# Supporting Information

## Electrocatalytic Reduction of Low Concentration $CO_2$

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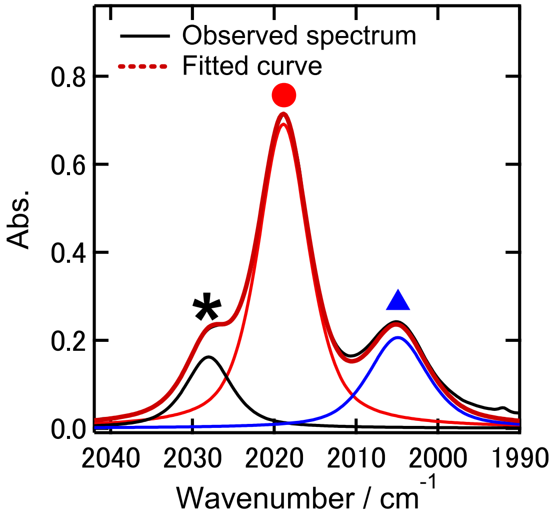

**Fig. S1.** Curve fitting of the FT-IR spectrum of the Re(I) complexes (5.0 mM) in a DMF-TEOA (5:1 v/v) solution containing 0.1 M $Et_4NBF_4$ after purging with 1% $CO_2$. Black asterisk (*), blue triangle (▲) and red circle (●) display the peaks attributed to **Re-DMF$^+$**, **Re-TEOA**, and **Re-$CO_2$TEOA**, respectively.

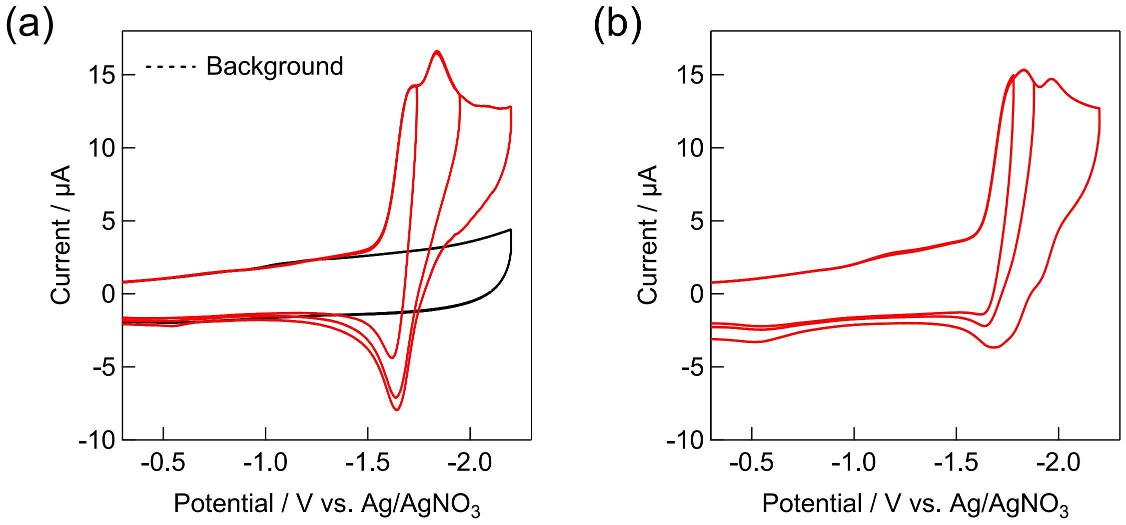

**Fig. S2.** CVs of the Re(I) complex (0.5 mM) in DMF (a) and in a DMF-TEOA mixed solution (5:1 v/v) (b) containing $Et_4NBF_4$ (0.1 M) as supporting electrolyte under an Ar atmosphere at a sweep rate of 200 mV $s^{-1}$. A glassy carbon electrode (diameter: 3 mm), a $Ag/AgNO_3$ (10 mM) electrode and a Pt wire were used as working, reference, and counter electrode, respectively.

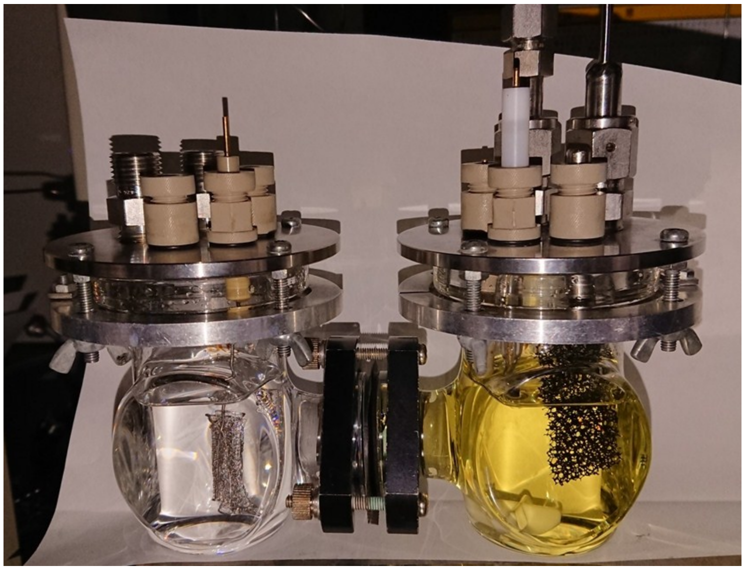

**Fig. S3.** Picture of the setup for the bulk electrolysis. The right side is the cathodic chamber for $CO_2$ reduction reaction.

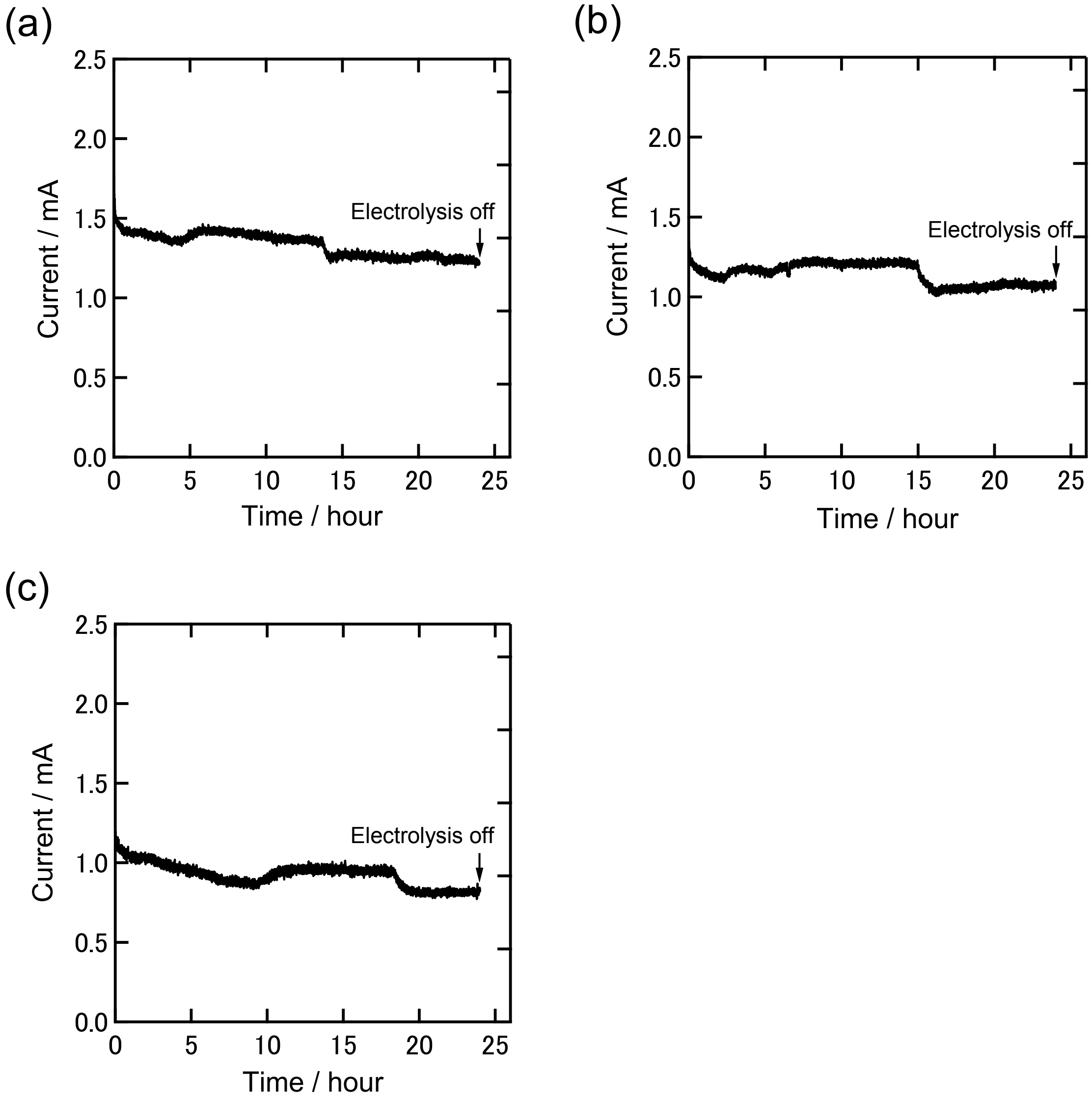

**Fig. S4.** Time courses of current during bulk electrolysis using the Re(I) catalyst (0.5 mM) at −1.82 V in a DMF-TEOA solution containing $Et_4NBF_4$ (0.1 M) under (a) 100%, (b) 10%, and (c) 1% $CO_2$ atmospheres (10 mL $min^{-1}$).

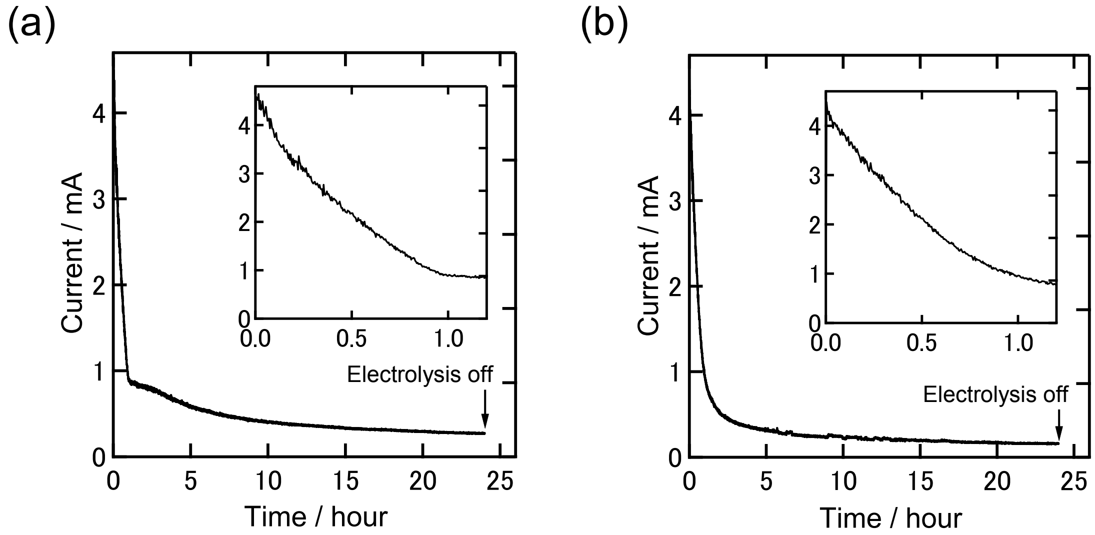

**Fig. S5.** Time courses of current during bulk electrolysis using **Re-DMF$^+$** (0.5 mM) at −1.82 V in a DMF solution containing $Et_4NBF_4$ (0.1 M) under (a) 100% and (b) 1% $CO_2$ atmospheres (10 mL min$^{-1}$).

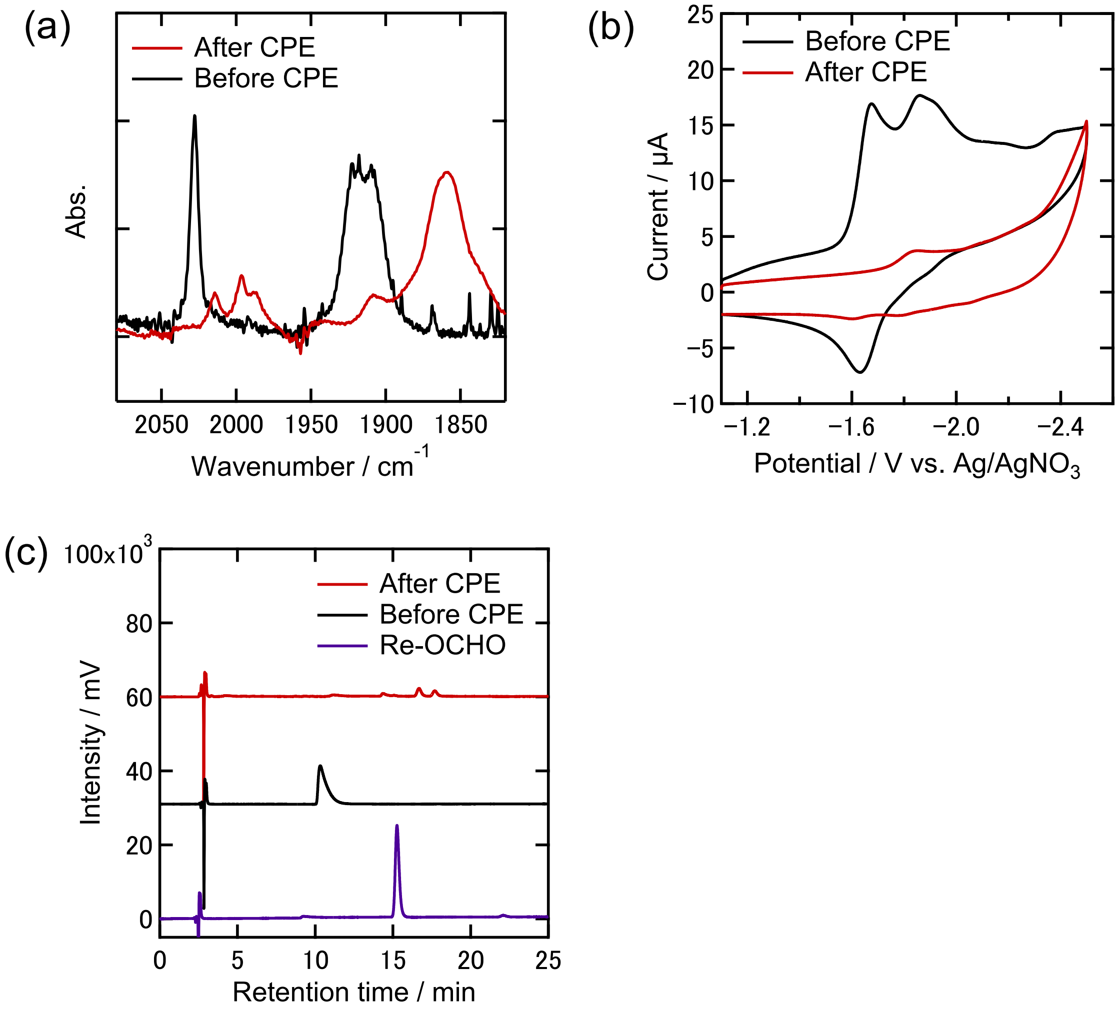

**Fig. S6.** (a) FT-IR spectra, (b) CVs, and (c), UHPLCs of the Re(I) complexes before and after the bulk electrolysis at -1.82 V under a 1% $CO_2$ atmosphere in DMF containing $Et_4NBF_4$ (0.1 M) as supporting electrolyte; black lines: before electrolysis, and red lines: after electrolysis. The blue line in (c) is UHPLC of **Re-OCHO**. The FT-IR spectra and CVs were measured by using the reaction solutions without any treatment. UHPLC: an ODS column: $\lambda_{det}$ = 400 nm, a MeOH-$H_2O$ mixed solution containing $KH_2PO_4$ buffer of pH5.9 (1:1 v/v) was used as the eluent. The blue line shows the analysis result of the isolated **Re-OCHO** as reference.

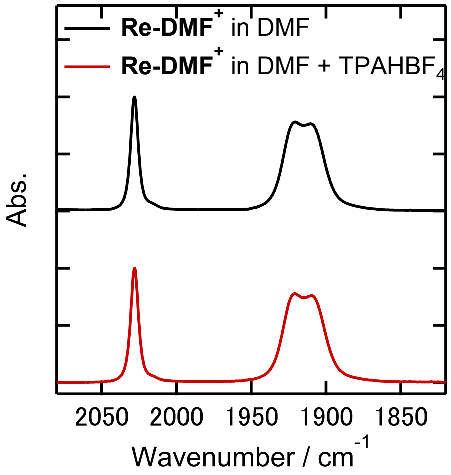

**Fig. S7.** FT-IR spectra (black) before and (red) after adding $TPAHBF_4$ (25 mM) into a DMF solution containing **Re-DMF**$^+$ (5.0 mM) and $Et_4NBF_4$ (0.1 M) under an Ar atmosphere.

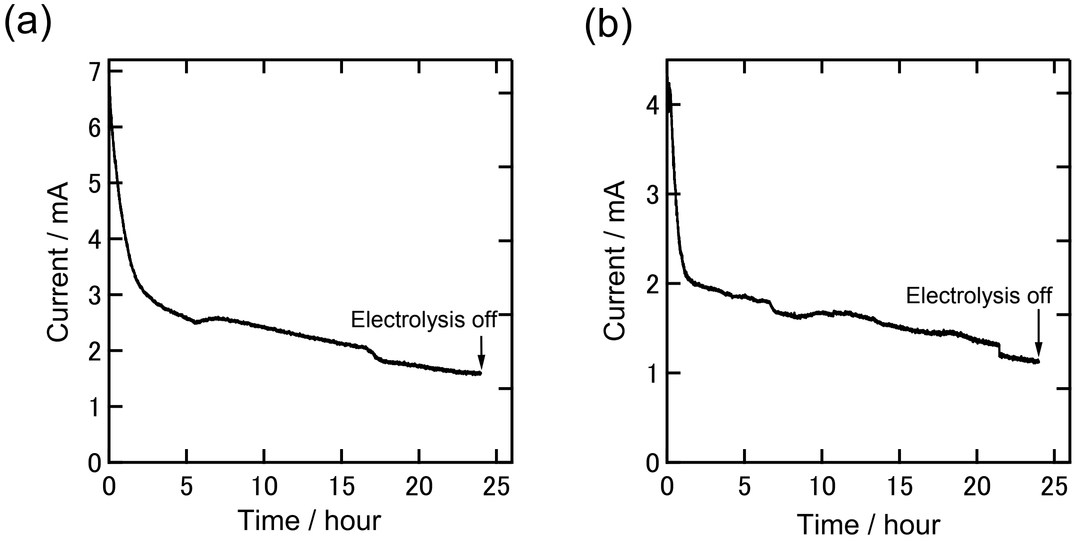

**Fig. S8.** Time courses of current during bulk electrolysis using **Re-DMF**$^+$ (0.5 mM) at −1.82 V in the DMF solution containing $Et_4NBF_4$ (0.1 M) and $TPAHBF_4$ (25 mM) under (a) 100% and (b) 1% $CO_2$ atmospheres (10 mL min$^{-1}$).

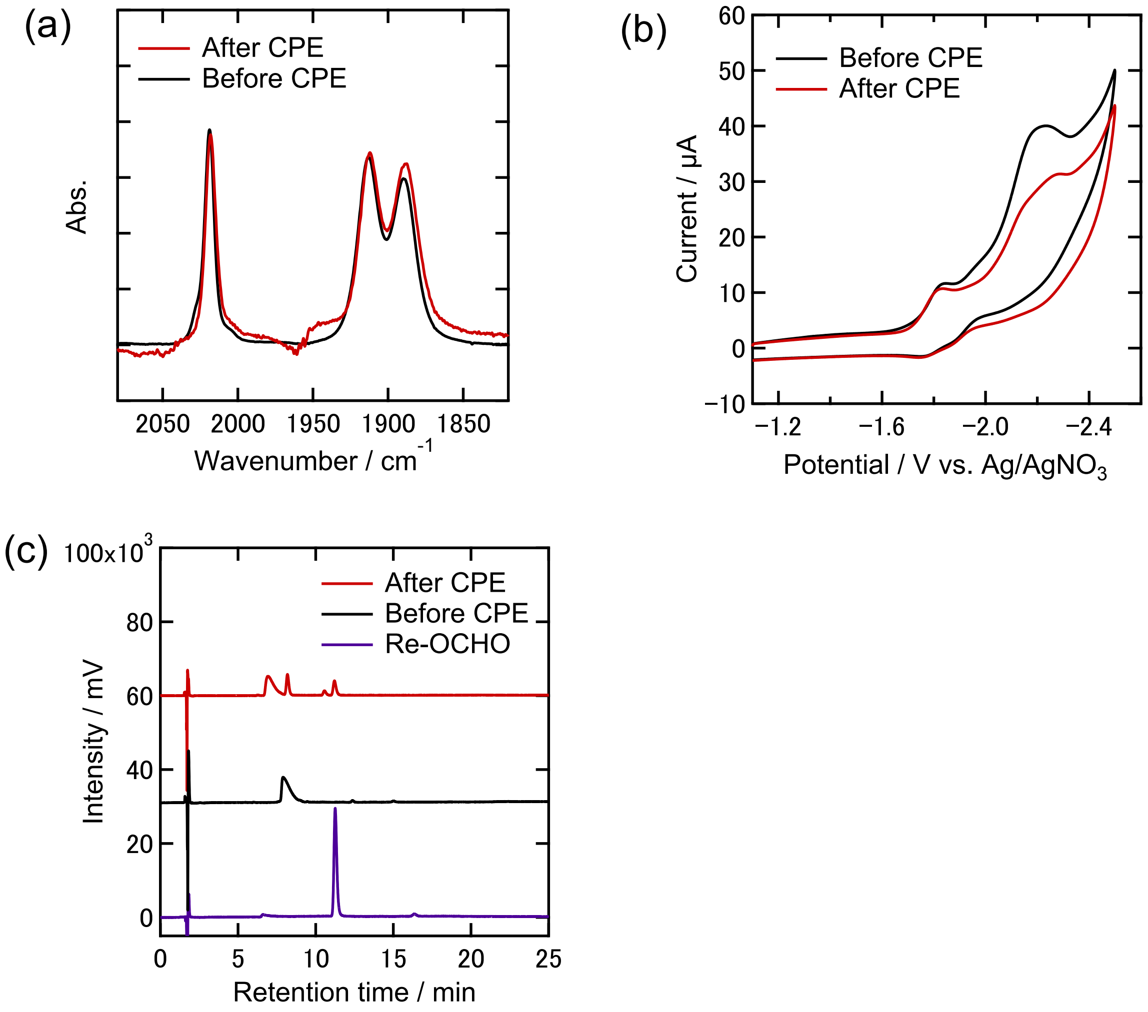

**Fig. S9.** (a) FT-IR spectra, (b) CVs, and (c), UHPLCs of the Re(I) complexes before and after the bulk electrolysis at -1.82 V under a 10% $CO_2$ atmosphere a DMF-TEOA mixed solution (5:1 v/v) containing $Et_4NBF_4$ (0.1 M) as supporting electrolyte; black lines: before electrolysis, and red lines: after electrolysis. The blue line in (c) is UHPLC of **Re-OCHO**. The FT-IR spectra and CVs were measured by using the reaction solutions without any treatment. UHPLC: an ODS column: $\lambda_{det}$ = 400 nm, a MeOH-$H_2O$ mixed solution containing $KH_2PO_4$ buffer of pH5.9 (1:1 v/v) was used as the eluent. The blue line shows the analysis result of the isolated **Re-OCHO** as reference.