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 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 hydrocarbons using H₂ by Fischer–Tropsch processes.† There have been extensive studies on the electrocatalytic reduction of CO₂ with cobalt and nickel macrocycles.† The selective electrocatalytic reduction of CO₂ to CO has been achieved using nickel macrocycles in water without the formation of H₂. In water, however, cobalt macrocycles have lacked the selectivity for CO₂ reduction to CO in organic solvents. In water, cobalt macrocycles can also act as good electrocatalysts for selective CO₂ reduction to CO with a Faradaic efficiency of 89% with hydrogen production accounting for the remaining 11% at pH 4.6.

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

The CoII(Ch)-modified electrode was prepared by drop casting a sonicated acetonitrile (MeCN) solution containing CoII(Ch) (1.0 mM), multi-walled carbon nanotubes (MWCNTs: 1.3 mg) as an electrolyte was performed and the formation of CO and H₂ was quantitated by the gas chromatography analyses.

Similarly the CoII(OEP)-modified electrode (OEP²⁻ = octaethylporphyrin dianion) was prepared by sonication in an MeCN solution containing CoII(OEP) (1.0 mM), MWCNT and Nafion. The CoII(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 CoII(Ch) was replaced by CoII(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 CoII(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 CoII(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.
preferentially rather than CO₂ reduction. The reason for a small TON at pH 6.8 is due to the slow proton-coupled electron-transfer 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 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 H₂ 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 initial 2 h was determined to be as high as 89%, whereas that for H₂ production was 11%. In the case of the Co(III)(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(III)(Ch)-modified electrode exhibits much higher electrocatalytic reactivity and selectivity for CO production than the Co(III)(OEP)-modified electrode.

The EPR spectra of Co(II)(Ch) in a solution and Co(II)(Ch) on MWCNTs are shown in Fig. 3 to observe the π–π interaction between Co(II)(Ch) and MWCNTs. An EPR spectrum of a frozen MeCN solution containing Co(II)(Ch) at 4.2 K exhibited well-resolved signals at $g = 2.293$ (Fig. 3a), which is a typical low-spin five-coordinate cobalt(II) complex. On the other hand, an EPR spectrum of Co(II)(Ch) on MWCNTs showed a new signal at $g = 2.039$. Table 1

<table>
<thead>
<tr>
<th>pH</th>
<th>TON⁺</th>
<th>TOF⁺ (h⁻¹)</th>
<th>CO : H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>140</td>
<td>87</td>
<td>1 : 32</td>
</tr>
<tr>
<td>2.8</td>
<td>350</td>
<td>87</td>
<td>11 : 17</td>
</tr>
<tr>
<td>3.6</td>
<td>540</td>
<td>100</td>
<td>4.2 : 1</td>
</tr>
<tr>
<td>4.6</td>
<td>1100</td>
<td>140</td>
<td>4.3 : 1</td>
</tr>
<tr>
<td>6.8</td>
<td>240</td>
<td>79</td>
<td>4.9 : 1</td>
</tr>
</tbody>
</table>

*Experimental errors are within 5%.*
and CoII(Ch) also provides a suitable hydrophobic environment for another Co(I) complex is also required for the two-electron transfer in the ESI† (preparation procedures are shown in the Experimental section).† A lower energy shift may be attributed to the reduction of Co(II) to form the low valent cobalt species.‡ Thus, the deactivation of CoII(Ch) on MWCNTs may be attributed to the formation of unreactive monomer cobalt(II) species after the electrolysis.

When MWCNTs were replaced by reduced graphene oxide (rGO), which is planar, as a support material of Co(II), the CO and H2 yields became much smaller (TON = 430 for CO and 250 for H2) (Fig. 4). Thus, the three dimensional assembly of MWCNTs with CoII(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 CoII(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 CO2−. Because another Co(i) complex is also required for the two-electron reduction of CO2, two CoII(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 CoII(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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Notes and references

23. The current efficiency in this work is higher than the reported values using cobalt tertiopride, porphyrin and phthalocyanine complexes.1,4,5,6
25. A signal in the high magnetic field at g = 1.964 in Fig. 3 is assigned to the Co(II) superoxo complex [CoII(Ch)-O2•−], which is generated by the electron-transfer oxidation of CoII(Ch) with a small amount of O2 at residual at low temperature. See: (a) D. Sazou, C. Araullo-McAdams, B. C. Han, M. M. Franken and K. M. Kadish, J. Am. Chem. Soc., 1990, 112, 7879; (b) J. P. Collman, K. E. Berg, C. J. Sunderland, A. Aukulo, M. A. Vance and E. I. Solomon, Inorg. Chem., 2002, 41, 6583.
26. We have examined EPR measurements in the presence of a lower concentration of CoII(Ch) on MWCNTs. The EPR signal at g = 4.2 was significantly smaller than the case of a high concentration of CoII(Ch).