Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Fourteen-Membered Macrocyclic Cobalt Complex for the Electrolysis of Low-Concentration Gaseous Carbon Dioxide with High Faradic Efficiency Toward Carbon Monoxide

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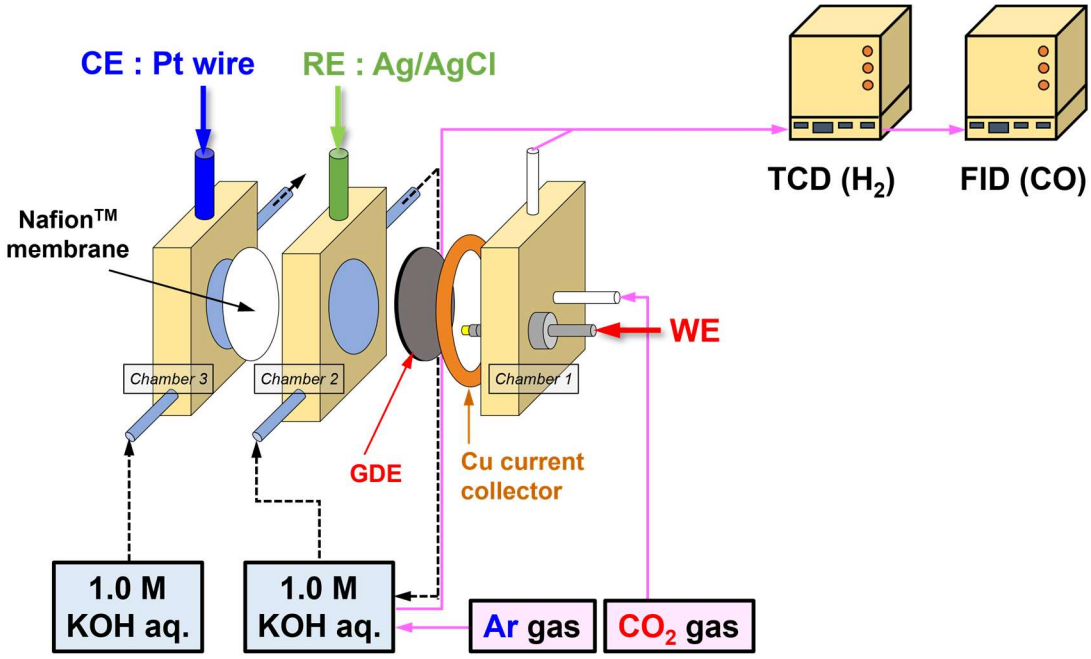

Figure S1. Schematic illustration of the electrolysis cell for CO_2 reduction using a GDE cathode. The paths of gas flow are indicated in pink. Gaseous products in the outlet gas were quantified by using on-line gas chromatography. For example, formation rate of CO was calculated by using following equation.

$$\text{Formation rate of CO / mol s}^{-1} = \frac{\text{Amount of CO in GC analysis / mol} \times \text{Injected volume of the outlet gas / mL}}{\text{Total flow rate of the outlet gas / mL s}^{-1}}$$

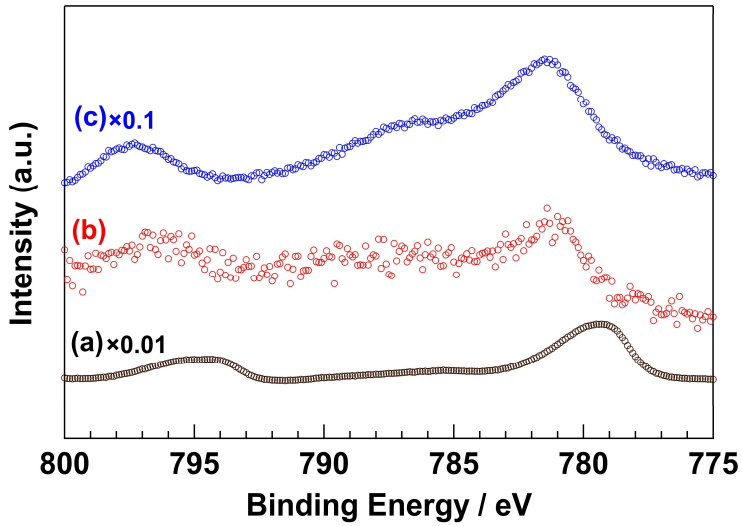

Figure S2. Co 2p X-ray photoelectron spectra of (a) Co powder, (b) Co−14MR, and (c) $Co(OH)_2$ measured by ESCA-3400 (Shimadzu Co. Ltd.) using Mg Kα as an X-ray source. Binding energy of spectra were calibrated by Au 4f peak, which was deposited on the samples prior to use.

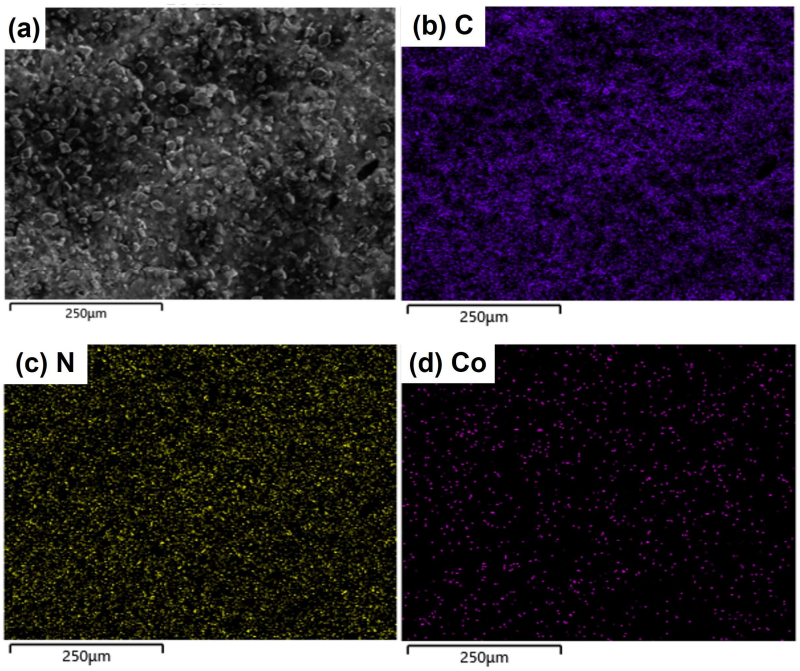

Figure S3. (a) SEM image and characteristic X-ray mappings corresponding to (b) C, (c) N, and (d) Co of Co−14MR/KB cathode.

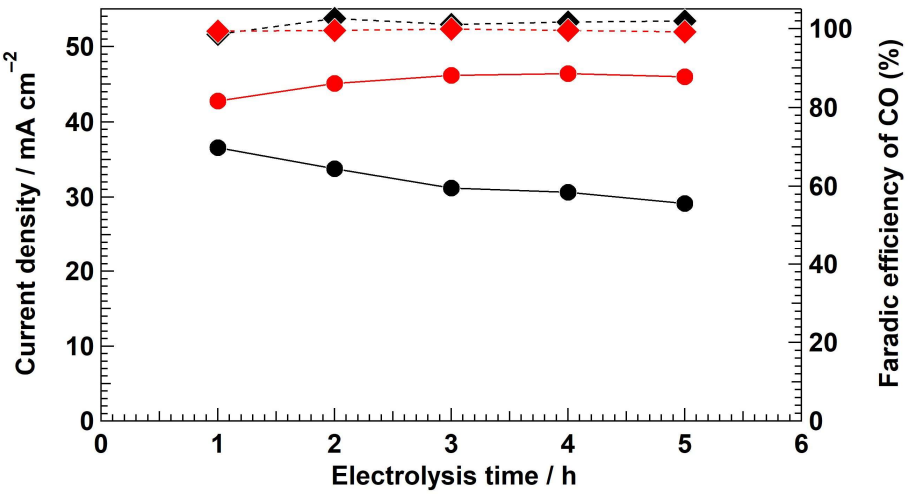

Figure S4. Time courses of the current density (circles) and Faradic efficiency for CO (diamonds) in the potentiostatic electrolysis of CO_2 using Co−14MR/KB (red) and CoTPP/KB (black) as cathode catalysts. Cathode potential: −1.65 V (Ag/AgCl, pH = 14); CO_2 supply to chamber 1: 10 mL min^{-1}; electrolyte solution of chamber 2 and 3: 1.0 M KOH aq.; electrode area (cathode): 1.9 cm^2.

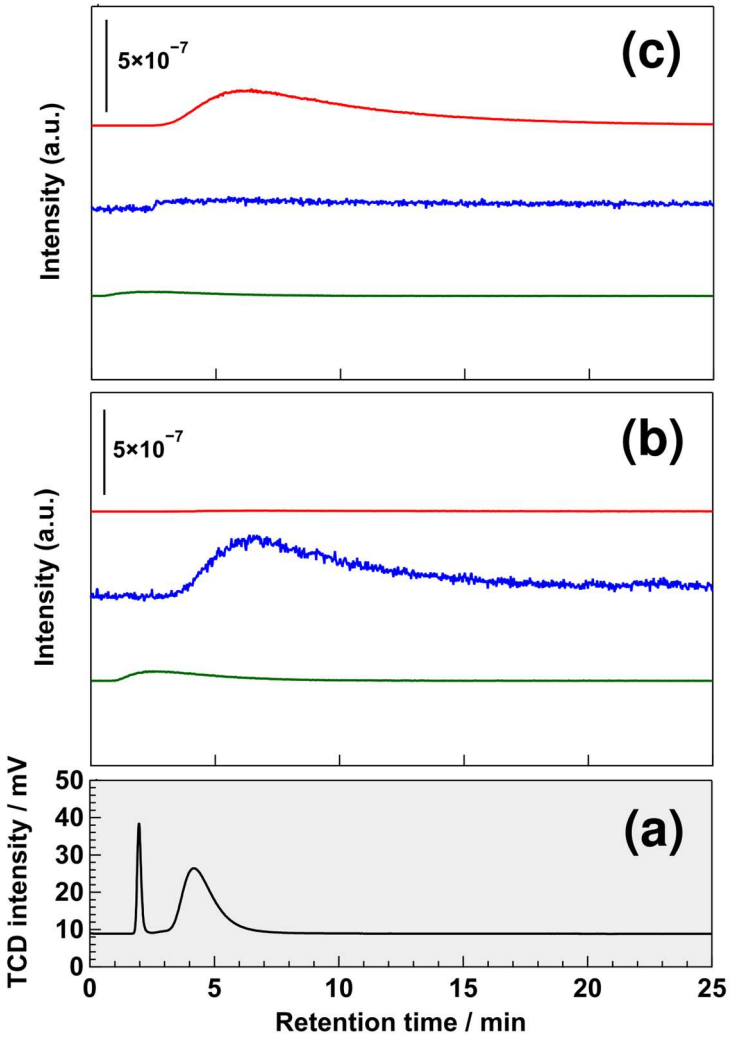

Figure S5. TCD-GC/Q-MS profiles for the isotope labelling experiment for CO_2 electrolysis using the Co−14MR cathode. (a) Chromatogram of TCD-GC. (b) and (c) MS profile of *m/z* = 2 (green), 28 (blue), and 29 (red). (b) and (c) were the results of the electrolysis of standard CO_2 and ^{13}C-labeled CO_2, respectively. The peak at 4 min in (a) and broad peaks starting at 4 min in *m/z* = 28 of (b) and *m/z* = 29 of (c) corresponded to CO.

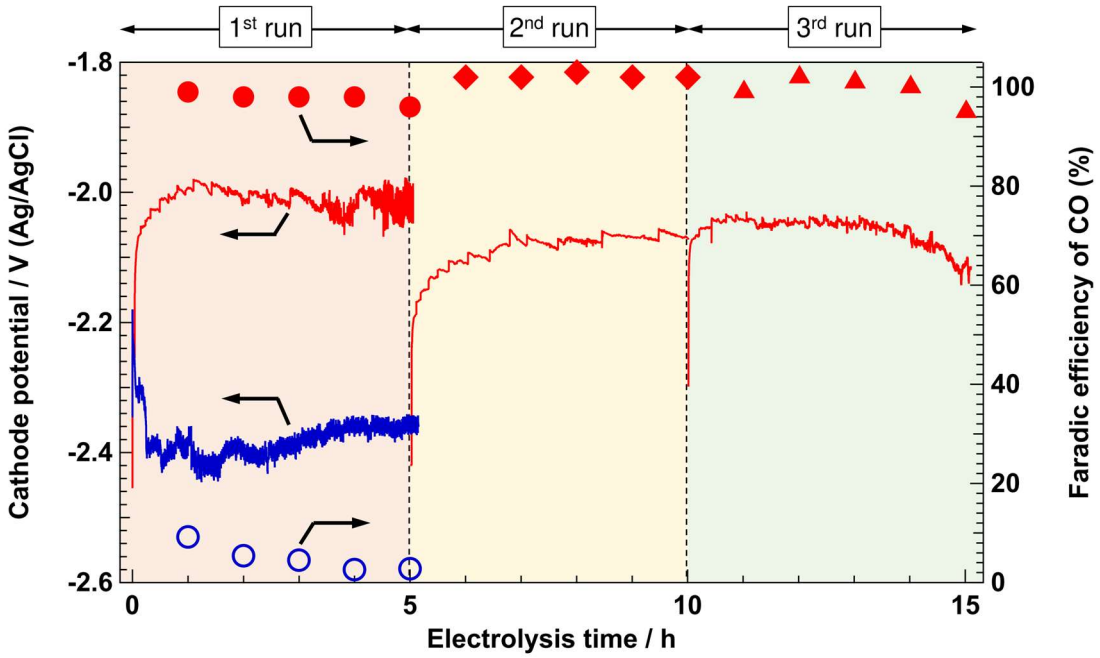

Figure S6. Time courses of the cathode potential and Faradic efficiency of CO in the galvanostatic CO_2 electrolysis at 100 mA cm^{-2} using Co−14MR (red) and CoPc (blue) as cathode catalysts.

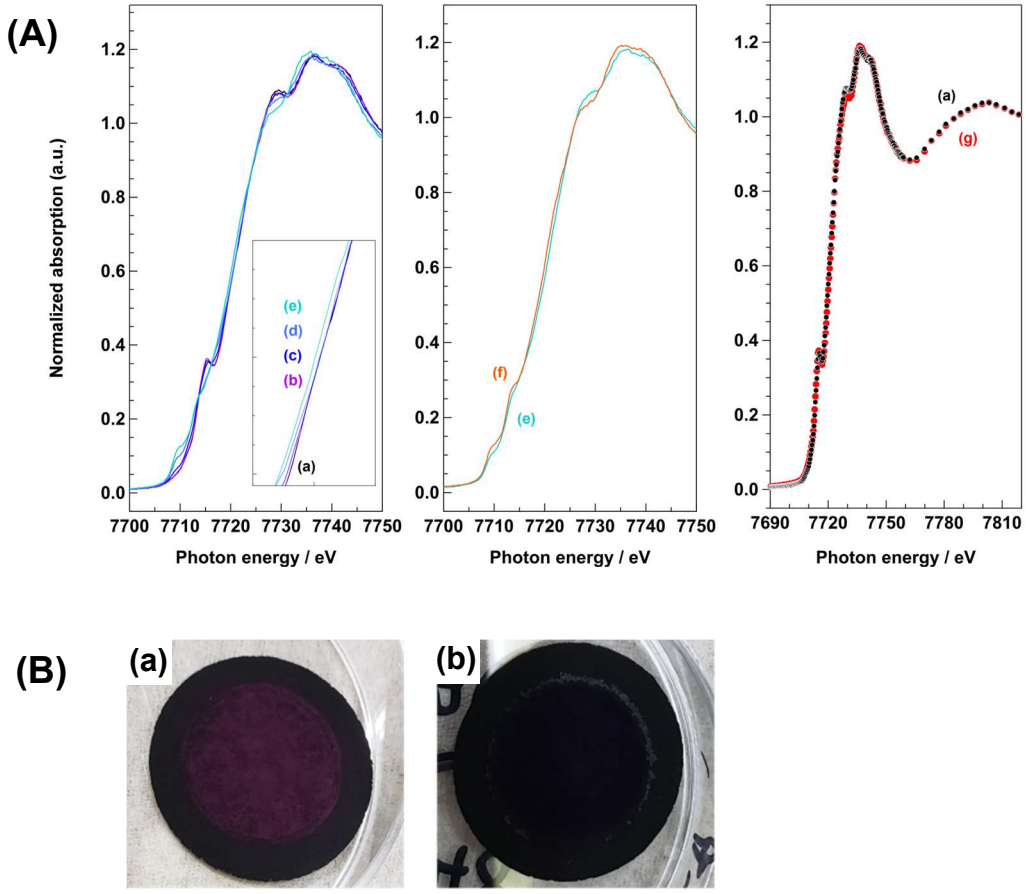

Figure S7. (A) *In-situ* XANES spectra of Co−14MR/KB cathode (a) before the electrolysis, during the potentiostatic electrolysis under He atmosphere at (b) −0.6 V (Ag/AgCl), (c) −0.9 V (Ag/AgCl), (d) −1.25 V (Ag/AgCl), (e) −1.65 V (Ag/AgCl), (f) under CO_2 atmosphere at −1.25 V (Ag/AgCl), and (g) after the electrolysis. (B) Photographs of CoPc/KB cathode (a) before the electrolysis and (b) after the electrolysis.

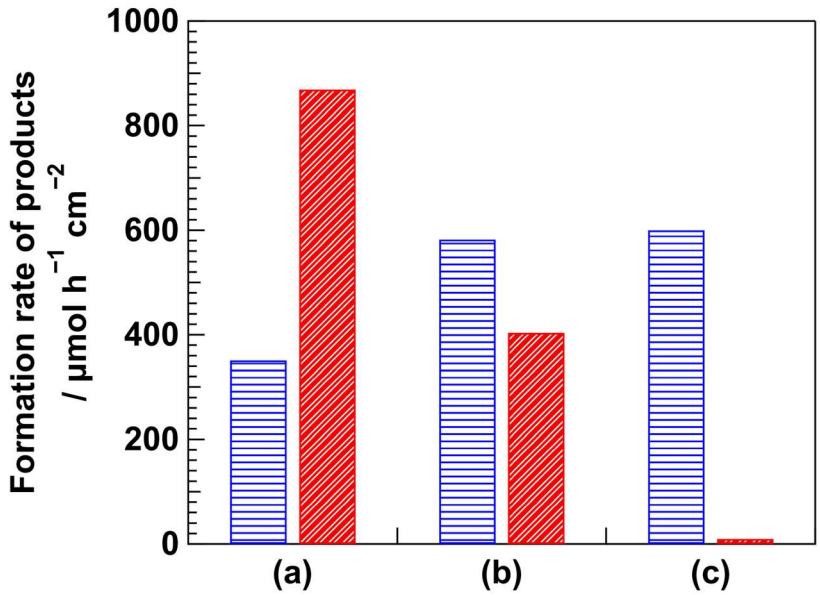

Figure S8. The formation rate of CO (red) and H_2 (blue) in the potentiostatic electrolysis at −1.65 V (Ag/AgCl) under a CO_2 atmosphere (CO_2 electrolysis condition) and an Ar atmosphere (H_2O electrolysis condition), respectively. (a) Co−14MR/KB, (b) CoPc/KB, and (c) Co/KB cathodes.

Table S1. Summary of low concentration CO_2 electrolysis using Co−14MR/KB, CoPc/KB, and Co/KB cathodes. Cathode potential: −1.65 V (Ag/AgCl, pH = 14); CO_2/Ar supply to chamber 1: 10 mL min^{-1}; electrolyte solution of chamber 2 and 3: 1.0 M KOH aq.; electrode area (cathode): 1.9 cm^2. I_d: current density, FE_{CO}: Faradic efficiency of CO.

CO_2 concentration		Cathode catalyst		
		Co-14MR/KB	CoPc/KB	Co/KB
25 % CO_2	I_d / mA cm^{-2}	34.5	23.4	23.3
	FE_{CO} (%)	97	76.0	0.24
10 % CO_2	I_d / mA cm^{-2}	26.7	20.4	25.0
	FE_{CO} (%)	95	58.5	0.04
5 % CO_2	I_d / mA cm^{-2}	21.3	19.8	26.8
	FE_{CO} (%)	88	36.3	0.02
1 % CO_2	I_d / mA cm^{-2}	12.8	25.3	33.6
	FE_{CO} (%)	41	3.3	0
0 % CO_2	I_d / mA cm^{-2}	18.4	30.3	33.2
	FE_{CO} (%)	0	0	0