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## COMMUNICATION

# Selective electrochemical reduction of CO<sub>2</sub> to CO with a cobalt chlorin complex adsorbed on multi-walled carbon nanotubes in water†

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Accepted 00th xxxx 2015Shoko Aoi,<sup>a</sup> Kentaro Mase,<sup>a</sup> Kei Ohkubo<sup>ab</sup> and Shunichi Fukuzumi<sup>\*abc</sup>

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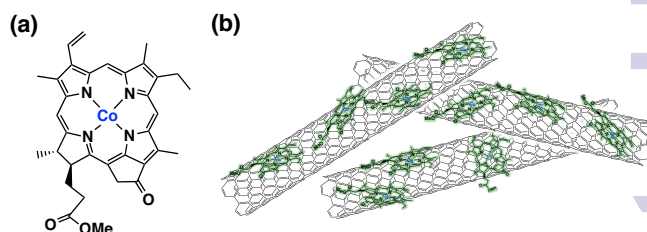
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Electrocatalytic reduction of CO<sub>2</sub> occurred efficiently using a glassy carbon electrode modified with a cobalt(II) chlorin complex adsorbed on multi-walled carbon nanotubes at an applied potential of  $-1.1$  V vs. NHE to yield CO with a Faradaic efficiency of 89% with hydrogen production accounting for the remaining 11% at pH 4.6.

Electrocatalytic two-electron reduction of CO<sub>2</sub> to CO has merited significant interest, because CO can be converted to liquid hydrocarbon fuels with H<sub>2</sub> by Fischer-Tropsch processes.<sup>1-3</sup> There have been extensive studies on electrocatalytic reduction of CO<sub>2</sub> with cobalt and nickel macrocycles.<sup>4-6</sup> The selective electrocatalytic reduction of CO<sub>2</sub> to CO has been achieved using nickel macrocycles in water without formation of H<sub>2</sub>.<sup>7-9</sup> Cobalt macrocycles can also act as good electrocatalysts for selective CO<sub>2</sub> reduction to CO in organic solvents.<sup>10-13</sup> In water, however, cobalt macrocycles have lacked selectivity for CO,<sup>13-15</sup> because cobalt complexes act as good catalysts for H<sub>2</sub> evolution.<sup>16-21</sup>

We report herein selective electrocatalytic reduction of CO<sub>2</sub> to CO using a glassy carbon electrode modified with a cobalt(II) chlorin complex (Co<sup>II</sup>(Ch): a chemical structure shown in Scheme 1) adsorbed on carbon nanotubes in water.

The Co<sup>II</sup>(Ch)-modified electrode was prepared by drop casting a sonicated acetonitrile (MeCN) solution containing Co<sup>II</sup>(Ch) (1.0 mM), multi-walled carbon nanotubes (MWCNTs: 1.3 mg) as a support material and 5% Nafion (12  $\mu$ L) as a proton exchange membrane and stabilization agent of Co<sup>II</sup>(Ch) on MWCNTs to a glassy carbon electrode (Experimental details are shown in the electronic supplementary information (ESI)). Similarly the Co<sup>II</sup>(OEP)-modified electrode (OEP<sup>2-</sup> = octaethylporphyrin dianion) was prepared by sonication in an MeCN solution containing Co<sup>II</sup>(OEP) (1.0 mM), MWCNT and Nafion. The Co<sup>II</sup>(Ch)-modified electrode exhibited a catalytic current at an applied potential at  $< -1.0$  V vs. NHE in a CO<sub>2</sub>-



Scheme 1 (a) Structure of Co<sup>II</sup>(Ch) and (b) Schematic image of Co<sup>II</sup>(Ch) on MWCNTs

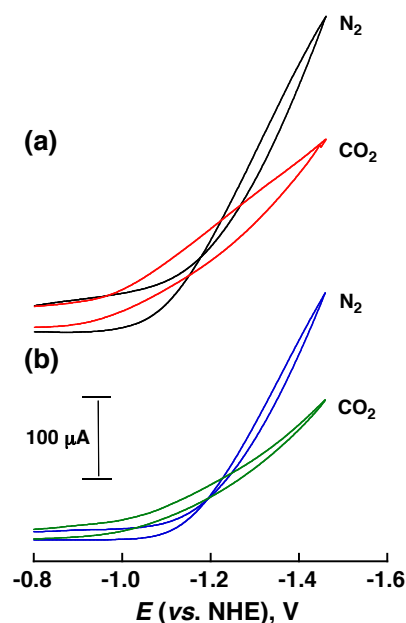


Fig. 1 Cyclic voltammograms (CV) of (a) a Co<sup>II</sup>(Ch)-modified and (b) a Co<sup>II</sup>(OEP)-modified electrode in CO<sub>2</sub>- and N<sub>2</sub>-saturated aqueous solutions containing Na<sub>2</sub>SO<sub>4</sub> (5.0 mM, pH 4.6). Sweep rate: 10 mV s<sup>-1</sup>; a working electrodes were modified Co complexes (0.01  $\mu$ mol) and MWCNTs (13  $\mu$ g) on a glassy carbon disk electrode.

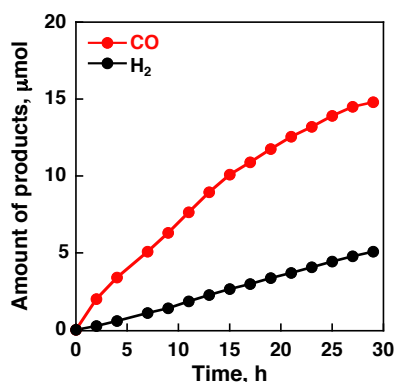
saturated aqueous solution at pH 4.6 as shown in Fig. 1 (red line). When  $\text{Co}^{\text{II}}(\text{Ch})$  was replaced by  $\text{Co}^{\text{II}}(\text{OEP})$  under otherwise the same experimental conditions, decrease of the catalytic current from 60  $\mu\text{A}$  (red line) to 30  $\mu\text{A}$  (green line) at  $-1.1\text{ V vs. NHE}$  was observed as shown in Fig. 1.

To assess the catalytic activity of  $\text{Co}^{\text{II}}(\text{Ch})$ , controlled-potential electrolysis of a  $\text{CO}_2$ -saturated aqueous solution with  $\text{Na}_2\text{SO}_4$  (5.0 mM) as an electrolyte was performed and formation of CO and  $\text{H}_2$  was quantitated by the gas chromatography analyses. No formation of the reduced products such as formaldehyde, methane, methanol and oxalate was observed in the present experimental conditions, however small amount of formic acid was detected by the formate dehydrogenase assay (Fig. S1 in the electronic supplementary information (ESI) †). We examined various experimental conditions such as pH of a  $\text{CO}_2$ -saturated aqueous solution, an applied potential and various amount of  $\text{Co}^{\text{II}}(\text{Ch})$  adsorbed on MWCNTs in a sonicated MeCN solution as summarized in Table 1. The time courses of formation of CO and  $\text{H}_2$  in electrolysis of a  $\text{CO}_2$ -saturated aqueous solution with  $\text{Na}_2\text{SO}_4$  at various pH were shown in Fig S2 in ESI †. The maximum turnover number (TON) was 1200 with a TOF of  $100\text{ h}^{-1}$  at pH 4.6. When the pH value is smaller than 4.6, proton reduction to evolve  $\text{H}_2$  occurred preferentially rather than  $\text{CO}_2$  reduction. The reason why small TON at pH 6.8 is slow proton-coupled electron-transfer reduction of  $\text{CO}_2$  to CO in the high pH

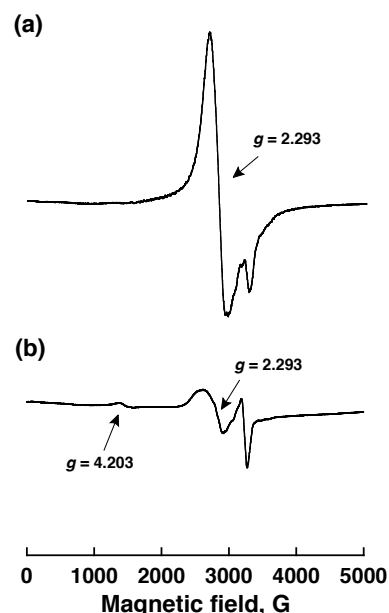
**Table 1** pH dependence of CO production and selectivities in electrocatalytic reduction in a  $\text{CO}_2$ -saturated aqueous solution on the  $\text{Co}^{\text{II}}(\text{Ch})$ -modified electrode at  $-1.1\text{ V vs. NHE}$ .

pH	TON <sup>a</sup>	TOF <sup>a</sup> ( $\text{h}^{-1}$ )	CO:H <sub>2</sub>
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

<sup>a</sup> Experimental errors are within 5%.



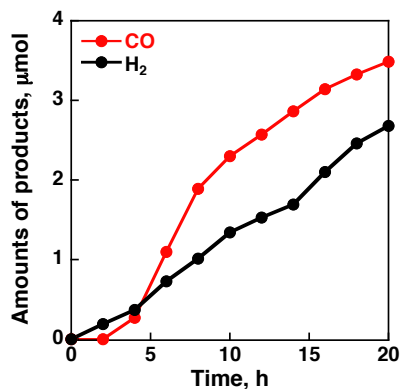
**Fig. 2** Time courses of evolution of CO and  $\text{H}_2$  in the electrocatalytic reduction of  $\text{CO}_2$  on the glassy carbon electrode modified with  $\text{Co}^{\text{II}}(\text{Ch})$  (0.01  $\mu\text{mol}$ ) adsorbed on MWCNTs (13  $\mu\text{g}$ ) in a  $\text{CO}_2$ -saturated aqueous solution containing  $\text{Na}_2\text{SO}_4$  (5.0 mM) at an applied potential of  $-1.1\text{ V vs. NHE}$ .  $\text{CO}_2$  was bubbled every 2 h.



**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  $\mu\text{L}$ ) in deaerated MeCN (250  $\mu\text{L}$ ) measured at 4.2 K.

conditions. The largest CO formation was observed when an applied potential was  $-1.1\text{ V vs. NHE}$  and concentration of  $\text{Co}^{\text{II}}(\text{Ch})$  was 1.0 mM (Figs. S3-S4 in ESI †). Fig. 2 shows the time courses of formation of CO and  $\text{H}_2$  in electrolysis of a  $\text{CO}_2$ -saturated aqueous solution with  $\text{Na}_2\text{SO}_4$  under optimised conditions (*i.e.* pH 4.6,  $-1.1\text{ V vs. NHE}$ ,  $[\text{Co}^{\text{II}}(\text{Ch})] = 1.0\text{ mM}$ ), indicating that the CO yield is significantly higher than the  $\text{H}_2$  yield with the maximum turnover number (TON) of 1500 and TOF of  $100\text{ h}^{-1}$ . The time course of formation of CO and  $\text{H}_2$  in  $\text{N}_2$ -saturated aqueous solution is shown in Fig. S5 in ESI †. GC data are shown in Fig S6 in ESI †. The CVs and time course of evolution of  $\text{H}_2$  under  $\text{N}_2$  and  $\text{CO}_2$  in the absence of  $\text{Co}^{\text{II}}(\text{Ch})$  or MWCNTs are shown in Figs S7 and S8 in ESI † as the control experiments. No catalytic current for the  $\text{CO}_2$  reduction and formation of CO in the electrolysis were observed without MWCNTs or  $\text{Co}^{\text{II}}(\text{Ch})$ . The current efficiency for CO production for the initial 2 h was determined to be as high as 89%, whereas that for  $\text{H}_2$  production was 11%.<sup>23</sup> In the case of the  $\text{Co}^{\text{II}}(\text{OEP})$ -modified electrode, the selectivity for CO production decreased to 50% and TON for CO production at 2 h electrolysis was only 20 (Fig. S9 in 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.

EPR spectra of  $\text{Co}^{\text{II}}(\text{Ch})$  in solution and  $\text{Co}^{\text{II}}(\text{Ch})$  on MWCNTs are shown in Fig. 3 to observe the  $\pi$ - $\pi$  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 a well-resolved signals at  $g = 2.293$  (Fig. 3a), which is a typical low spin five-coordinated cobalt(II) complex.<sup>24,25</sup> On the other hand, an EPR spectrum of  $\text{Co}^{\text{II}}(\text{Ch})$  on MWCNTs showed a new signal at  $g = 4.203$  in addition of signal at  $g = 2.293$  to the low



**Fig. 4** Time courses of formation of CO and H<sub>2</sub> in the electrocatalytic reduction of CO<sub>2</sub> on the glassy carbon electrode modified with Co<sup>II</sup>(Ch) (0.01 μmol) adsorbed on rGO (13 μg) in a CO<sub>2</sub>-saturated aqueous solution containing Na<sub>2</sub>SO<sub>4</sub> (5.0 mM) at an applied potential of -1.1 V vs. NHE.

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

We also examined the XPS measurements to confirm the situation of cobalt complex on MWCNTs after electrolysis. The XPS signal of the binding energy at 781 eV due to the Co(2p<sub>3/2</sub>) was shifted to at 779 eV after electrolysis (Fig. S10 in ESI). The lower energy shift may be attributed to the reduction of Co(II) to form the low valent cobalt species.<sup>27</sup> Thus, the deactivation of Co<sup>II</sup>(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<sup>II</sup>(Ch) (Preparation procedures are shown in the experimental section in ESI), the CO and H<sub>2</sub> yields became much smaller (TON = 300 for CO and 200 for H<sub>2</sub>) (Fig. 4). Thus, the three dimensional assembly of MWCNTs with Co<sup>II</sup>(Ch) (Scheme 1b) on the electrode surface may play an important role for the selective electrocatalytic reduction of CO<sub>2</sub> to CO. The  $\pi$ - $\pi$  interaction between MWCNT and Co<sup>II</sup>(Ch) also provides a suitable hydrophobic environment for binding of CO<sub>2</sub> instead of proton, because the binding of CO<sub>2</sub> to the Co(I) complex is required for formation of CO.<sup>22</sup> Because another Co(I) complex is also required for the two-electron reduction of CO<sub>2</sub>,<sup>22a</sup> two Co<sup>I</sup>(Ch) molecules located in close to each other on MWCNTs facilitate CO<sub>2</sub> reduction to CO (Scheme 1). Such situations may not be attained by a large two-dimensional  $\pi$ -system such as rGO, which afforded inefficient electrocatalytic reactivity for CO<sub>2</sub> reduction with Co<sup>II</sup>(Ch).

In conclusion, a cobalt(II) chlorin complex adsorbed on MWCNTs acts as an efficient catalyst for selective electrocatalytic reduction of CO<sub>2</sub> to CO in H<sub>2</sub>O (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 selective electrocatalytic reduction of CO<sub>2</sub> to CO over proton reduction to H<sub>2</sub>.

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#### Notes and references

<sup>a</sup> 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: fukuzumi@chem.eng.osaka-u.ac.jp; Fax: +81-6-6879-7370

<sup>b</sup> Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea.

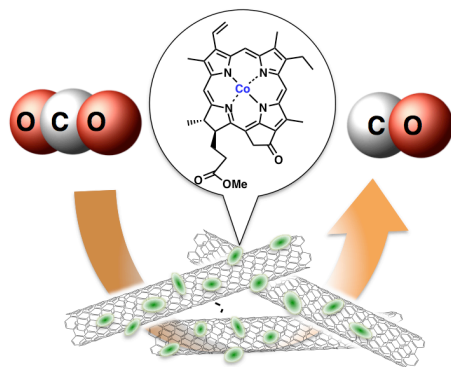
<sup>c</sup> Faculty of Science and Technology, Meijo University, ALCA and SENTAN, Japan Science and Technology Agency (JST), Nagoya, Aichi 468-8502, Japan

† Electronic Supplementary Information (ESI) available: UV-Vis absorption spectra for detection of formic acid (Fig. S1) and time courses of evolution of CO and H<sub>2</sub> in various conditions (Figs. S2- S9). XPS of working electrode (Fig. S10) See DOI: 10.1039/c000000x/

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## TOC



Selective electrocatalytic reduction of CO<sub>2</sub> to CO occurred efficiently using a glassy carbon electrode modified with a cobalt(II) chlorin complex adsorbed on multi-walled carbon nanotubes in water.