II}(Me₂phen)₃]^{2+*} was hardly quenched by Co^{II}(Ch) (Fig. S3 in the ESI[†]). The emission lifetime of $[Ru^{II}(Me_2phen)_3]^{2+*}$ remained the same in the presence of $Co^{II}(Ch)$ (100 µM) as that in the absence of $Co^{II}(Ch)$. The oneelectron oxidation potential $(E_{\alpha x}^*)$ of $[Ru^{II}(Me_2phen)_3]^{2+*}$ was determined from the one-electron oxidation potential of the ground state (1.12 V vs. SCE) and the excitation energy



Scheme 1 Mechanism of photocatalytic CO evolution from TEA with [Ru^{II}(Me₂phen)₃]²⁺ and Co^{II}(Ch).

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

[†] Electronic supplementary information (ESI) available: Experimental details and UV-vis absorption spectra (Fig. S1, S2 and S6), emission decay profiles (Fig. S3), cyclic voltammograms (Fig. S4 and S5), FTIR spectra (Fig. S7) and kinetic data (Fig. S8). See DOI: 10.1039/c6cy00376a



Fig. 1 Time courses of the production of (a) CO and (b) H₂ by photoirradiation of a CO₂-saturated MeCN solution of [Ru^{II}(Me₂phen)₃]²⁺ (2.0 mM), Co^{II}(Ch) (5.0, 40 and 60 μ M) and TEA (0.50 M) containing 5% (v/v) H₂O using a xenon lamp with a cut off filter ($\lambda > 420$ nm) at 298 K.



Fig. 2 Time courses of the production of CO and H₂ by photoirradiation of a CO₂-saturated MeCN solution of [Ru^{II}(Me₂phen)₃]²⁺ (2.0 mM), TEA (0.50 M), Co^{II}(Ch) (10 μ M) adsorbed on MWCNTs (1.0 mg) (red) and Co^{II}(Ch) (10 μ M) without MWCNTs (black) containing 5% (v/v) H₂O using a xenon lamp with a cut off filter ($\lambda > 420$ nm) at 298 K.

(2.1 eV) to be $-0.98 \text{ V} \nu s$. SCE.²³ The E_{ox}^* value is less negative than the one-electron reduction potential of Co^{II}(Ch) ($E_{red} \nu s$. SCE = -0.89 V), when the electron transfer from $[\text{Ru}^{II}(\text{Me}_2\text{phen})_3]^{2+*}$ to Co^{II}(Ch) is exergonic (Fig. S4 in the ESI†).

On the other hand, the emission of [Ru^{II}(Me₂phen)₃]^{2+*} was quenched by TEA by electron transfer from TEA to $[Ru^{II}(Me_2phen)_3]^{2+*}$. The one-electron reduction potential (E_{red}^*) of $[\text{Ru}^{\text{II}}(\text{Me}_2\text{phen})_3]^{2+*}$ was determined from the oneelectron reduction potential of the ground state (-1.47 V vs. SCE) and the excitation energy (2.1 eV) to be 0.67 V vs. SCE. Because the E_{ox} value of TEA (0.74 V vs. SCE), which was determined by second harmonic ac voltammetry (SHACV; Fig. S5 in the ESI[†]), is more positive than the E_{red}^* value, the electron transfer from TEA to [Ru^{II}(Me₂phen)₃]^{2+*} is slightly endergonic. The rate constant of electron transfer from TEA to [Ru^{II}(Me₂phen)₃]^{2+*} was determined from the Stern-Volmer plot (Fig. 3) to be 1.7×10^6 M⁻¹ s⁻¹ in MeCN at 298 K. The quantum yield of the photocatalytic reduction of CO₂ to CO under photoirradiation of light at λ = 450 nm was determined to be 0.10% using a ferric oxalate actinometer (see the Experimental section in the ESI[†]).



Fig. 3 (a) Emission spectra of $[Ru^{II}(Me_2phen)_3]^{2+}$ (8.8 μ M) with various concentrations of TEA (0–0.50 M) in deaerated MeCN containing 5% (v/v) H₂O at 298 K. (b) Stern–Volmer plot.

The photocatalytic mechanism of the CO₂ reduction is shown in Scheme 1. Upon photoexcitation of $[Ru^{II}(Me_2phen)_3]^{2+}$, electron transfer from TEA to $[Ru^{II}(Me_2phen)_3]^{2+*}$ occurs to produce a TEA radical cation and $[Ru(Me_2phen)_3]^+$, the latter of which reduces $Co^{II}(Ch)$ to [Co^I(Ch)]⁻. The TEA radical cation may be deprotonated to produce a neutral radical that may be further oxidized. Thus, the endergonic electron transfer from TEA $[Ru^{II}(Me_2phen)_3]^{2+*}$ (vide supra) is irreversible. We have previously reported that CO₂ is reduced to CO when Co^{II}(Ch) is electrochemically reduced to [CoI(Ch)]-.22 At the same time [Co^I(Ch)]⁻ was reported to react with H⁺ to produce the hydride complex ([Co^{III}(H)(Ch)]), which reacts with H⁺ to produce H₂.²⁴ [Co^{III}(H)(Ch)] is also an intermediate for H₂ evolution in the photocatalytic reduction of H₂O to H₂.²⁶

In order to examine the reaction of $[\text{Co}^{\text{I}}(\text{Ch})]^{-}$ with CO₂, $[\text{Co}^{\text{I}}(\text{Ch})]^{-}$ was prepared independently by the one-electron reduction of Co^{II}(Ch) with decamethylcobaltocene $[\text{Co}(\text{Cp}^*)_2]$ in MeCN as reported previously.²⁴ The UV-vis absorption band of $[\text{Co}^{\text{I}}(\text{Ch})]^{-}$ (green line in Fig. 4a; $\lambda_{\text{max}} = 510$ nm) decreased, accompanied by an increase in absorbance at 660 nm due to $[\text{Co}^{\text{II}}(\text{Ch})(\text{CO}_2)]^{-}$ (blue line) at 65 ms upon introduction of CO₂ by mixing.²⁷ Then, this absorption band finally blue shifted to $\lambda_{\text{max}} = 652$ nm, which is due to $[\text{Co}^{\text{III}}(\text{Ch})(\text{CO})]^{+}$



Fig. 4 (a) UV-vis absorption spectral changes of $[Co^{I}(Ch)]^{-}$ (20 μ M) upon introduction of CO_2 -saturated MeCN containing 5% (v/v) H₂O at 298 K. The blue and red lines show the spectra taken at 65 ms and 2 s after mixing, respectively. The green line shows the UV-vis absorption spectrum of $[Co^{I}(Ch)]^{-}$ (15 μ M) formed by the electron-transfer reduction of Co^{II}(Ch) (15 μ M) with Co(Cp^{*})₂ (300 μ M) in deaerated MeCN at 298 K.²⁴ (b) Decay time profile of absorbance at 660 nm due to $[Co^{III}(Ch)(CO_2)]^{-}$.



Fig. 5 (a) UV-vis absorption spectral changes in the electron-transfer reduction of $[Co^{III}(Ch)]^+$ (20 μ M) with TEA (0.10 M) in deaerated MeCN containing 5% (v/v) H₂O at 298 K at 65 ms and 25 s after mixing. (b) Decay time profiles of absorbance at 652 nm due to $[Co^{III}(Ch)]^+$ in the presence of various concentrations of TEA in deaerated MeCN containing 5% (v/v) H₂O at 298 K.

(red line). This absorption band matched with that of $[Co^{III}(Ch)(CO)]^+$ which was produced by introducing CO to $[Co^{III}(Ch)]^+$ in MeCN (Fig. S6 in the ESI[†]). When N₂ was introduced to $[Co^{III}(Ch)(CO)]^+$, the spectrum returned to $[Co^{III}(Ch)]^+$. This indicates that the binding of CO to $[Co^{III}(Ch)]^+$ is reversible. The CO stretching frequency of $[Co^{III}(Ch)]^+$ is reversible. The CO stretching frequency of $[Co^{III}(Ch)(CO)]^+$ was also measured in MeCN under an appropriate CO pressure (Fig. S7 in the ESI[†]). *v*CO is located at 2158 cm⁻¹, which is nearly the same as the "free" CO molecule (*v*CO = 2155 cm⁻¹),²⁸ suggesting a weak reversible coordination. Finally, $[Co^{III}(Ch)(CO_2)]^-$ was converted to $[Co^{III}(Ch)]^+$ and CO by protonation with dehydration (Scheme 1). The rate constant of the formation of $[Co^{III}(Ch)(CO)]^+$ was determined from the change in absorbance at 660 nm to be 3.4 s⁻¹ (Fig. 4b).

 $[Co^{III}(Ch)]^+$, which was prepared by one-electron oxidation of $Co^{II}(Ch)$ with (p-BrC₆H₄)₃N⁺⁺SbCl₆⁻, was thermally reduced by TEA to produce $Co^{II}(Ch)$ (Scheme 1) as shown in Fig. 5a. The rate of reduction of $[Co^{III}(Ch)]^+$ by a large excess of TEA obeyed first-order kinetics and the pseudo-first-order rate constant was proportional to the concentration of TEA. From the slope of the linear plot of the pseudo-first-order rate constant *vs.* concentration of TEA, the second-order rate constant was determined to be 0.64 M⁻¹ s⁻¹ (Fig. S8 in the ESI†).

In conclusion, $Co^{II}(Ch)$ adsorbed on MWCNTs acts as an efficient catalyst for photocatalytic CO_2 reduction to CO as well as H_2 evolution from TEA in MeCN containing 5% (v/v) water. The present study paves a new way to produce synthetic gas from CO_2 and H_2O using an earth-abundant metal complex catalyst for CO_2 reduction under visible light irradiation.

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