

# Aqueous electrocatalytic CO<sub>2</sub> reduction using metal complexes dispersed in polymer ion gels

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## **Experimental**

### **Materials**

All reagents and solvents were purchased from Sigma Aldrich and used without further purification.

*fac*-[Re(bpy)(CO)<sub>3</sub>Cl] ([Re-Cl]) and [Ir(tpy)(ppy)Cl] ([Ir]) were synthesized according to literature methods.<sup>1,2,33</sup>

## **Preparation of Polymer Ion Gel Electrodes**

### **[Re]-PIG/CC Electrode**

The precursor solution was made by combining monomer and [Re-Cl] in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). [Re-Cl] (8 mg, 0.017 mmol), ammonium trifluoromethanesulfonate (38 mg) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (0.5 ml) were dissolved in 1 mL of  $\text{CH}_2\text{Cl}_2$  solution containing silicone rubber ( $20 \text{ mg mL}^{-1}$ ). Then, 50  $\mu\text{L}$  of formic acid ( $\text{HCOOH}$ ) and Tetraethyl orthosilicate (TEOS, 38  $\mu\text{L}$ ) were added, and the solution was stirred for five minutes. Dimethylacrylamide/methylenebisacrylamide (0.4 mol % dimethylacrylamide) solution (0.17 mL) and 2,2'-azodiisobutyronitrile (12 mg) as a radical initiator were added to the solution. 0.1 mL of the precursor solution was drop cast onto carbon cloth (CC) on a Teflon seat. The area of CC was about  $2.0 \text{ cm}^2$  ( $1.0 \text{ cm} \times 2.0 \text{ cm}$ ). The coating procedure was repeated three times (to yield approximately  $1.49 \mu\text{mol cm}^{-2}$  of [Re-Cl]), and the resulting polymer solution on CC was heated on a hot plate at 393 K for twelve hours, after which the [Re]-PIG was rinsed with distilled water and dried for 1 day. Copper wire was connected to the [Re]-PIG/CC electrode using copper tape, and the edges of the electrode and all connection points were coated with hot glue. A schematic illustration of the [Re]-PIG electrode is shown in **Scheme S1**.

### **[Re]/CC Electrode**

[Re-Cl] (8 mg) and ammonium trifluoromethanesulfonate (38 mg) were dissolved in 1 mL of  $\text{CH}_2\text{Cl}_2$ . Then, 50  $\mu\text{L}$  of formic acid ( $\text{HCOOH}$ ) and TEOS (38  $\mu\text{L}$ ) were added, and the solution

was stirred for 5 minutes. After stirring, 0.1 mL of solution was drop cast on CC. The area of CC was about 2.0 cm<sup>2</sup> (1.0 cm × 2.0 cm). The coating procedure was repeated three times, and the resulting electrode was heated on a hot plate at 393 K for 12 hours. The [Re]/CC electrode was then rinsed with distilled water and dried for 1 day. Copper wire was connected to the [Re]/CC electrode using copper tape, and the edges of the [Re]/CC electrode and the connection points were coated with hot glue.

### **PIG/CC Electrode**

Ammonium trifluoromethanesulfonate (38 mg) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (0.5 mL) were dissolved in 1 mL of CH<sub>2</sub>Cl<sub>2</sub> containing silicone rubber (20 mg/ml). Then, 50 μL of formic acid (HCOOH) and TEOS (38 μL) were added, and the solution was stirred for five minutes. After stirring, dimethylacrylamide/methylenebisacrylamide (0.4 mol % in dimethylacrylamide) solution (0.17 ml) and 2,2'-azodiisobutyronitrile (12 mg) as a radical initiator were added. The precursor mixed solution (0.1 mL) was drop cast on CC. The area of CC was about 2.0 cm<sup>2</sup> (1.0 cm × 2.0 cm). The coating procedure was repeated three times, and the resulting electrode was heated on a hot plate at 393 K for 12 hours, after which the PIG/CC electrode was rinsed with distilled water and dried for 1 day. Copper wire was connected to the electrode using copper tape, and the edges of the electrode and the connection points were covered with hot glue.

### **[Ir]-PIG/CC Electrode**

[Ir] (4 mg, 0.0052 mmol) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (0.5 ml) were dissolved in 1 mL of  $\text{CH}_2\text{Cl}_2$  containing silicone rubber ( $20 \text{ mg mL}^{-1}$ ). Then, 50  $\mu\text{L}$  of formic acid ( $\text{HCOOH}$ ) and TEOS (38  $\mu\text{L}$ ) were added, and the solution was stirred for five minutes. After stirring, dimethylacrylamide/methylenebisacrylamide (0.4 mol % dimethylacrylamide) solution (0.17 mL) and 2,2'-azodiisobutyronitrile (12 mg) as a radical initiator were added. The solution (0.1 mL) was drop cast on CC. The area of the CC electrode was about  $2.0 \text{ cm}^2$  ( $1.0 \text{ cm} \times 2.0 \text{ cm}$ ). The coating procedure was repeated three times (to yield an approximately  $0.45 \mu\text{mol cm}^{-2}$  of [Ir]), and the resulting electrode was heated on a hot plate at 393 K for 12 hours. Then, the electrode was rinsed with distilled water and dried for 1 day. Copper wire was connected to the electrode using copper tape, and the edges of the [Ir]-PIG electrode and the connection points were coated with hot glue.

### **CoO(OH)/CP Electrode**

CoO(OH) nanoparticles were synthesized according to literature procedure.<sup>40</sup>  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.095 g, 0.4 mmol) was dissolved in 125 mL of distilled water. The solution was purged with nitrogen for 30 minutes, after which the solution was heated at  $60 \text{ }^\circ\text{C}$  for 15 minutes. NaOH (0.64 M in  $\text{H}_2\text{O}$ , 12.5 mL) and  $\text{H}_2\text{O}_2$  (2.4 % in  $\text{H}_2\text{O}$ , 5 mL) were added to the solution while stirring at  $60 \text{ }^\circ\text{C}$ . Then, the reaction solution was cooled to room temperature. CoO(OH) nanoparticles were coated on hydrophilic treatment carbon paper (CP) by immersion of the CP into the CoO(OH) reaction

solution. The CoO(OH)/CP electrode was dried overnight, and the electrode was annealed at 423 K for one hour in atmosphere, followed by rinsing with distilled water. Copper wire was connected to the CoO(OH)/CP electrode using copper tape, and the edges of the electrode and the connection points were coated with hot glue. A schematic illustration of the CoO(OH)/CP electrode is shown in **Scheme S2**.

### **Electrochemistry**

Electrocatalytic reactions were performed at atmospheric pressure in a flow reactor with a Bio-Logic VSP-300 potentiostat. The [Re]-PIG, [Re]/CC, PIG/CC, [Ir]-PIG/CC and CoOOH/CP electrodes (electrode size of about  $1.0 \times 2.0$  cm, reaction area of about  $0.9\text{--}1.1$  cm<sup>2</sup>) were used as the working electrode. A leak less Ag/AgCl reference electrode and platinum wire counter electrode were used. A Pyrex glass cell was used as the electrochemical cell, and 0.1 M potassium hydroxide (KOH)/0.1 M potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) aqueous solution was used as the electrolyte. CO<sub>2</sub> or N<sub>2</sub> gas was bubbled into the reactor for 60 minutes prior to the measurement and allowed to flow at 20 sccm during the measurement period. The amounts of CO, H<sub>2</sub>, and O<sub>2</sub> gas produced were determined *in situ* using a flow reactor combined with a gas chromatograph (SRI Instruments Multiple Gas Analyzer TCD-FID) and oxygen sensor (NeoFOX Oxygen Sensor, Ocean Optics). CO<sub>2</sub> reduction coupled to water oxidation was conducted using a two electrode configuration (**Figure 3a**). The [Re]-PIG/CC cathode and CoO(OH)/CP anode were connected with a potentiostat in a single compartment flow reactor.

### **Calculation of Potential Values vs. RHE**

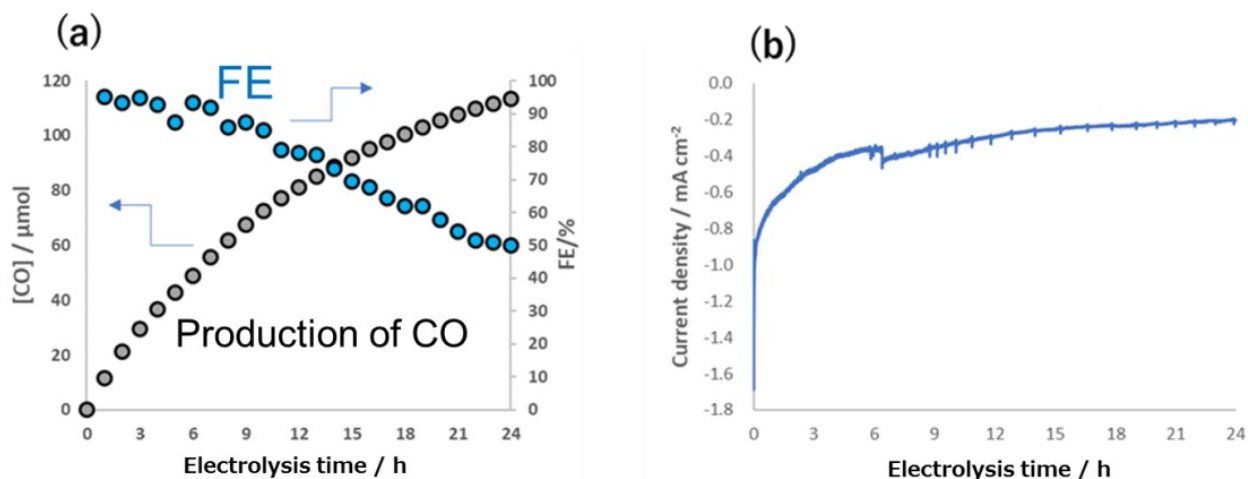
Potential values expressed versus RHE were obtained using the following equation:

$$E_a \text{ (vs. RHE)} = E_a + 0.059 \times pH + 0.199 \text{ V (for Ag/AgCl)}$$

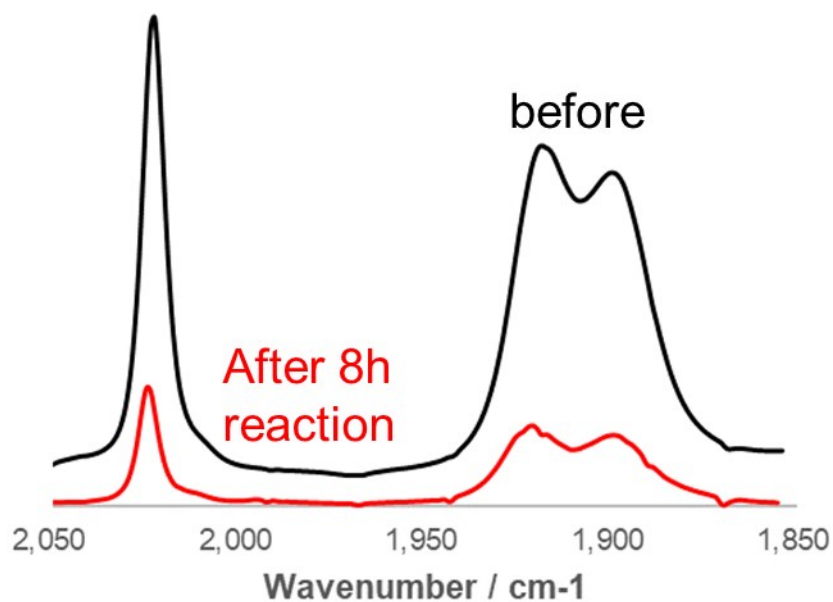
where  $E_a$  is the applied potential.

The pH of the 0.1 M KOH + 0.1 M K<sub>2</sub>CO<sub>3</sub> solution saturated with CO<sub>2</sub> was approximately 7.2. The

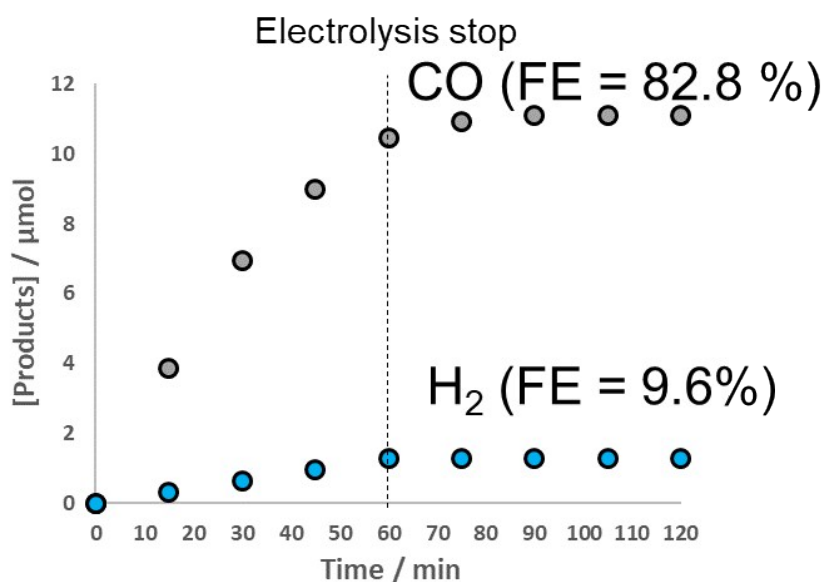
pH of the 0.1 M KOH + 0.1 M K<sub>2</sub>CO<sub>3</sub> solution saturated with N<sub>2</sub> was approximately 11.8.



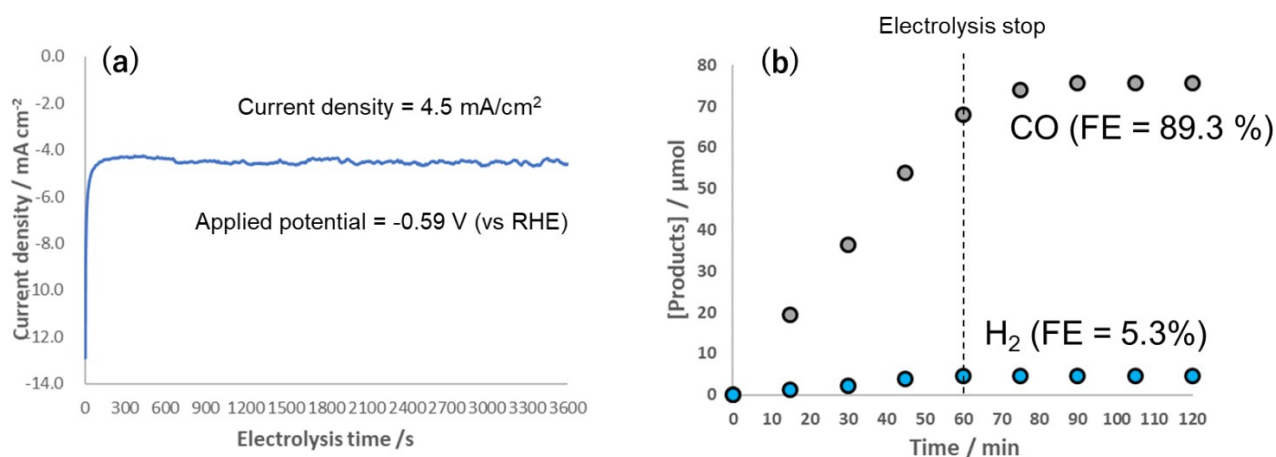
**Figure S1.** Bulk electrolysis for 24 hours at  $-0.68$  V vs. RHE in a solution of  $\text{CO}_2$ -saturated  $0.1$  M  $\text{KOH} + 0.1$  M  $\text{K}_2\text{CO}_3$ . (a) The plot shows the volume of carbon monoxide (gray) produced and Faradaic efficiency for CO production (blue) using the [Re]-PIG electrocatalyst. (b) Chronoamperograms using [Re]-PIG electrode for 24 h.



**Figure S2.** IR spectra of [Re]-PIG electrode before (black) and after 8h reaction (red).

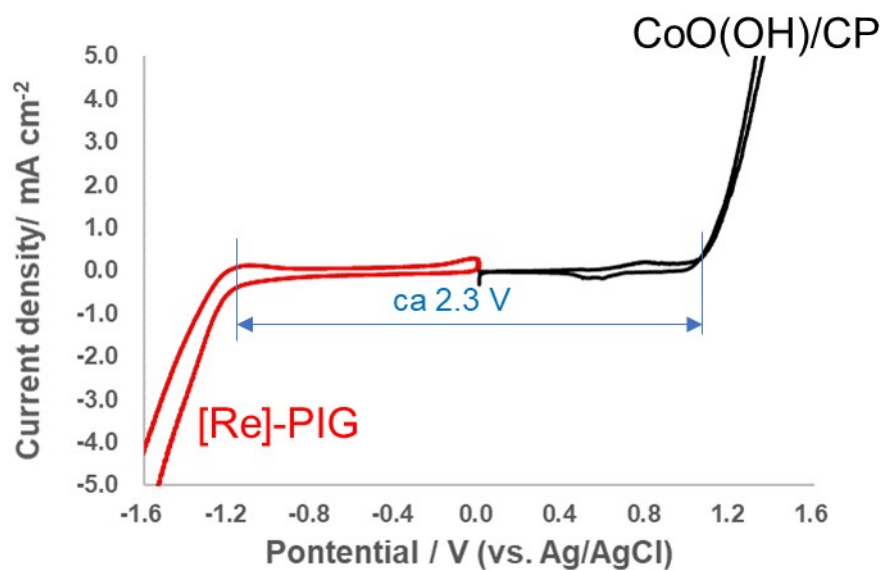


**Figure S3.** Electrocatalytic activity of [Ir]-PIG electrode in 0.1 M KOH + 0.1 M K<sub>2</sub>CO<sub>3</sub> mixed solution. Bulk electrolysis for one hour at -0.68 V vs. RHE in a solution of CO<sub>2</sub>-saturated 0.1 M KOH + 0.1 M K<sub>2</sub>CO<sub>3</sub> indicating volume of carbon monoxide (black) and hydrogen (blue) produced using the [Ir]-PIG electrocatalyst.

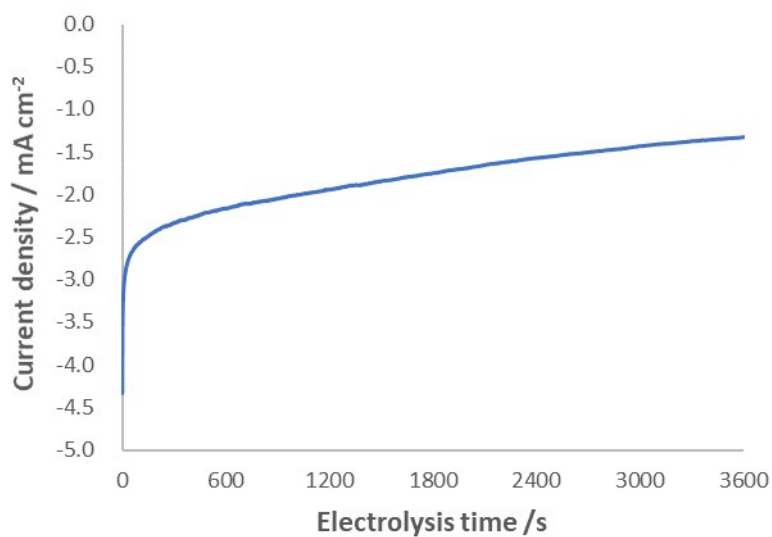


**Figure S4.** (a) Chronoamperograms using [Co(TPP)]-PIG electrode for 1 h at -0.59 V (*vs.* RHE) under CO<sub>2</sub> atmosphere in 0.1 M K<sub>2</sub>B<sub>4</sub>O<sub>7</sub> + 0.2 M K<sub>2</sub>SO<sub>4</sub> mixed solution. (b) Time courses of H<sub>2</sub> (blue) and CO (black) production during electrolysis at -0.59 V *vs.* RHE for 1h under CO<sub>2</sub> atmosphere in 0.1 M K<sub>2</sub>B<sub>4</sub>O<sub>7</sub> + 0.2 M K<sub>2</sub>SO<sub>4</sub> mixed solution.

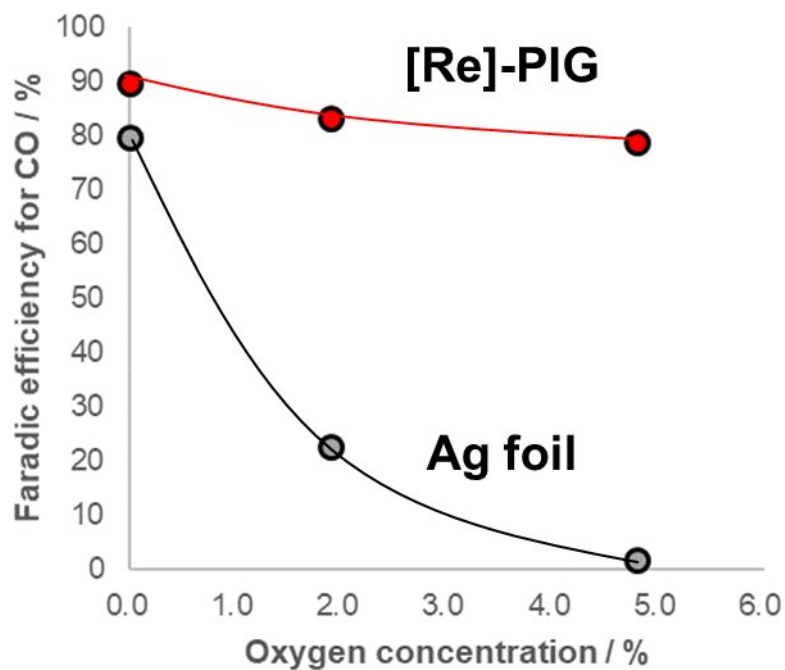




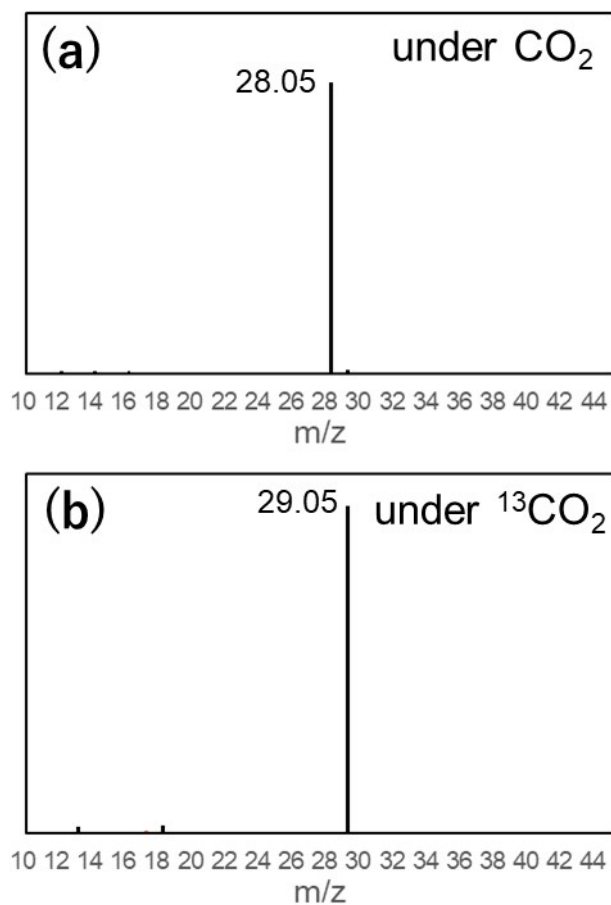
**Figure S5.** Cyclic voltammograms of the CoO(OH)/CP (black) and [Re]-PIG (red) electrodes in CO<sub>2</sub>-saturated 0.1 M KOH + 0.1 M K<sub>2</sub>CO<sub>3</sub> solution.



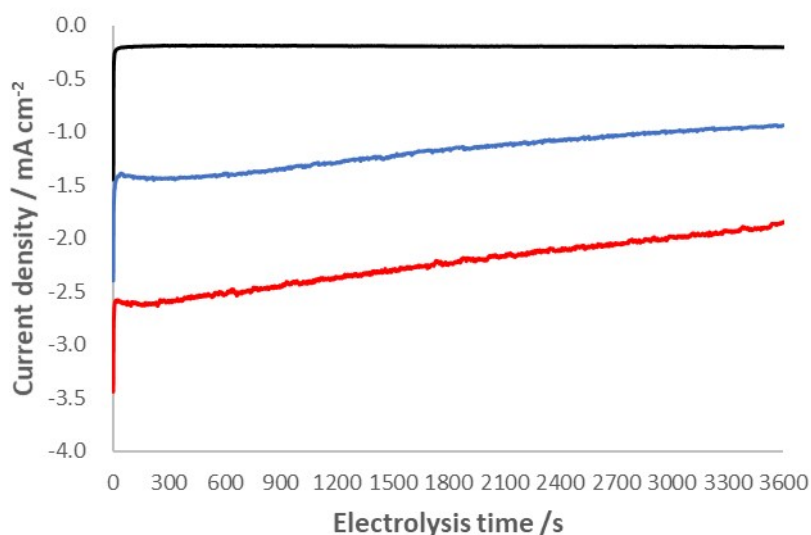
**Figure S6.** Chronoamperometry for CO<sub>2</sub> reduction coupled to water oxidation using [Re]-PIG and CoO(OH)/CP electrodes at 2.5 V cell bias in 0.1 M KOH + 0.1 M K<sub>2</sub>CO<sub>3</sub> solution under CO<sub>2</sub>.



**Figure S7.** (A) Current efficiency for CO formation as a function of oxygen concentration in CO<sub>2</sub> flow over [Re]-PIG electrode and Ag foil in 0.1M KOH + 0.1M K<sub>2</sub>CO<sub>3</sub> mix solution (for [Re]-PIG) and 0.1 M KHCO<sub>3</sub> solution (for Ag foil). Bulk electrolysis for one hour at -0.78 V vs. RHE.



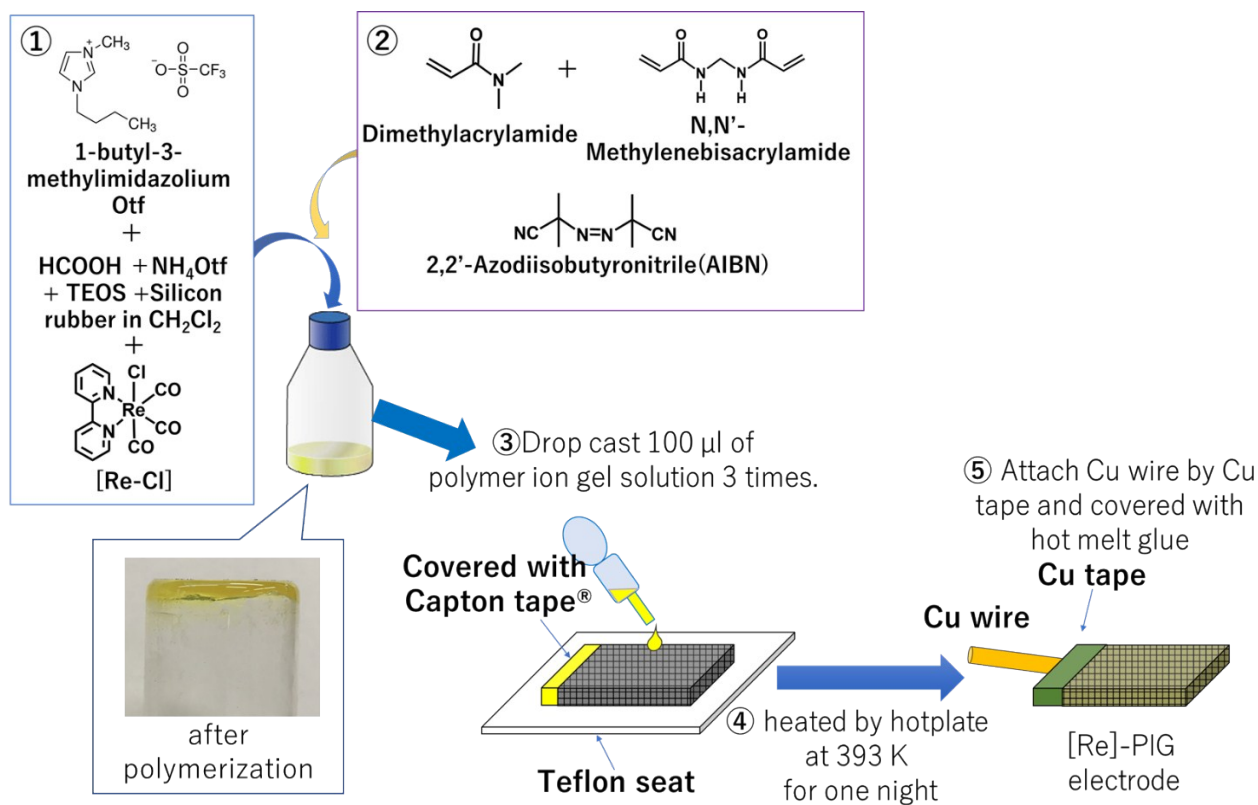
**Figure S8.** MS spectra of bulk electrolysis for 1 hours at -0.68 V vs. RHE. (a) MS spectrum under CO<sub>2</sub> in 0.1 M KOH + 0.1 M K<sub>2</sub>CO<sub>3</sub>; (b) MS spectrum under <sup>13</sup>CO<sub>2</sub> in 0.1 M KOH + 0.1 M K<sub>2</sub><sup>13</sup>CO<sub>3</sub>.



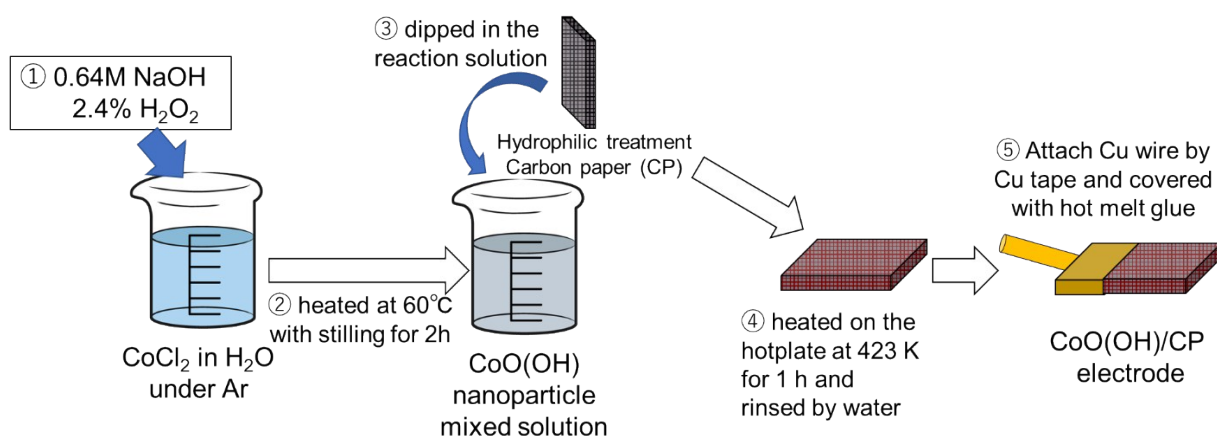
**Figure S9.** Chronoamperometry of CO<sub>2</sub> reduction by [Re]-PIG electrodes at various bias voltages [-0.58 V (black), -0.68 V (blue) and -0.78 V (red)].

**Table S1.** Summary of electrocatalytic CO<sub>2</sub> reduction using PIG based electrodes at several concentrations of [Re-Cl]. Electrocatalytic CO<sub>2</sub> reduction for one hour using [Re]-PIG electrodes at -0.68 V vs. RHE in 0.1 M KOH + 0.1 M K<sub>2</sub>CO<sub>3</sub> purged with CO<sub>2</sub>.

Electrode	Amount of Catalyst / $\mu\text{mol cm}^{-2}$	FE of CO / %	FE of H <sub>2</sub> / %	Current Density / mA cm <sup>-2</sup>
[Re]-PIG	0.75	55.4	33.8	0.77
[Re]-PIG	1.49	90.8	trace	1.19
[Re]-PIG	2.24	92.1	trace	1.08



**Scheme S1.** Schematic illustration of [Re]-PIG electrode preparation. (Capitalize the T in OTf)



**Scheme S2.** Schematic illustration of CoO(OH)/CP electrode preparation.