## ESI:

## In-situ growth of $Cu_2O$ with honeycomb structure on roughed graphite paper for efficient electroreduction of $CO_2$ to $C_2H_4$

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Fig. S1 SEM image of pristine GP.



Fig. S2 Cross-sectional SEM image of RGP and the corresponding elemental mapping of Al, C and O.



**Fig. S3** CVs of RGP (a), Cu-Cu<sub>2</sub>O/RGP (b), Cu<sub>2</sub>O/RGP (c) and Cu<sub>2</sub>O/NGP (d) in CO<sub>2</sub> saturated 0.1 M KHCO<sub>3</sub> solution. (e) Estimation of  $C_{dl}$  by plotting the current density against scan rate to fit a linear regression for RGP, Cu-Cu<sub>2</sub>O/RGP, Cu<sub>2</sub>O/RGP and Cu<sub>2</sub>O/NGP.



Fig. S4 Comparison of LSVs of RGP (a), Cu-Cu<sub>2</sub>O/RGP (b), Cu<sub>2</sub>O/RGP (c) and Cu<sub>2</sub>O/NGP (d) in

Ar and CO<sub>2</sub> saturated 0.1 M KHCO<sub>3</sub> with a scan rate of 5 mV  $s^{-1}.$ 



Fig. S5 CVs of Cu-Cu<sub>2</sub>O/RGP (a), Cu<sub>2</sub>O/RGP (b) and Cu<sub>2</sub>O/NGP (c) before and after electrolysis

in Ar saturated 0.1 M KHCO<sub>3</sub> with a scan rate of 50 mV s<sup>-1</sup>.



Fig. S6 FEs of  $Cu_2O/RGP$  (a) and  $Cu-Cu_2O/RGP$  (b) toward  $CO_2RR$ .



Fig. S7 FEs of HCOOH for Cu-Cu<sub>2</sub>O/RGP, Cu<sub>2</sub>O/RGP and Cu<sub>2</sub>O/NGP.



Fig. S8 Partial current density of each product vs. applied potentials for Cu-Cu<sub>2</sub>O/RGP (a) and

Cu<sub>2</sub>O/RGP (b).



Fig. S9 Stability tests of Cu-Cu<sub>2</sub>O/RGP (a) and Cu<sub>2</sub>O/RGP (b) at -0.9 V over 10 h and corresponding FEs of C<sub>2</sub>H<sub>4</sub> production.



Fig. S10 XRD patterns of  $Cu_2O/NGP$  before and after  $CO_2RR$ .



Fig. S11 SEM image of  $Cu_2O/NGP$  after  $CO_2RR$ .



Fig. S12 TEM images of  $Cu_2O/NGP$  before (a, b) and after (c, d)  $CO_2RR$ . And the corresponding

selected area electron diffraction patterns exhibited in the inset of b and d.

Samples	BET surface area $(m^2 g^{-1})$	Pore volume (cm <sup>3</sup> g <sup><math>-1</math></sup> )
Cu-Cu <sub>2</sub> O/RGP	4.9	0.31
Cu <sub>2</sub> O/RGP	5.2	0.39
Cu <sub>2</sub> O/NGP	5.3	0.42

Table S1 Specific surface area and pore volume of three samples.

Samples	С	Κ	O K		Cu K		N K	
	wt%	at%	wt%	at%	wt%	at%	wt%	at%
Cu-Cu <sub>2</sub> O/RGP	5.41	22.23	1.87	5.76	92.72	72.01	-	-
Cu <sub>2</sub> O/RGP	5.51	16.89	17.65	38.63	76.84	44.48	-	-
Cu <sub>2</sub> O/NGP	4.14	13.82	12.72	31.85	82.12	51.41	1.02	2.92

Table S2 Element contents of three samples determined by EDS.