

Aqueous electrocatalytic CO₂ 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)₃Cl] ([Re-Cl]) and [Ir(tpy)(ppy)Cl] ([Ir]) were synthesized according to literature methods.^{1,2,33}

Preparation of Polymer Ion Gel Electrodes

[Re]-PIG/CC Electrode

The precursor solution was made by combining monomer and [Re-Cl] in dichloromethane (CH_2Cl_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 CH_2Cl_2 solution containing silicone rubber (20 mg mL^{-1}). Then, 50 μL of formic acid (HCOOH) and Tetraethyl orthosilicate (TEOS, 38 μL) 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 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 CH_2Cl_2 . Then, 50 μL of formic acid (HCOOH) and TEOS (38 μL) 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 cm² (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 CH₂Cl₂ 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 cm² (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 CH_2Cl_2 containing silicone rubber (20 mg mL^{-1}). 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 % 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 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.⁴⁰ $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (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 H_2O , 12.5 mL) and H_2O_2 (2.4 % in H_2O , 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 1.0×2.0 cm, reaction area of about $0.9\text{--}1.1$ cm²) 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 (K₂CO₃) aqueous solution was used as the electrolyte. CO₂ or N₂ 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, H₂, and O₂ 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). CO₂ 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:

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

where E_a is the applied potential.

The pH of the 0.1 M KOH + 0.1 M K₂CO₃ solution saturated with CO₂ was approximately 7.2. The

pH of the 0.1 M KOH + 0.1 M K₂CO₃ solution saturated with N₂ was approximately 11.8.

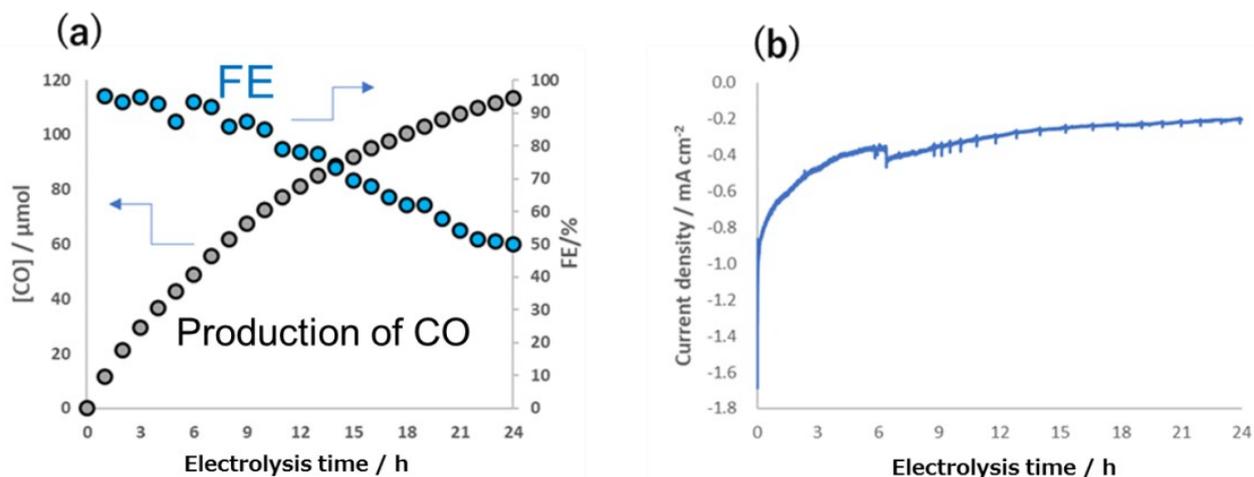


Figure S1. Bulk electrolysis for 24 hours at -0.68 V vs. RHE in a solution of CO_2 -saturated 0.1 M $\text{KOH} + 0.1$ M K_2CO_3 . (a) The plot shows the volume of carbon monoxide (gray) produced and Faradaic efficiency for CO production (blue) using the [Re]-PIG electrocatalyst. (b) Chronoamperograms using [Re]-PIG electrode for 24 h.

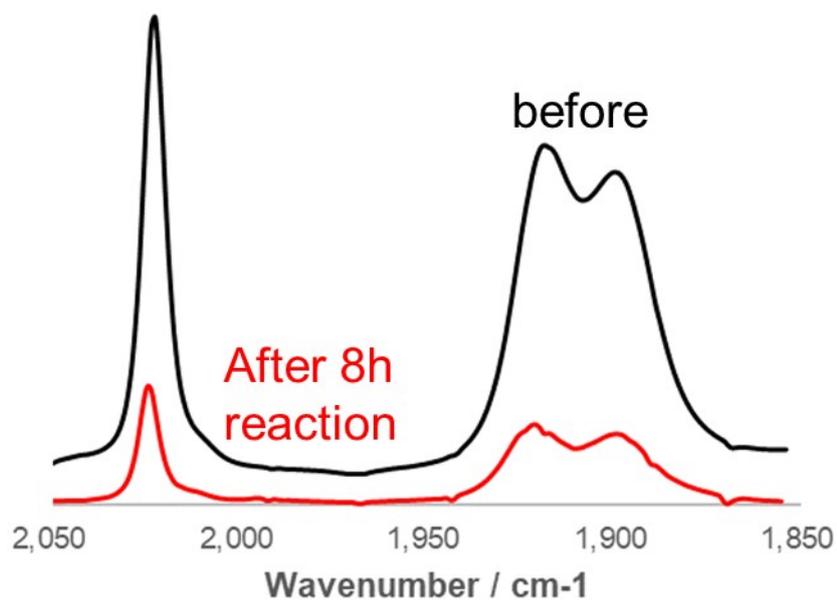


Figure S2. IR spectra of [Re]-PIG electrode before (black) and after 8h reaction (red).

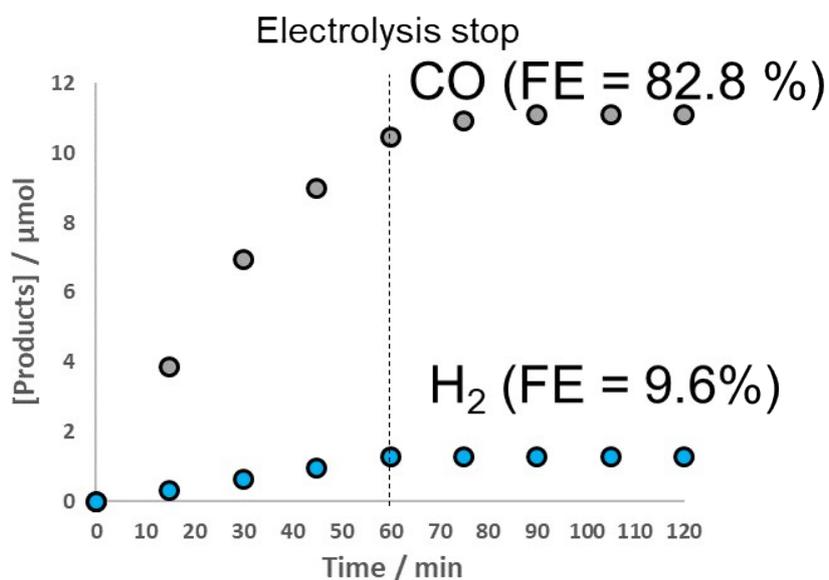


Figure S3. Electrocatalytic activity of [Ir]-PIG electrode in 0.1 M KOH + 0.1 M K₂CO₃ mixed solution. Bulk electrolysis for one hour at -0.68 V vs. RHE in a solution of CO₂-saturated 0.1 M KOH + 0.1 M K₂CO₃ indicating volume of carbon monoxide (black) and hydrogen (blue) produced using the [Ir]-PIG electrocatalyst.

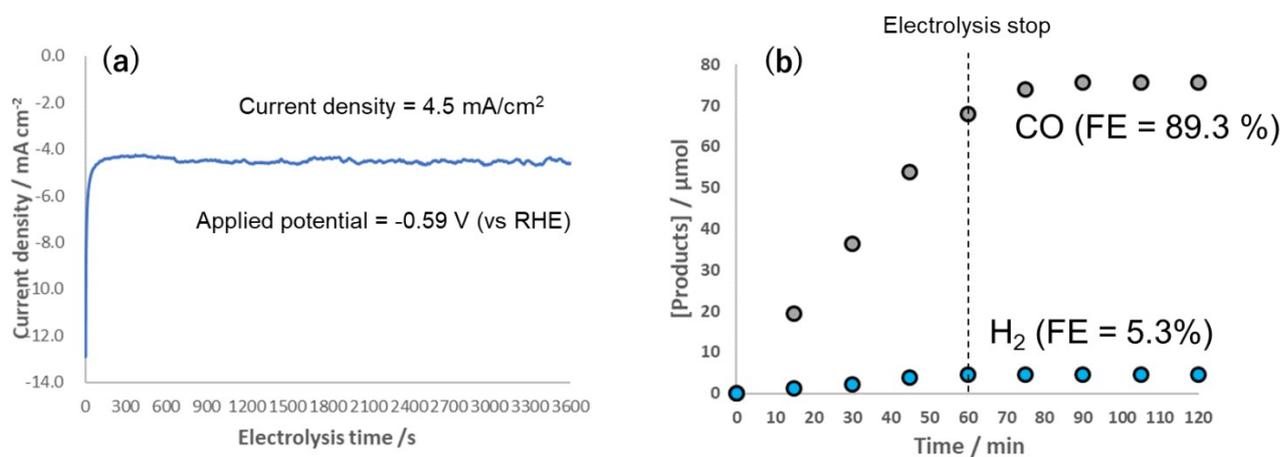


Figure S4. (a) Chronoamperograms using [Co(TPP)]-PIG electrode for 1 h at -0.59 V (vs. RHE) under CO₂ atmosphere in 0.1 M K₂B₄O₇ + 0.2 M K₂SO₄ mixed solution. (b) Time courses of H₂ (blue) and CO (black) production during electrolysis at -0.59 V vs RHE for 1h under CO₂ atmosphere in 0.1 M K₂B₄O₇ + 0.2 M K₂SO₄ mixed solution.

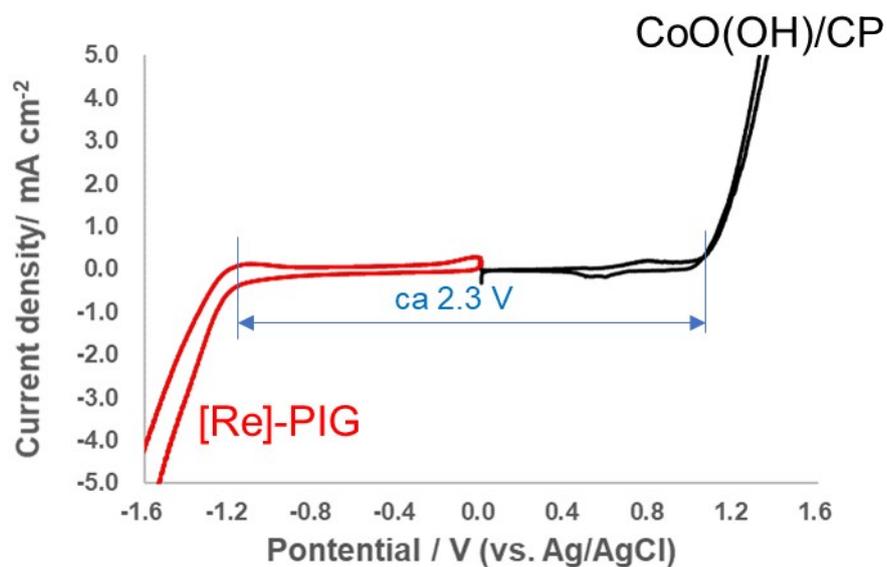


Figure S5. Cyclic voltammograms of the CoO(OH)/CP (black) and [Re]-PIG (red) electrodes in CO₂-saturated 0.1 M KOH + 0.1 M K₂CO₃ solution.

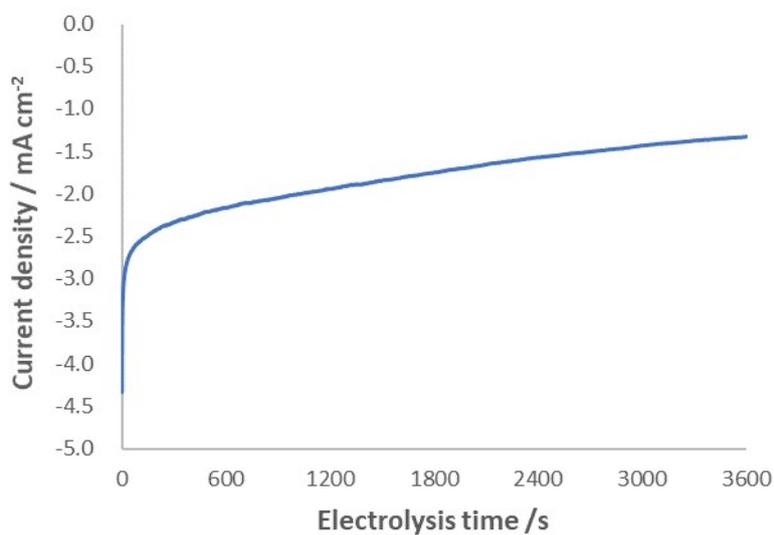


Figure S6. Chronoamperometry for CO₂ reduction coupled to water oxidation using [Re]-PIG and CoO(OH)/CP electrodes at 2.5 V cell bias in 0.1 M KOH + 0.1 M K₂CO₃ solution under CO₂.

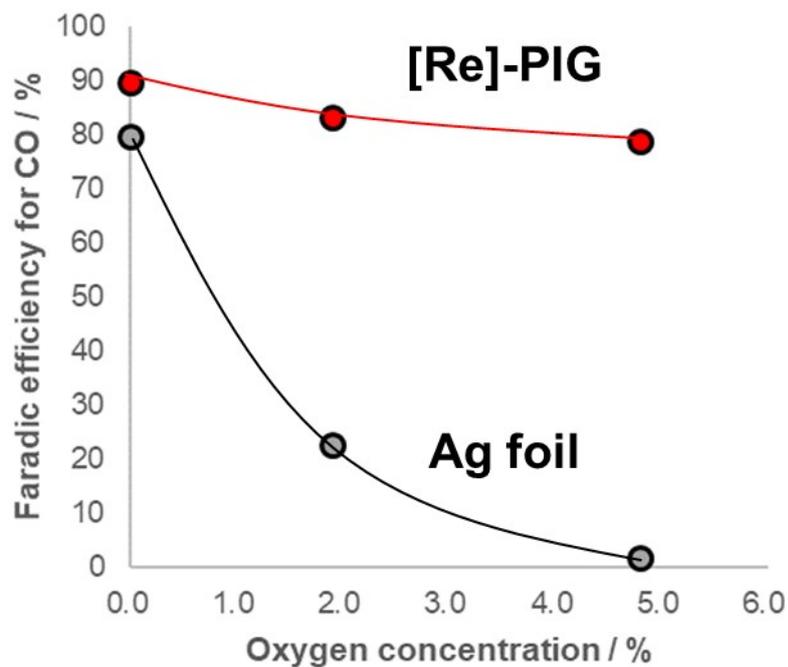


Figure S7. (A) Current efficiency for CO formation as a function of oxygen concentration in CO₂ flow over [Re]-PIG electrode and Ag foil in 0.1M KOH + 0.1M K₂CO₃ mix solution (for [Re]-PIG) and 0.1 M KHCO₃ solution (for Ag foil). Bulk electrolysis for one hour at -0.78 V vs. RHE.

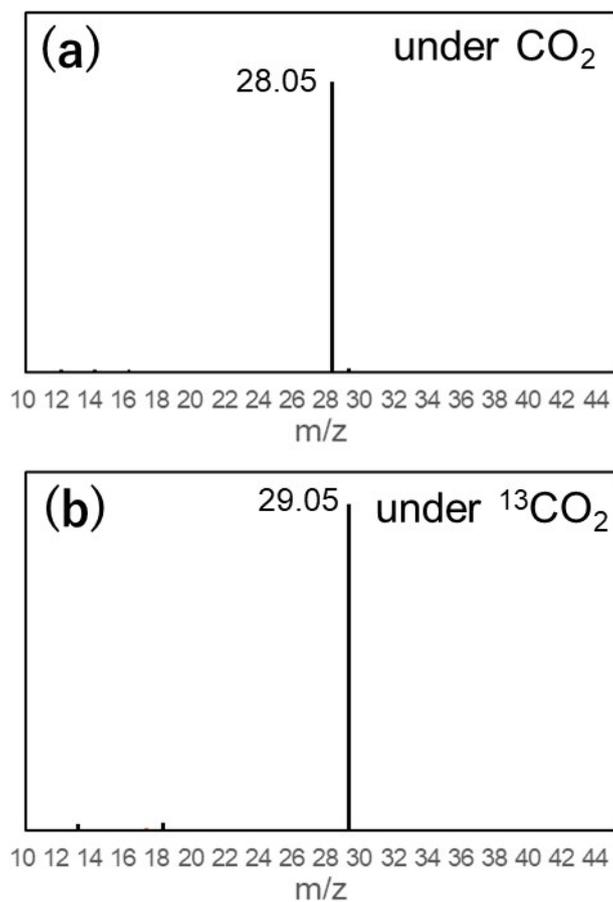


Figure S8. MS spectra of bulk electrolysis for 1 hours at -0.68 V vs. RHE. (a) MS spectrum under CO₂ in 0.1 M KOH + 0.1 M K₂CO₃; (b) MS spectrum under ¹³CO₂ in 0.1 M KOH + 0.1 M K₂¹³CO₃.

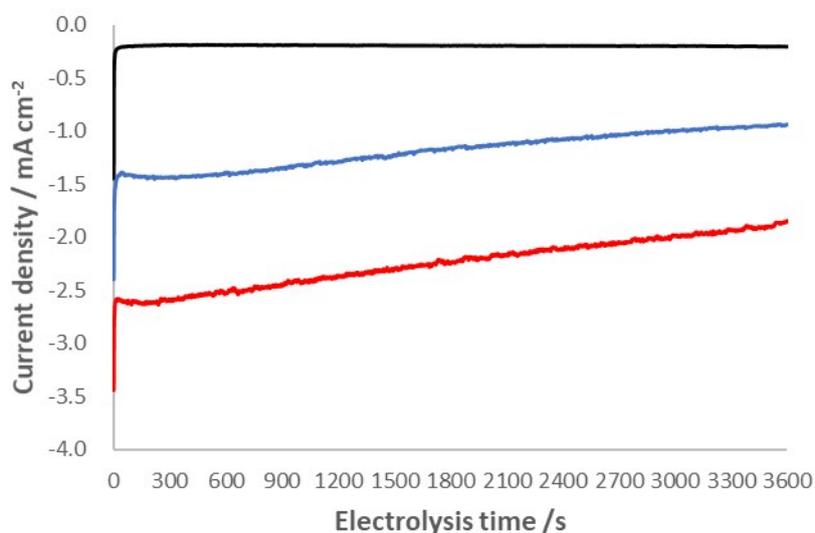
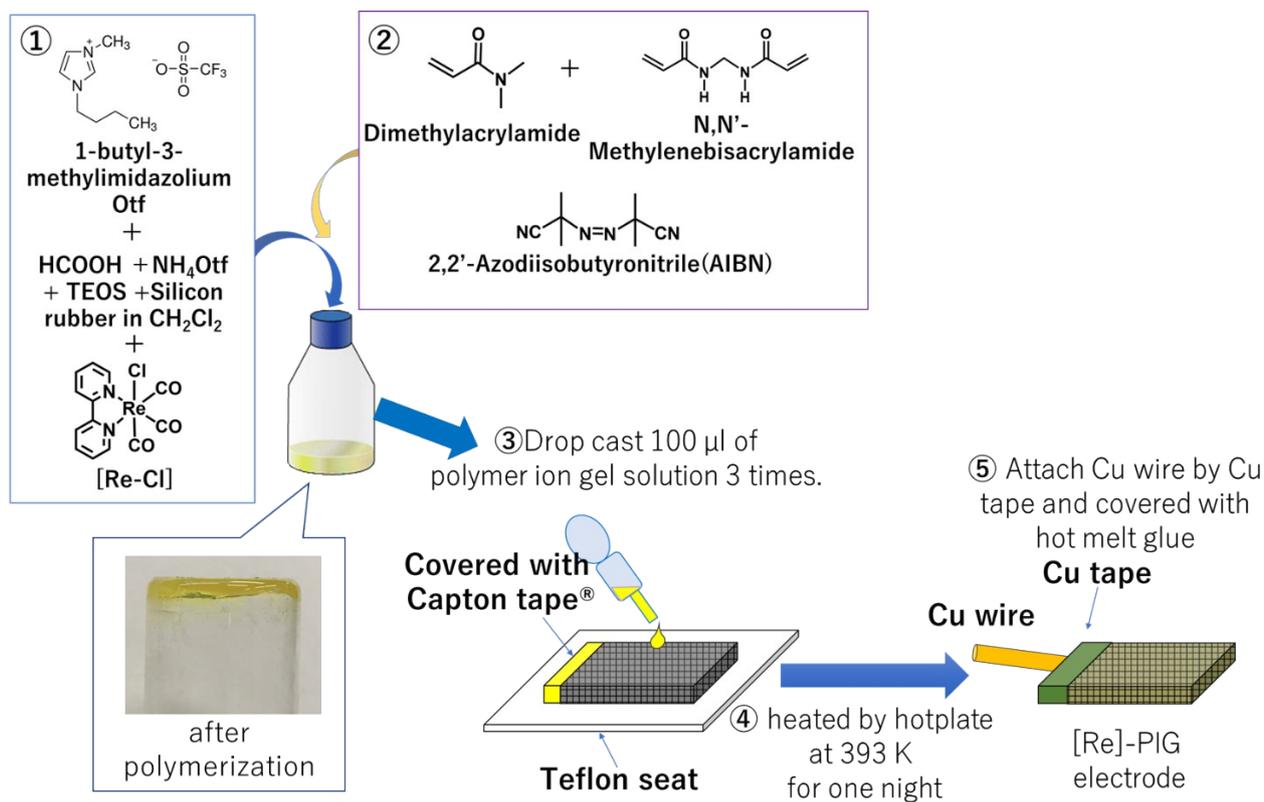


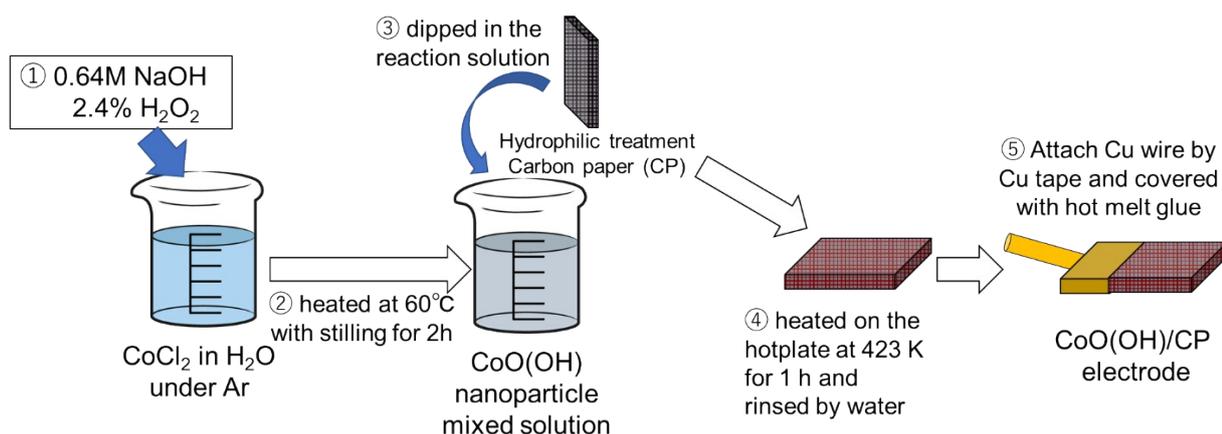
Figure S9. Chronoamperometry of CO₂ reduction by [Re]-PIG electrodes at various bias voltages [-0.58 V (black), -0.68 V (blue) and -0.78 V (red)].

Table S1. Summary of electrocatalytic CO₂ reduction using PIG based electrodes at several concentrations of [Re-Cl]. Electrocatalytic CO₂ reduction for one hour using [Re]-PIG electrodes at -0.68 V vs. RHE in 0.1 M KOH + 0.1 M K₂CO₃ purged with CO₂.

Electrode	Amount of Catalyst / $\mu\text{mol cm}^{-2}$	FE of CO / %	FE of H ₂ / %	Current Density / mA cm ⁻²
[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.