Supporting information

Controlling C-C coupling in Electrocatalytic Reduction of CO_2 over $Cu_{1-x}Zn_x/C$

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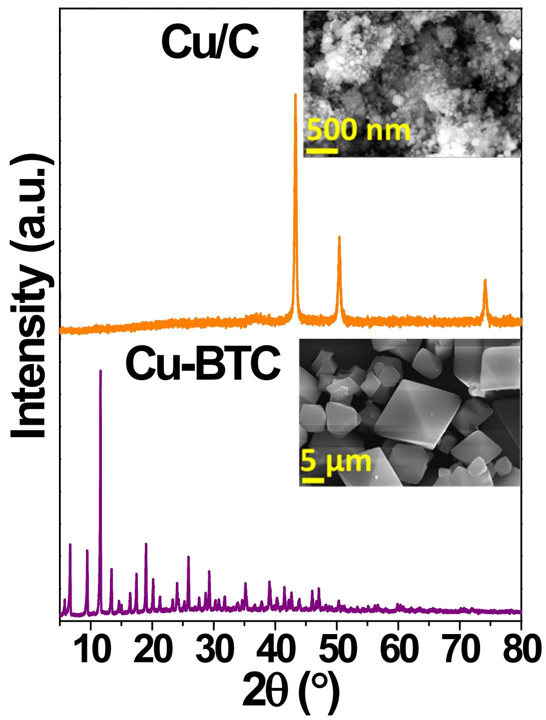

Fig. S1 XRD patterns and SEM micrographs of pristine Cu-BTC MOFs and Cu/C NPs

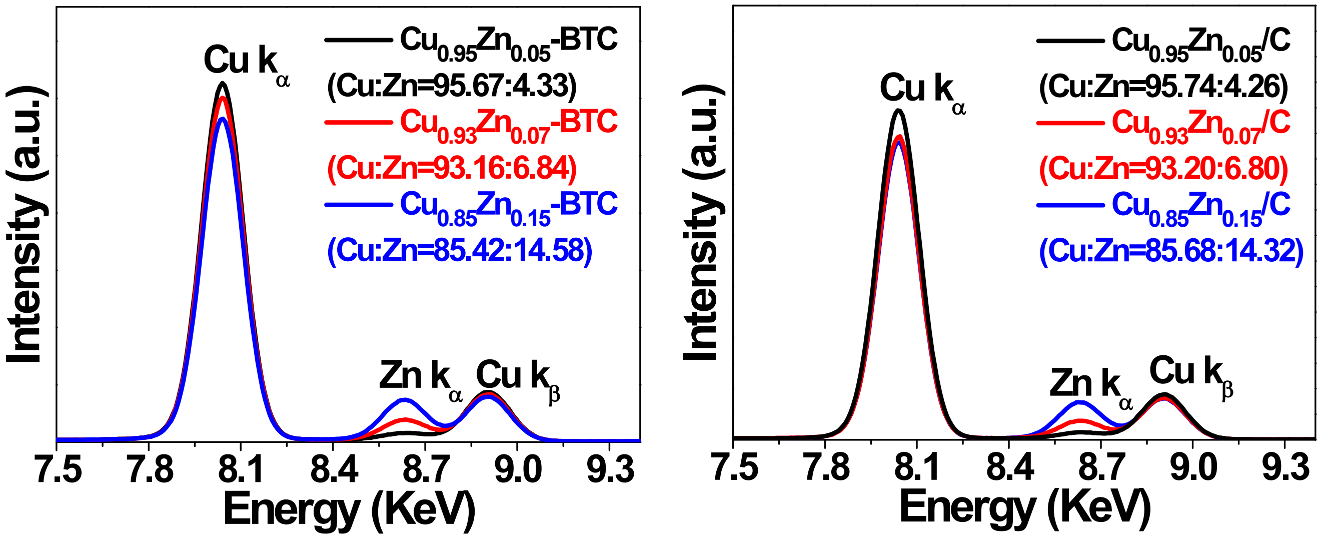

Fig. S2 XRF data of $Cu_{1-x}Zn_x$-BTC MOFs and $Cu_{1-x}Zn_x/C$ NPs.

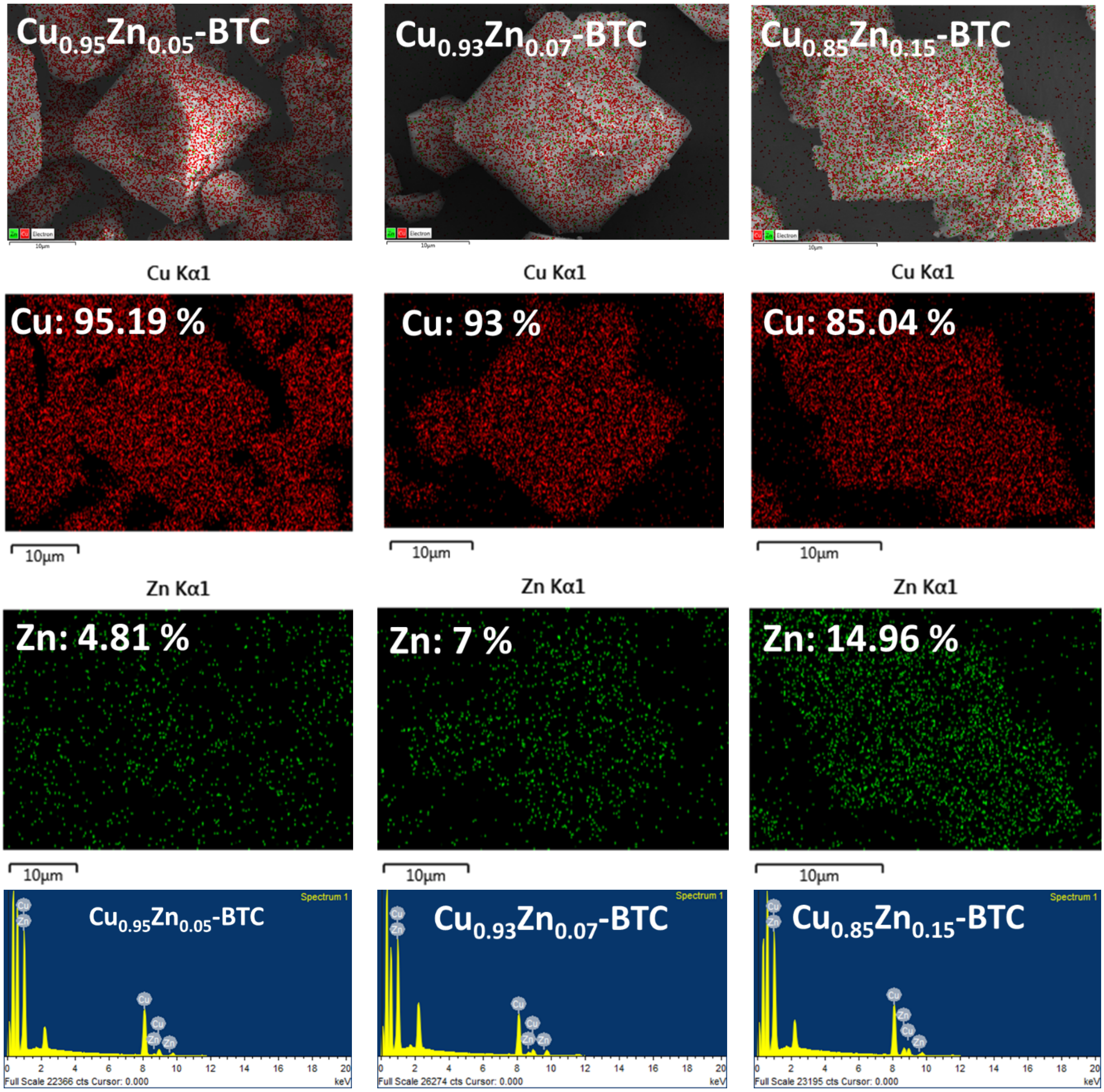

Fig. S3 EDS elemental mapping of $Cu_{1-x}Zn_x$-BTC MOFs.

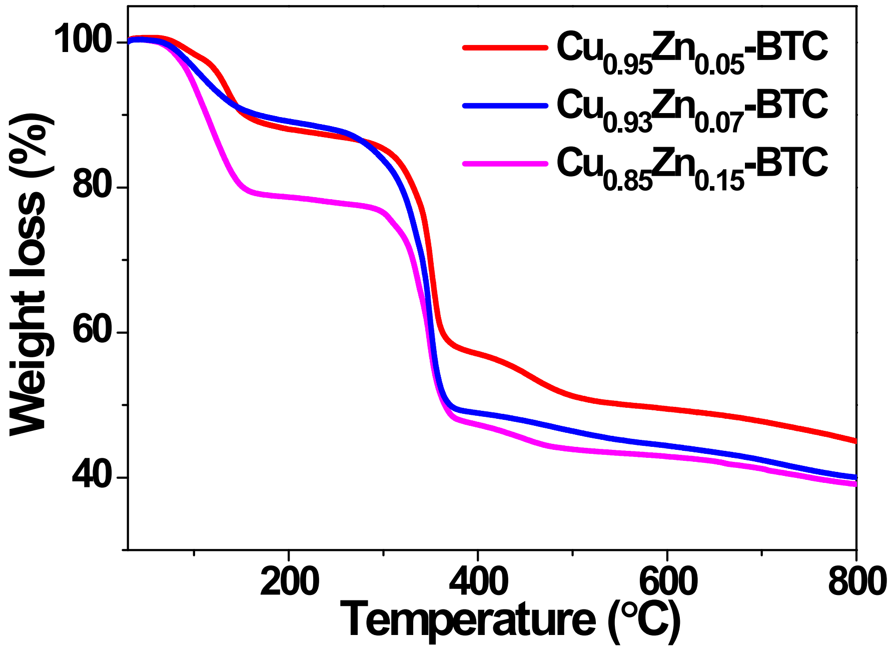

Fig. S4 TGA plot of $Cu_{1-x}Zn_x$-BTC MOFs.

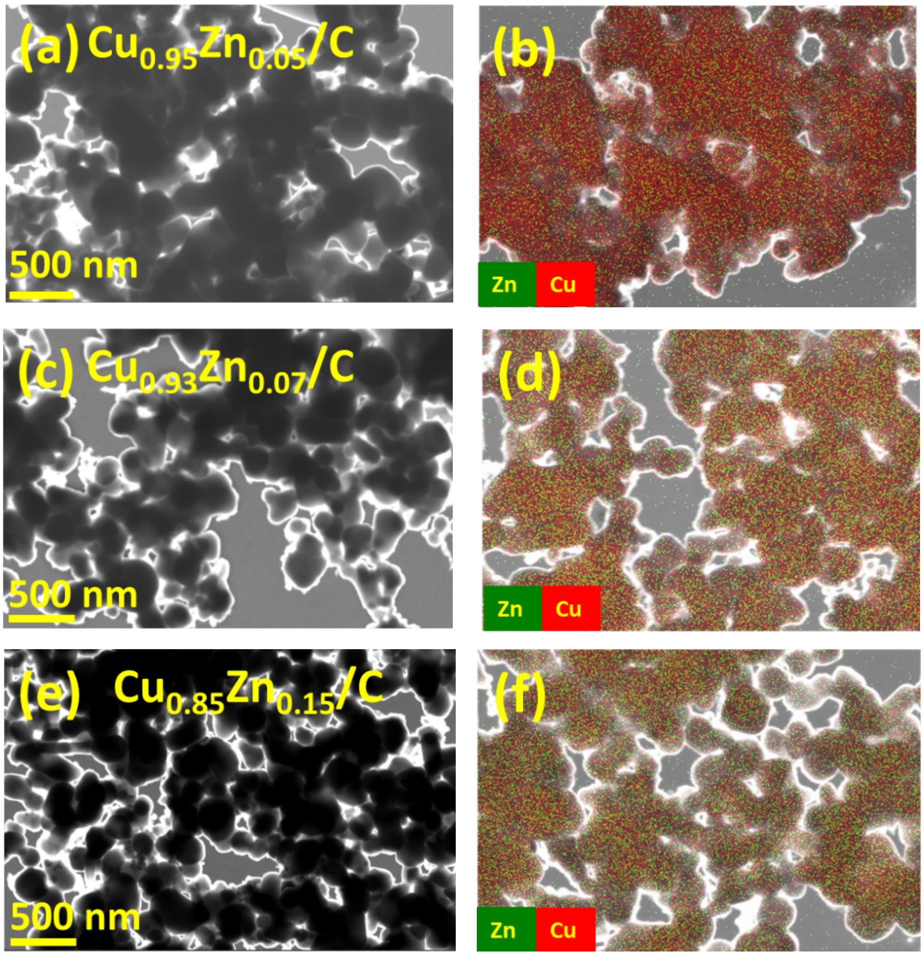

Fig. S5 STEM micrographs and elemental mapping of (a,b) $Cu_{0.95}Zn_{0.05}/C$, (c,d) $Cu_{0.93}Zn_{0.07}/C$, and (e,f) $Cu_{0.85}Zn_{0.15}/C$.

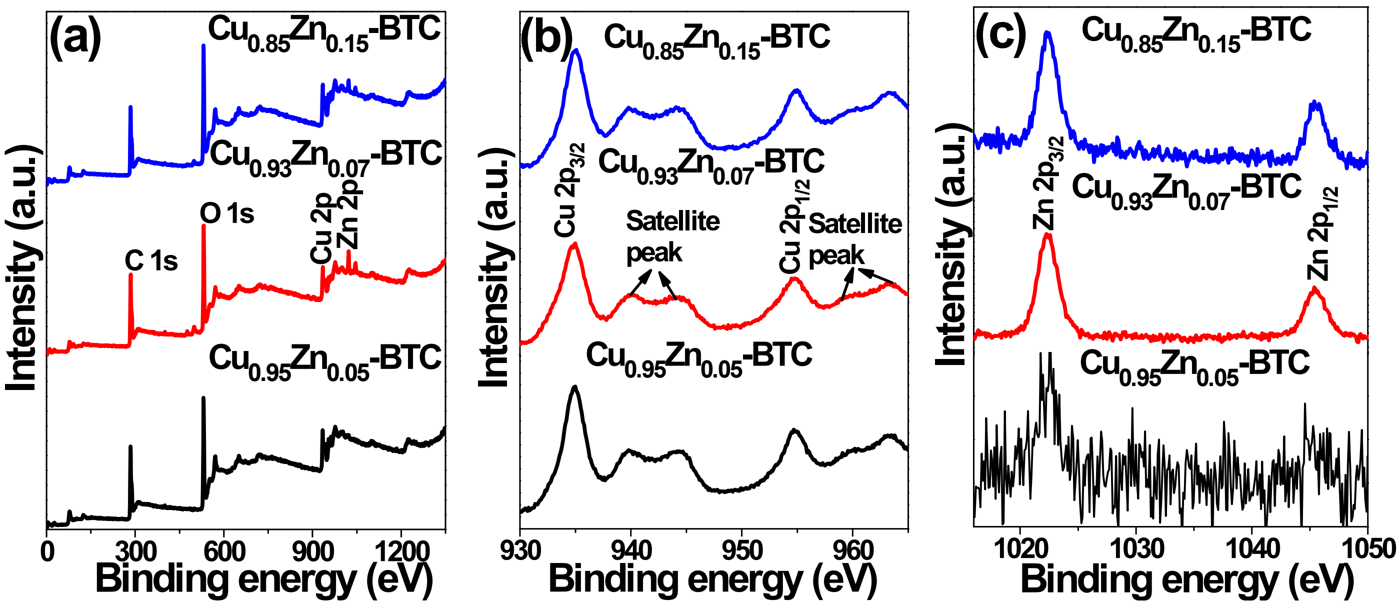

Fig. S6 (a) XPS survey spectra, (b) Cu 2*p* and (c) Zn 2*p* core-level spectrum of bimetallic $Cu_{1-x}Zn_x$-BTC MOFs.

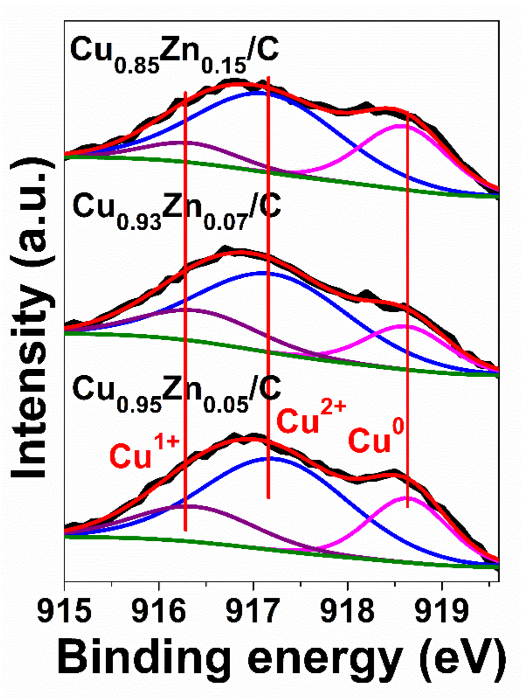

Fig. S7 The Auger Cu LM2 spectra of synthesized $Cu_{1-x}Zn_x$/C.

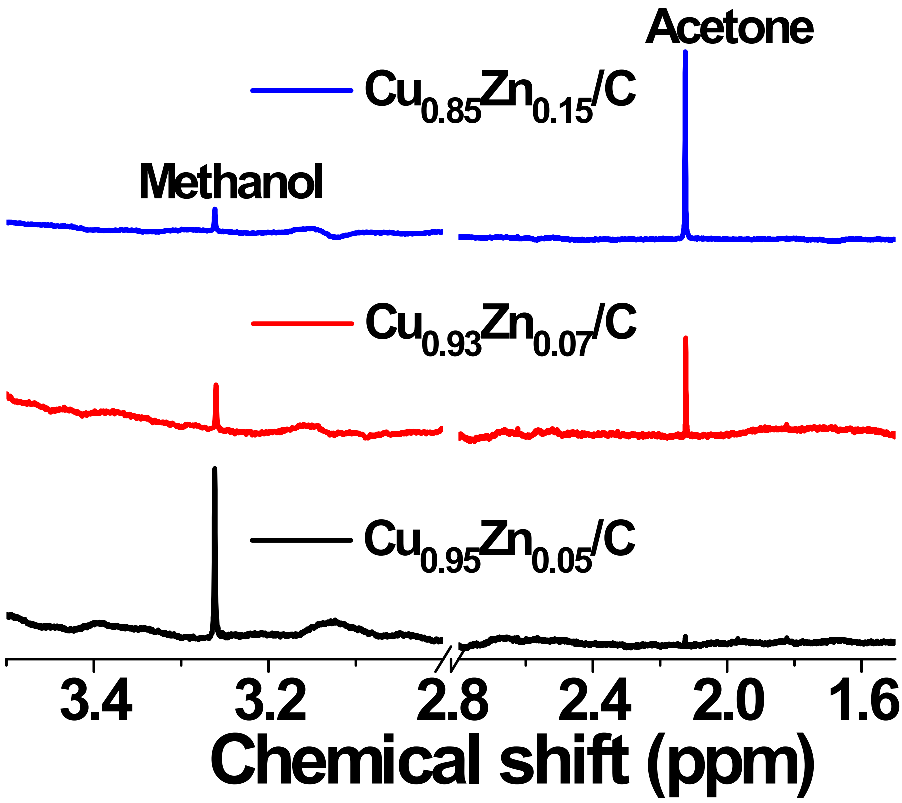

Fig. S8 ^{1}H NMR plot after 4 h electrolysis of the $Cu_{1-x}Zn_x/C$ at a potential -0.40 V vs. RHE.

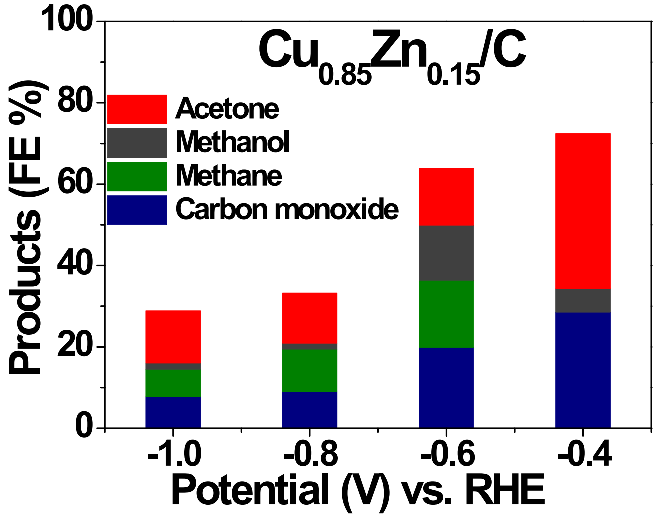

Fig. S9 Faraday efficiency of CO_2RR products as a function of potential over $Cu_{0.85}Zn_{0.15}$/C.

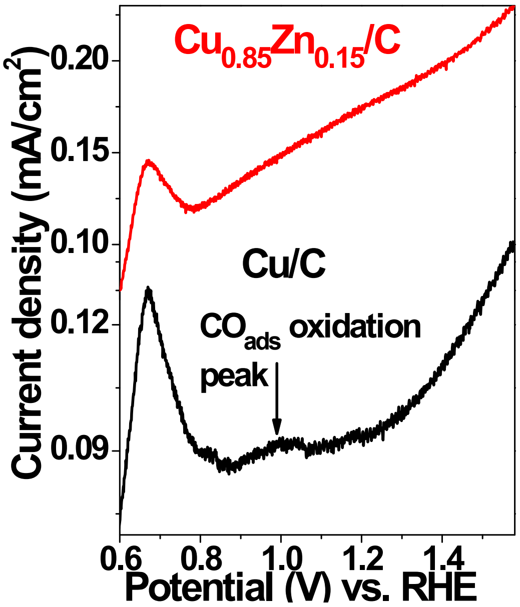

Fig. S10 LSV plot of CO stripping over Cu/C and $Cu_{0.85}Zn_{0.15}/C$ in presence of 0.1 M $NaHCO_3$ as an electrolyte at 50 mV/s scan rate. In this experiment, CO was adsorbed over both the catalysts and then the electrocatalytic oxidation of adsorbed CO was performed over both the materials. The LSV data exhibited an anodic peak due to the oxidation of adsorbed CO over Cu/C, whereas the similar peak was absent over the $Cu_{0.85}Zn_{0.15}/C$ nano-alloy. This strongly suggests that presence of Zn in the lattice desorbs the adsorbed CO, and therefore no anodic peak was observed in CO stripping experiment over $Cu_{0.85}Zn_{0.15}/C$.

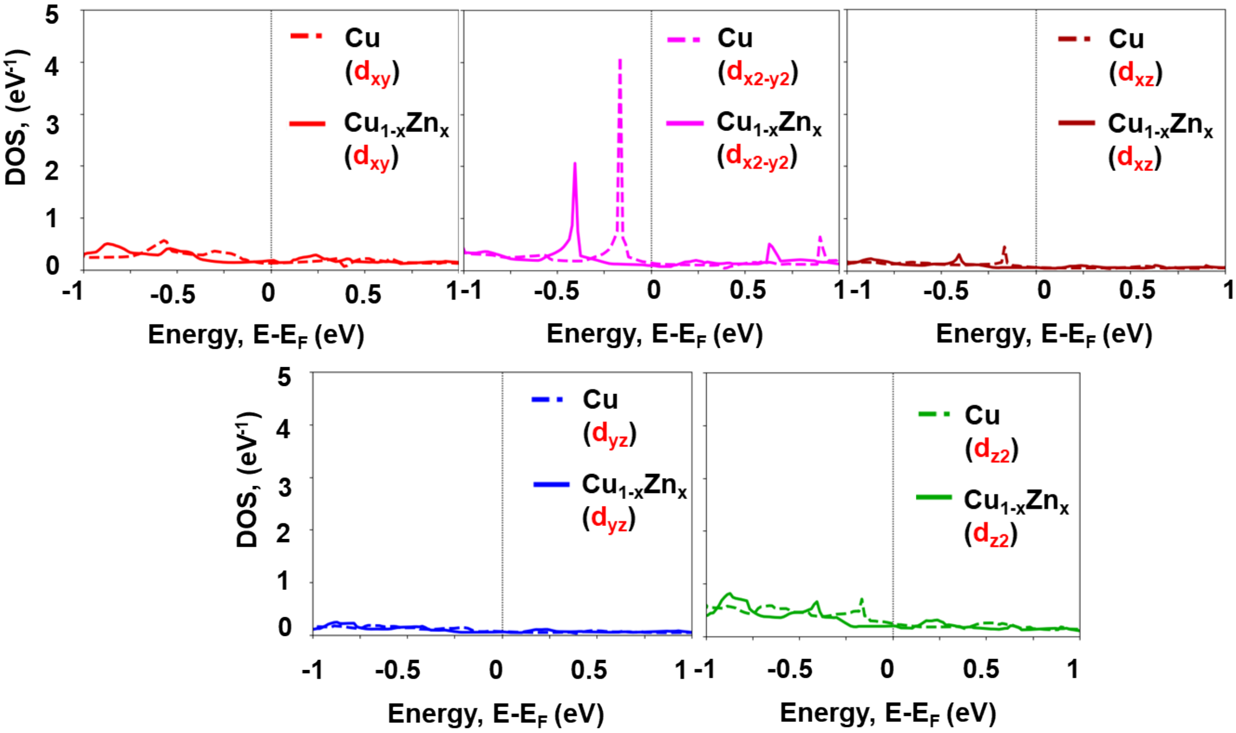

Fig. S11 DOS of Cu(111) and $C_{1-x}Zn_x$ (111).

Table S1: Comparison of the present catalyst with the literature on electrochemical reduction of CO_2 using various electrodes and electrolytes.

Catalyst	Electrolyte	Electrode potential	Faradaic efficiency (%)	Ref.
Cu-SA/NPC	0.1 M $KHCO_3$	-0.36 (vs. RHE)	$FE_{CH_3OH} = 3.27$ $FE_{CH_3COCH_3} = 36.7$	1
$Cu_{75}Zn_{25}$-C	0.1 M $KHCO_3$	-0.99 (vs. RHE)	$FE_{HCO_2H} = 5.2$ $FE_{C_2H_5OH} = 7.2$ $FE_{C_2H_4} = 15.4$	2
OD-$Cu_{75}Zn_{25}$ (cubes)	0.1 M $KHCO_3$	-1.1 (vs. RHE)	$FE_{HCO_2H} = 2.5$ $FE_{CH_4} = 18.2$ $FE_{C_2H_5OH} = 16.1$ $FE_{C_2H_4} = 41.1$ $FE_{C_3H_7OH} = 2.2$	3
CuZn alloy	0.1 M $KHCO_3$	-1.1 (vs. RHE)	$FE_{CO} = 14.1$ $FE_{C_2H_5OH} = 0.8$ $FE_{C_2H_4} = 33.3$	4
Cu_4Zn	0.1 M $KHCO_3$	-1.05 (vs. RHE)	$FE_{CO} = 10.36$ $FE_{CH_4} = 0.42$ $FE_{HCO_2H} = 0.32$ $FE_{C_2H_4} = 10.75$ $FE_{C_2H_5OH} = 29.14$ $FE_{C_3H_7OH} = 4.39$	5
TLHP Cu_5Zn_8	0.1 M $KHCO_3$	-0.8 (vs. RHE)	$FE_{CO} = 14.3$ $FE_{HCO_2H} = 4.3$ $FE_{CH_3CO_2H} = 11.7$ $FE_{C_2H_5OH} = 46.6$	6
$CuZn_{20}$/NGN	0.1 M $KHCO_3$	-0.8 (vs. RHE)	$FE_{C_2H_5OH} = 34.25$	7
Cu_2O	0.5 M $KHCO_3$	-1.30 (vs. Ag/AgCl)	$FE_{CH_3OH} = 45.7$	8
Cu_2O/ZnO (1:1)			$FE_{CH_3OH} = 17.7$	
$Cu_{0.95}Zn_{0.05}$/C	0.1 M $NaHCO_3$	-0.40 V (vs. RHE)	$FE_{CH_3OH} = 29.1$ $FE_{CH_3COCH_3} = 12.3$	This work
$Cu_{0.93}Zn_{0.07}$/C			$FE_{CH_3OH} = 16.37$ $FE_{CH_3COCH_3} = 19.0$	

$Cu_{0.85}Zn_{0.15}/C$			$FE_{CH_3OH} = 5.8$ $FE_{CH_3COCH_3} = 38.1$	

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