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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 H₂ 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.

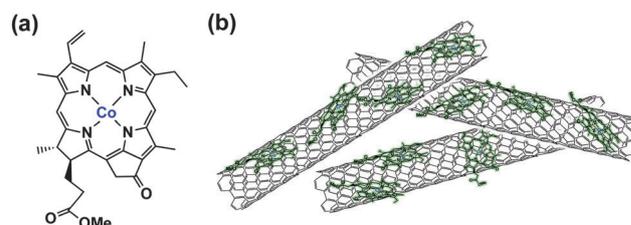
The Co^{II}(Ch)-modified electrode was prepared by drop casting a sonicated acetonitrile (MeCN) solution containing Co^{II}(Ch) (1.0 mM), multi-walled carbon nanotubes (MWCNTs: 1.3 mg) as a support material and 5% Nafion (12 μL) as a proton exchange membrane and stabilization agent of Co^{II}(Ch) on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

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† 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



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 (OEP²⁻ = 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 μA (red line) to 30 μA (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 H₂ 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 CO₂-saturated 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



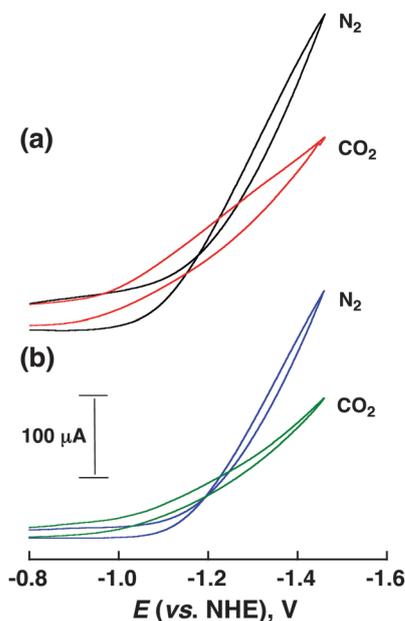


Fig. 1 Cyclic voltammograms (CV) of (a) a $\text{Co}^{\text{II}}(\text{Ch})$ -modified and (b) a $\text{Co}^{\text{II}}(\text{OEP})$ -modified electrode in CO_2 - and N_2 -saturated aqueous solutions containing Na_2SO_4 (5.0 mM, pH = 4.6). Sweep rate: 10 mV s^{-1} ; working electrodes were modified with 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 CO_2 -saturated aqueous solution on the $\text{Co}^{\text{II}}(\text{Ch})$ -modified electrode at -1.1 V vs. NHE

pH	TON ^a	TOF ^a (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

^a Experimental errors are within 5%.

preferentially rather than CO_2 reduction. The reason for a small TON at pH 6.8 is due to the slow proton-coupled electron-transfer reduction of CO_2 to CO under high pH conditions. An applied potential and the concentration of $\text{Co}^{\text{II}}(\text{Ch})$ 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 H_2 in electrolysis of a CO_2 -saturated aqueous solution with Na_2SO_4 under optimised conditions (*i.e.* pH 4.6, -1.1 V vs. NHE , $[\text{Co}^{\text{II}}(\text{Ch})] = 1.0 \text{ mM}$), indicating that the CO yield is significantly higher than the H_2 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 N_2 -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 H_2 under N_2 and CO_2 in the absence of $\text{Co}^{\text{II}}(\text{Ch})$ or MWCNTs are shown in Fig. S7 and S8 in the ESI[†] as control experiments. No catalytic current for CO_2 reduction and CO formation in the electrolysis was observed without MWCNTs or $\text{Co}^{\text{II}}(\text{Ch})$. The current efficiency for CO production for the

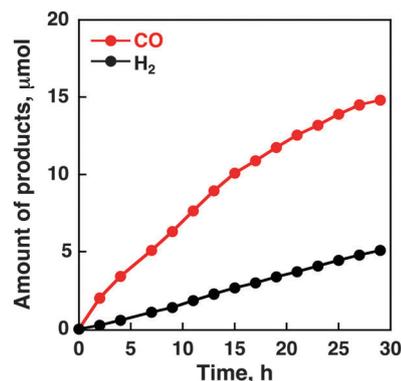


Fig. 2 Time courses of evolution of CO and H_2 in the electrocatalytic reduction of CO_2 on the glassy carbon electrode modified with $\text{Co}^{\text{II}}(\text{Ch})$ (0.01 μmol) adsorbed on MWCNTs (13 μg) in a CO_2 -saturated aqueous solution containing Na_2SO_4 (5.0 mM) at an applied potential of -1.1 V vs. NHE . CO_2 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 $\text{Co}^{\text{II}}(\text{OEP})$ -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 $\text{Co}^{\text{II}}(\text{Ch})$ -modified electrode exhibits much higher electrocatalytic reactivity and selectivity for CO production than the $\text{Co}^{\text{II}}(\text{OEP})$ -modified electrode.

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

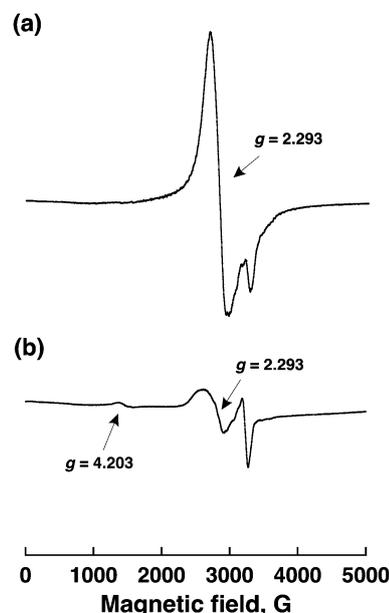


Fig. 3 EPR spectra of (a) $\text{Co}^{\text{II}}(\text{Ch})$ (1.0 mM) in deaerated MeCN measured at 4.2 K and (b) $\text{Co}^{\text{II}}(\text{Ch})$ (1.0 mM) adsorbed on MWCNTs (0.30 mg) and Nafion (3.0 μL) in deaerated MeCN (250 μL) measured at 4.2 K.



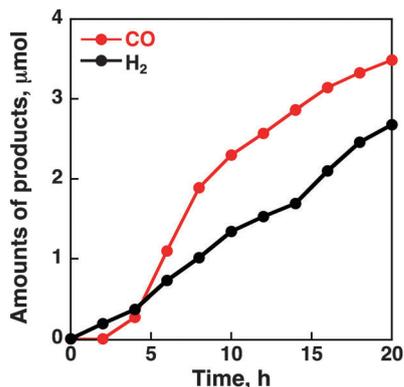


Fig. 4 Time courses of formation of CO and H₂ in the electrocatalytic reduction of CO₂ on the glassy carbon electrode modified with Co^{II}(Ch) (0.01 μmol) adsorbed on rGO (13 μg) in a CO₂-saturated aqueous solution containing Na₂SO₄ (5.0 mM) at an applied potential of −1.1 V vs. NHE.

$g = 4.203$ 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(II) 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(I) 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†), the CO and H₂ yields became much smaller (TON = 350 for CO and 250 for H₂) (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(I) complex is required for the formation of CO.²² Because another Co(I) 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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