Supporting Information

Controlling C_{2+} Products Selectivity of Electrochemical CO_2 Reduction on Electrosparyed Cu Catalyst

Si Young Lee[a, b], Sang Youn Chae[a], Hyejin Jung[a, b], Chan Woo Lee[a, c], Dang Le Tri Nguyen[a ,b, d], Hyung-Suk Oh[a, b], Byoung Koun Min[a, e ,f], Yun Jeong Hwang[a, b,g]*

[a] Clean Energy Research Center, Korea Institute of Science and Technology, 5, Hwarang-ro 14-gil, Seongbuk-gu, Seoul, 02792, Republic of Korea

[b] Division of Energy and Environmental Technology, KIST School, Korea University of Science and Technology, Hwarang-ro 14 gil 5, Seongbuk-gu, Seoul, 02792, Republic of Korea

[c] Department of Chemistry, Kookmin University, Seoul 02707, Republic of Korea

[d] Institute of Research and Development, Duy Tan University, Da Nang 550000, Vietnam

[e] National Research Agenda Division, Korea Institute of Science and Technology, 5, Hwrang-ro 14 gil, Seongbuk-gu, Seoul, 02792, Republic of Korea

[f] Green School, Korea University, 145, Anam-ro, Seonbuk-gu, Seoul, 02842, Republic of Korea

[g] Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 03722, Republic of Korea

*Corresponding author. Tel: +82-2-958-5227. Fax: +82-2-958-5809.

E-mail address: yjhwang@kist.re.kr (Y. J. Hwang)

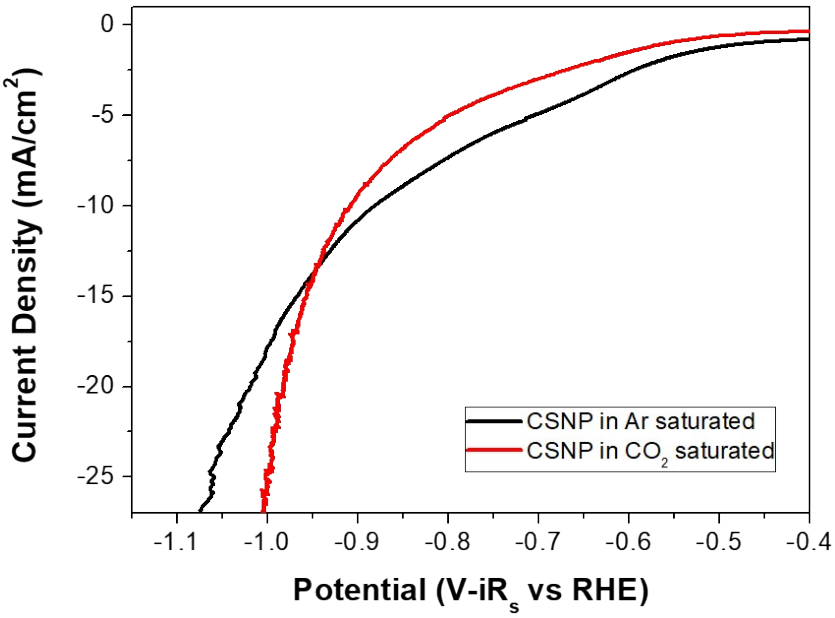

Fig. S1 LSV comapred with Ar and CO_2 atmosphere for CSNP/CP sample

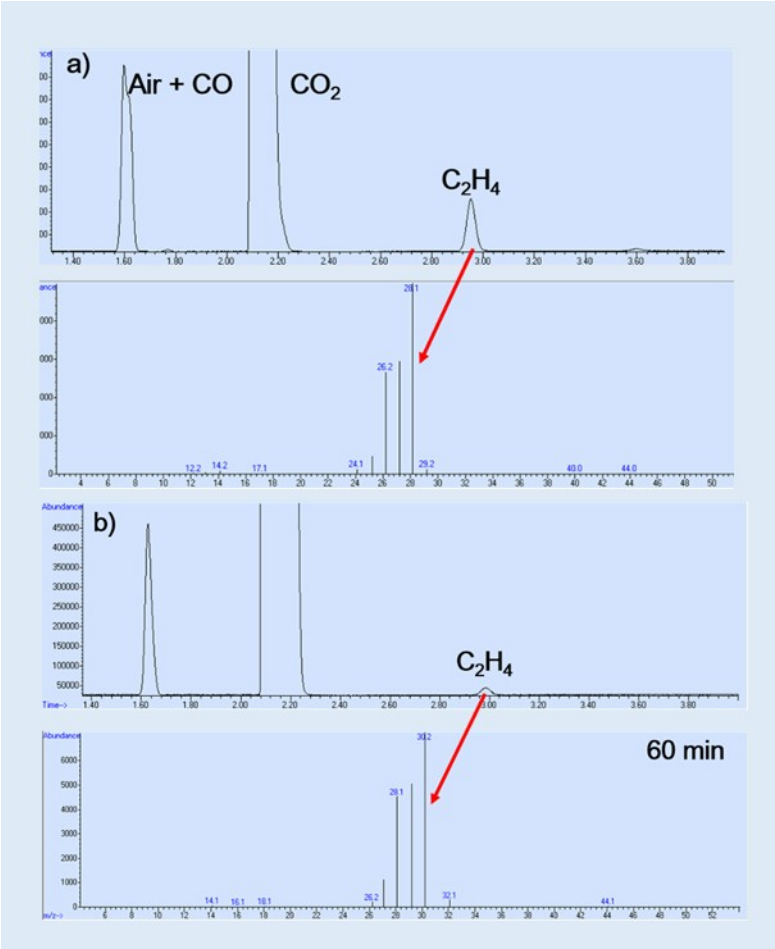

Fig. S2 Chromatogram and mass spectroscopy measured by GC-MS with CSNP/CP; a) when $^{12}CO_2$ was used, and b) $^{13}CO_2$ was used for CO_2RR.

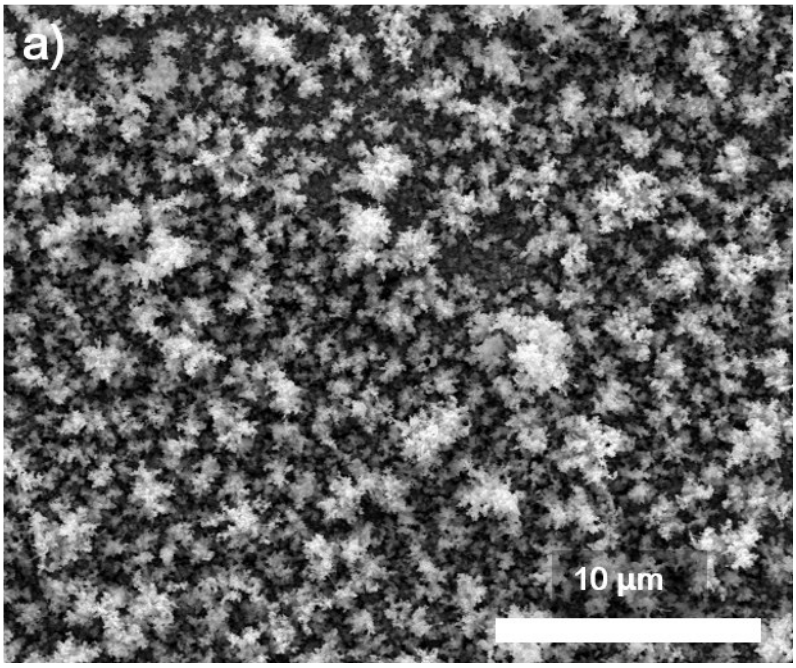

Figure S3 SEM image of CSNP/Cu sample

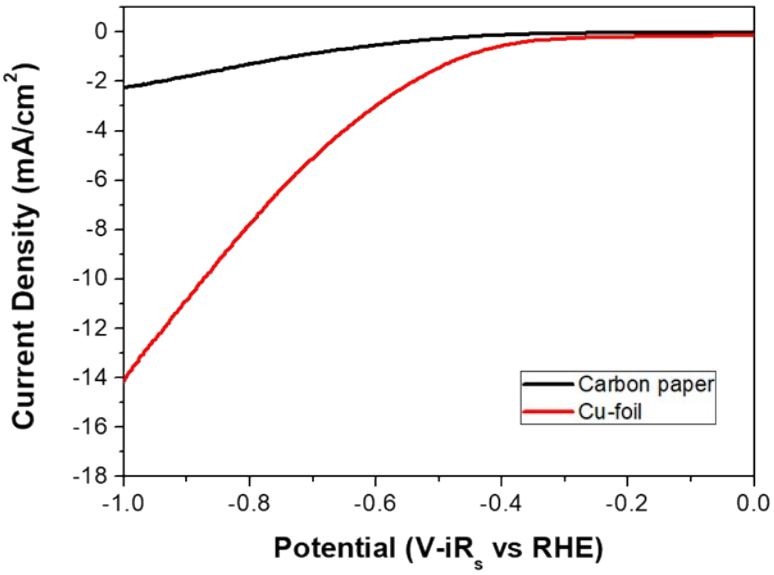

Fig. S4 HER activity of each substrate in 0.1M $KHCO_3$ N_2 pursing condition

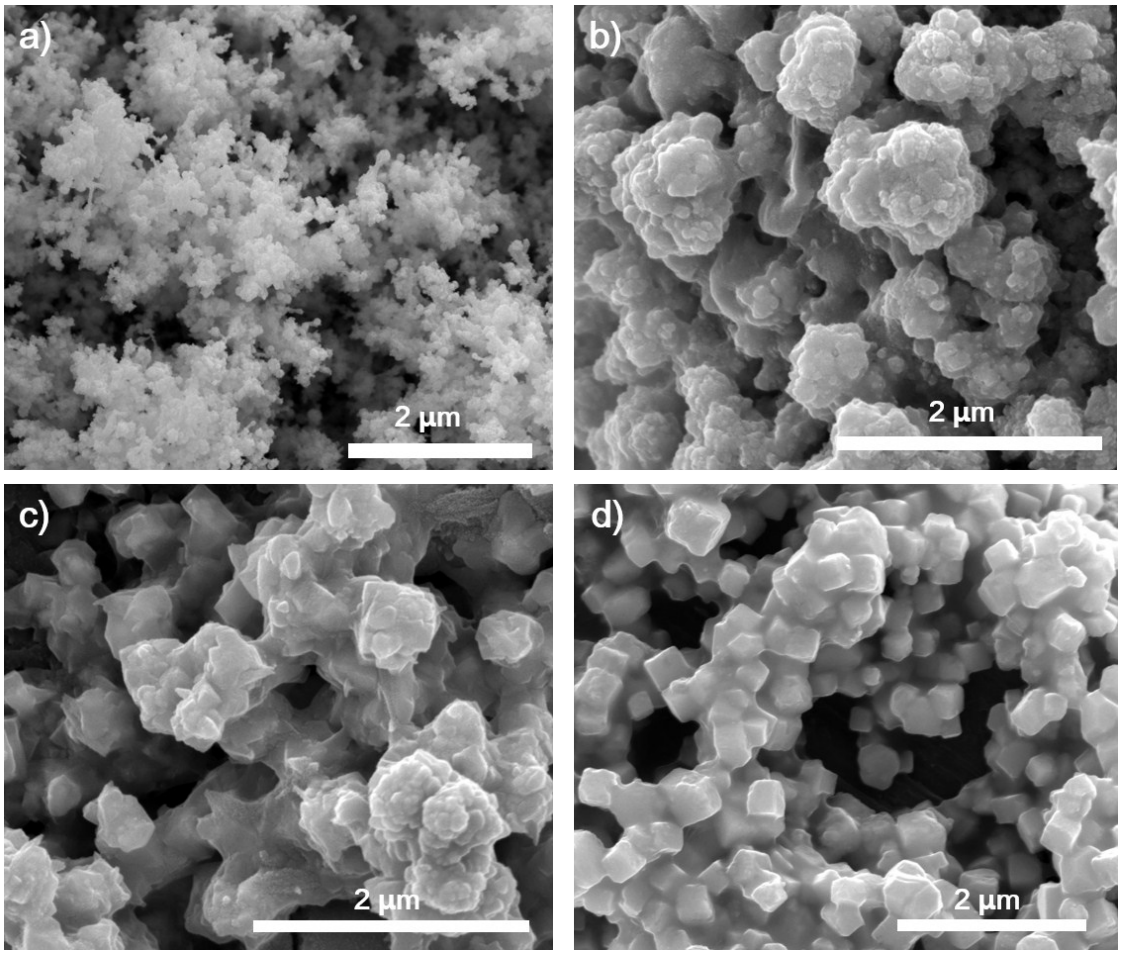

Fig. S5 Morphology change of CSNP/CP by reaction time; a) 2 hours CO_2RR post; b) 15 hours CO_2RR post; c) 30 hours CO_2RR post; 60 hours CO_2RR post

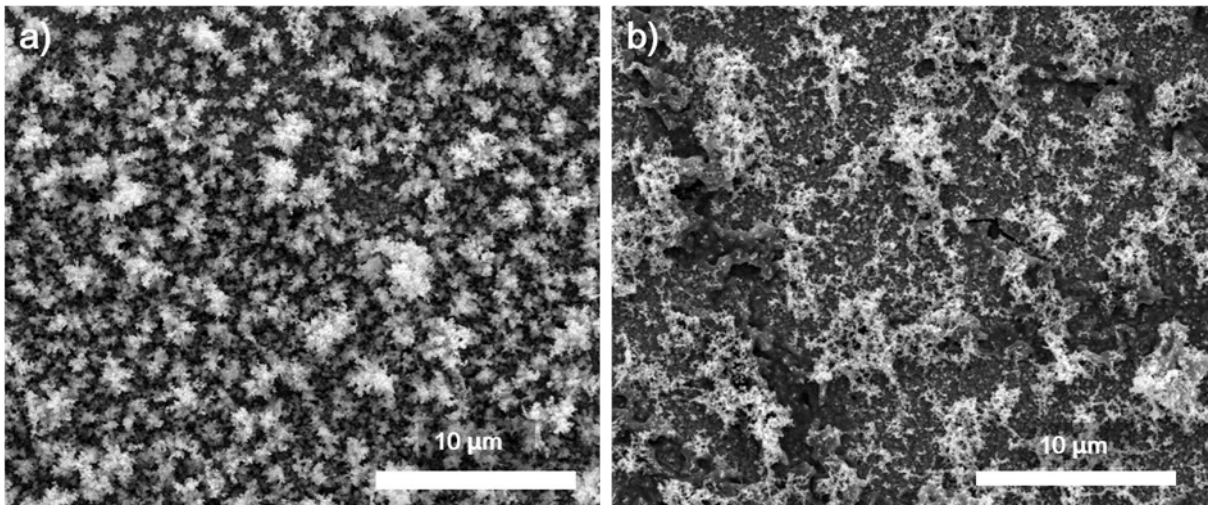

Fig. S6 SEM image of each catalyst sample a) CSNP/Cu before CO_2RR, b) CSNP/Cu 2 hour after CO_2RR

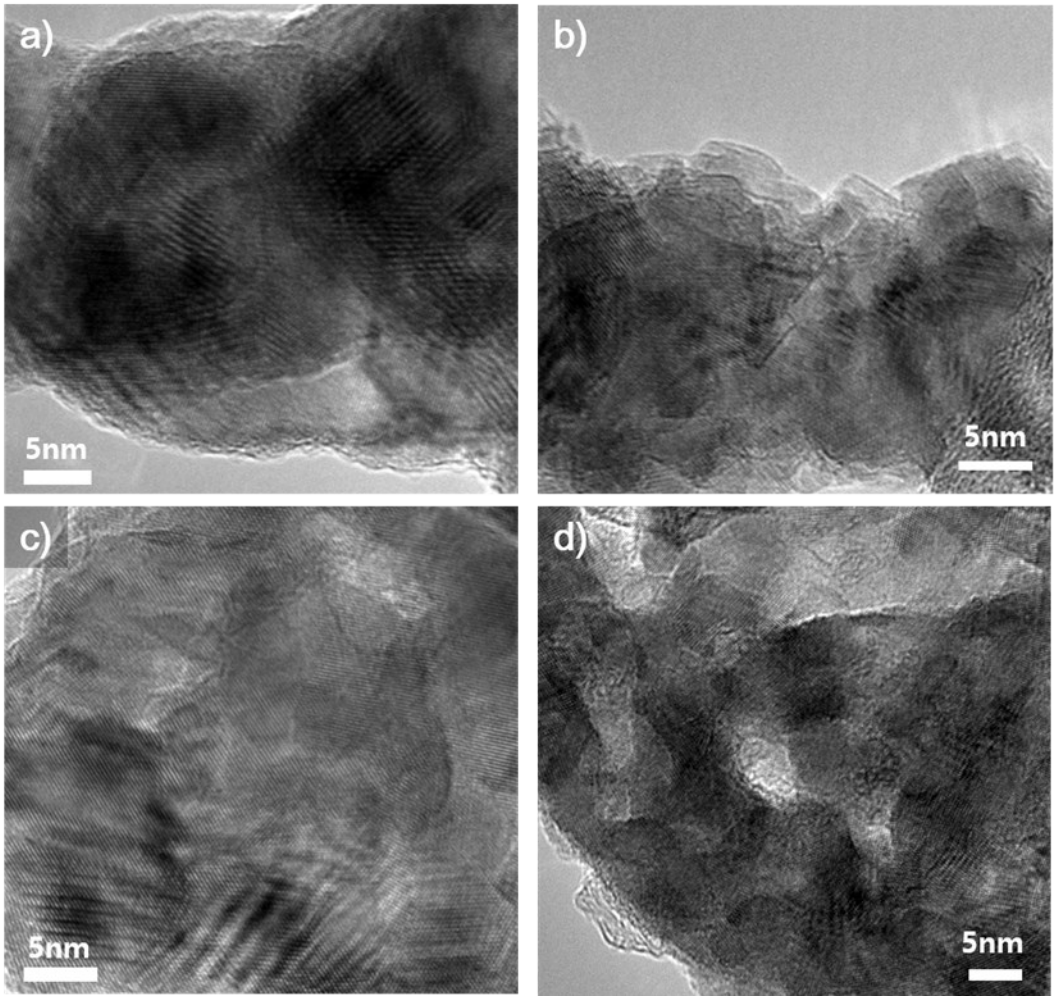

Fig. S7 HR-TEM image of each catalyst sample a) CSNP/Cu before CO_2RR, b) CSNP/Cu 2 hour after CO_2RR, c) CSNP/CP before CO_2RR, d) CSNP/CP 2 hour after CO_2RR

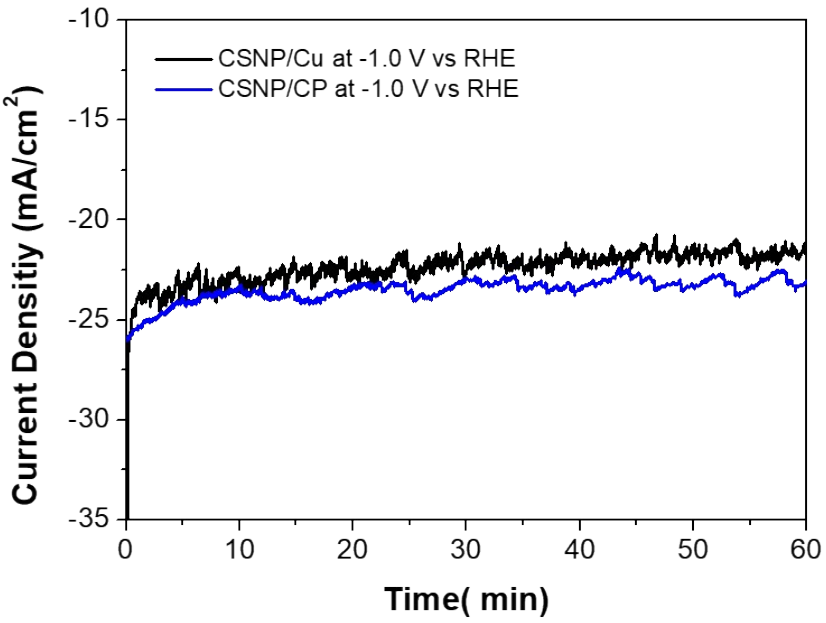

Fig. S8 Total current density compared with CSNP/Cu and CSNP/CP

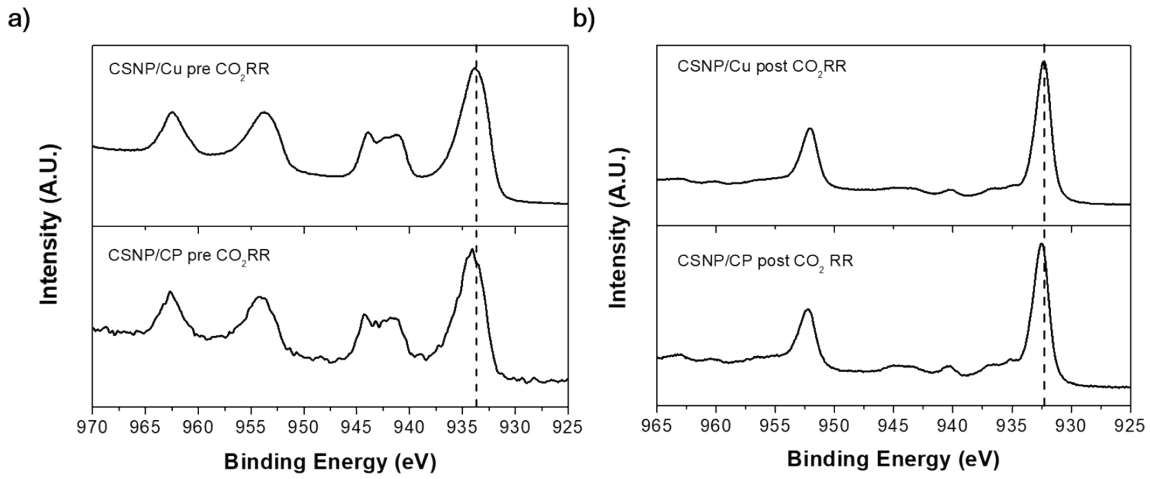

Fig. S9 The Cu 2p XPS peak of each catalyst-substrate module sample a) CSNP Cu 2p peak compared with CO_2RR pre-post condition b)) CSNP Cu 2p peak compared with CO_2RR pre-post condition

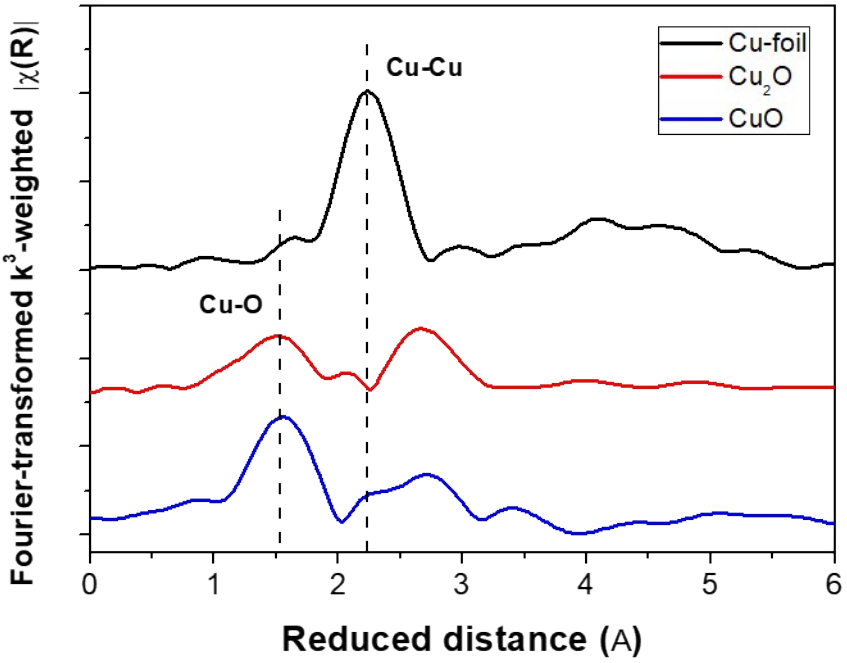

Fig. S10 Cu based reference materials Cu K-edge EXAFS spectra

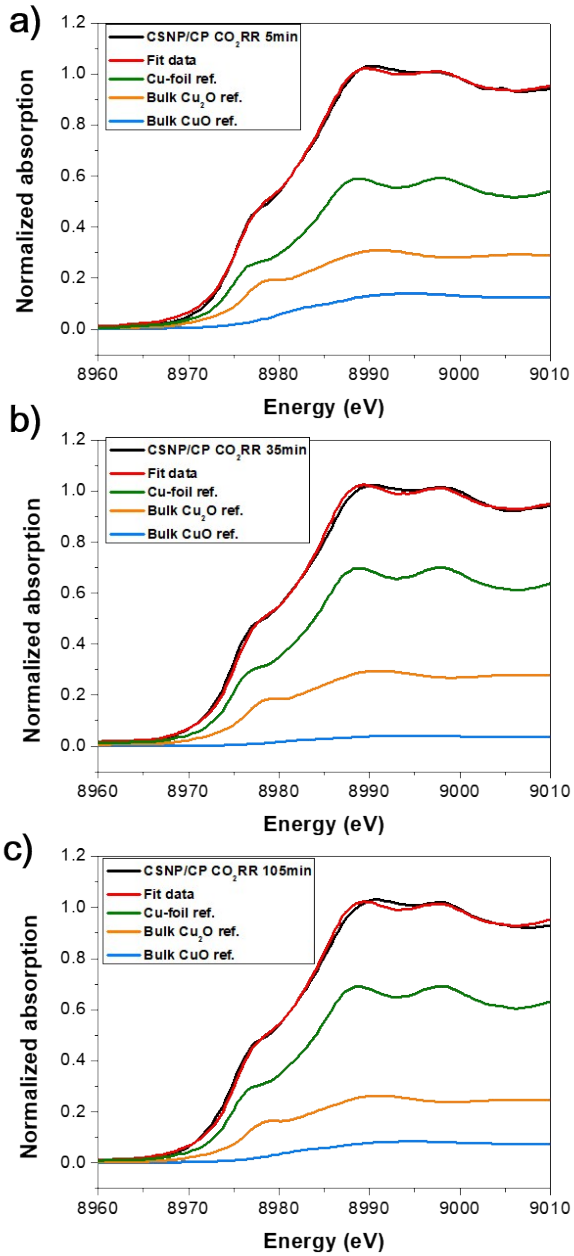

Fig. S11 Linear combination fitting (LCF) results of in situ/operando CSNP/CP sample; a) 5min CO_2RR sample results; b) 35min CO_2RR sample results; c) 105min CO_2RR sample results

	5 min	35 min	105 min
Cu^0	58.4%	67.9%	68.8%
Cu_2O	28.7%	24.3%	27.4%
CuO	12.9%	7.9%	3.8%

Table S1 LCF results of *in situ/operando* CSNP/CP data

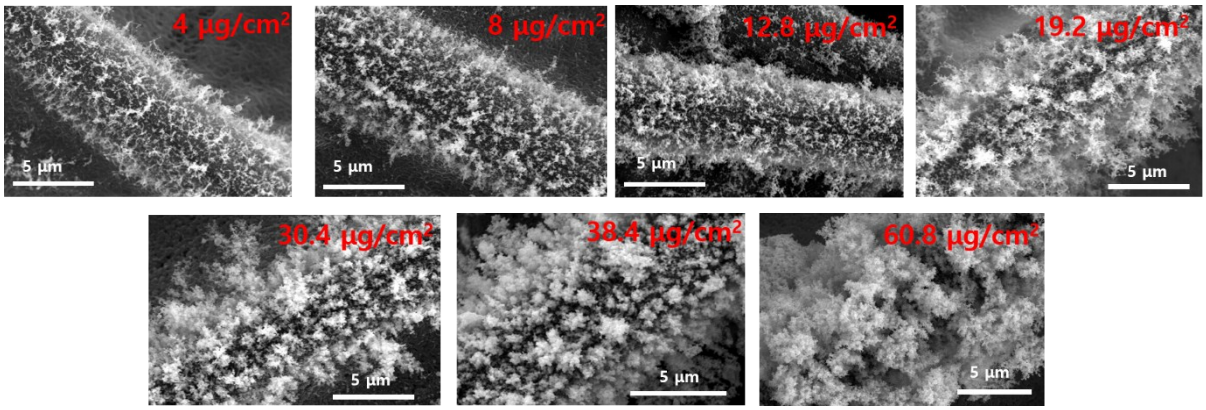

Fig. S12 Surface morphology SEM image of CSNP/CP catalyst depending on spray amount

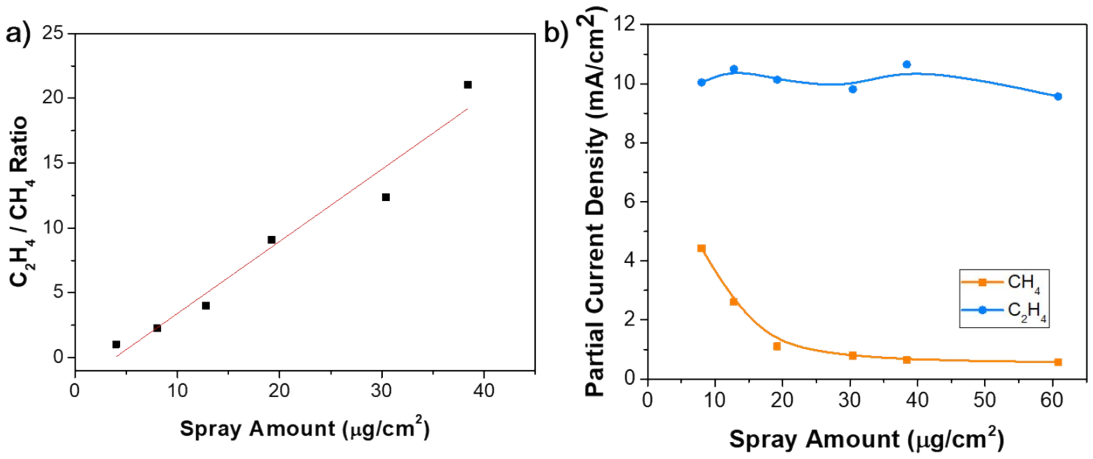

Fig. S13 C_2H_4 to CH_4 ratio and partial current density depending on spray amount in CSNP/CP catalyst; a) C_2H_4 / CH_4 ratio trend; b) C_2H_4 and CH_4 partial current densitiy trend

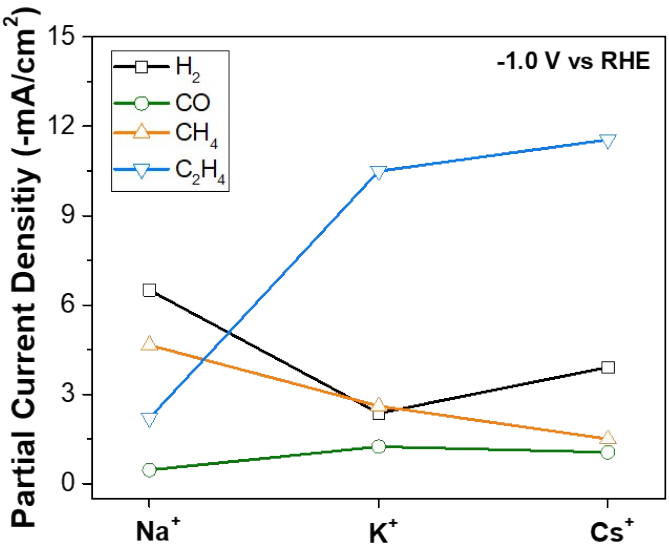

Fig. S14 The partial current densitiy of CSNP gas products in each cation electrolyte

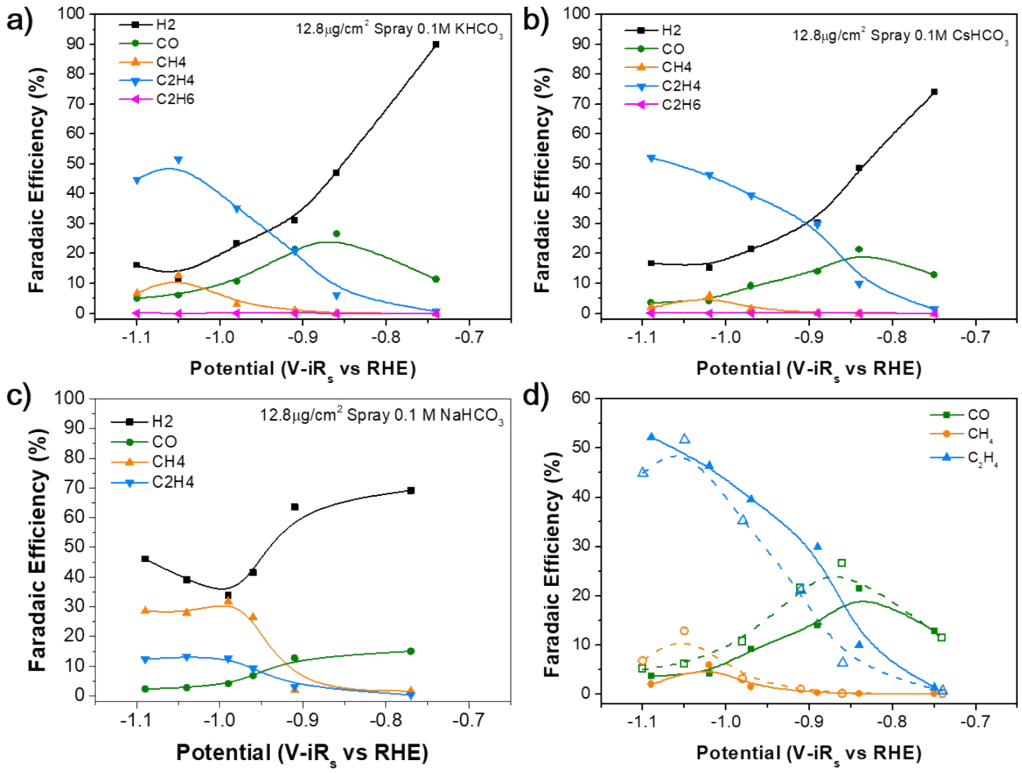

Fig. S15 The potential dependent faradaic efficiency of 12.8 μg/cm^2 applied CSNP/CP; a) 12.8 μg/cm^2 CSNP/CP in 0.1 M $KHCO_3$; b) 12.8 μg/cm^2 CSNP/CP in 0.1 M $CsHCO_3$; c) 12.8 μg/cm^2 CSNP/CP in 0.1 M $NaHCO_3$ d) compared except hydrogen

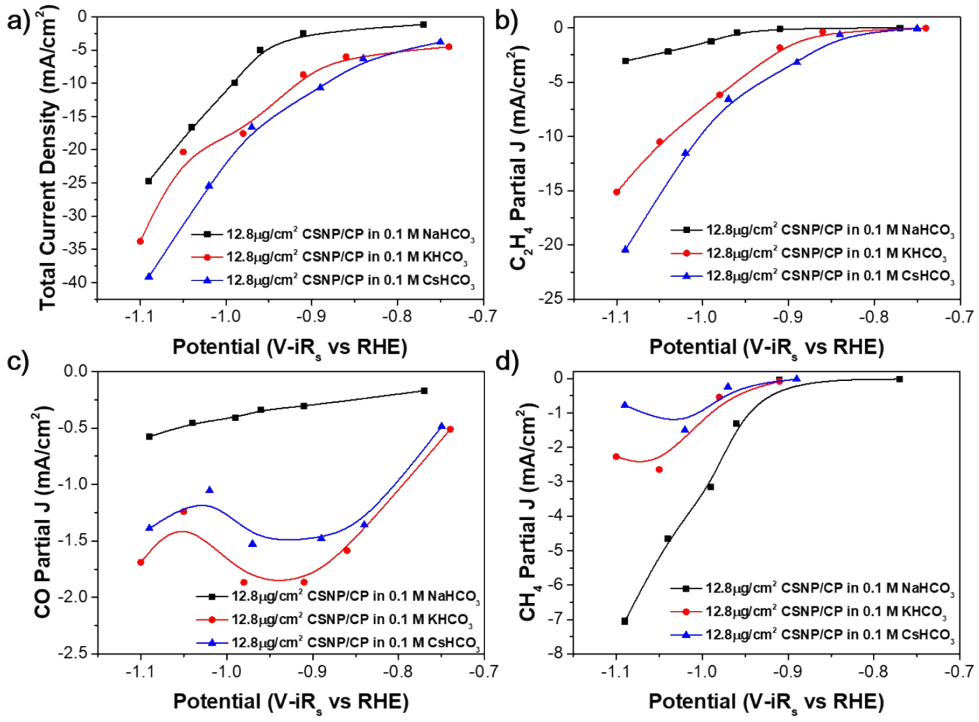

Fig. S16 Total and partial current density of each electrolyte condition in 12.8 μg/cm^2 CSNP/CP in 0.1 M (Cs, K, Na)HCO_3 CSNP/CP a) total current density b) C_2H_4 partial current density c) CO partial current density d) CH_4 partial current density

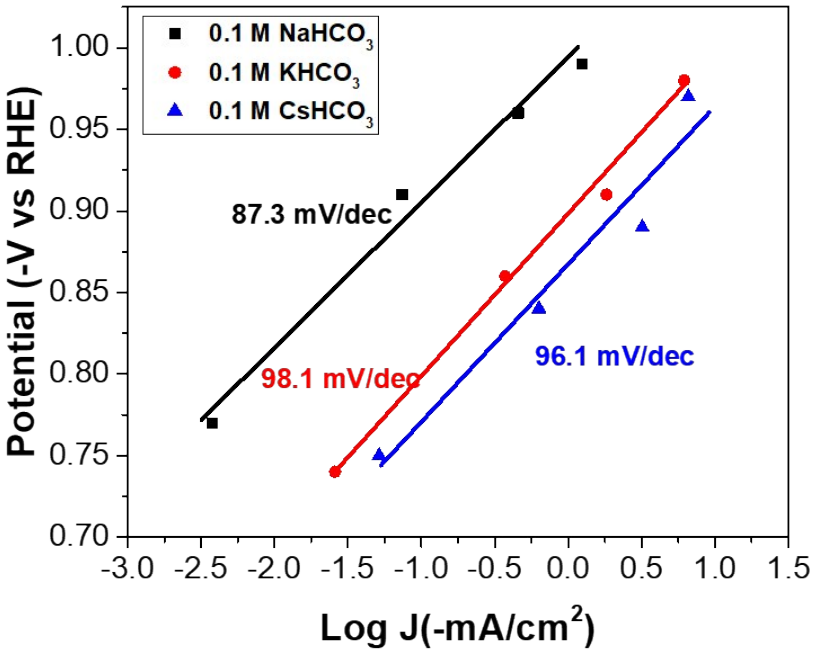

Fig. S17 Tafel slope of C_2H_4 in each cation electrolyte

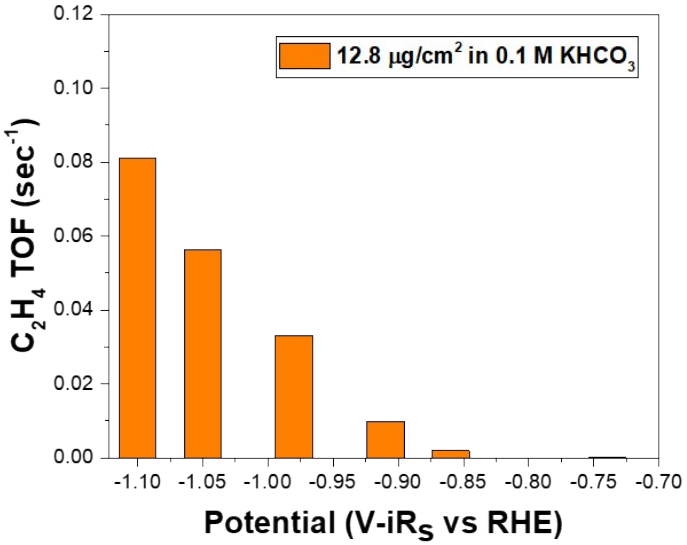

Fig. S18 TOF of C_2H_4 for applied potential in 0.1 M $KHCO_3$ electrolyte

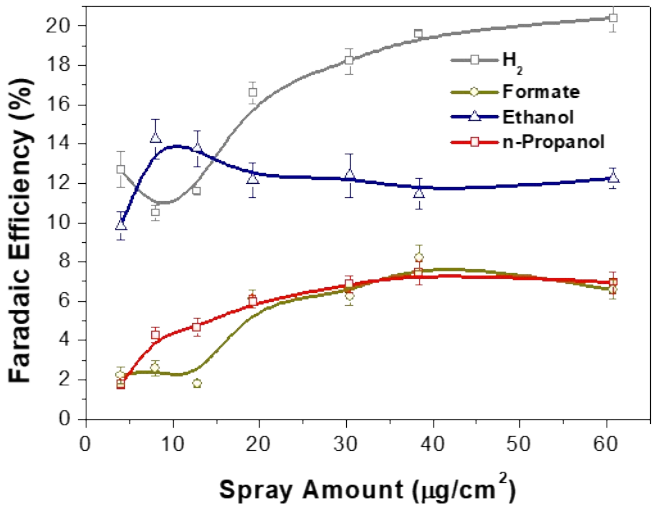

Fig. S19 The liquid products faradaic efficiency trend with spray amount