Electronic supplementary information (ESI)

Selective electrochemical reduction of CO_2 to CO with a cobalt chlorin complex adsorbed on multi-walled carbon nanotubes in water

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Experimental Section

General Procedure. Chemicals were purchased from commercial sources and used without further purification unless otherwise noted. Acetonitrile (MeCN) used for spectroscopic and electrochemical measurements was dried according to published procedures and distilled under N_2 prior to use.[S1] Nafion® perfluorinated ion exchange resin solution and Nafion perfluorinated membrane (Nafion 117) were received from Sigma Aldrich. Multi-walled carbon nanotubes (L 6-9 nm × 5 μm, > 95%) was obtained from Aldrich Chemicals Co. Purified water was provided by a Millipore Milli-Q water purification system (Millipore, Direct-Q 3 UV) with an electronic conductance of 18.2 MΩ cm. A cobalt chlorin complex [Co^{II}(Ch)] was prepared by the published methods.[S2]

Electrochemical measurements. Cyclic voltammetry (CV) measurements of Co^{II}(Ch) were performed on an ALS 630B electrochemical analyzer and voltammograms were measured in deaerated water (5.0 mL) containing 5.0 mM Na_2SO_4 as a supporting electrolyte at room temperature. A conventional three-electrode cell was used with a glassy carbon (GC) working electrode (surface area of 7.1 mm^2) and a platinum wire as the counter electrode. The glassy carbon working electrode (BAS) was routinely polished with BAS polishing alumina suspension and rinsed with acetone before use. The potentials were measured with respect to the saturated calomel electrode (SCE).

Electrochemical performance of a thin film of Co^{II}(Ch) deposited on the glassy carbon working electrode for the catalytic CO_2 reduction was evaluated in a CO_2-saturated aqueous solution (5.0 mL) containing Na_2SO_4 (5.0 mM) as a supporting electrolyte at 298 K using a conventional three-electrode cell consisting of a working electrode and a platinum coil as the counter electrode. All the electrochemical measurements were conducted using a saturated calomel reference electrode (SCE) and all results in this work are presented against the SCE. The conversion of potentials vs. SCE to vs. NHE was performed according to the following equation (1).

$$E\ (\textit{vs.}\ \text{SCE at measured pH}) = E\ (\textit{vs.}\ \text{NHE at pH 0}) - 0.241\ \text{V} - 0.059\ \text{V} \times \text{pH} \qquad (1)$$

A modified working electrode for electrochemical reduction of CO_2 was prepared by drop-cast method. A mother MeCN (1.0 mL) solution consists of $\mathrm{Co^{II}(Ch)}$ (1.0 mM), MWCNTs (1.3 mg) and 5% Nafion (12 μL) on the glassy carbon working electrode. The solution was sonicated for 20 min and then a 10 μL drop was applied on the surface of a polished glassy carbon working electrode and allowed to evaporate to afford a thin film containing a MWCNTs loading of 0.18 mg $\mathrm{cm^{-2}}$ and a catalyst loading of 10 nmol. When the glassy carbon electrode modified with $\mathrm{Co^{II}(Ch)}$ adsorbed on reduced graphene oxide (rGO) was prepared, MWCNT was replaced by reduced graphene oxide under otherwise the same experimental conditions.

Gas chromatography. The gas phase of the reaction vessel was analyzed by Shimadzu GC-17A gas chromatograph [Ar carrier, a capillary column with molecular sieves (Agilent Technologies, 19095PMS0, 30 m " 0.53 mm) at 313 K] equipped with a thermal conductivity detector. 200 μL from the headspace of the reaction vessel (7.5 mL) was injected in the column. The amount of gas was quantified through calibration curves.

Detection of formic acid. Detection and determinations of quantity of formic acid were performed on the indicator kit purchased from J. K. International. In the presence of formic acid and formate dehydrogenase, $\mathrm{NAD^+}$ is reduced to NADH as following equation (2).

$$\mathrm{HCOOH + NAD^+ + H_2O \rightarrow HCO_3^- + NADH + H^+} \qquad (2)$$

The concentration of formic acid formed in an aqueous solution after electrolysis was calculated from increase of absorbance at λ = 340 nm due to formation of NADH (NADH: λ_{max} = 340 nm, 6300 $\mathrm{M^{-1}\,cm^{-1}}$). Calcium phosphate buffer (1.0 mL) was poured to lithium salts of $\mathrm{NAD^+}$ (19 mg). The resulting solution (1.0 mL) is denoted as ①. Distilled water (2.0 mL) was added to ① (1.0 mL) and UV-Vis absorption spectra of the mixture (3.0 mL) before and after addition of formate dehydrogenase (50 μL) were measured. Increase of absorbance at λ = 340 nm before and after addition of formate dehydrogenase (50 μL) were 0.004 (ΔA Blank). An aqueous solution (2.0 mL) after electrolysis was added to ① (1.0 mL) and UV-Vis absorption spectra of the mixture (3.0 mL) before and after addition of formate dehydrogenase (50 μL) were measured. Increase of absorbance at λ = 340 nm before and after addition of formate dehydrogenase (50 μL) was 0.10 (ΔAbs sample solution) at pH 4.6. The authentic ΔAbs was calculated as following equation (3).

$$Abs\ (\text{sample solution}) - Abs\ (\text{blank}) = \Delta Abs \qquad (3)$$

The concentration of formic acid was calculated as following equation (4).

The concentration of formic acid (g $\mathrm{L^{-1}}$) = $(V \times MW \times \Delta Abs) / (\varepsilon \times d \times v \times 1000)$

V (Volume of solution in UV-cell): 3.05 mL

MW (Molecular weight of formate acid): 46.0

d (Optical pass length): 1.0 cm

ε (Absorption coefficient): 6300 $\mathrm{M^{-1}\,cm^{-1}}$

v (Volume of solution after electrolysis): 2.0 mL

$$\text{The concentration of formate acid (g L}^{-1}) = (3.05 \times 46.0 \times \Delta Abs) / (6300 \times 1.00 \times 2.00 \times 1000) = 0.0111 \times \Delta Abs \quad (4)$$

Spectroscopic Measurements. UV-vis spectroscopy was carried out on a Hewlett Packard 8453 diode array spectrophotometer at room temperature using quartz cell (light path length = 1 cm).

EPR Measurements. The EPR spectra were performed on a JEOL X-band EPR spectrometer (JES-ME-LX) using a quartz EPR tube containing a deaerated sample frozen solution at 4.2 K. The internal diameter of the EPR tube is 4.0 mm, which is small enough to fill the EPR cavity but large enough to obtain good signal-to-noise ratios during the EPR measurements at low temperatures (at 4.2 K). The EPR spectra were measured under nonsaturating microwave power conditions. The amplitude of modulation was chosen to optimize the resolution and the signal-to-noise (S/N) ratio of the observed spectra. The g values were calibrated with a Mn^{2+} marker.

XPS Measurements. XP spectra (XPS) were observed by a ULVAC-PHI ESCA5600 X-ray photoelectron spectrophotometer. The incident radiation was Mg Ka X-ray (1253.6 eV) at 400 W and a charge neutralizer was turned on for acquisition. The binding energy of each element was corrected by C 1s peak (284.8 eV) from carbon in the sample. A modified working electrode for electrochemical reduction of CO_2 was prepared by drop-cast method. A mother MeCN (1.0 mL) solution consists of Co^{II}(Ch) (1.0 mM), MWCNTs (1.3 mg) and 5% Nafion (12 μL) on the glassy carbon plate electrode. The solution was sonicated for 20 min and then a 100 μL drop was applied on the surface of a polished glassy carbon working electrode and allowed to evaporate to afford a thin film containing a MWCNTs loading of 0.18 mg cm^{-2} and a catalyst loading of 100 nmol.

References

[S1] W. L. F. Armarego and C. L. L. Chai, *Purification of Laboratory Chemicals*, 7th ed., Pergamon Press, Oxford, 2013.

[S2] K. Mase, K. Ohkubo and S. Fukuzumi, *J. Am. Chem. Soc.*, 2013, **135**, 2800.

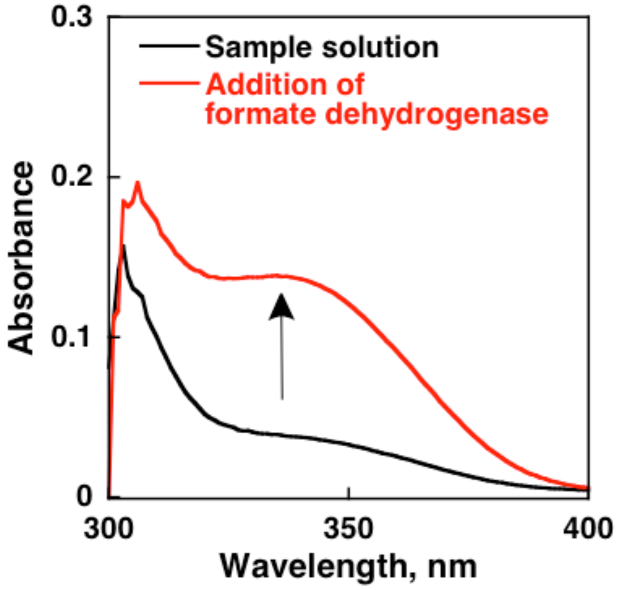

Fig. S1 UV-vis absorption spectral changes of solutions after electrolysis on the glassy carbon electrode modified with Co^{II}(Ch) adsorbed on MWCNTs at 298 K at pH 4.6. Black and red lines show the spectra before and after addition of formate dehydrogenase.

Comment: The amount of formate acid formed in aqueous solution (5.0 mL) after electrolysis was 0.12 μmol at pH 4.6. Thus, TON for formate acid was determined as 12 (pH 4.6).

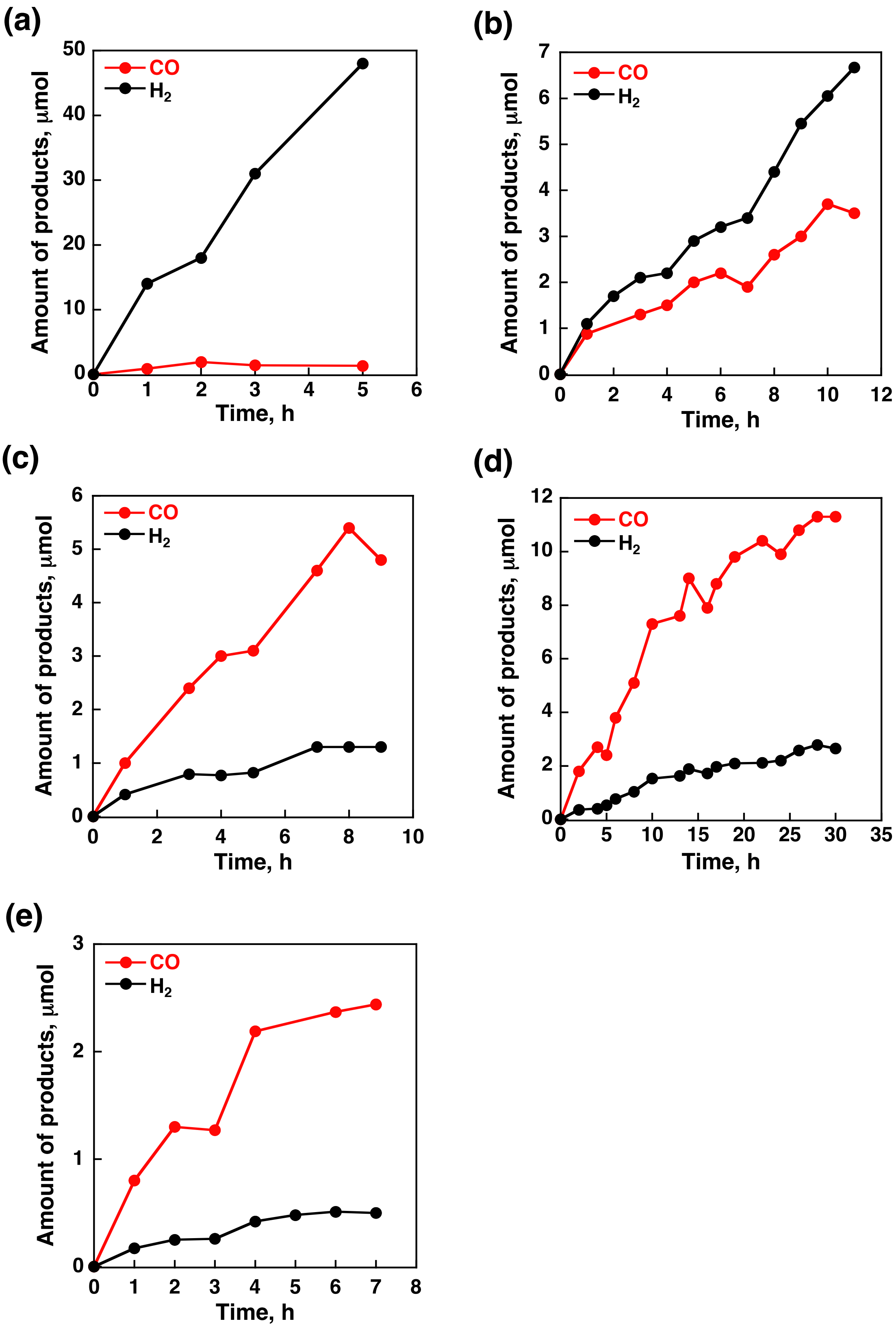

Fig. S2. Time courses of evolution of CO (red) and H_2 (black) in the electrolysis at –1.1 V *vs.* NHE in a CO_2-saturated aqueous solution containing Na_2SO_4 (5.0 mM) on the glassy carbon electrode modified with Co^{II}(Ch) (0.01 µmol) adsorbed on MWCNTs (13 µg) at 298 K at pH (a) 2.0, (b) 2.8, (c) 3.6, (d) 4.6 and (e) 6.8. pH of a CO_2-saturated aqueous solution containing Na_2SO_4 (5.0 mM) was adjusted by a 1000 times diluted H_2SO_4 aqueous solution.

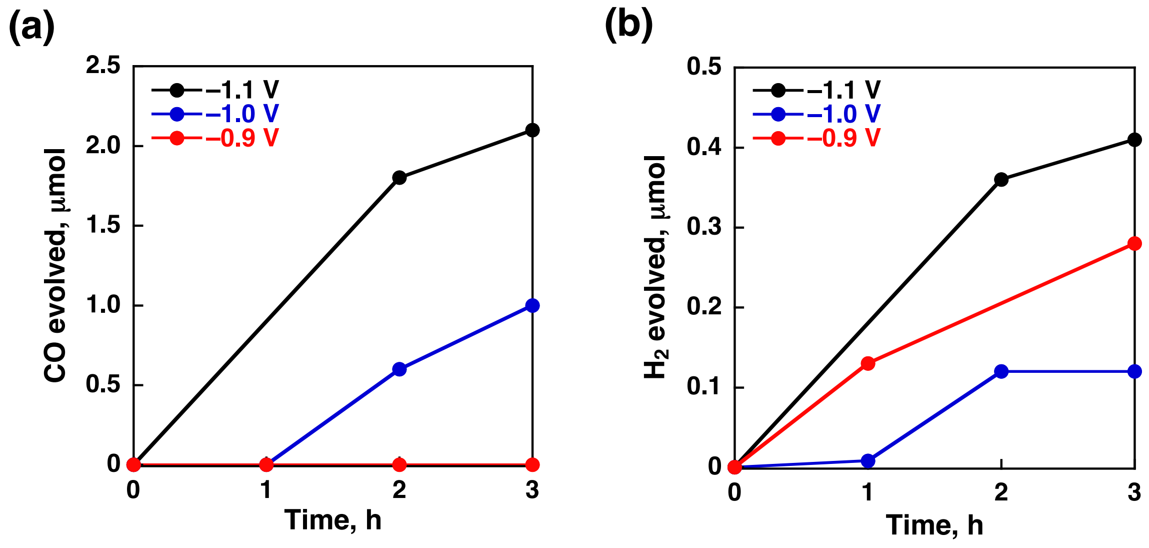

Fig. S3. Time courses of evolution of (a) CO and (b) H_2 in the electrocatalytic reduction of CO_2 at pH 4.6 on the glassy carbon electrode modified with $Co^{II}(Ch)$ (0.01 µmol) adsorbed on MWCNTs (13 µg) in CO_2-saturated aqueous solutions containing Na_2SO_4 (5.0 mM) at 298 K. Controlled-potential electrolysis of a CO_2-saturated aqueous solution with Na_2SO_4 (5.0 mM) was performed at –0.9 V, –1.0 V and –1.1 V *vs*. NHE.

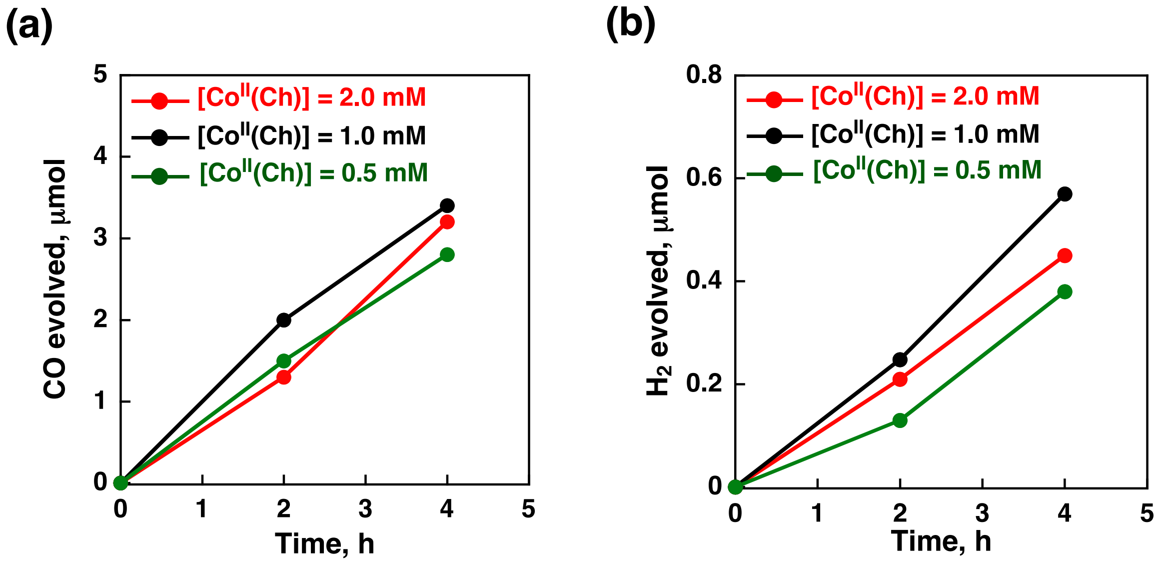

Fig. S4. Time courses of evolution of (a) CO and (b) H_2 in the electrocatalytic reduction of CO_2 at –1.1 V *vs*. NHE at pH 4.6 on the glassy carbon electrode modified with various amount of $Co^{II}(Ch)$ (0.01 µmol) adsorbed on MWCNTs (13 µg) in CO_2-saturated aqueous solutions containing Na_2SO_4 (5.0 mM) at 298 K. Concentrations of $Co^{II}(Ch)$ in a sonicated MeCN solution were 0.5, 1.0 and 2.0 mM.

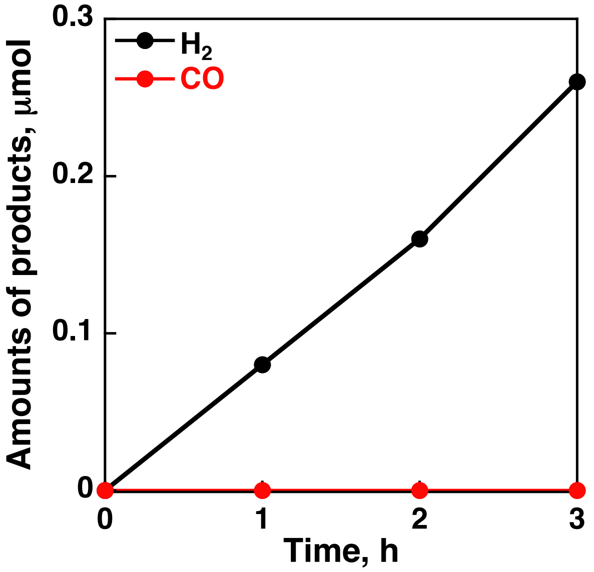

Fig. S5 Time courses of evolution of CO (red) and H_2 (black) in the electrolysis at –1.1 V *vs*. NHE in a N_2-saturated aqueous solution containing Na_2SO_4 (5.0 mM) on the glassy carbon electrode modified with Co^{II}(Ch) (0.01 μmol) adsorbed on MWCNTs (13 μg) at 298 K at pH 4.6.

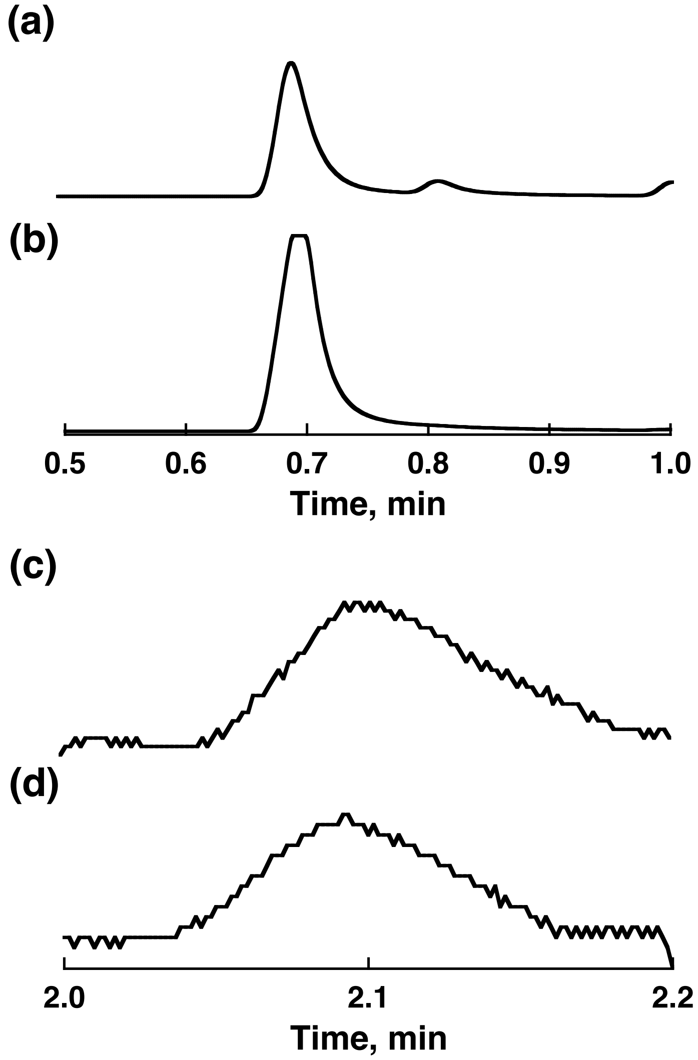

Fig. S6 GC charts of (a) evolved hydrogen after electrolysis on the glassy carbon electrode modified with $Co^{II}(Ch)$ (0.01 μmol) adsorbed on MWCNTs (13 μg) at −1.1 V *vs.* NHE in a CO_2-saturated aqueous solution containing Na_2SO_4 (5.0 mM) at 298 K, (b) H_2 as a control experiment, (c) evolved CO after electrolysis on the glassy carbon electrode modified with $Co^{II}(Ch)$ (0.01 μmol) adsorbed on MWCNTs (13 μg) at −1.1 V *vs.* NHE in a CO_2-saturated aqueous solution containing Na_2SO_4 (5.0 mM) at 298 K and (d) CO as control experiment.

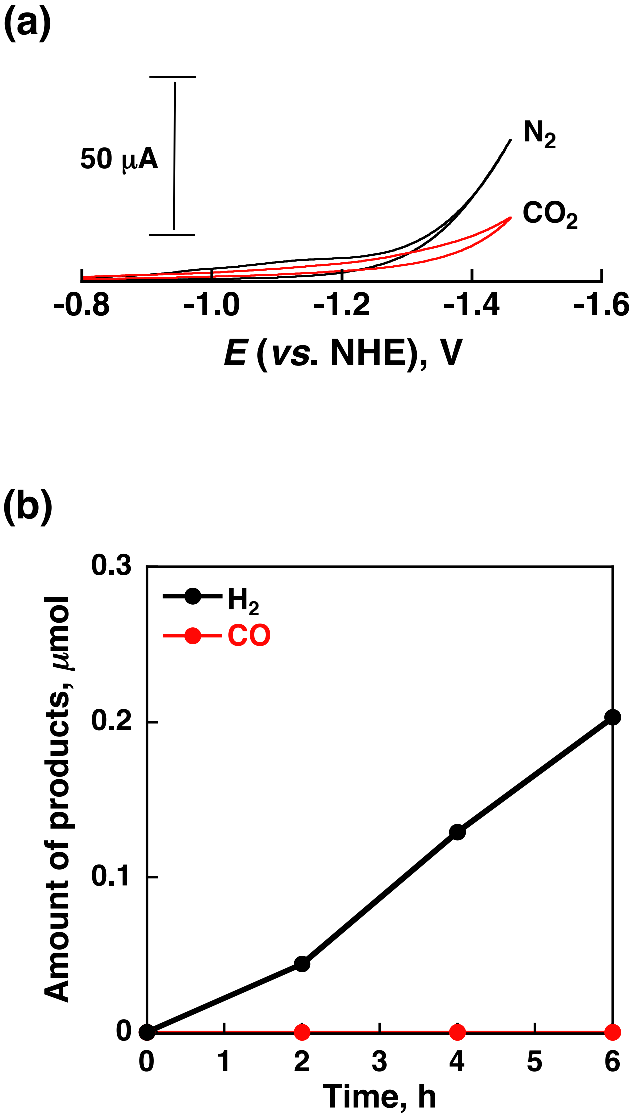

Fig. S7 (a) CV of Co^{II}(Ch)-modified electrode in CO$_2$- and N$_2$-saturated aqueous solutions containing Na_2SO_4 (5.0 mM, pH = 4.6). Sweep rate: 10 mV s^{-1}; modified electrode was prepared by drop casting a sonicated MeCN solution containing Co^{II}(Ch) (1.0 mM) and 5% Nafion (12 μL). (b) Time courses of evolution of H$_2$ and CO in the electrolysis of a CO$_2$-saturated aqueous solution with Na_2SO_4 (5.0 mM) at −1.1 V *vs*. NHE at pH 4.6 on the Co^{II}(Ch)-modified electrode.

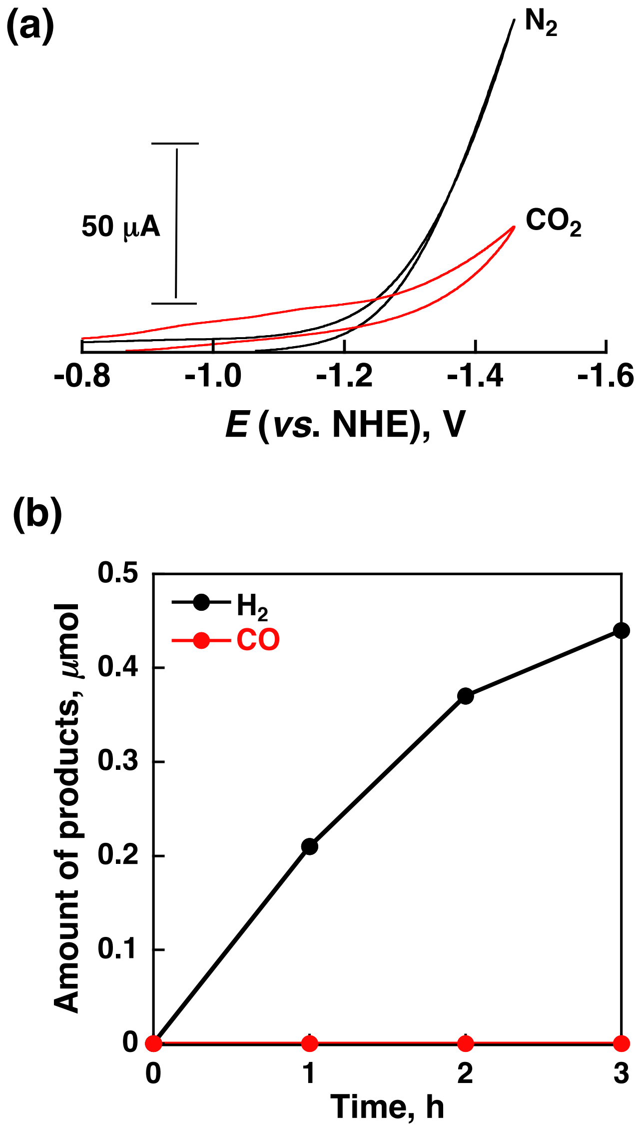

Fig. S8 (a) CV of modified electrode in CO_2- and N_2-saturated aqueous solutions containing Na_2SO_4 (5.0 mM, pH = 4.6). Sweep rate: 10 mV s^{-1}; modified electrode was prepared by drop casting a sonicated MeCN solution containing MWCNTs (1.3 mg) and 5% Nafion (12 μL). (b) Time courses of evolution of H_2 and CO in the electrolysis of a CO_2-saturated aqueous solution with Na_2SO_4 (5.0 mM) at –1.1 V *vs*. NHE at pH 4.6 on the modified electrode.

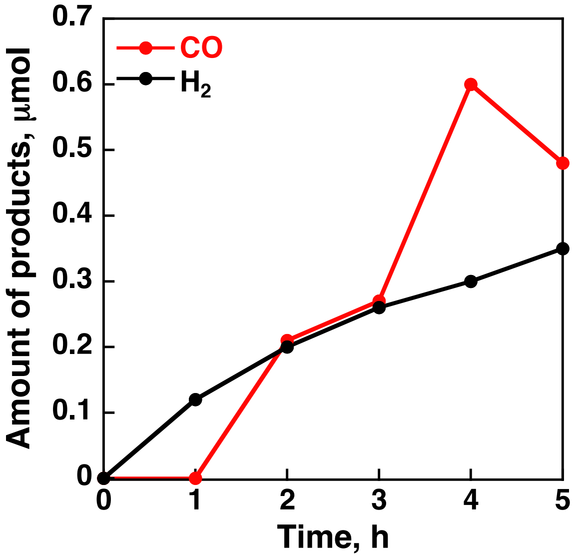

Fig. S9. Time courses of evolution of H_2 and CO in the electrocatalytic reduction of CO_2 at –1.1 V *vs*. NHE at pH 4.6 on the glassy carbon electrode modified with Co^{II}(OEP) (0.01 μmol) adsorbed on MWCNTs (13 μg) in a CO_2-saturated aqueous solution containing Na_2SO_4 (5.0 mM) at 298 K.

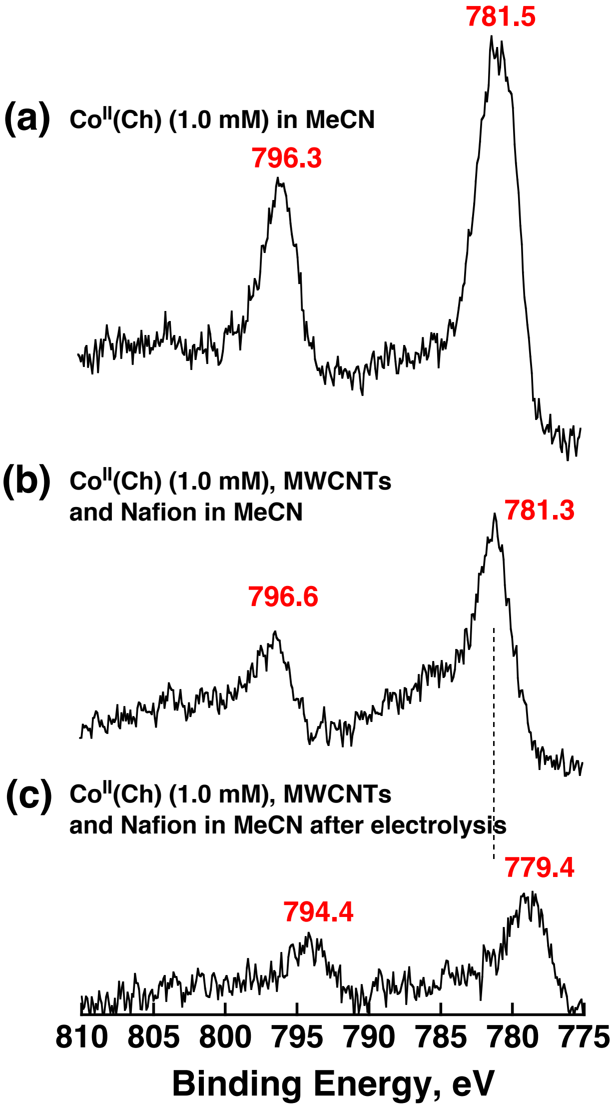

Fig. S10 Co $2p_{3/2}$ XP spectra (XPS) of (a) $Co^{II}(Ch)$ (1.0 mM) in MeCN, (b) a sonicated MeCN solution (100 μL) containing $Co^{II}(Ch)$ (1.0 mM), MWCNTs (1.3 mg) and Nafion (12 μL) and (c) a sonicated MeCN solution (100 μL) containing $Co^{II}(Ch)$ (1.0 mM), MWCNTs (1.3 mg) and Nafion (12 μL) after electrolysis at –1.1 V *vs*. NHE for 32 h in a CO_2-saturated aqueous solution containing Na_2SO_4 (5.0 mM).