Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

1D/2D nitrogen-doped carbon nanorod arrays/ultrathin carbon nanosheets: outstanding catalysts for highly efficient electroreduction CO_2 to CO

Ying zhu,[a] Kuilin Lv,[a] Xingpu Wang,[a] Hequn Yang,[a] Guozheng Xiao,[a] Ying Zhu*[ab]

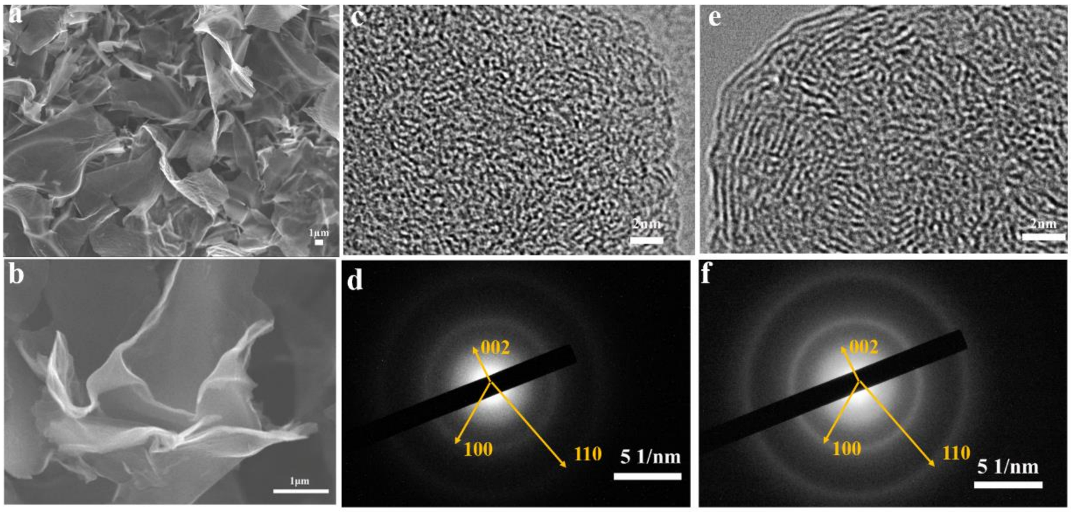

Fig. S1 (a, b) SEM images of CS, (c, e) HRTEM images of the 1D/2D NR/CS-800, 1D/2D NR/CS-1000, (d, f) SAED of the1D/2D NR/CS-800, 1D/2D NR/CS-1000.

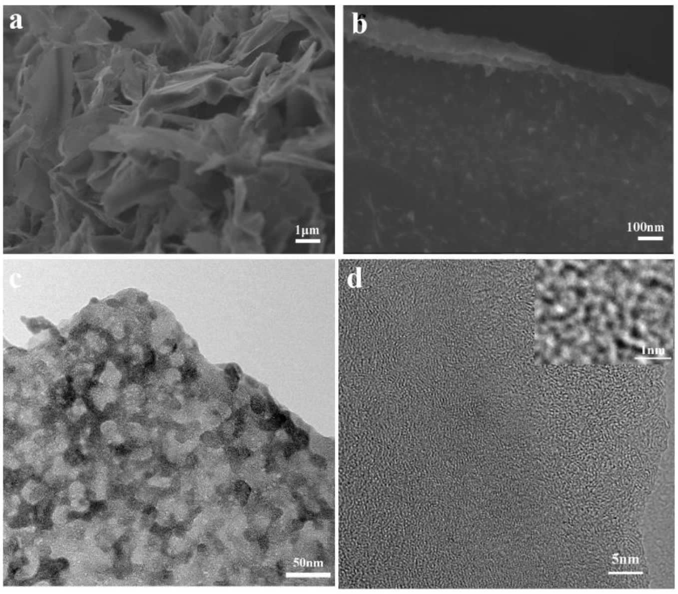

Fig. S2 (a, b) ESEM, (c) STEM and (d) HRTEM images of 1D/2D NR/CS-900 after 30 h stability test in CO_2-saturated 0.5 M $KHCO_3$ at -0.45 V.

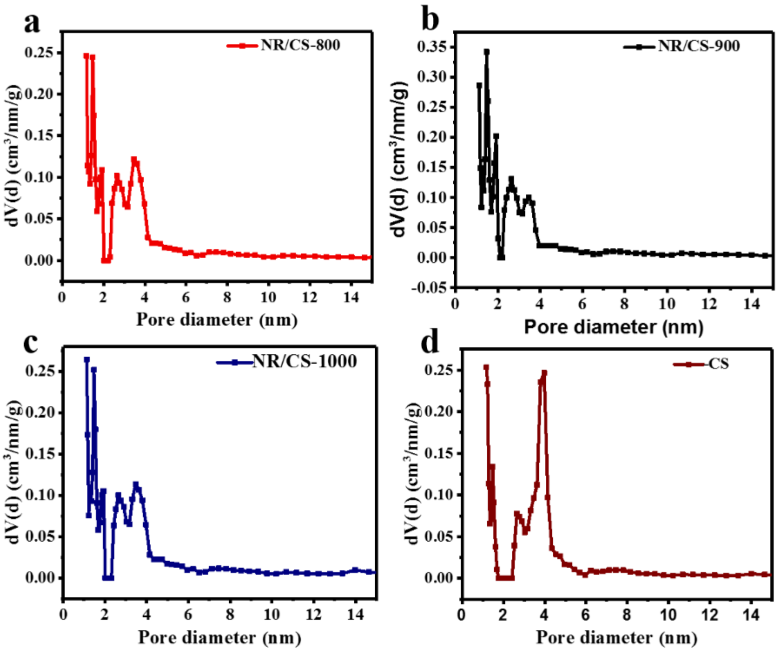

Fig. S3 (a-d) Pore size distributions of 1D/2D NR/CS-X and CS calculated from the N_2 adsorption isotherms by the BJH method using a slit pore model.

Table S1. SSA and I_D/I_G ratios of 1D/2D NR/CS-X and CS.

Samples	NR/CS-800	NR/CS-900	NR/CS-1000	CS
SSA(m^2/g)	741.93	859.97	743.45	689.68
I_D/I_G	1.04	1.17	1.07	0.97

Table S2. Atomic percentage (at %) of different N species in 1D/2D NR/CS-X.

Samples	Pyridinic N	Pyrrolic N	Graphitic N	Oxidized N	Total
NR/CS -800	1.31	1.60	2.16	0.72	5.79
NR/CS -900	1.49	0.88	2.07	0.86	5.30
NR/CS -1000	0.52	0.72	1.11	0.93	3.28

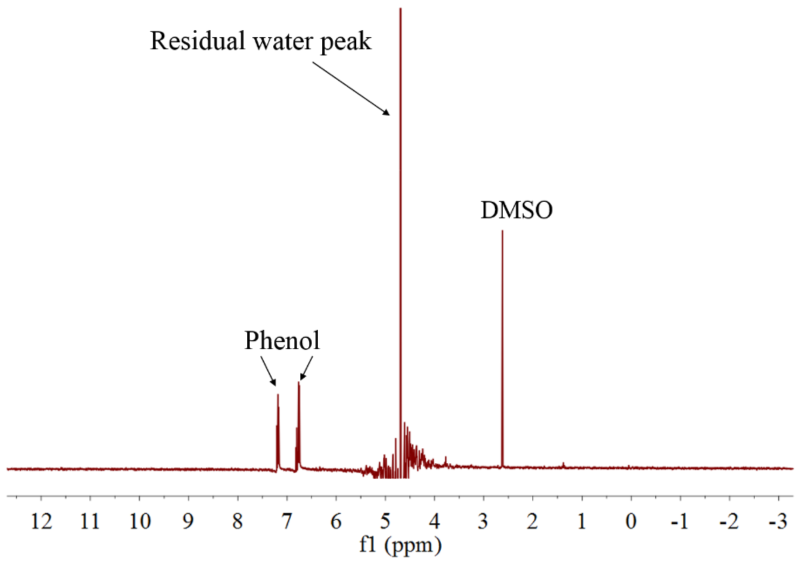

Fig. S4 The [1]HNMR spectrum of the 0.5M $KHCO_3$ solution on 1D/2D NR/CS-X. Potential applied = -0.35-0.95 V (vs RHE).

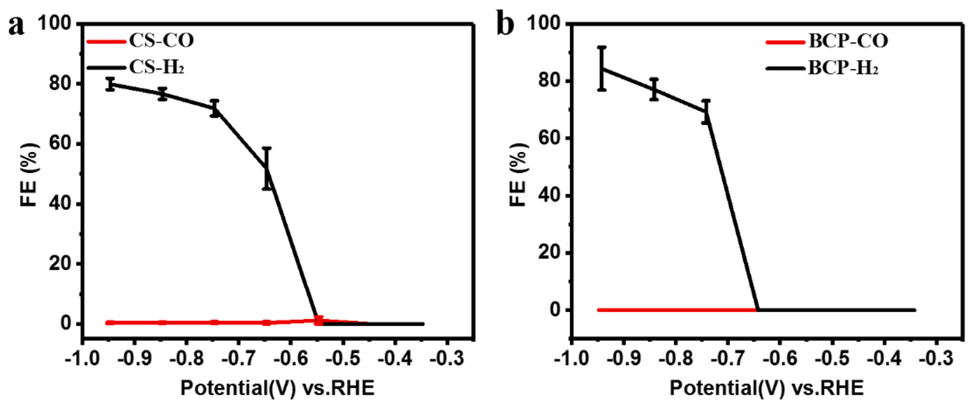

Fig. S5 (a, b) FEs of CO and H_2 at different applied potentials for CS, Blank carbon paper (BCP, MGL190), respectively.

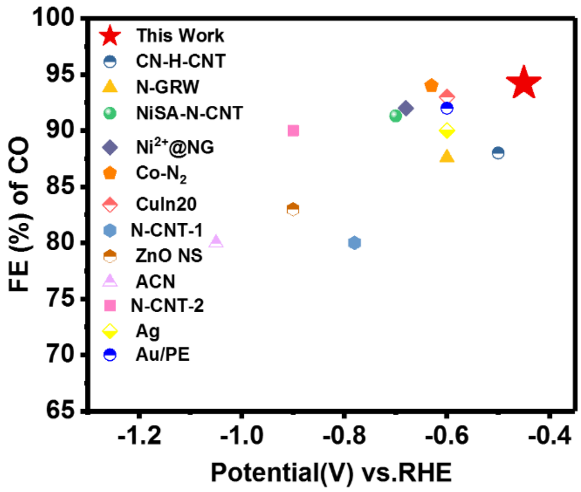

Fig. S6 Comparison of potentials and FE of formation of CO on 1D/2D NR/CS-900 with other electrocatalysts reported in the recently literatures.

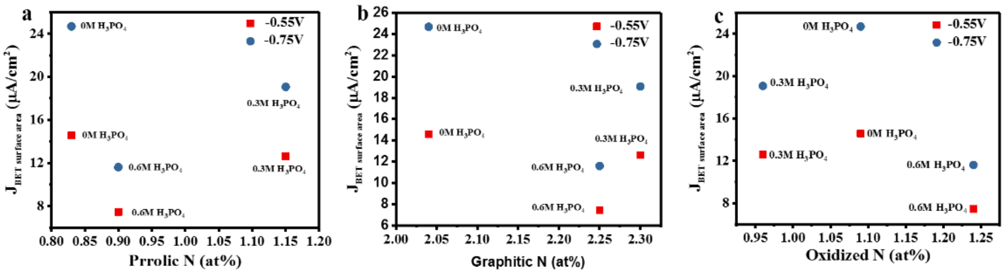

Fig. S7 The relationship between the CO normalized partial current density and contents of the pyrrolic N (a), graphitic N (b), oxidized N (c) in 1D/2D NR/CS-900 (YM H_3PO_4) at -0.55 and -0.75 V. 1D/2D NR/CS-900 (YM H_3PO_4) represents NR/CS-900 being soaked in Y M H_3PO_4 solution for 3 h. The full-filled blue circles and the full-filled red square represent 1D/2D NR/CS-900 (0 M H_3PO_4), 1D/2D NR/CS-900 (0.3 M H_3PO_4) and 1D/2D NR/CS-900 (0.6 M H_3PO_4) at -0.55 and -0.75 V from right to left, respectively.

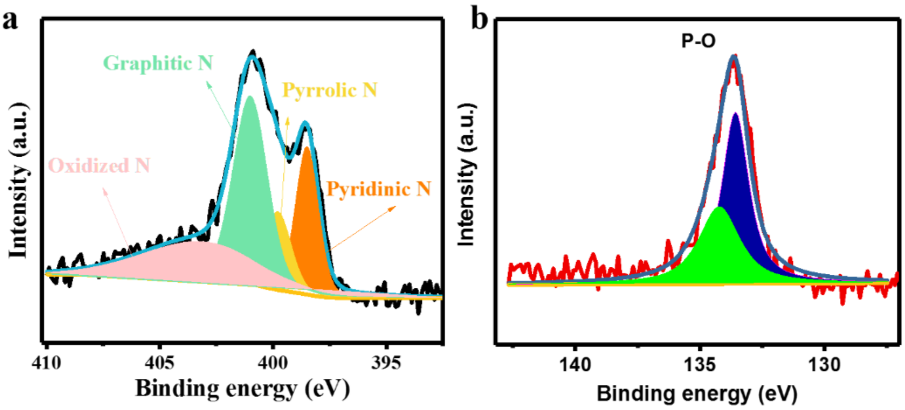

Fig. S8 (a, b) N1s and P 2p XPS spectra of 1D/2D NR/CS-900 (0.3 M H_3PO_4).

Table S3 Atomic percentage (at %) of different nitrogen 1D/2D NR/CS-900 (Y M H_3PO_4).

Samples	Pyridinic N	Pyrrolic N	Graphitic N	Oxidized N	Total
NR/CS-900 (0 M H_3PO_4)	1.49	0.88	2.07	0.86	5.30
NR/CS-900 (0.3 M H_3PO_4)	1.20	0.76	2.29	1.48	5.73
NR/CS-900 (0.6 M H_3PO_4)	1.14	0.90	2.22	1.34	5.6

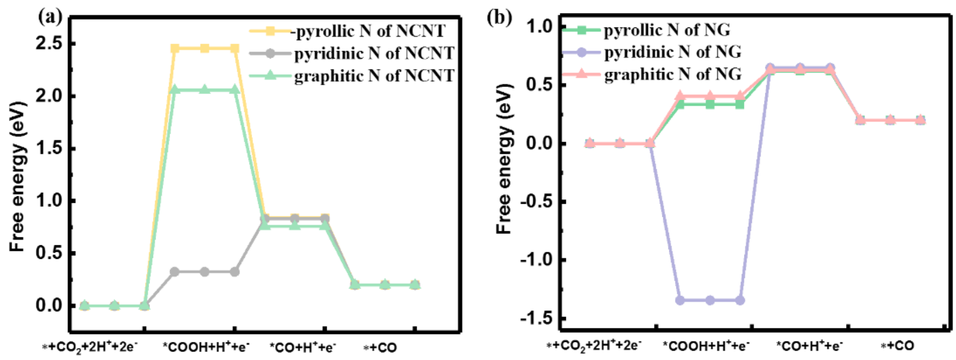

Fig. S9 (a, b) Free energy diagrams of CO_2RR on NCNT and NG catalysts.

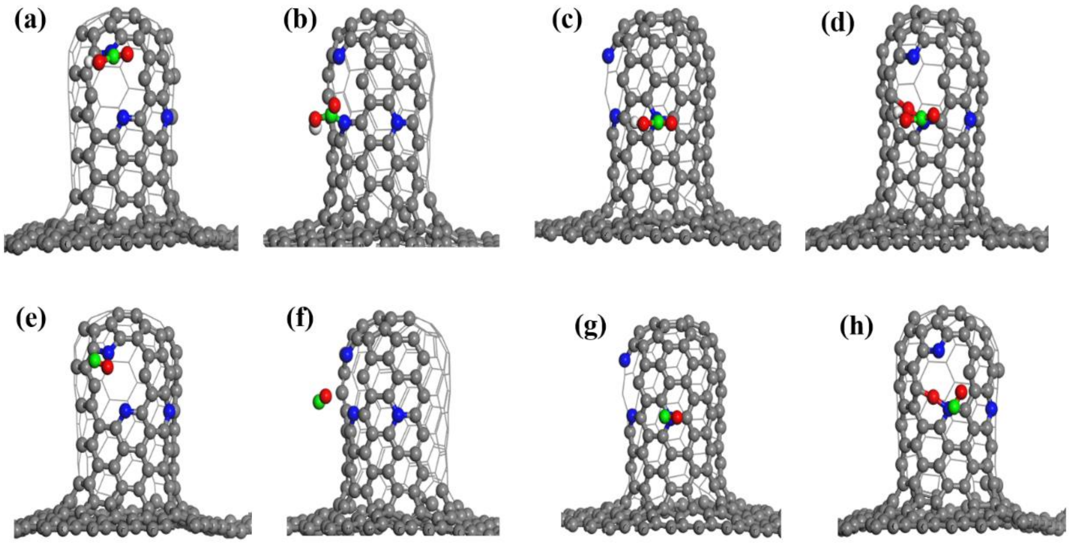

Fig. S10 Optimized configurations of 1D/2D NR/CS-X catalysts. The ground state configurations of *COOH intermediate adsorbed on active sites of (a) pyrrolic N, (b) pyridinic N, (c) graphitic N and (d) oxidized N. The ground state configurations of intermediate *CO adsorbed on active sites (e) pyrrolic N, (f) pyridinic N and (g) graphitic N and (h) oxidized N. The balls colored in green, blue, red, and white represent C, N, O, and H atoms, respectively.

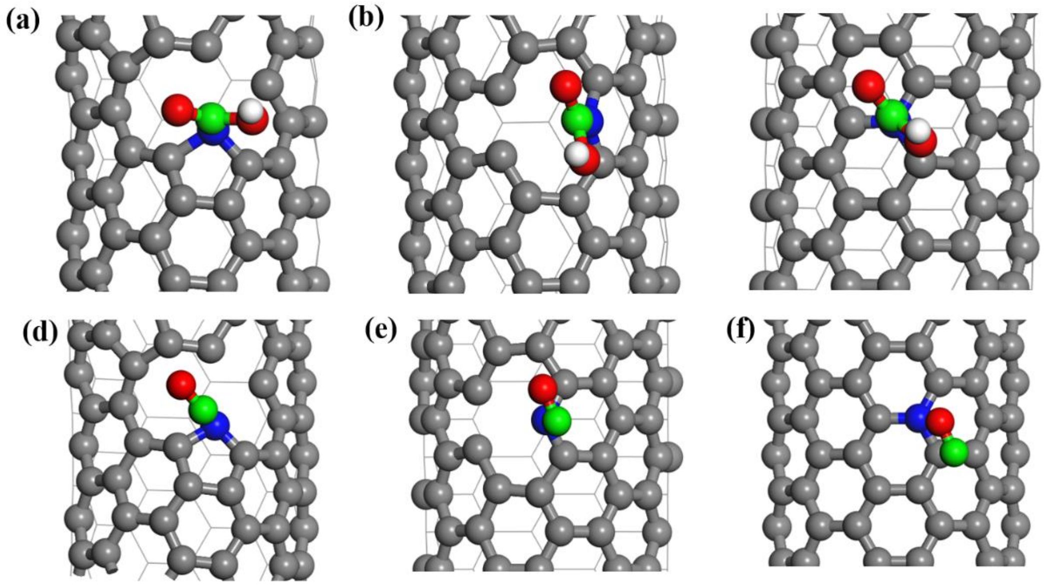

Fig. S11 Optimized configuration of NCNT. The ground state configurations of COOH intermediate adsorbed on active sites of (a) pyrrolic N, (b) pyridinic N, (c)graphitic N. The ground state configurations of CO intermediate adsorbed on active sites (d) pyrrolic N, (e) pyridinic N and (f) graphitic N. The balls colored in green, blue, red, and white represent C, N, O, and H atoms, respectively.

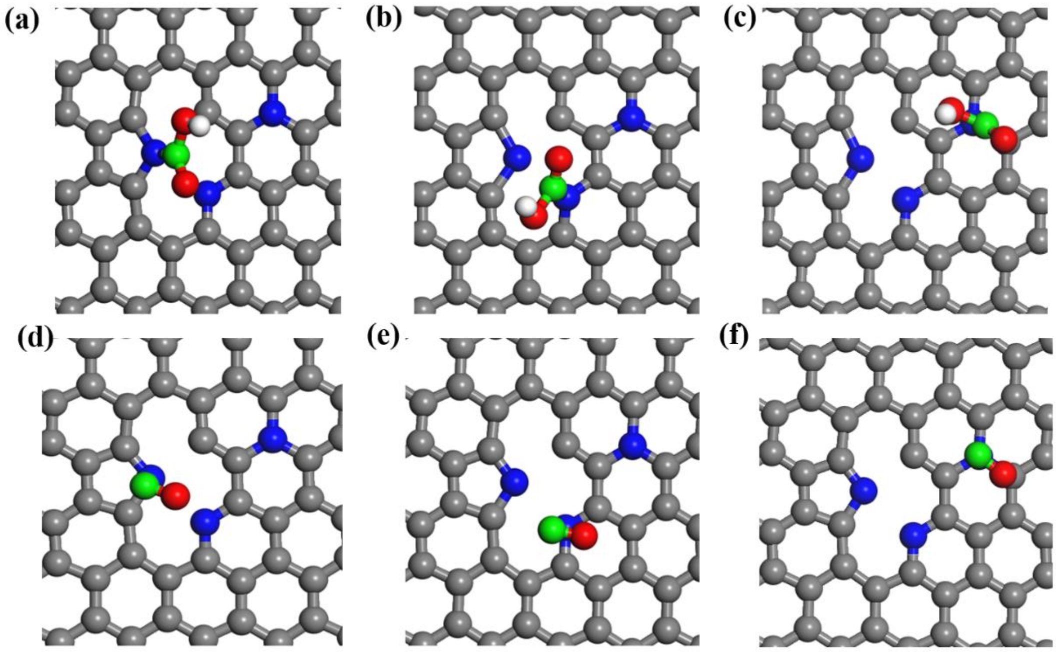

Fig. S12 Optimized configuration of NG. The ground state configurations of COOH intermediate adsorbed on active sites of (a) pyrrolic N, (b) pyridinic N, (c) graphitic N. The ground state configurations of CO intermediate adsorbed on active sites of (d) pyrrolic N, (e) pyridinic N, (f) graphitic N. The balls colored in green, blue, red, and white represent C, N, O, and H atoms, respectively.

Table S4 Bond length (Å) between COOH intermediate and pyrrolic N, pyridinic N, graphitic N and oxidized N.

Bond length(Å)	Pyrrolic N-C	Pyridinic N-C	Graphitic N-C	Oxidized N-C
1D/2D NR/CS-X	1.431	1.443	1.640	1.443
NCNT	1.546	1.430	1.583	------
NG	1.394	1.402	3.257	------

Table S5. The details about the energy (eV) employed in free energy.

Materials	N Species	Intermediate	E_{DFT}	E_{ZPE}	TΔS	G
NCNT	Pyrrolic N	COOH*	-875.88	0.76	0.34	-875.46
		CO*	-866.55	0.21	0.16	-866.52
	Pyridinic N	COOH*	-886.76	0.69	0.27	-886.34
		CO*	-875.29	0.27	0.24	-875.26
	Graphitic N	COOH*	-897.78	0.67	0.27	-897.38
		CO*	-888.02	0.25	0.33	-888.10
1D/2D NR/CS-X	Pyrrolic N	COOH*	-2102.75	0.61	0.20	-2102.34
		CO*	-2090.56	0.17	0.34	-2090.73
	Pyridinic N	COOH*	-2102.01	0.66	0.24	-2101.59
		CO*	-2090.56	0.15	0.31	-2090.72
	Graphitic N	COOH*	-2101.32	0.67	0.21	-2100.86
		CO*	-2090.56	0.16	0.29	-2090.69
	Oxidized N	COOH*	-2110.75	0.75	0.30	-2110.3
		CO*	-2098.97	0.27	0.34	-2099.04
NG	Pyrrolic N	COOH*	-302.18	0.66	0.21	-301.73
		CO*	-290.69	0.15	0.33	-305.08
	Pyridinic N	COOH*	-305.57	0.66	0.17	-886.34
		CO*	-290.68	0.16	0.32	-875.26
	Graphitic N	COOH*	-301.83	0.55	0.38	-301.66
		CO*	-290.66	0.15	0.35	-290.86

Table S6 Free energy (eV) corrections for species.

Species	E_{DFT}	E_{ZPE}	TΔS	G
H_2O	-14.21	0.56	0.67	-14.32
CO_2	-22.95	0.31	0.66	-22.85
CO	-14.79	0.13	0.60	-15.26
*CO	-	0.19	0.12	0.07
*COOH	-	0.61	0.16	0.45
H_2	-6.76	0.27	0.40	-6.98

Table S7 Free energy（eV）of CO_2 electroreduction reactions for the NR/CS-X, NCNT and NG.

Materials	N Species	ΔG(*COOH)	ΔG (*CO)
1D/2D NR/CS-X	Pyrrolic N	-0.525	1.035
	Pyridinic N	0.225	0.295
	Graphitic N	0.955	-0.405
	Oxidized N	-1.445	0.685
NCNT	Pyrrolic N	2.455	-1.615
	Pyridinic N	0.325	0.505
	Graphitic N	2.055	-1.295
NG	Pyrrolic N	0.335	0.285
	Pyridinic N	-1.345	1.995
	Graphitic N	0.405	0.225