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Electronic Supplementary Information

Evaluating the efficacy of nanosized CuZnAl and CuZnZr mixed oxides for electrocatalytic CO_2 reduction

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Table S1:

Catalyst	Theoretical (mol%)				Actual (mol%)			
	Cu	**Zn**	**Al**	**Zr**	**Cu**	**Zn**	**Al**	**Zr**
CuZnAl	0.675	0.275	0.05	--	0.674	0.274	0.06	--
CuZnZr	0.675	0.275	--	0.05	0.673	0.273	--	0.07

Theoretical and actual composition of the synthesized catalysts.

Table S2: The size of different crystallites in CuZnAl and CuZnZr samples calcined at different temperature.

Phase	*Crystallite size (nm)					
	CuZnAl-500	**CuZnAl-600**	**CuZnAl-700**	**CuZnZr-500**	**CuZnZr-600**	**CuZnZr-700**
CuO	111.8	44.7	40.6	28.6	47.3	55.3
ZnO	112.7	71.4	46.2	51.7	57.2	57.4
Al_2O_3	-	-	-	-	-	-
$CuAl_2O_4$	-	-	34.5	-	-	-
ZrO_2	-	-	-	35.4	42.8	50.6

*Calculated using Scherrer equation and XRD data

Table S3: Textural properties of catalysts from N_2-physisorption and chemical composition of catalysts

Catalyst	Calcination temperature (˚C)	S_{BET} (m^2/g)	V_t (cc/g)	Av. pore diameter (nm)
CuZnAl	500	17	0.130	18.4
	600	12	0.002	3.0
	700	3	0.005	2.8
CuZnZr	500	26	0.075	7.8
	600	8	0.003	5.7
	700	2	0.001	3.5

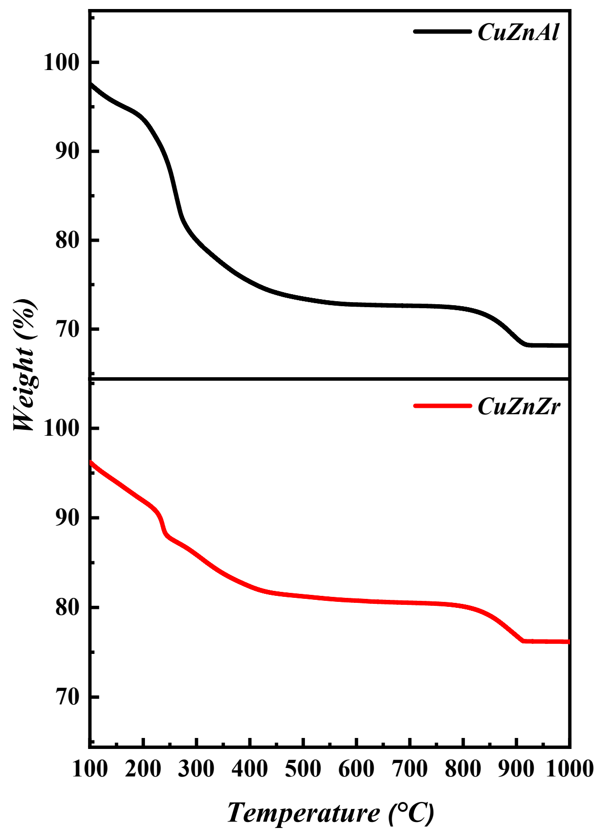

Fig S1: Thermograms of as-synthesized CuZnAl, and CuZnZr catalysts

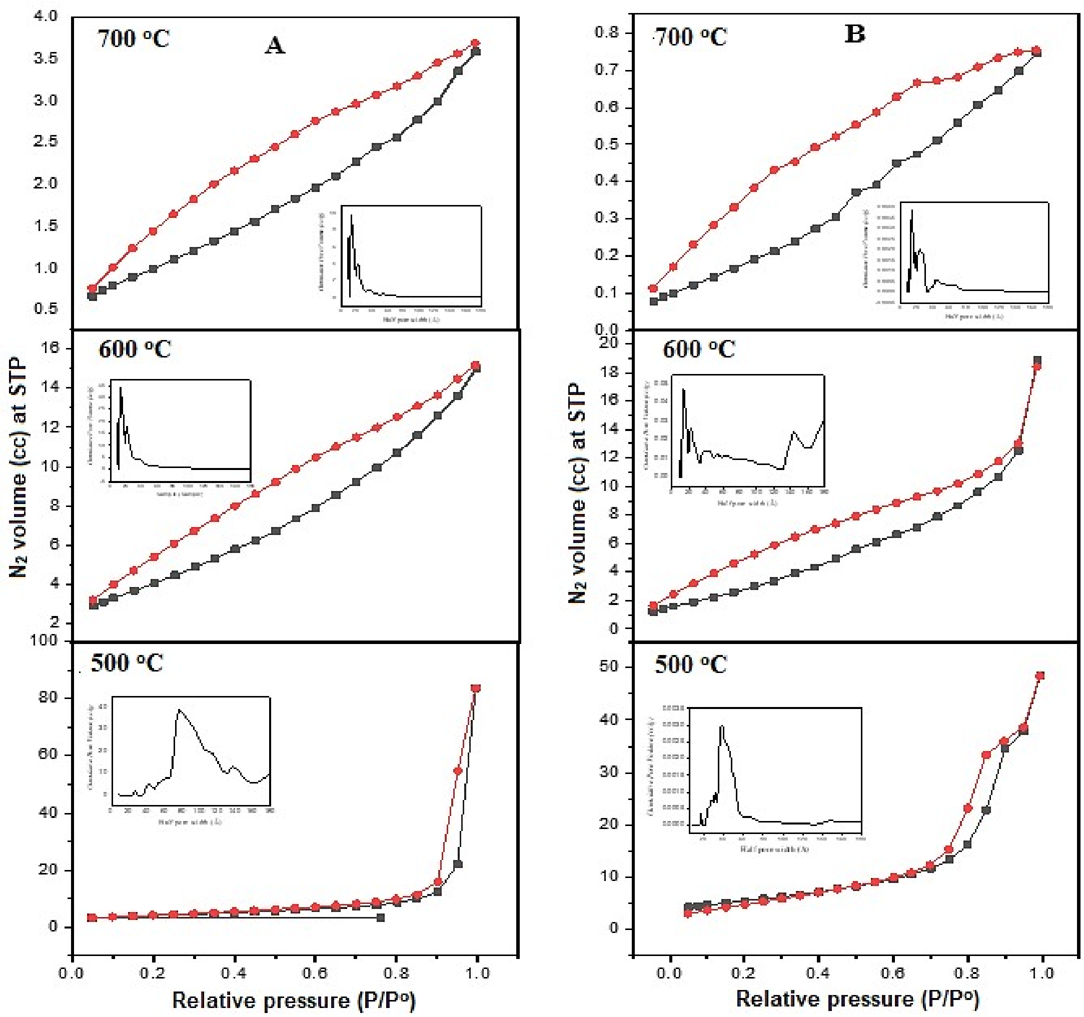

Fig. S2: N_2 adsorption-desorption isotherms for (A) CuZnAl and (B) CuZnZr catalysts calcined in air at 500, 600, and 700 ˚C.

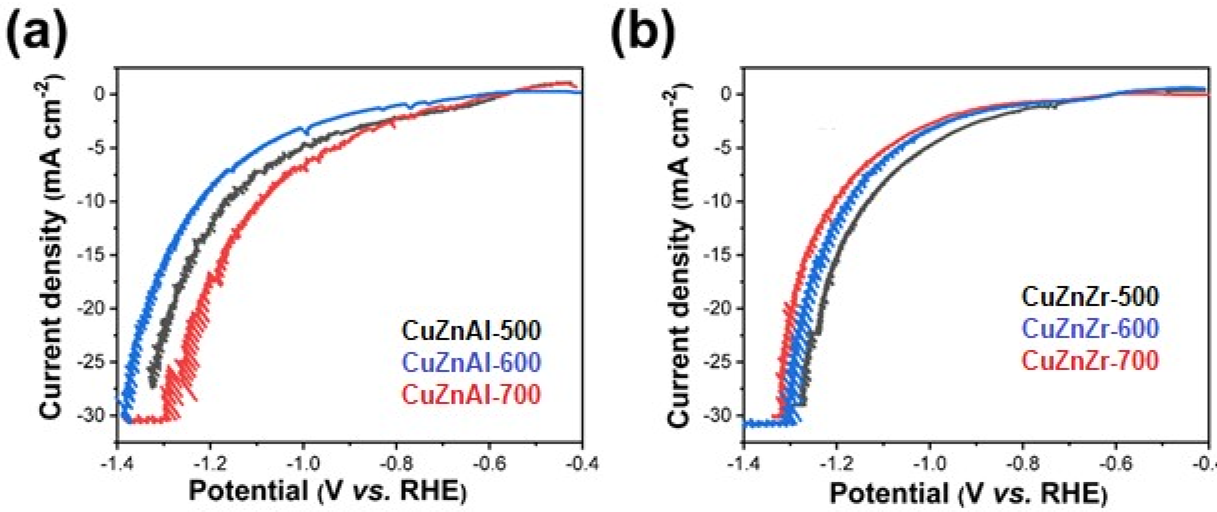

Fig. S3: (a) LSV curves of CuZnAl-x (temperature x=500/600/700 °C) in CO_2-saturated 0.1 $KHCO_3$ solution, (b) LSV curves of CuZnZr-x (temperature x=500/600/700 °C) in CO_2-saturated 0.1 $KHCO_3$ solution.

Table S4: Comparison between the performance of nanosized and non-nanosized CuZn-based catalysts

Catalyst	Nanosized copper catalysts									Non-nanosized copper catalysts					
	CO$_2$R products									CO$_2$R products					
	CO, FE(%)		CH_3OH, FE(%)	CH_4, FE(%)		C_2H_5OH, FE(%)	C_2H_4, FE(%)	Ref.	Catalyst	CO, FE(%)	CH_3OH, FE(%)	CH_4, FE(%)	C_2H_5OH, FE(%)	C_2H_4, FE(%)	Ref.
7CuO/3ZnO/C	50	at -0.46 V (vs RHE)	-	3	at -0.76 V (vs RHE)		47	[1]	**PcCu-O$_8$-Zn/CNT**	89	-	-	-	-	[5]
8CuO/2ZnO/C	38		-	5			50								
9CuO/1ZnO/C	35		-	29			46 at -0.9 V (vs RHE)								
Cu/ZnO x	-		-	36% at 1.1 V (vsRHE)		-	-	[2]	**Cu/ZnO**	5.4	2.8	1	10.2	10	[6]
CuZn	38	at -1.46 V (vs RHE)	-	-		-	-	[3]	**Cu/ZnO**	5	2	-	12	6	[7]
CuZn_240	36		-	-			-								
CuZn_300	37		-	-			-								
CuO-ZnO$_{10}$	-		15 at -0.6 V (vs RHE)			22 at -0.8 V (vs RHE)	-	[4]							

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