Supporting Information

Aligned Carbon Nanotube / Copper Sheet: A Novel Electrocatalyst for CO_2 Reduction to Hydrocarbons

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1. Characterization of funtionalized CNT sheets

1.1 Raman

Raman analysis was performed to reveal the structure before and after functionalization of the MWCNT sheets surface. As shown in Fig. S1, the peak at 1328 cm^{-1} is assigned to the defects and disordered graphite structures, while the peaks at 1589 cm^{-1} and 2654 cm^{-1} are attributed to the graphite band which is common to all sp^2 systems and second-order Rama scattering process, respectively. Intensity ratio of defect band and graphite band is a signature of the degree of functionalization of the CNT sheets. Defect/graphite ratios (I_D/I_G ratios) of pristine

CNT (P-CNT) sheets, CNT sheets treated with O_2 plasma (O-CNT) and CNT sheets treated with electrochemical redox cycling after treatment with O_2 plasma (OE-CNT) were 0.83, 1.15, and 1.25 respectively.

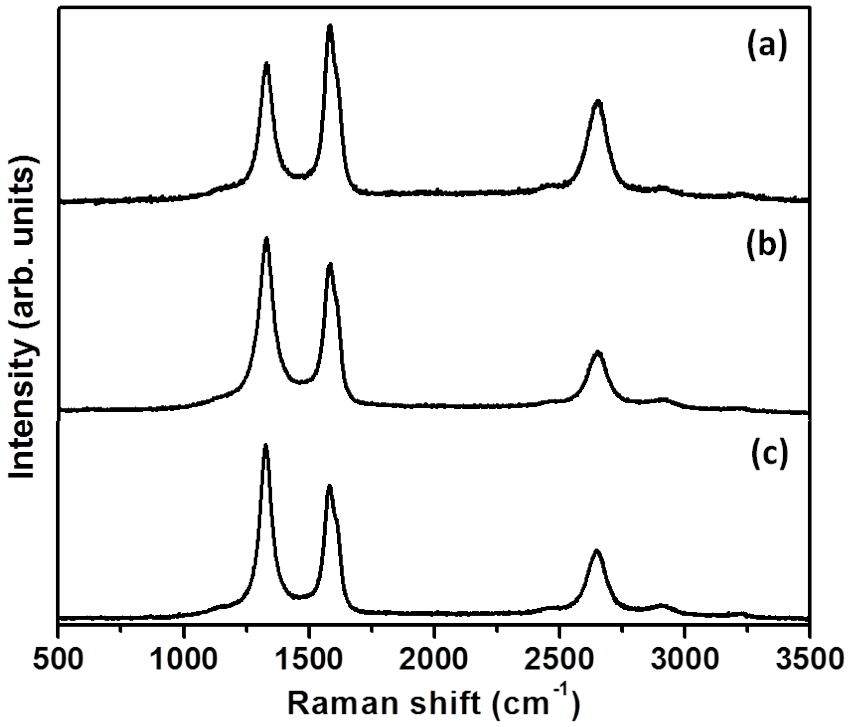

Figure S1. Raman spectra of CNT sheets substrate electrodes by different pretreatment. (a) P-CNT sheets (I_D/I_G ratio = 0.83), (b) O-CNT sheets (I_D/I_G ratio = 1.15), (c) OE-CNT sheets (I_D/I_G ratio = 1.25).

1.2 Cyclic voltammetry

The CV behavior of CNT sheets was observed before/after O_2 plasma functionalization at $\pm$ 1.5 V. Reduction and oxidation peak currents were increased with O_2 plasma functionalization because of enhanced electron transfer on the activated CNT area.

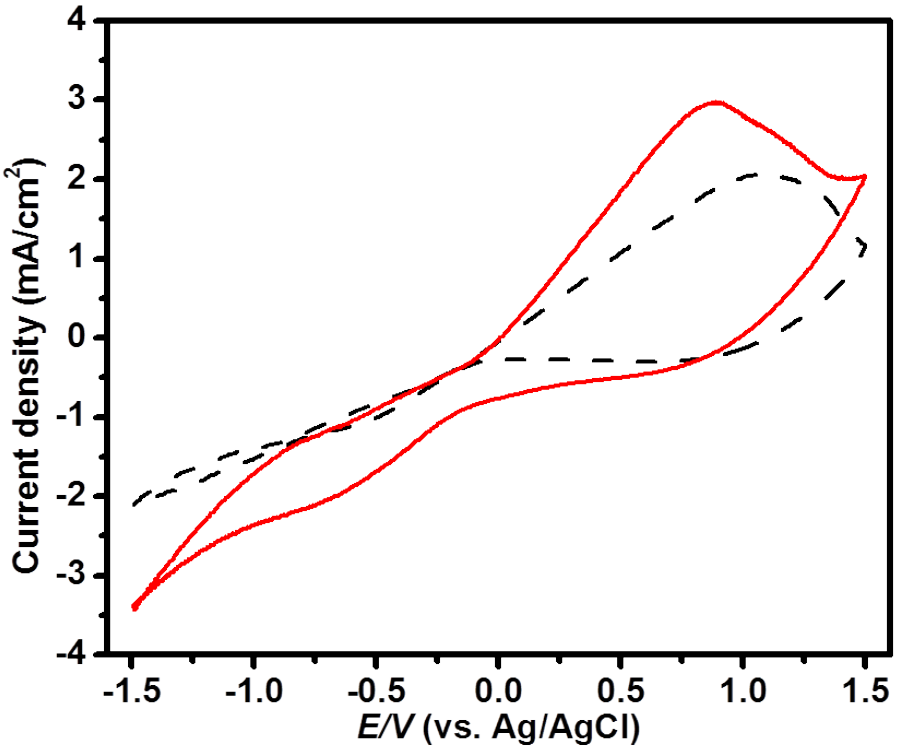

Figure S2. Cyclic volatmmetry (CV) CNT sheets. (a) P-CNT sheets (dash line), (b) O-CNT sheets (solid line).

2. Surface area calculation

Figure S3 shows the drawing for definition of surface area of the deposited Cu particles and the coverage ratio on CNT sheets. These were calculated from SEM images based on simplified morphologies and shapes (Fig. S3b, Table S1, S2). Coverage ratio is the covered Cu particle area (blue dashed-line area in Fig. S3a) divided by the CNT sheets area (red solid line area in Fig. S3a).

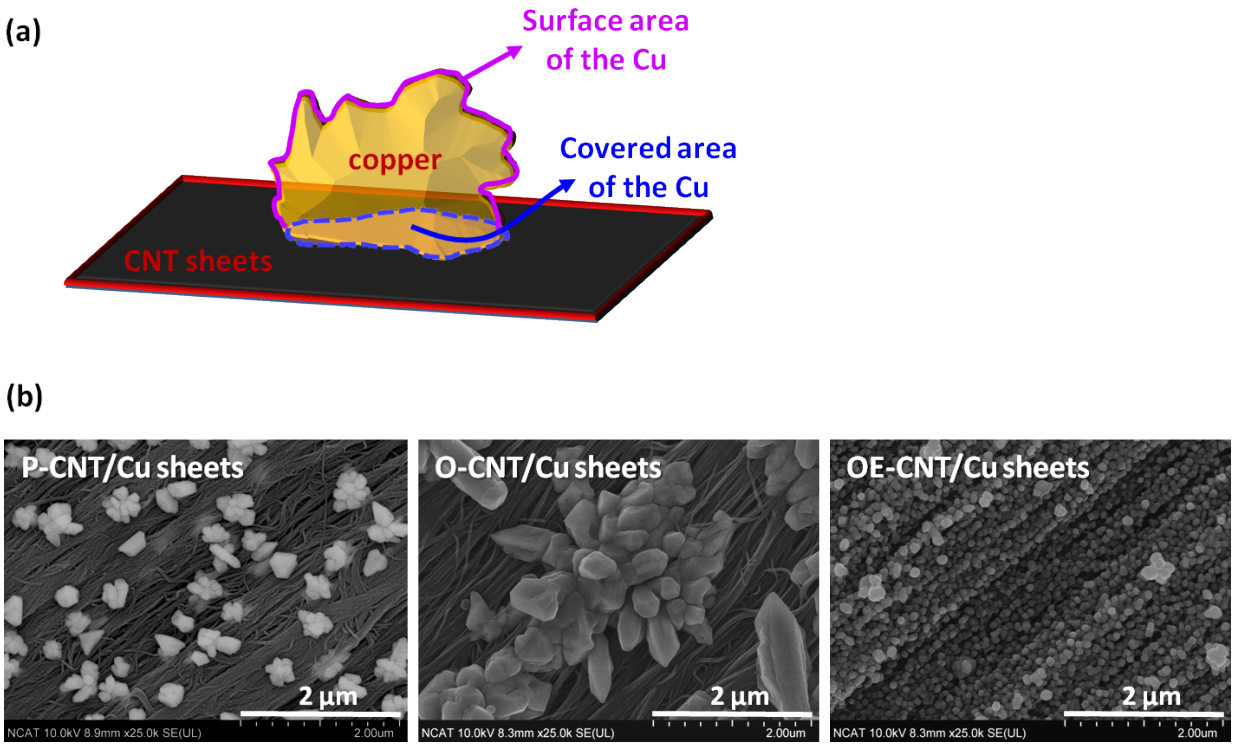

Figure S3. Surface area of the electrochemical depostied Cu particles and the CNT sheets coverage ratios of Cu particles. (a) shematic for definition, (b) SEM images of three different CNT/Cu sheets.

Table S1. Calculation of surface area of Cu particles

	Surface area of Cu particles				
Electrocatalysts	Shape	Diameter (nm)	Height (μm)	Area in 25k SEM (cm^2)	Area in CNT sheets of both sides (cm^2)
P-CNT/Cu	Sphere	130	-	1.27×10^{-7}	5.4
O-CNT/Cu	Cylinder	400	1	5.27×10^{-7}	24.7
OE-CNT/Cu	Hemisphere	80	-	2.75×10^{-7}	12.2

Table S2. Calculation of CNT sheets coverage ratios of Cu particles

	Coverage ratios				
Electrocatalysts	Shape (bundle)	Diameter (μm)	Area of covered Cu (cm^2)	CNT sheets area of both sides (cm^2)	Coverage ratios (Cu/CNT sheets, %)
P-CNT/Cu	Circle	0.42	1.2	7.5	0.16
O-CNT/Cu	Circle	3.3	4.0	8.2	0.49
OE-CNT/Cu	square	- (All covered)	7.8	7.8	1

3. Characterization of the three differet CNT/Cu sheets.

3.1 XRD

A typical XRD pattern of as-prepared P-CNT sheets and the three different CNT/Cu sheets are shown in Fig. S4. The peak corresponding to P-CNT sheets is marked at $2\Theta = 26.0^{\circ}$ and can be attributed to the diffraction from C(002) facets of CNTs [1, 2]. The diffraction pattern

clearly shows three main peaks at 43.3º, 50.5º, and 74.1º in the range of 20º to 80º, which can be assigned to the diffraction from the (111), (200), and (220) planes, respectively, of the face-centered cubic lattice of Cu(0) [3].

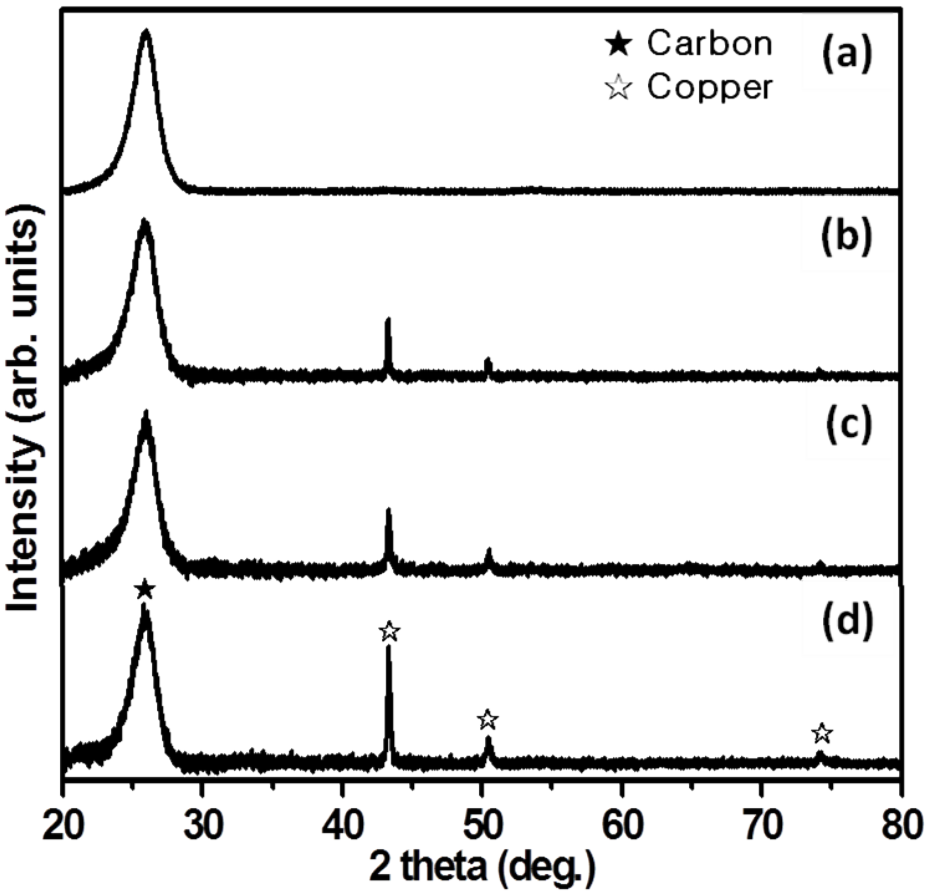

Figure S4. XRD patterns of pulse-electrodeposited CNT/Cu sheets after the different pretreatment. (a) P-CNT sheets, (b) P-CNT/Cu sheets, (c) O-CNT/Cu sheets, (d) OE-CNT/Cu sheets .

3.2 EDS

A comparative compositional analysis from the EDS result is given in Table S3. The results show that the deposited Cu on OE-CNT/Cu sheets is covered uniformly. This is also confirmed using SEM images as shown in Fig. 2c. Oxygen element was found in all electrodes, but Cu_2O/CuO oxides were not found in the XRD results. This could potentially mean that the surface of the CNT/Cu sheets was slightly oxidized during the washing process after electrochemical depositon or that oxygen, which was self-contained on the CNT sheets was detected.

Table S3. EDS spectra analysis of electrodeposited Cu on CNT sheets after different pretreatments.

Element	P-CNT sheets	P-CNT/Cu sheets	O-CNT/Cu sheets	OE-CNT/Cu sheets
C	97.29	94.12	93.47	60.36
O	2.71	3.16	3.53	8.84
Cu		2.72	3.00	30.80

* The content represents the at. %.

Figure S5 shows the energy-dispersive X-ray spectroscopy (EDS) mapping profile of the side view of three different CNT/Cu sheets containing Cu partlces of different geometrical shapes on the CNT sheets. Pulsed electrochemically deposited Cu on the CNT sheets was also observed. Oxygen is observed regardless of the location of Cu from the mapping profiles as shown with Table S1 results.

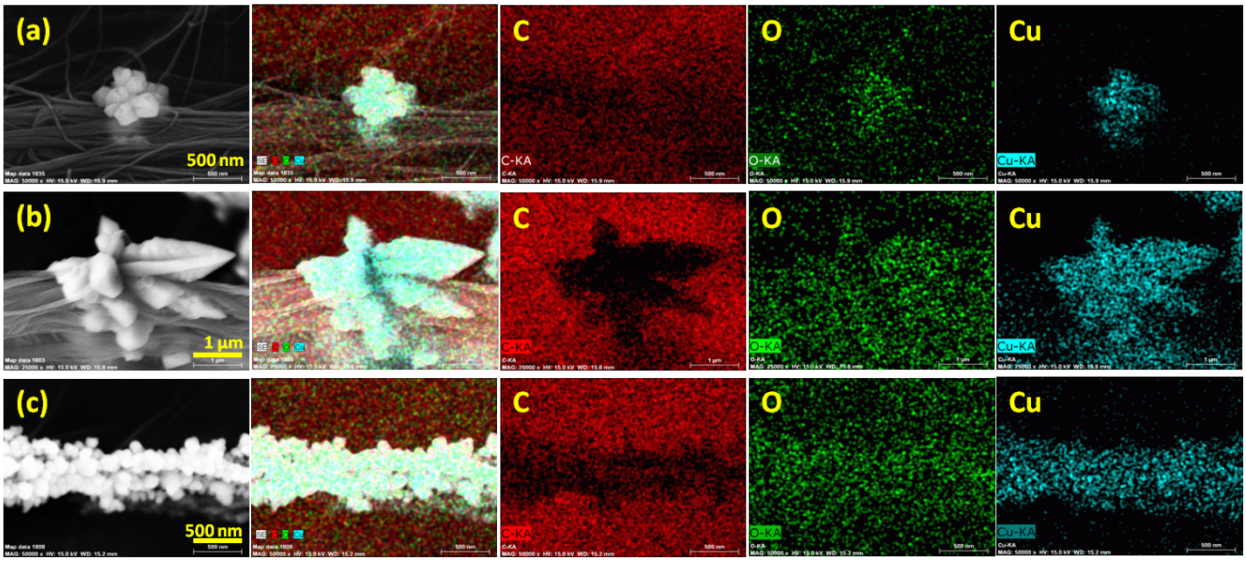

Figure S5. EDS mapping profiles of side view of electrodeposited Cu on CNT sheets after different pretreatment. (a) P-CNT/Cu sheets, (b) O-CNT/Cu sheets, (c) OE-CNT/Cu sheets.

4. Electrochemical reaction of CO_2

4.1 Efficiency of CO_2 reduction

The electrochemical CO_2 reduction was performed according to the various current densities using P-CNT and the three different CNT/Cu sheets. Figure 5S show the gas product results of the CO_2 conversion to hydrocarbons. CO_2 reduction activities of Cu deposited on CNT sheet electrodes were determined by a 15 min reaction in CO_2 saturated 0.1 M $NaHCO_3$ (380 mL) bulk aqueous solution with pH of 6.5. The products were analyzed in the gas phase after electrolyses by an interfaced gas chromatograph (GC) with an electrochemical reaction cell. Table S4-S7 show Faradaic efficiencies of all products for the different electrodes.

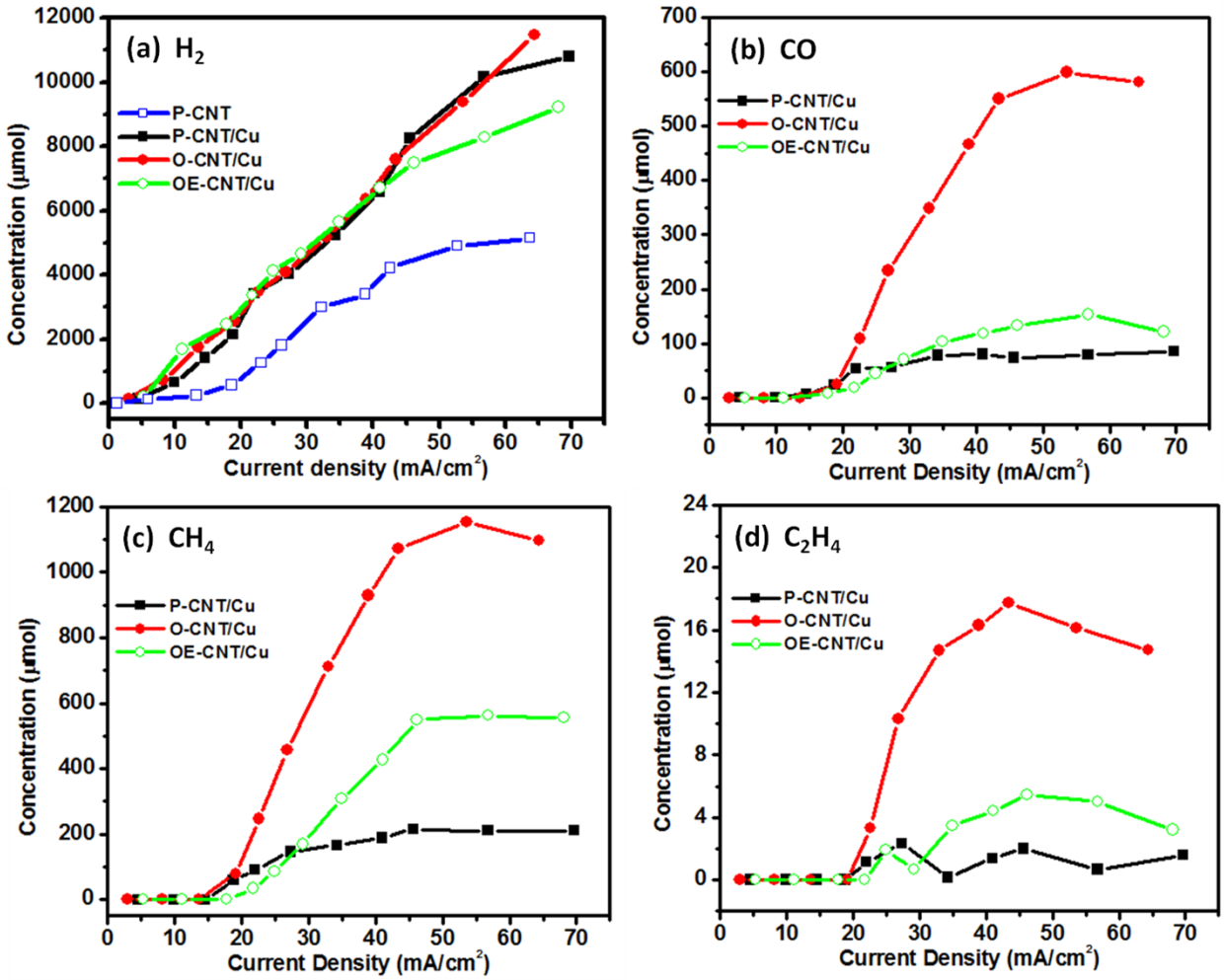

Figure S6. Electrocatalytic reaction efficiency for H_2 evolution and CO, CH_4, and C_2H_4 formation of P-CNT sheets and the three different CNT/Cu sheets in CO_2 saturated 0.1 M $NaHCO_3$ solution at 25 °C. (a) H_2, (b) CO, (c) CH_4, (d) C_2H_4.

Table S4. Faradaic efficiencies for the products by electrochemical reduction of CO_2 at P-CNT sheet substrate electrode.

Potential (E/V)	current density (mA/cm^2)	Faradaic efficiency (%)				
		CO	CH_4	C_2H_4	H_2	total
-1.5	1.3				0	0.0
-2.0	6.0				54.6	54.6
-2.5	13.3				55.5	55.5
-2.8	18.6				62.6	62.6
-3.0	23.0				85.4	85.4
-3.2	26.2				99.5	99.5
-3.5	32.2				95.7	95.7
-3.8	38.8				92.2	92.2
-4.0	42.6				88.6	88.6
-4.5	52.7				83.2	83.2
-5.0	63.8				71.6	71.6

Table S5. Faradaic efficiencies for the products by electrochemical reduction of CO_2 at copper depostied on P-CNT sheet substrate electrode (P-CNT/Cu sheets).

Potential (E/V)	current density (mA/cm^2)	Faradaic efficiency (%)				
		CO	CH_4	C_2H_4	H_2	total
-1.5	4.5				51.5	51.5
-2.0	9.9				55.3	55.3
-2.5	14.6	1.4			66.0	67.4
-2.8	18.8	2.0	7.1		67.8	76.9
-3.0	22.0	1.9	5.3	2.0	54.9	64.2
-3.2	27.3	2.3	9.1	2.5	73.8	87.7
-3.5	34.2	2.3	7.5	1.6	70.3	81.7
-3.8	41.0	1.9	6.7	1.4	69.3	79.3
-4.0	45.6	1.4	6.4	1.2	72.2	81.2
-4.5	56.8	1.2	4.7	0.8	67.3	74.0
-5.0	69.7	1.0	3.7	0.7	56.7	62.1

Table S6. Faradaic efficiencies for the products by electrochemical reduction of CO_2 at Copper deposited on CNT sheet substrate electrode with O_2 plasma pretreatment (O-CNT/Cu sheets).

Potential (E/V)	current density (mA/cm^2)	Faradaic efficiency (%)				
		CO	CH_4	C_2H_4	H_2	total
-1.5	3.8				50.2	50.2
-2.0	8.2				49.4	49.4
-2.5	13.6				59.9	59.9
-2.8	19.1	1.6	6.8		61.4	69.8
-3.0	22.6	8.0	24.8	3.5	57.5	93.9
-3.2	26.8	6.9	21.4	3.0	60.2	91.5
-3.5	32.9	7.7	24.9	2.7	57.1	92.4
-3.8	38.9	8.0	25.4	2.2	54.6	90.2
-4.0	43.4	8.0	24.9	2.0	55.5	90.4
-4.5	53.6	6.6	20.4	1.4	52.0	80.4
-5.0	64.4	5.1	15.5	1.1	50.6	72.3

Table S7. Faradaic efficiencies for the products by electrochemical reduction of CO_2 at Copper deposited on CNT sheet substrate electrode with O_2 plasma/cyclic voltammetry pretreatment (OE-CNT/Cu sheets).

Potential (E/V)	current density (mA/cm^2)	Faradaic efficiency (%)				
		CO	CH_4	C_2H_4	H_2	total
-1.5	5.3				55.4	55.4
-2.0	11.1				80.4	80.4
-2.5	17.8	1.2			84.5	85.7
-2.8	21.7	1.4	4.0		86.6	92.0
-3.0	24.9	2.2	6.6	2.8	86.6	98.2
-3.2	29.1	2.7	9.8	2.1	79.8	94.3
-3.5	34.9	2.9	13.4	1.9	75.1	93.4
-3.8	41.1	2.6	14.5	1.6	70.5	89.3
-4.0	46.2	2.5	16.0	1.5	67.5	87.5
-4.5	56.8	2.3	12.9	1.1	59.0	75.4
-5.0	68.1	1.5	10.2	0.8	52.5	65.0

References

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2. L. Ai and J. Jiang, *Chemical Engineering Journal*, 2012, **192**, 156-163.
3. X. Kang, Z. Mai, X. Zou, P. Cai and J. Mo, *Analytical Biochemistry*, 2007, **363**, 143-150.