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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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Photocatalytic reduction of CO_2 and H_2O with triethylamine occurred efficiently using a cobalt(II) chlorin complex adsorbed on multi-walled carbon nanotubes as a CO_2 reduction catalyst and $[Ru^{II}(Me_2phen)_3]^{2+}$ (Me_2phen = 4,7-dimethyl-1,10-phenanthroline) as a photocatalyst to yield CO and H_2 with a ratio of 2.4:1 and the high turnover number of 710.

Photocatalytic reduction of carbon dioxide (CO_2) and water (H_2O) to produce synthesis gas, which is a fuel gas mixture consisting primarily of hydrogen (H_2) 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 the CO_2 reduction.[7-13] The much more earth abundant metal complexes such as Co complexes have also been used as catalysts for the photocatalytic CO_2 reduction.[14-21] However, the turnover number has yet to be much improved for the photocatalytic reduction of CO_2 and H_2O to produce synthetic gas with earth-abundant metal complexes.

We report herein efficient photocatalytic reduction of CO_2 and H_2O using triethylamine as a reductant, a cobalt(II) chlorin complex adsorbed on multi-walled carbon nanotubes (MWCNTs) as a CO_2 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 H_2 with a 2.4 to 1 ratio and high turnover number. The photocatalytic mechanism is clarified by examining each step of the catalytic cycle.

Visible light irradiation of a CO_2-saturated MeCN solution of $[Ru^{II}(Me_2phen)_3]^{2+}$, a cobalt(II) chlorin complex $Co^{II}(Ch)$ (the chemical structure is shown in Scheme 1) and triethylamine (TEA) containing 5% (v/v) H_2O resulted in formation of CO and H_2 as shown in Fig. 1. The optimised concentration of $Co^{II}(Ch)$ was 40 μM and the larger concentration of $Co^{II}(Ch)$ absorbed more light than $[Ru^{II}(Me_2phen)_3]^{2+}$ to retard the photocatalytic reaction (Fig. S1 in the electronic supplementary information (ESI)†). When $Co^{II}(Ch)$ was adsorbed on MWCNTs by adding

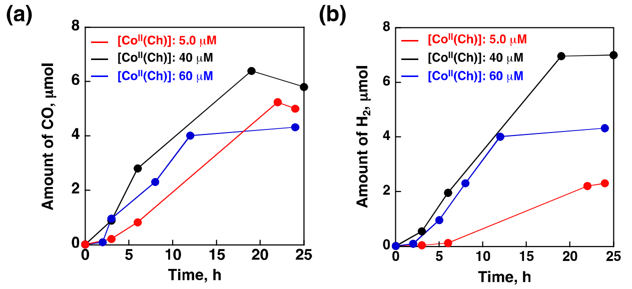

Fig. 1 Time courses of production of (a) CO and (b) H_2 by photoirradiation of a CO_2-saturated MeCN solution of $[Ru^{II}(Me_2phen)_3]^{2+}$ (2.0 mM), $Co^{II}(Ch)$ (5.0, 40 and 60 μM) and TEA (0.50 M) containing 5% (v/v) H_2O using a xenon lamp with a cut off filter ($\lambda >$ 420 nm) at 298 K.

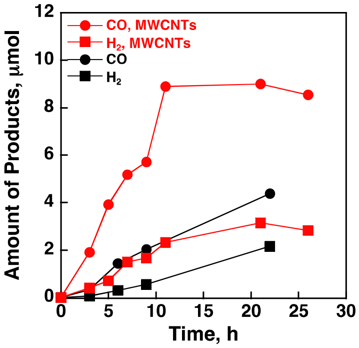

Fig. 2 Time courses of production of CO and H_2 by photoirradiation of a CO_2-saturated MeCN solution of $[Ru^{II}(Me_2phen)_3]^{2+}$ (2.0 mM), TEA (0.50 M), $Co^{II}(Ch)$ (10 μM) adsorbed on MWCNTs (1.0 mg) (red) and $Co^{II}(Ch)$ (10 μM) without MWCNTs (black) containing 5% (v/v) H_2O using a xenon lamp with a cut off filter ($\lambda >$ 420 nm) at 298 K.

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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/x0xx00000x

MWCNTs to the reaction solution and then stirring it (Fig. S2 in 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 binding of CO_2 instead of proton, because the binding of CO_2 to the Co(I) complex is required for formation of CO.[14]

The emission of $[Ru^{II}(Me_2phen)_3]^{2+*}$ was hardly quenched by Co^{II}(Ch) (Fig. S3 in 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 one-electron oxidation potential (E_{ox}^*) 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 (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 electron transfer from $[Ru^{II}(Me_2phen)_3]^{2+*}$ to Co^{II}(Ch) is exergonic (Fig. S4 in ESI†).

On the other hand, the emission of $[Ru^{II}(Me_2phen)_3]^{2+*}$ was quenched by TEA by electron transfer from TEA to $[Ru^{II}(Me_2phen)_3]^{2+*}$. The one-electron reduction potential (E_{red}^*) of $[Ru^{II}(Me_2phen)_3]^{2+*}$ 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 ESI†), is more positive than the E_{red}^* value, electron transfer from TEA to $[Ru^{II}(Me_2phen)_3]^{2+*}$ is slightly endergonic. The rate constant of electron transfer from TEA to $[Ru^{II}(Me_2phen)_3]^{2+*}$ 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 CO_2 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 ESI†).

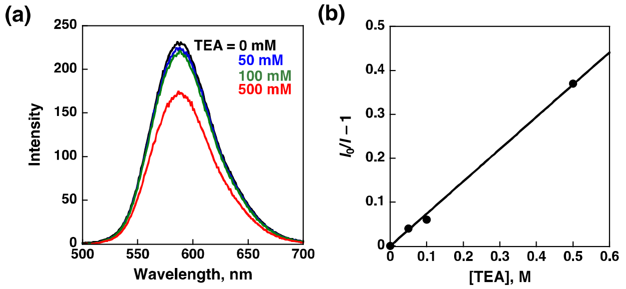
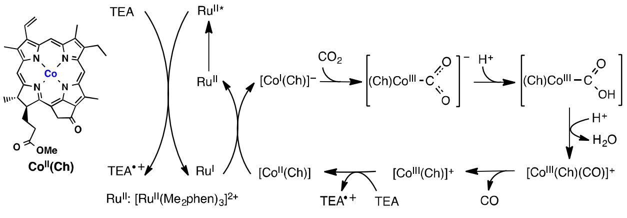


Fig. 3 (a) Emission spectra of $[Ru^{II}(Me_2phen)_3]^{2+}$ (8.8 μM) with various concentration of TEA (0-0.50 M) in deaerated MeCN containing 5% (v/v) H_2O at 298 K. (b) Stern-Volmer plot.



Scheme 1 Mechanism of photocatalytic CO evolution from TEA with $[Ru^{II}(Me_2phen)_3]^{2+}$ and Co^{II}(Ch).

The photocatalytic mechanism of the CO_2 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 TEA radical cation and $[Ru(Me_2phen)_3]^+$, the latter of which reduces Co^{II}(Ch) to $[Co^I(Ch)]^-$. TEA radical cation may be deprotonated to produce the neutral radical that may be further oxidized. Thus, the endergonic electron transfer from TEA to $[Ru^{II}(Me_2phen)_3]^{2+}$* (vide supra) is irreversible. We have previously reported that CO_2 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 H_2.[24] $[Co^{III}(H)(Ch)]$ is also intermediate for H_2 evolution in this photocatalytic reduction of H_2O to H_2.[26]

In order to examine the reaction of $[Co^I(Ch)]^-$ with CO_2, $[Co^I(Ch)]^-$ 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; λ_{max} = 510 nm) decreased, accompanied by an increase in absorbance at 660 nm due to $[Co^{III}(Ch)(CO_2)]^-$ (blue line) at 65 ms upon introduction of CO_2 by mixing.[27] Then, this absorption band was finally blue shifted

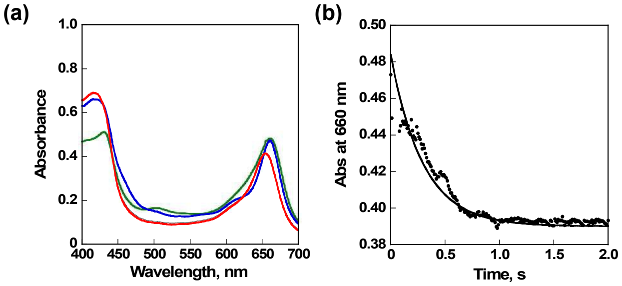


Fig. 4 (a) UV-vis absorption spectral changes of $[Co^I(Ch)]^-$ (20 μM) upon introduction of CO_2-saturated MeCN containing 5% (v/v) H_2O at 298 K. The blue and red lines show the spectra taken at 65 ms and 2 s after mixing, respectively. The green line shows UV-vis absorption spectrum of $[Co^I(Ch)]^-$ (15 μM) formed by the electron-transfer reduction of Co^{II}(Ch) (30 μM) with $Co(Cp^*)_2$ (600 μM) in deaerated MeCN at 298 K.[24] (b) Decay time profile of absorbance at 660 nm due to $[Co^{III}(Ch)(CO_2)]^-$.

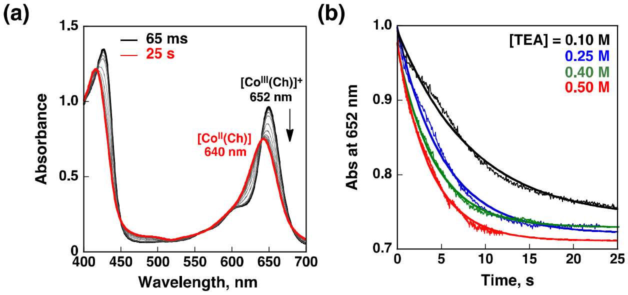


Fig. 5 (a) UV-vis absorption spectral changes in the electron-transfer reduction of $[Co^{III}(Ch)]^+$ (20 μM) with TEA (0.10 M) in deaerated MeCN containing 5% (v/v) H_2O at 298 K at 65 ms and 25 s after mixing. (b) Decay time profiles of absorbance at 652 nm due to $[Co^{III}(Ch)]^+$ in the presence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

to λ_{max} = 652 nm, which is due to $[Co^{III}(Ch)(CO)]^+$ (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 ESI†). When N_2 was introduced to $[Co^{III}(Ch)(CO)]^+$, the spectrum returned to $[Co^{III}(Ch)]^+$. This indicates that binding of CO to $[Co^{III}(Ch)]^+$ is reversible. The CO stretching frequency of $[Co^{III}(Ch)(CO)]^+$ was also measured in MeCN under an appropriate CO pressure (Fig. S7 in ESI†). The νCO is located at 2158 cm^{-1}, which is nearly the same as the “free” CO molecule (νCO = 2155 cm^{-1}),[28] suggesting the 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).

$[Co^{III}(Ch)]^+$ that was prepared by the one-electron oxidation of $Co^{II}(Ch)$ with $(p\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$ 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 large excess TEA obeyed first-order kinetics and the pseudo-first-order rate constant was proportional to 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 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 triethylamine 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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25 TON for CO formation was improved by adsorption of cobalt chlorin complexes on MWCNTs, because two $[Co^{I}(Ch)]^-$ are located close to each other when 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 Co(0) species was produced because Co(I)/Co(0) couple was not observed in the CV measurements. Thus, the catalytic active species for proton reduction may be Co(III)-H.[24]
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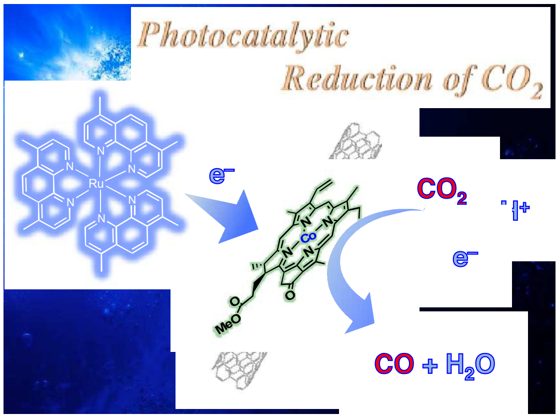

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