Supporting Information

Selective Conversion of Carbon Dioxide to Formate Using Few-Layer Nitrogen-Doped Graphene on Copper Foam with Enhanced Suppression of Hydrogen Evolution Reaction

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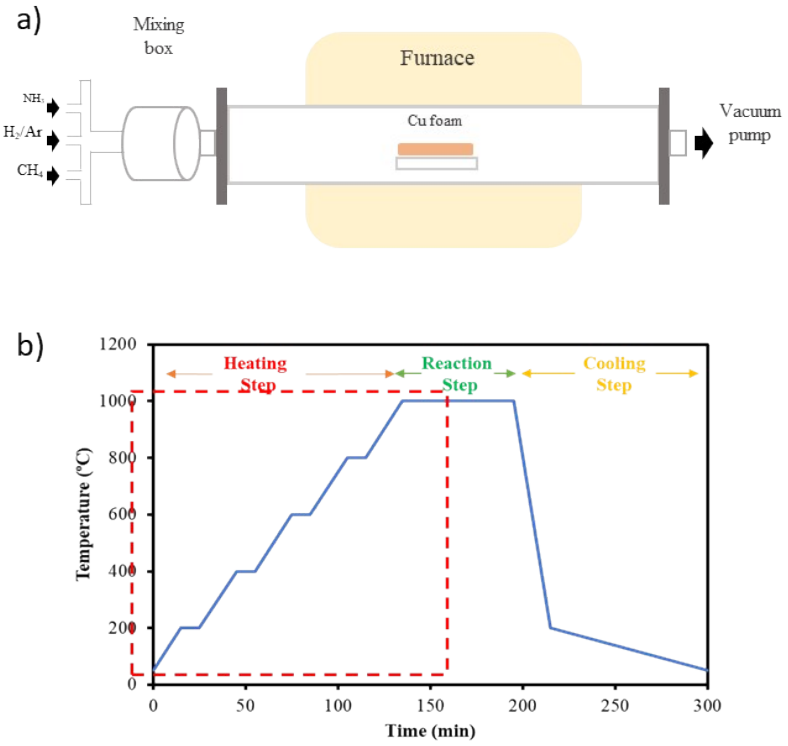

Fig. S1. Schematic diagram of a) the chemical vapor deposition (CVD) process set up, and b) three main steps of CVD process.

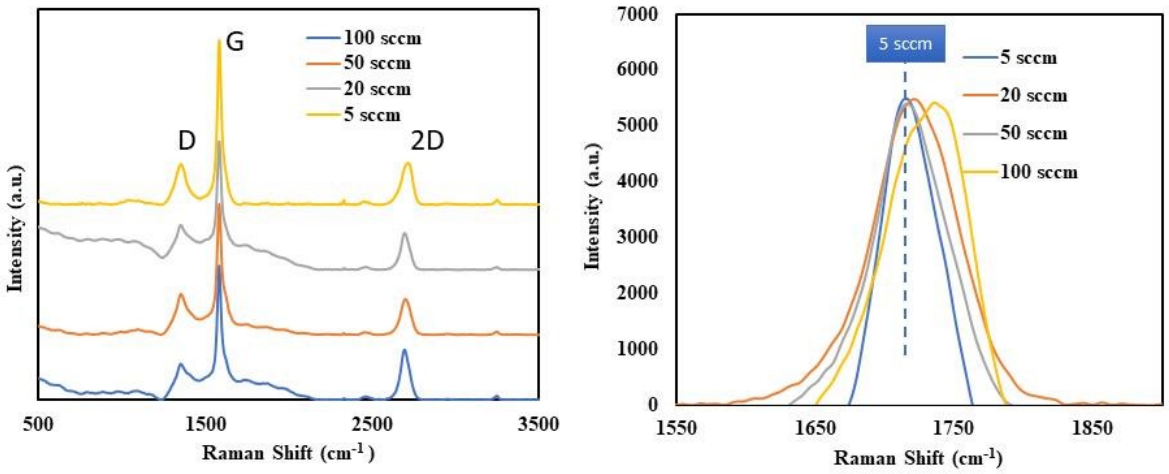

Fig. S2. (a) Raman spectra of Graphene supported on Cu foam (GP/CuF) with compared flowrate of methane, and (b) comparison of 2D band with flow rate of methane at 5, 20, 50, and 100 sccm.

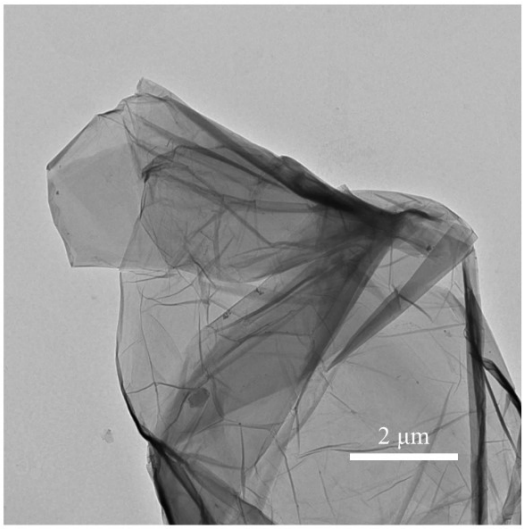

Fig. S3. TEM images of graphene that coated on copper foam.

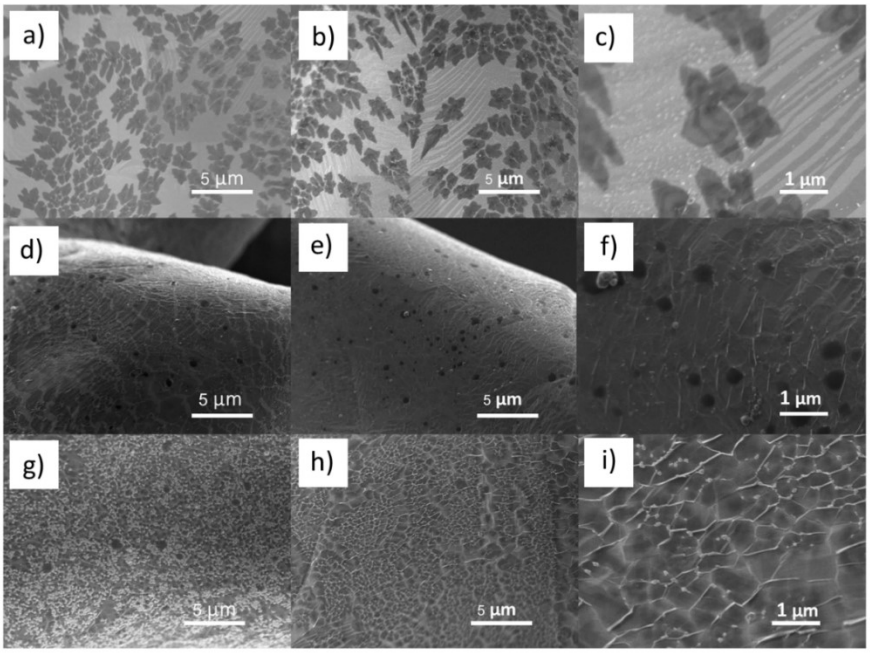

Fig. S4. SEM images of the morphology on copper foam surface when vary the reaction time of a-c), d-f) and g-i) related to 1, 10, and 30 min, respectively.

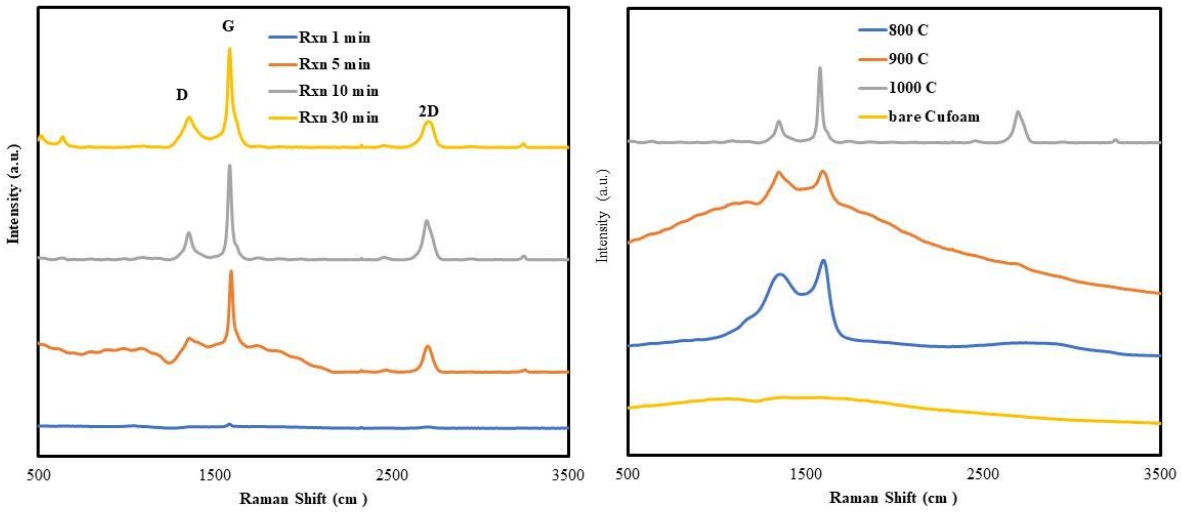

Fig. S5. Raman spectra of GP/CuF (a) with reaction time of 1, 5, 10 and 30 min. (b) Reaction temperature variation at 800, 900 and 1000 °C when compared to bare Cu foam.

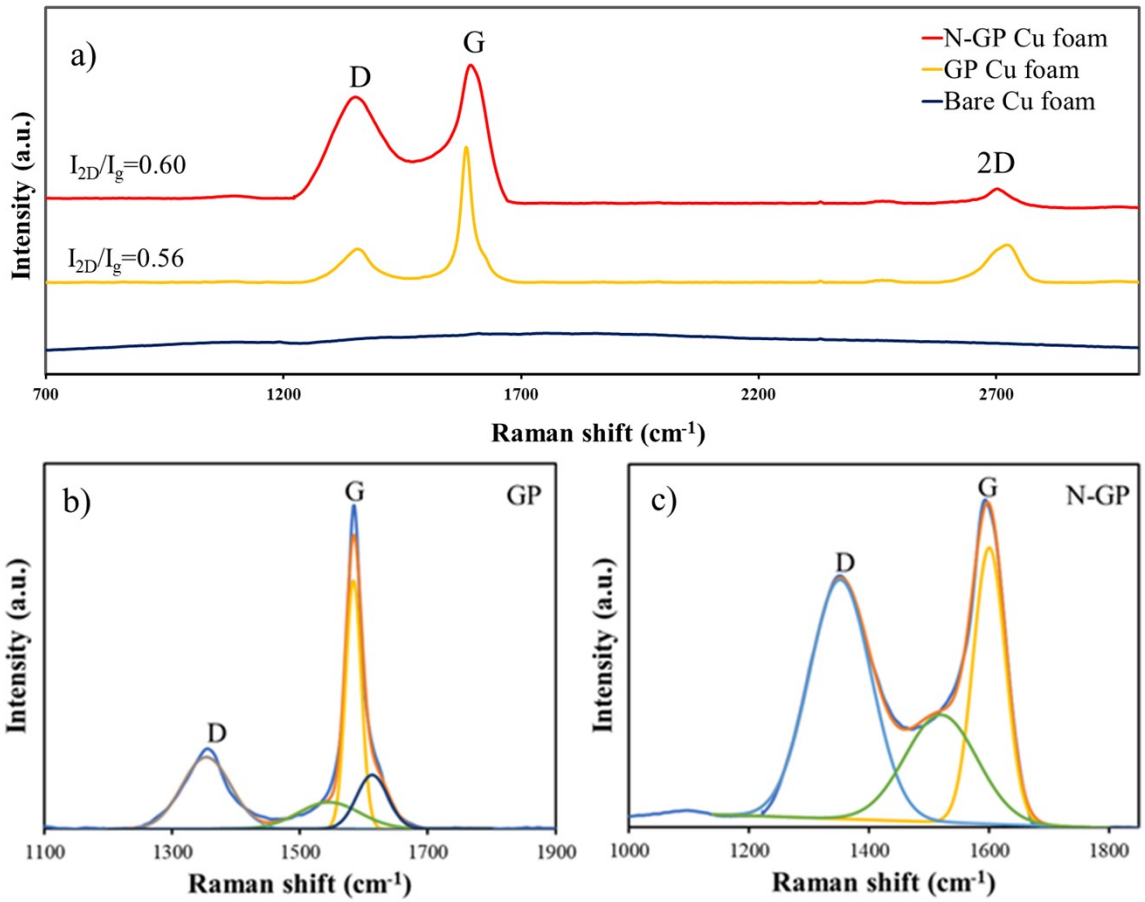

Fig. S6. (a) Raman spectra of all catalysts and deconvoluted Raman spectra of D band and G band of a) GP/CuF and b) N-GP/CuF.

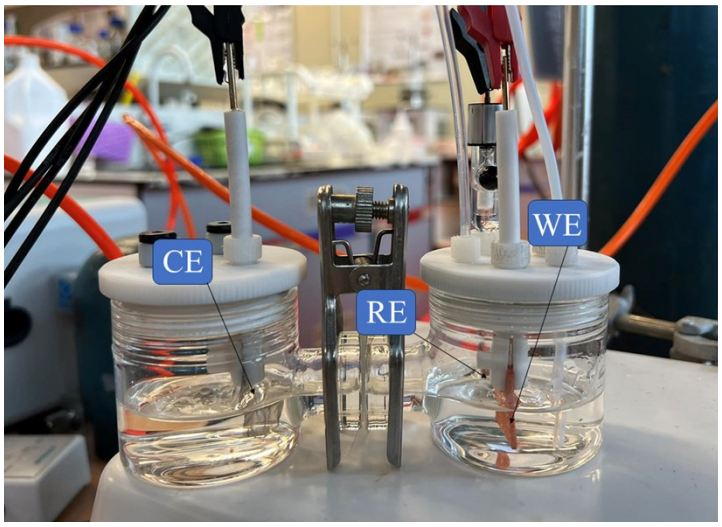

Fig. S7. Experimental setup of electrocatalytic reduction of CO_2.

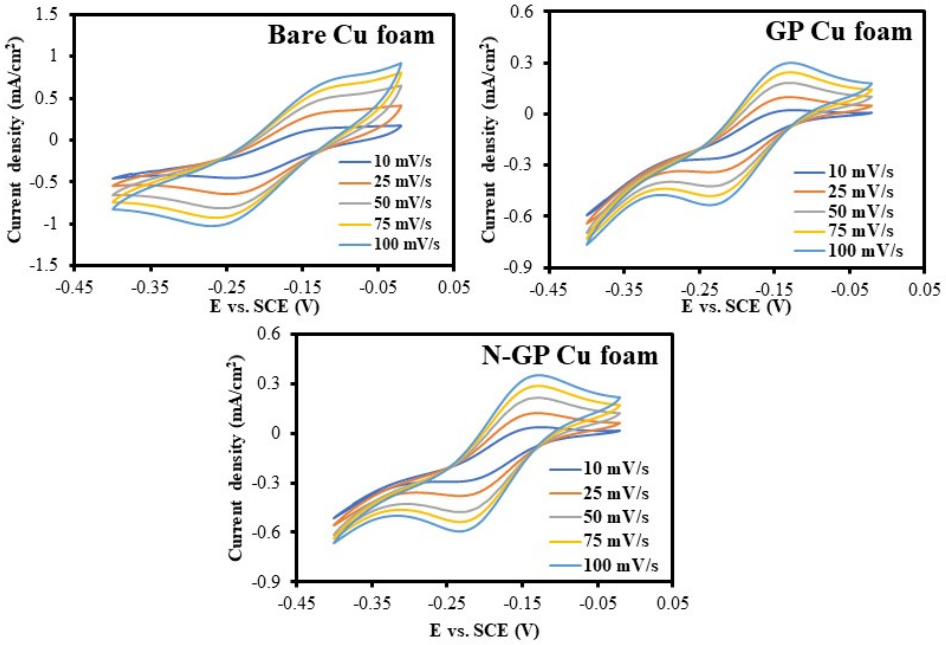

Fig. S8. Cyclic voltammetry (CV) curve s of CuF, GP/CuF, and N-GP/CuF at different scan rate (10-100 mV S^{-1}) in the presence of 0.1mM $[Ru(NH_3)]_3^{+/2+}$ in 1M KCl supporting electrolyte.

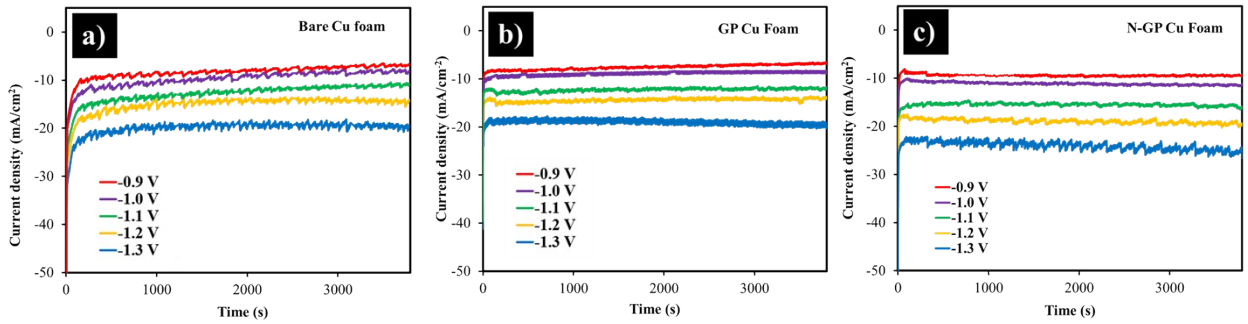

Fig. S9. Current density changes in (a) CuF, (b) GP/CuF and (c) N-GP/CuF at various applied potentials.

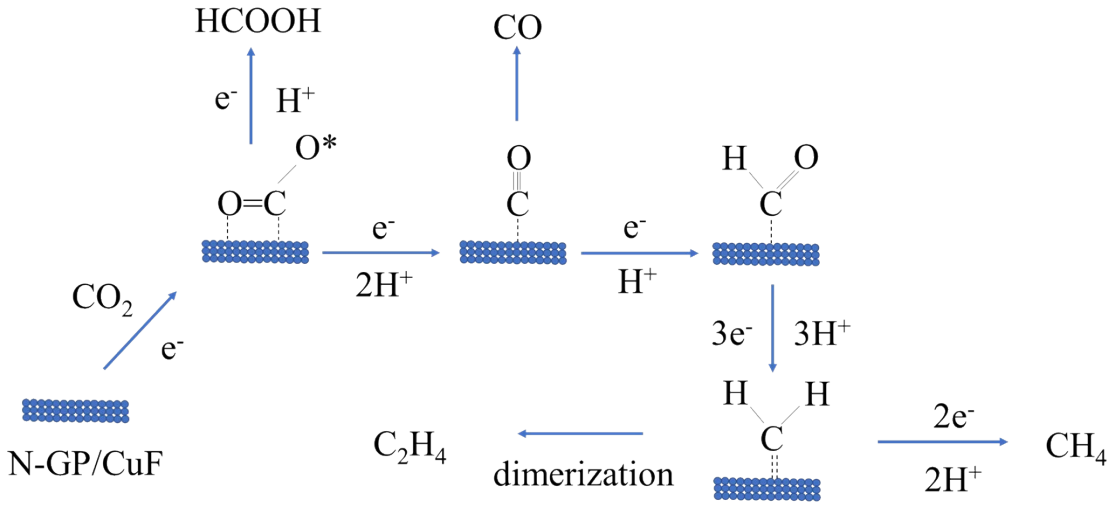

Fig. S10. Schematic of proposed CO_2 reduction mechanism

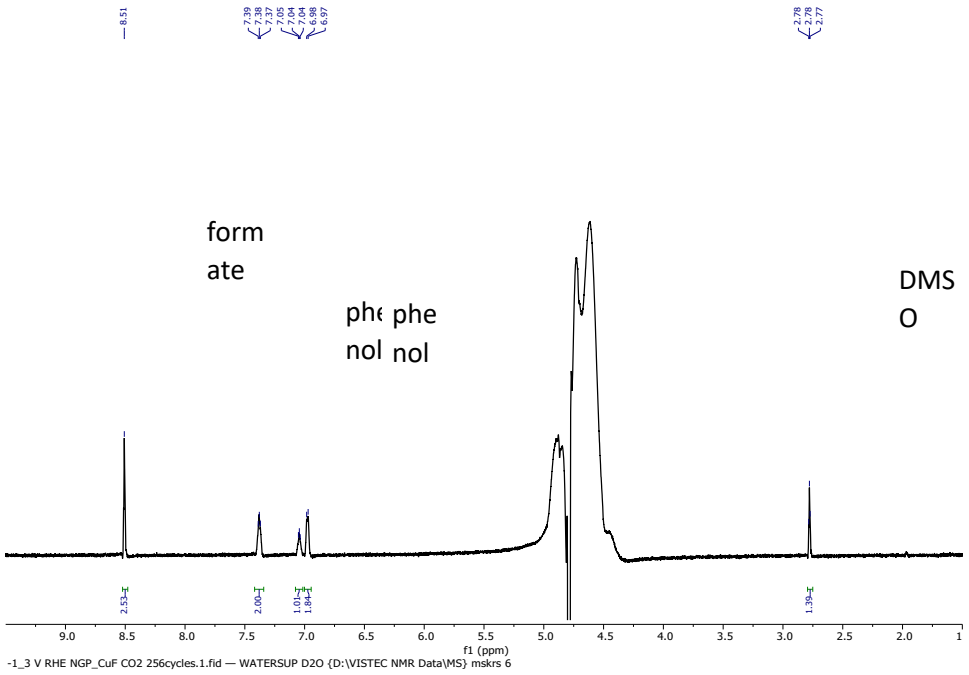

Fig. S11. NMR spectra of liquid fraction after electrocatalytic reduction of CO_2 on N-GP/CuF at -1.3 V (vs. RHE).

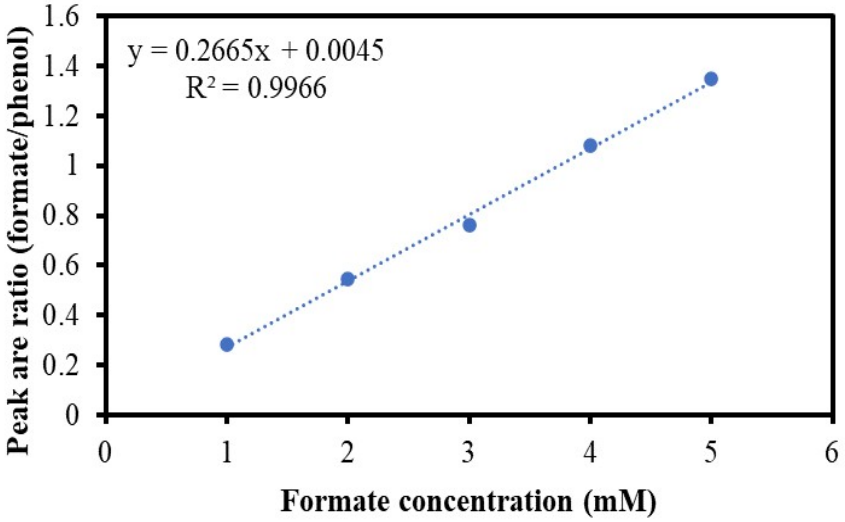

Fig. S12. Calibration curve of formate using phenol as internal standard.

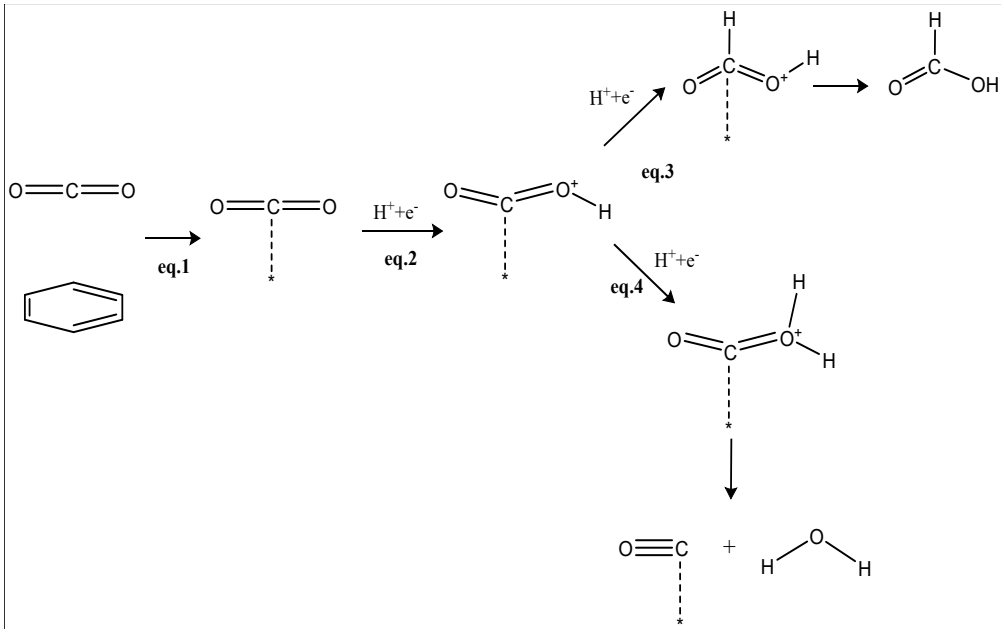

Fig. S13. Proposed hydrogenation mechanism for CO_2 electrochemical reduction on graphene and N-doped graphene, producing HCOOH in top-line and CO + H_2O in lower-line.

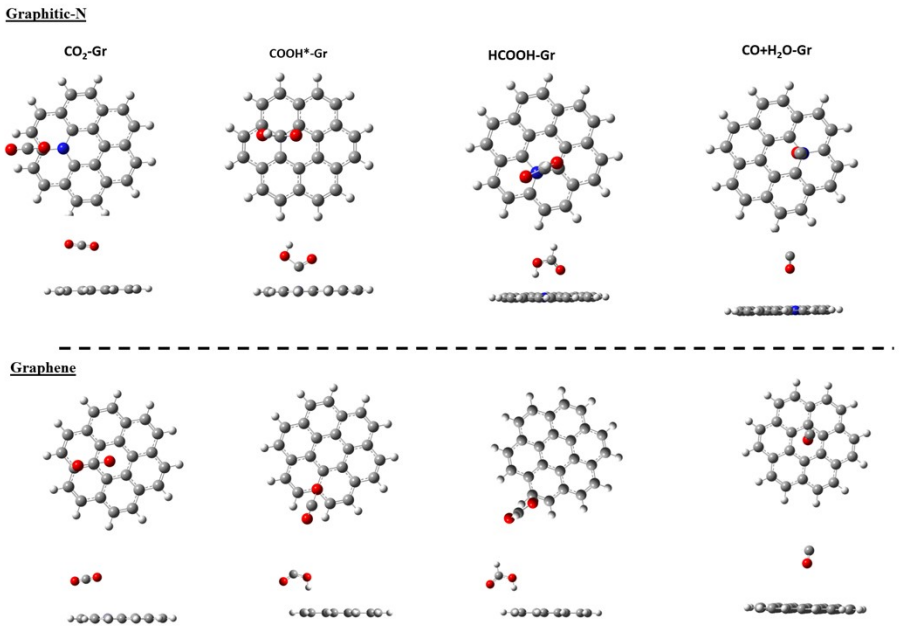

Fig. S14. Schematic of interaction between CO_2 molecules and both N-Gr (top) and Gr (bottom) catalyst after simulation process

Table S1. A representative data of gaseous products from online-gas chromatography for CO_2 reduction reaction using N-GP/CuF catalyst at -1.3V (vs. RHE).

			Amount of gaseous products (mol)				
Sampling No.	Time of sample injection (s)	Current (mA)	CH_4	C_2H_4	C_2H_6	CO	H_2
1	690	23.124	3.27×10^{-9}	7.11×10^{-8}	0.00	1.92×10^{-8}	7.56×10^{-8}
2	1335	23.431	4.90×10^{-9}	1.10×10^{-7}	0.00	2.08×10^{-8}	8.50×10^{-8}
3	1980	23.720	6.54×10^{-10}	8.34×10^{-8}	0.00	1.92×10^{-8}	8.42×10^{-8}
4	2625	24.214	8.17×10^{-9}	1.37×10^{-7}	0.00	2.04×10^{-8}	1.09×10^{-7}
5	3270	24.901	8.17×10^{-9}	1.47×10^{-7}	0.00	2.00×10^{-8}	1.05×10^{-7}
6	3915	25803	9.81×10^{-9}	1.62×10^{-7}	0.00	2.13×10^{-8}	1.06×10^{-7}
Average (3-6)			8.17×10^{-9}	1.32×10^{-7}	0.00	2.02×10^{-8}	1.01×10^{-7}

Table S2. Faradaic efficiencies of electrocatalytic reduction of CO_2 on N-GP/CuF.

Faradaic Efficiencies (%)							
Sampling No	CH_4	C_2H_4	C_2H_6	CO	H_2	Formate (accumulative)	Total
1	0.58	12.69	0.00	3.43	13.49	50.86	
2	1.09	19.46	0.00	3.68	15.00		
3	1.14	14.50	0.00	3.34	14.65		
4	1.39	23.40	0.00	3.48	18.60		
5	1.35	24.38	0.00	3.32	17.34		
6	1.57	25.88	0.00	3.40	16.99		
Average (3~6)	1.36	22.04	0.00	3.39	16.89	50.86	94.55

Table S3. Literature review on N-doped GP Cu foam.

Catalyst	Electrolyte	Current density (J)	Main product	Onset	Refs
Cu NPs coated on rGO support	0.1 M $KHCO_3$	7.5 mA cm^{-2} @ -1.4V (vs. RHE)	CO ~50% @ -1.0V (vs.RHE)	~ -1.5 V (vs. RHE)	[1]
N-doped graphene	0.5 M $KHCO_3$	7.5mA cm^{-2} @ -0.84V (vs. RHE)	HCOOH: ~73% @-0.84V (vs. RHE)	~0.3 V (vs. RHE)	[2]
NG foam	0.1 M $KHCO_3$	~1.8mA cm^{-2} @ -1.0V (vs. RHE)	CO ~85% @ -0.58V (vs.RHE)	-0.3V (vs. RHE)	[3]
Cu NPs on graphene	0.1 M $KHCO_3$	~0.2mA cm^{-2} @ -1.0V (vs. RHE)	CO: ~40% @ -1.0V (vs. RHE)	-0.42 V (vs. RHE)	[4]
B doped graphene	0.1 M $KHCO_3$	~1.4mA cm^{-2} @ -0.7V (vs. RHE)	HCOOH 66% @-0.76V (vs. RHE)	-0.4 V (vs.RHE)	[5]
Cu_2O/ZnO	0.1 M $KHCO_3$	N/A	CO with FF of 65.7% at − 1.4 V_{RHE}	N/A	[6]
Sn@SnS_2-NF	0.5 M $KHCO_3$	N/A	Formate, 93% FF at −1.4 V	N/A	[7]
In_2O clusters on Ag NPs	0.1 M $KHCO_3$	3.53 mA cm^{-2} at -0.9 V (vs RHE)	Formate 95.5% FF@ at -0.9 V (vs RHE)	N/A	[8]
InAs Quantum Dots	1.0 M $KHCO_3$	N/A	formate 100%FF@ at 100 mA cm^{-2} (vs RHE)	N/A	[9]
Cu Foam	0.5 M $CsHCO_3$	N/A	HCOOH 70% FF @25bar @18.2 mA/cm^2 (-1V vs. RHE)	N/A	[10]

Catalyst	Electrolyte	Current density (J)	Main product	Onset	Refs
CDU Foam	0.5 M $KHCO_3$	N/A	HCOOH 30%FF @25bar @18.2 mA/cm^2 (-1V vs. RHE)	N/A	[10]
Cu Foam	0.5 M $CsHCO_3$	N/A	HCOOH 51 %FF @25bar @9.1 mA/cm^2 (-1V vs. RHE)	N/A	[10]
Cu Foam	0.5 M $KHCO_3$	N/A	HCOOH 55% @25 bar @9.1 mA/cm^2 (-1V vs. RHE)	N/A	[10]
N doped GP Cu Foam	0.1 M $KHCO_3$	~10mA cm^{-2} @ -1.0V (vs. RHE)	Formate 65.5% @-1.0V (vs. RHE)	-0.47 V (vs. RHE)	This work

Note. FF is Faradaic efficiency.

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