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Supplementary Materials

Electrochemical CO_2 Reduction in Methanol at Cu and Cu_2O-Deposited Carbon Black Electrodes

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Table S1. Apparatus and experimental conditions.

Electrochemical reduction	
Cell	H-type cell
Potentiostat/galvanostate	Hokuto HA-3001A
Coulometer	Integrator 1109 (Fusou Seisakujyo, Inc., Japan)
Working electrode	Cu or Cu_2O-deposited carbon black/ carbon plate (10 mm × 10 mm)
Counter electrode	Pt foil (30 mm × 20 mm, 0.1 mm thickness, 99.98% purity)
Reference electrode	Ag quasi-reference electrode (Q.R.E.)
Electrolyte	
catholyte	0.15 M NaCl in methanol
anolyte	1.0 M $NaHCO_3$ in water
Carbon dioxide	99.9999 % purity
Potential	–1.7 to –2.0 V vs. Ag/AgCl sat. KCl
Temperature	298 K
Product analysis	
Gas products	Gas chromatography TCD (GL Sciences GC-320, Molecular Sieve 5A; 13X-S, Ar and He carrier gas) FID (GL Sciences GC-353B, Porapak Q, N_2 carrier gas)
Liquid products	HPLC with UV detector (Shimazu LC-10AT)

Table S2. Effect of electrode on the Faradaic efficiencies of products by the electrochemical reduction of CO_2.

Electrodes	Faradaic efficiency (%)					
	CH_4	C_2H_4	$HCOOCH_3$	CO	H_2	Total
Carbon black	–	–	17.9	25.8	41.5	85.3
Cu foil	15.8	6.8	14.8	5.8	45.5	88.5

Potential: –1.9 V, catholyte: 0.15 M of NaCl in methanol.

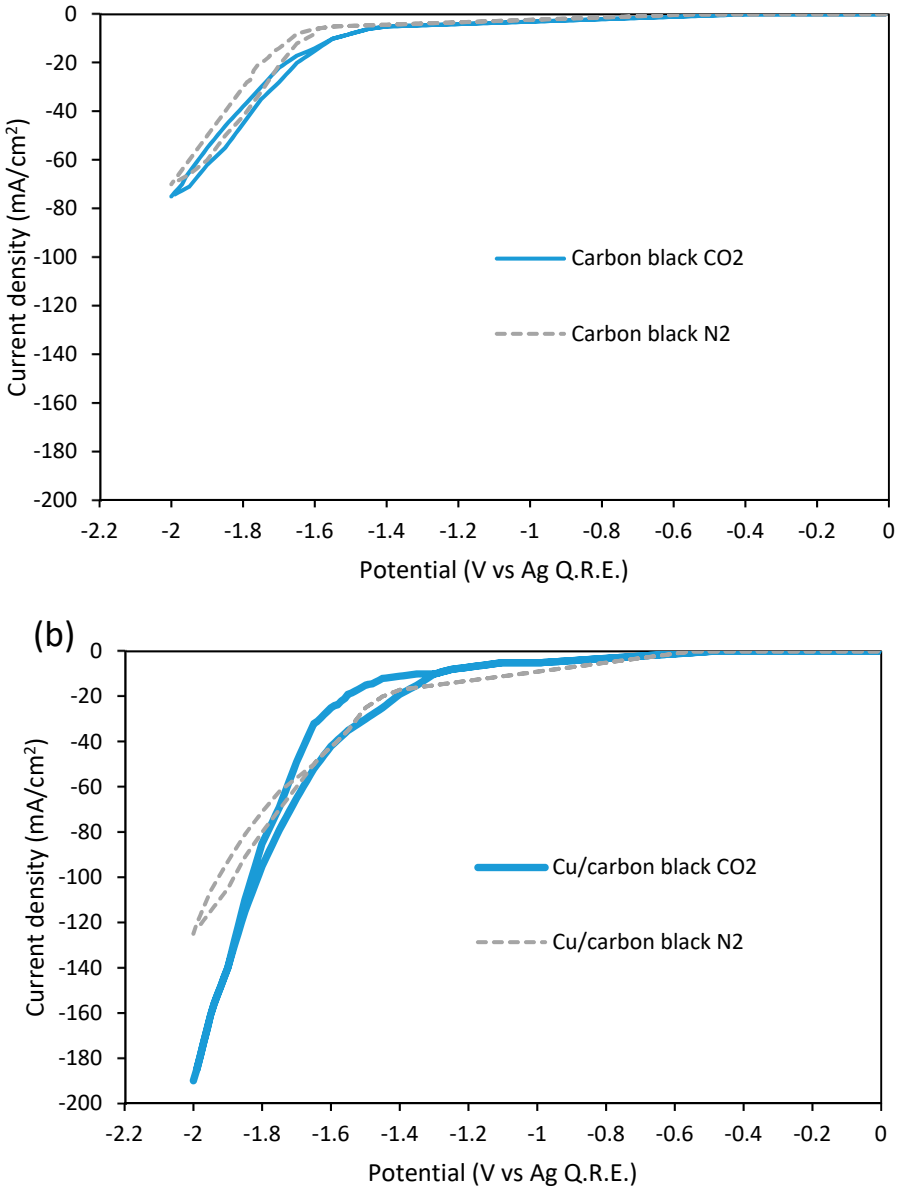

Figure S1. Current–potential curves in CO_2-saturated and N_2-purged methanol. (a) Carbon black electrode; (b) Cu/carbon black electrode.

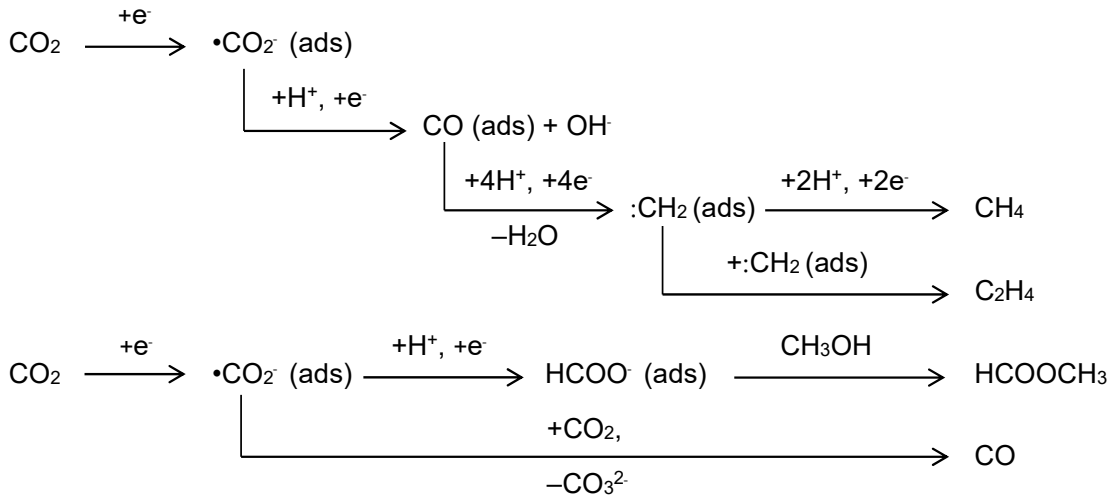

Figure S2. Reaction mechanism of the electrochemical reduction of CO_2 at the Cu and Cu_2O-deposited carbon black electrodes in methanol.

Table S3. Effect of electrode on the Faradaic efficiencies of products by the electrochemical reduction of CO_2.

Electrodes	Faradaic efficiency (%)						
	CH_4	C_2H_4	HCOOH[1]	CO	H_2	Total	
Cu/carbon black	26.9	13.4	14.6	9.5	25.6	85.3	This work
Cu_2O/carbon black	32.3	6.8	8.4	7.8	34.7	88.5	This work
Cu plate	17.8	12.7	10.2	5.4	52.0	98.1	[1]
GDE[2]	0.2	-	2.1	-	84.4	86.7	[2]
PorCu electrode[3]	27	17	-[4]	10	-[4]	54	[3]

[1] In this work, $HCOOCH_3$ was formed in the methanol electrolyte.

[2] Carbon gas diffusion electrode.

[3] Copper–porphyrin complex electrode.

[4] Not determined.

References

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