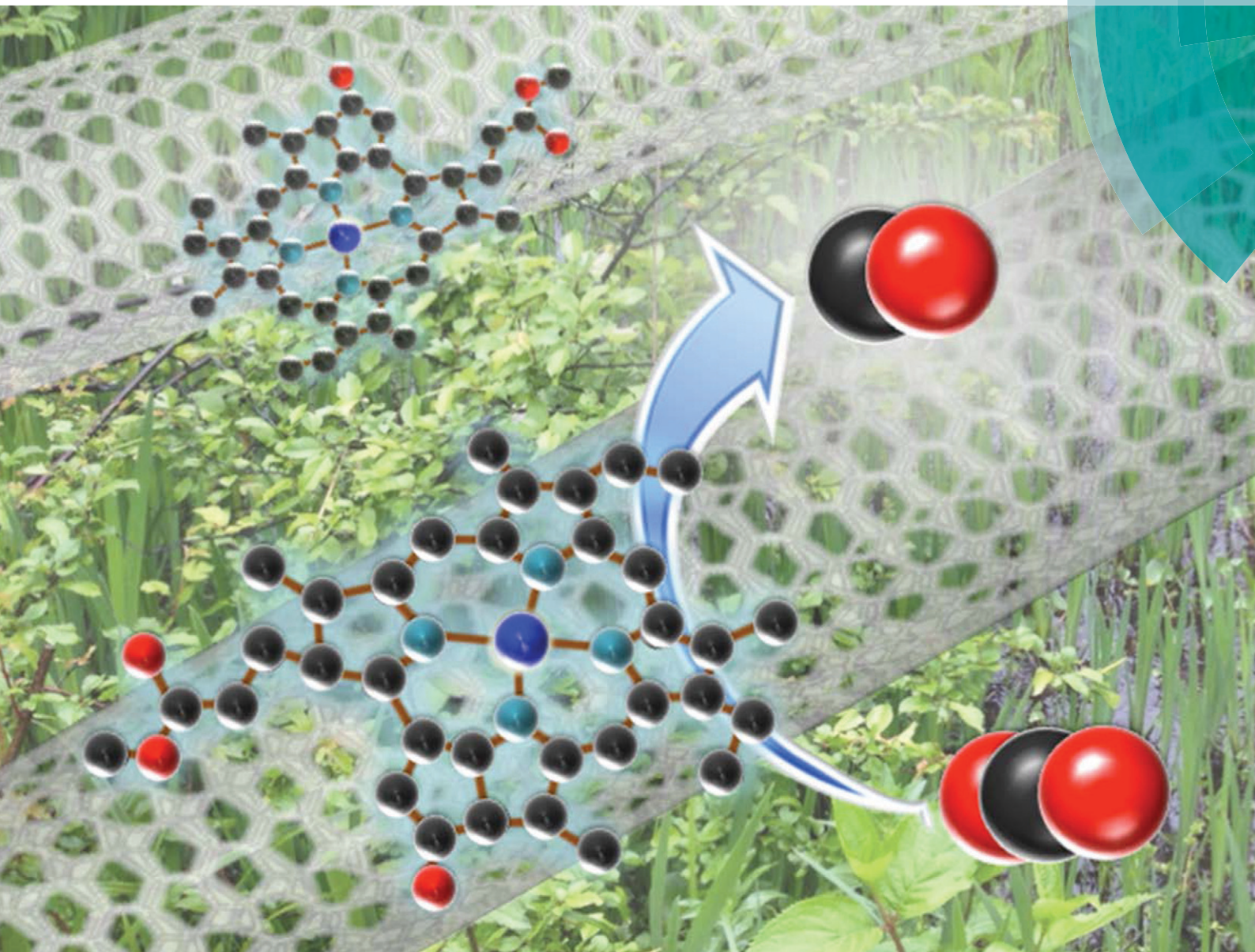


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COMMUNICATION

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Photocatalytic reduction of CO_2 and H_2O to CO and H_2 with a cobalt chlorin complex adsorbed on multi-walled carbon nanotubes

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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}(Me₂phen)₃]²⁺ (Me₂phen = 4,7-dimethyl-1,10-phenanthroline) as a photocatalyst to yield CO and H₂ with a ratio of 2.4 : 1 and a high turnover number of 710.

Photocatalytic reduction of carbon dioxide (CO₂) and water (H₂O) 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 CO₂ and H₂O 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}(Me₂phen)₃]²⁺ (Me₂phen = 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

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}

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

Visible light irradiation of a CO₂-saturated MeCN solution of [Ru^{II}(Me₂phen)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}(Me₂phen)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(I) complex is required for the formation of CO.¹⁴

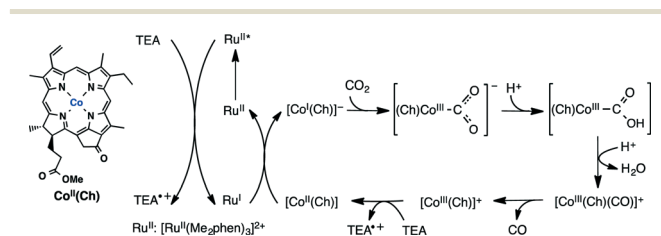
The emission of [Ru^{II}(Me₂phen)₃]^{2+*} was hardly quenched by Co^{II}(Ch) (Fig. S3 in the ESI†). The emission lifetime of [Ru^{II}(Me₂phen)₃]^{2+*} remained the same in the presence of Co^{II}(Ch) (100 μM) as that in the absence of Co^{II}(Ch). The one-electron oxidation potential (*E*_{ox}^{*}) of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

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† 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



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



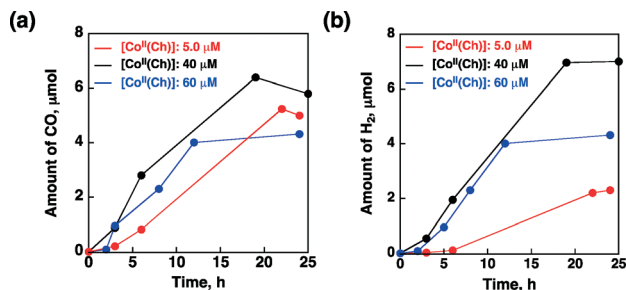


Fig. 1 Time courses of the production of (a) CO and (b) H₂ by photoirradiation of a CO₂-saturated MeCN solution of [Ru^{II}(Me₂phen)₃]²⁺ (2.0 mM), Co^{II}(Ch) (5.0, 40 and 60 μM) and TEA (0.50 M) containing 5% (v/v) H₂O using a xenon lamp with a cut off filter ($\lambda > 420$ nm) at 298 K.

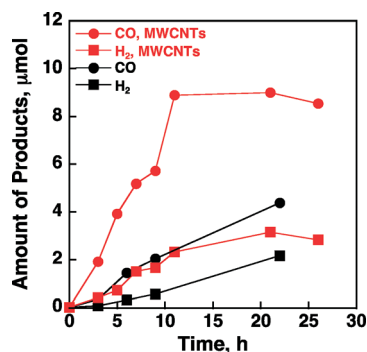


Fig. 2 Time courses of the production of CO and H₂ by photoirradiation of a CO₂-saturated MeCN solution of [Ru^{II}(Me₂phen)₃]²⁺ (2.0 mM), TEA (0.50 M), Co^{II}(Ch) (10 μM) adsorbed on MWCNTs (1.0 mg) (red) and Co^{II}(Ch) (10 μM) without MWCNTs (black) containing 5% (v/v) H₂O using a xenon lamp with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

(2.1 eV) to be -0.98 V vs. SCE.²³ The E_{ox}^* value is less negative than the one-electron reduction potential of Co^{II}(Ch) (E_{red} vs. SCE = -0.89 V), when the electron transfer from [Ru^{II}(Me₂phen)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}(Me₂phen)₃]^{2+*}. The one-electron reduction potential (E_{red}^*) of [Ru^{II}(Me₂phen)₃]^{2+*} was determined from the one-electron 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 $\lambda = 450$ nm was determined to be 0.10% using a ferric oxalate actinometer (see the Experimental section in the ESI[†]).

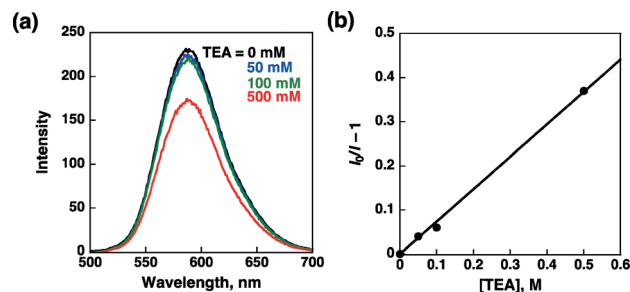


Fig. 3 (a) Emission spectra of [Ru^{II}(Me₂phen)₃]²⁺ (8.8 μM) with various concentrations of TEA (0–0.50 M) in deaerated MeCN containing 5% (v/v) H₂O at 298 K. (b) Stern–Volmer plot.

The photocatalytic mechanism of the CO₂ reduction is shown in Scheme 1. Upon photoexcitation of [Ru^{II}(Me₂phen)₃]²⁺, electron transfer from TEA to [Ru^{II}(Me₂phen)₃]^{2+*} occurs to produce a TEA radical cation and [Ru(Me₂phen)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 to [Ru^{II}(Me₂phen)₃]^{2+*} (*vide supra*) is irreversible. We have previously reported that CO₂ is reduced to CO when Co^{II}(Ch) is electrochemically reduced to [Co^I(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 [Co^I(Ch)]⁻ with CO₂, [Co^I(Ch)]⁻ was prepared independently by the one-electron reduction of Co^{II}(Ch) with decamethylcobaltocene [Co(Cp^{*})₂] in MeCN as reported previously.²⁴ The UV-vis absorption band of [Co^I(Ch)]⁻ (green line in Fig. 4a; $\lambda_{\text{max}} = 510$ nm) decreased, accompanied by an increase in absorbance at 660 nm due to [Co^{III}(Ch)(CO₂)]⁻ (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 [Co^{III}(Ch)(CO)]⁻

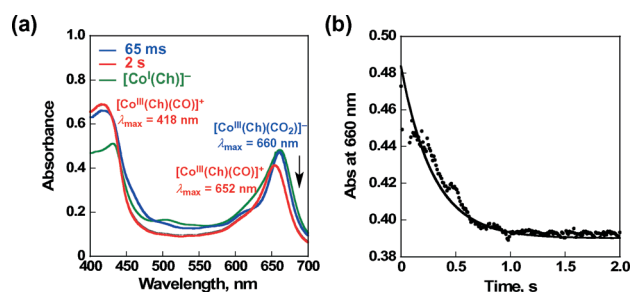


Fig. 4 (a) UV-vis absorption spectral changes of [Co^I(Ch)]⁻ (20 μM) upon introduction of CO₂-saturated MeCN containing 5% (v/v) H₂O at 298 K. The blue and red lines show the spectra taken at 65 ms and 2 s after mixing, respectively. The green line shows the UV-vis absorption spectrum of [Co^I(Ch)]⁻ (15 μM) formed by the electron-transfer reduction of Co^{II}(Ch) (15 μM) with Co(Cp^{*})₂ (300 μM) in deaerated MeCN at 298 K.²⁴ (b) Decay time profile of absorbance at 660 nm due to [Co^{III}(Ch)(CO₂)]⁻.



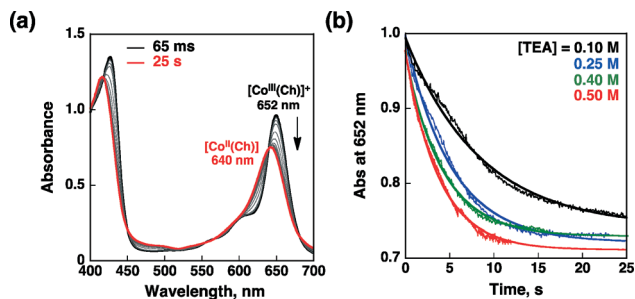


Fig. 5 (a) UV-vis absorption spectral changes in the electron-transfer reduction of $[\text{Co}^{\text{III}}(\text{Ch})]^+$ ($20 \mu\text{M}$) with TEA (0.10 M) in deaerated MeCN containing 5% (v/v) H_2O at 298 K at 65 ms and 25 s after mixing. (b) Decay time profiles of absorbance at 652 nm due to $[\text{Co}^{\text{III}}(\text{Ch})]^+$ in the presence of various concentrations of TEA in deaerated MeCN containing 5% (v/v) H_2O at 298 K.

(red line). This absorption band matched with that of $[\text{Co}^{\text{III}}(\text{Ch})(\text{CO})]^+$ which was produced by introducing CO to $[\text{Co}^{\text{III}}(\text{Ch})]^+$ in MeCN (Fig. S6 in the ESI[†]). When N_2 was introduced to $[\text{Co}^{\text{III}}(\text{Ch})(\text{CO})]^+$, the spectrum returned to $[\text{Co}^{\text{III}}(\text{Ch})]^+$. This indicates that the binding of CO to $[\text{Co}^{\text{III}}(\text{Ch})]^+$ is reversible. The CO stretching frequency of $[\text{Co}^{\text{III}}(\text{Ch})(\text{CO})]^+$ was also measured in MeCN under an appropriate CO pressure (Fig. S7 in the ESI[†]). νCO is located at 2158 cm^{-1} , which is nearly the same as the “free” CO molecule ($\nu\text{CO} = 2155 \text{ cm}^{-1}$),²⁸ suggesting a weak reversible coordination. Finally, $[\text{Co}^{\text{III}}(\text{Ch})(\text{CO}_2)]^-$ was converted to $[\text{Co}^{\text{III}}(\text{Ch})]^+$ and CO by protonation with dehydration (Scheme 1). The rate constant of the formation of $[\text{Co}^{\text{III}}(\text{Ch})(\text{CO})]^+$ was determined from the change in absorbance at 660 nm to be 3.4 s^{-1} (Fig. 4b).

$[\text{Co}^{\text{III}}(\text{Ch})]^+$, which was prepared by one-electron oxidation of $\text{Co}^{\text{II}}(\text{Ch})$ with $(p\text{-BrC}_6\text{H}_4)_3\text{N}^+\text{SbCl}_6^-$, was thermally reduced by TEA to produce $\text{Co}^{\text{II}}(\text{Ch})$ (Scheme 1) as shown in Fig. 5a. The rate of reduction of $[\text{Co}^{\text{III}}(\text{Ch})]^+$ 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 $0.64 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. S8 in the ESI[†]).

In conclusion, $\text{Co}^{\text{II}}(\text{Ch})$ 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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- 24 S. Aoi, K. Mase, K. Ohkubo and S. Fukuzumi, *Chem. Commun.*, 2015, **51**, 15145.
- 25 The TON for CO formation was improved by the adsorption of the cobalt chlorin complex on MWCNTs, because two $[\text{Co}^{\text{I}}(\text{Ch})]^-$ molecules are located close to each other where the two-electron reduction of CO_2 to CO may occur. The optimized amount of MWCNTs was 1.0 mg under the present experimental conditions, because the amounts of CO and H_2 produced in the present photocatalytic system became smaller when 0.5 mg and 1.5 mg of MWCNTs were employed instead of 1.0 mg of MWCNTs.
- 26 No $\text{Co}(0)$ species was produced because a $\text{Co}(\text{i})/\text{Co}(0)$ couple was not observed in CV measurements. Thus, the catalytically active species for proton reduction maybe $\text{Co}(\text{iii})-\text{H}$.²⁴
- 27 An X-ray absorption near-edge spectroscopy (XANES) study of the $\text{Co}(\text{iii})-\text{CO}_2$ adducts clearly indicated a significant charge-transfer from $\text{Co}(\text{i})$ to the bound CO_2 (see: E. Fujita, L. R. Furenlid and M. W. Renner, *J. Am. Chem. Soc.*, 1997, **119**, 4549).
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