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Selective electrochemical reduction of CO₂ to CO with a cobalt chlorin complex adsorbed on multi-walled carbon nanotubes in water[†]

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Electrocatalytic reduction of CO₂ occurred efficiently using a glassy carbon electrode modified with a cobalt(II) chlorin complex adsorbed on multi-walled carbon nanotubes at an applied potential of -1.1 V vs. NHE to yield CO with a Faradaic efficiency of 89% with hydrogen production accounting for the remaining 11% at pH 4.6.

Electrocatalytic two-electron reduction of CO2 to CO has merited significant interest, because CO can be converted to liquid hydrocarbon fuels using H₂ by Fischer-Tropsch processes.¹⁻³ There have been extensive studies on the electrocatalytic reduction of CO2 with cobalt and nickel macrocycles.^{4–6} The selective electrocatalytic reduction of CO2 to CO has been achieved using nickel macrocycles in water without the formation of H₂.^{7–9} Cobalt macrocycles can also act as good electrocatalysts for selective CO₂ reduction to CO in organic solvents.^{10–13} In water, however, cobalt macrocycles have lacked the selectivity for CO,13-15 because cobalt complexes act as good catalysts for H_2 evolution.^{16–21}

We report herein the selective electrocatalytic reduction of CO₂ to CO using a glassy carbon electrode modified with a cobalt(II) chlorin complex (Co^{II}(Ch): a chemical structure shown in Scheme 1) adsorbed on carbon nanotubes in water.

The Co^{II}(Ch)-modified electrode was prepared by drop casting a sonicated acetonitrile (MeCN) solution containing Co^{II}(Ch) (1.0 mM), multi-walled carbon nanotubes (MWCNTs: 1.3 mg) as a support material and 5% Nafion (12 µL) as a proton exchange membrane and stabilization agent of Co^{II}(Ch) on MWCNTs to a glassy carbon electrode (experimental details are shown in the ESI[†]).

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Japan Science and Technology Agency (JST), Nagoya, Aichi 468-8502, Japan † Electronic supplementary information (ESI) available: UV-Vis absorption spectra for the detection of formic acid (Fig. S1) and time courses of evolution of CO and H₂ under various conditions (Fig. S2–S9). XPS of the working electrode (Fig. S10). See DOI: 10.1039/c5cc03340c

(b) (a)

Scheme 1 (a) Structure of Co^{II}(Ch) and (b) schematic image of Co^{II}(Ch) on MWCNTs

Similarly the $Co^{II}(OEP)$ -modified electrode (OEP^{2-} = octaethylporphyrin dianion) was prepared by sonication in an MeCN solution containing Co^{II}(OEP) (1.0 mM), MWCNT and Nafion. The Co^{II}(Ch)-modified electrode exhibited a catalytic current at an applied potential of <-1.0 V vs. NHE in a CO₂-saturated aqueous solution at pH 4.6 as shown in Fig. 1 (red line). When Co^{II}(Ch) was replaced by Co^{II}(OEP) under otherwise the same experimental conditions, a decrease of the catalytic current from 60 μ A (red line) to 30 μ A (green line) at -1.1 V vs. NHE was observed as shown in Fig. 1.

To assess the catalytic activity of Co^{II}(Ch), controlled-potential electrolysis of a CO₂-saturated aqueous solution with Na₂SO₄ (5.0 mM) as an electrolyte was performed and the formation of CO and H_2 was quantitated by the gas chromatography analyses. No formation of the reduced products such as formaldehyde, methane, methanol and oxalate was observed under the present experimental conditions; however, a small amount of formic acid was detected by the formate dehydrogenase assay (Fig. S1 in the ESI⁺). We investigated various experimental conditions such as the pH of a CO₂-saturated aqueous solution, an applied potential and various amounts of Co^{II}(Ch) adsorbed on MWCNTs in a sonicated MeCN solution as summarized in Table 1. The time courses of formation of CO and H₂ in electrolysis of a CO₂saturated aqueous solution with Na2SO4 at various pH values are shown in Fig. S2 in the ESI.† The maximum turnover number (TON) was 1100 with a TOF of 140 h^{-1} at pH 4.6. When the pH value is smaller than 4.6, proton reduction to evolve H2 occurred



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Fig. 1 Cyclic voltammograms (CV) of (a) a Co^{II}(Ch)-modified and (b) a Co^{II}(OEP)-modified electrode in CO₂- and N₂-saturated aqueous solutions containing Na₂SO₄ (5.0 mM, pH = 4.6). Sweep rate: 10 mV s⁻¹; working electrodes were modified with Co complex (0.01 µmol) and MWCNTs (13 µg) on a glassy carbon disk electrode.

Table 1 pH dependence of CO production and selectivities in electrocatalytic reduction in a CO₂-saturated aqueous solution on the Co^{II}(Ch)modified electrode at -1.1 V vs. NHE

pН	TON ^a	$\operatorname{TOF}^{a}(\operatorname{h}^{-1})$	$CO: H_2$
2.0	140	87	1:32
2.8	350	87	11:17
3.6	540	100	4.2:1
4.6	1100	140	4.3:1
6.8	240	79	4.9:1

preferentially rather than CO₂ reduction. The reason for a small TON at pH 6.8 is due to the slow proton-coupled electrontransfer reduction of CO₂ to CO under high pH conditions. An applied potential and the concentration of Co^{II}(Ch) for the CO formation were optimised to be -1.1 V vs. NHE and 1.0 mM, respectively (Fig. S3 and S4 in ESI[†]). Fig. 2 shows the time courses of formation of CO and H₂ in electrolysis of a CO₂-saturated aqueous solution with Na2SO4 under optimised conditions (*i.e.* pH 4.6, -1.1 V vs. NHE, $[Co^{II}(Ch)] = 1.0 \text{ mM}$), indicating that the CO yield is significantly higher than the H₂ yield with the maximum turnover number (TON) of 1500 and a TOF of 100 $h^{-1}\!.$ The time courses of formation of CO and H_2 in N₂-saturated aqueous solution are shown in Fig. S5 in the ESI.† GC data are shown in Fig. S6 in the ESI.† The CVs and time courses of evolution of H₂ under N₂ and CO₂ in the absence of Co^{II}(Ch) or MWCNTs are shown in Fig. S7 and S8 in the ESI[†] as control experiments. No catalytic current for CO₂ reduction and CO formation in the electrolysis was observed without MWCNTs or Co^{II}(Ch). The current efficiency for CO production for the



Fig. 2 Time courses of evolution of CO and H₂ in the electrocatalytic reduction of CO₂ on the glassy carbon electrode modified with Co^{II}(Ch) (0.01 µmol) adsorbed on MWCNTs (13 µg) in a CO₂-saturated aqueous solution containing Na₂SO₄ (5.0 mM) at an applied potential of -1.1 V vs. NHE. CO₂ was bubbled every 2 h.

initial 2 h was determined to be as high as 89%, whereas that for H_2 production was 11%.²³ In the case of the Co^{II}(OEP)-modified electrode, the selectivity for CO production decreased to 50% and the TON for CO production at 2 h of electrolysis was only 20 (Fig. S9 in the ESI†). Thus, the Co^{II}(Ch)-modified electrode exhibits much higher electrocatalytic reactivity and selectivity for CO production than the Co^{II}(OEP)-modified electrode.

The EPR spectra of $\text{Co}^{II}(\text{Ch})$ in a solution and $\text{Co}^{II}(\text{Ch})$ on MWCNTs are shown in Fig. 3 to observe the π - π interaction between $\text{Co}^{II}(\text{Ch})$ and MWCNTs. An EPR spectrum of a frozen MeCN solution containing $\text{Co}^{II}(\text{Ch})$ at 4.2 K exhibited wellresolved signals at *g* = 2.293 (Fig. 3a), which is a typical low-spin five-coordinated cobalt(π) complex.^{24,25} On the other hand, an EPR spectrum of $\text{Co}^{II}(\text{Ch})$ on MWCNTs showed a new signal at



Fig. 3 EPR spectra of (a) Co^{II}(Ch) (1.0 mM) in deaerated MeCN measured at 4.2 K and (b) Co^{II}(Ch) (1.0 mM) adsorbed on MWCNTs (0.30 mg) and Nafion (3.0 μ L) in deaerated MeCN (250 μ L) measured at 4.2 K.



Fig. 4 Time courses of formation of CO and H₂ in the electrocatalytic reduction of CO₂ on the glassy carbon electrode modified with Co^{II}(Ch) (0.01 μ mol) adsorbed on rGO (13 μ g) in a CO₂-saturated aqueous solution containing Na₂SO₄ (5.0 mM) at an applied potential of -1.1 V vs. NHE.

g = 4.203 in addition to the signal at g = 2.293 to the low-spin Co(II). The g = 4.203 signal is a triplet marker of two molecules of cobalt(II) complexes (S = 1/2) located close to each other. This indicates that the selective reduction of CO₂ to CO results from involvement of two cobalt(I) complexes for two-electron transfer reduction of CO₂.²⁶

We also investigated the XPS measurements to confirm the state of the cobalt complex on MWCNTs after electrolysis. The XPS signal of the binding energy at 781 eV due to the $Co(2p_{3/2})$ was shifted to 779 eV after electrolysis (Fig. S10 in the ESI†). The lower energy shift may be attributed to the reduction of $Co(\pi)$ to form the low valent cobalt species.²⁷ Thus, the deactivation of $Co^{II}(Ch)$ on MWCNTs may be attributed to the formation of unreactive monomer cobalt(1) species after the electrolysis.

When MWCNTs were replaced by reduced graphene oxide (rGO), which is planar, as a support material of Co^{II}(Ch) (preparation procedures are shown in the Experimental section in the ESI^{\dagger}), the CO and H₂ yields became much smaller (TON = 350 for CO and 250 for H_2 (Fig. 4). Thus, the three dimensional assembly of MWCNTs with Co^{II}(Ch) (Scheme 1b) on the electrode surface may play an important role for the selective electrocatalytic reduction of CO₂ to CO. The π - π interaction between MWCNTs and Co^{II}(Ch) also provides a suitable hydrophobic environment for binding of CO₂ instead of proton, because the binding of CO₂ to the Co(1) complex is required for the formation of CO.²² Because another Co(1) complex is also required for the two-electron reduction of CO₂,^{22a} two Co^I(Ch) molecules located close to each other on MWCNTs facilitate CO₂ reduction to CO (Scheme 1). Such situations may not be attained by a large two-dimensional π -system such as rGO, which afforded inefficient electrocatalytic reactivity for CO₂ reduction with Co^{II}(Ch).

In conclusion, a cobalt(II) chlorin complex adsorbed on MWCNTs acts as an efficient catalyst for selective electrocatalytic reduction of CO₂ to CO in H₂O (pH = 4.6) at an applied potential of -1.1 V vs. NHE with a high faraday efficiency of 89%. The present study provides a unique strategy for the selective electrocatalytic reduction of CO₂ to CO over proton reduction to H₂.

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