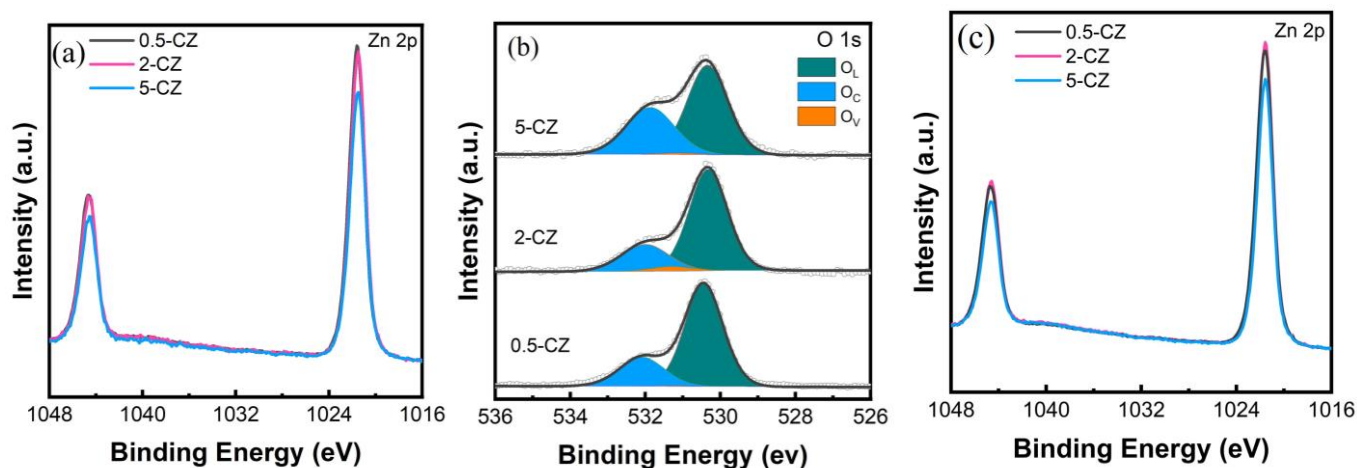


# Size Effect of Cu Particles on Interface Formation in Cu/ZnO Catalysts for Methanol Synthesis

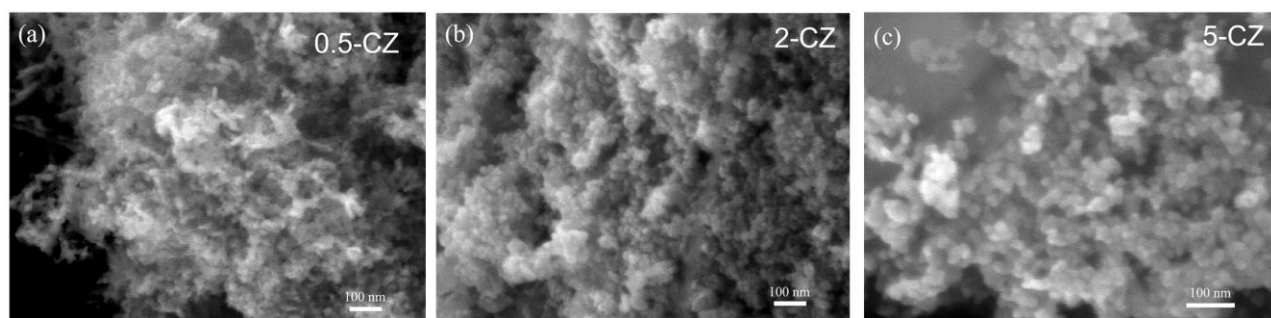
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## XPS of catalysts



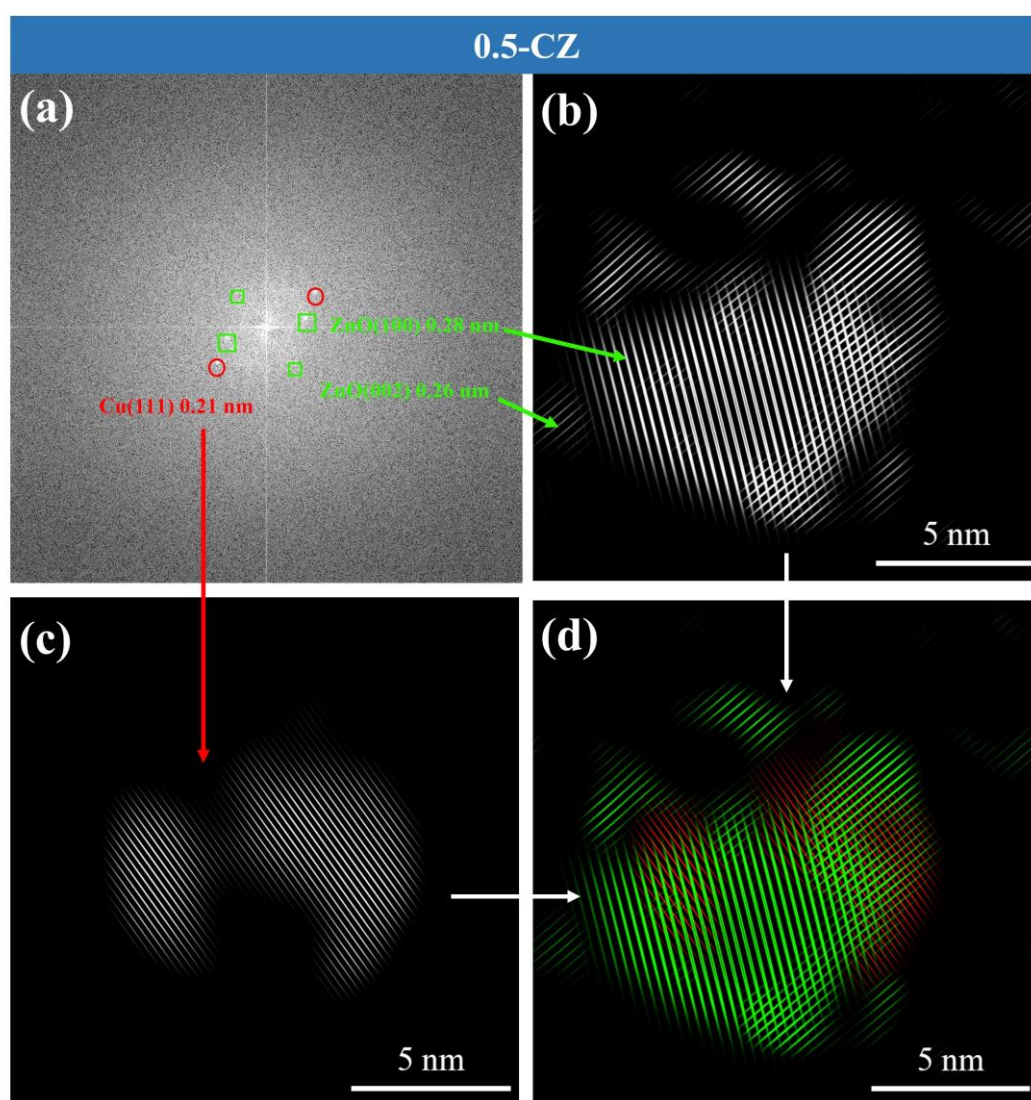
**Figure S1.** XPS spectra of (a) Zn 2p and (b) O 1s of the calcined Cu/ZnO catalysts. (c) XPS spectra of Zn 2p for reduced catalysts.

### SEM Images of Calcined Catalysts.

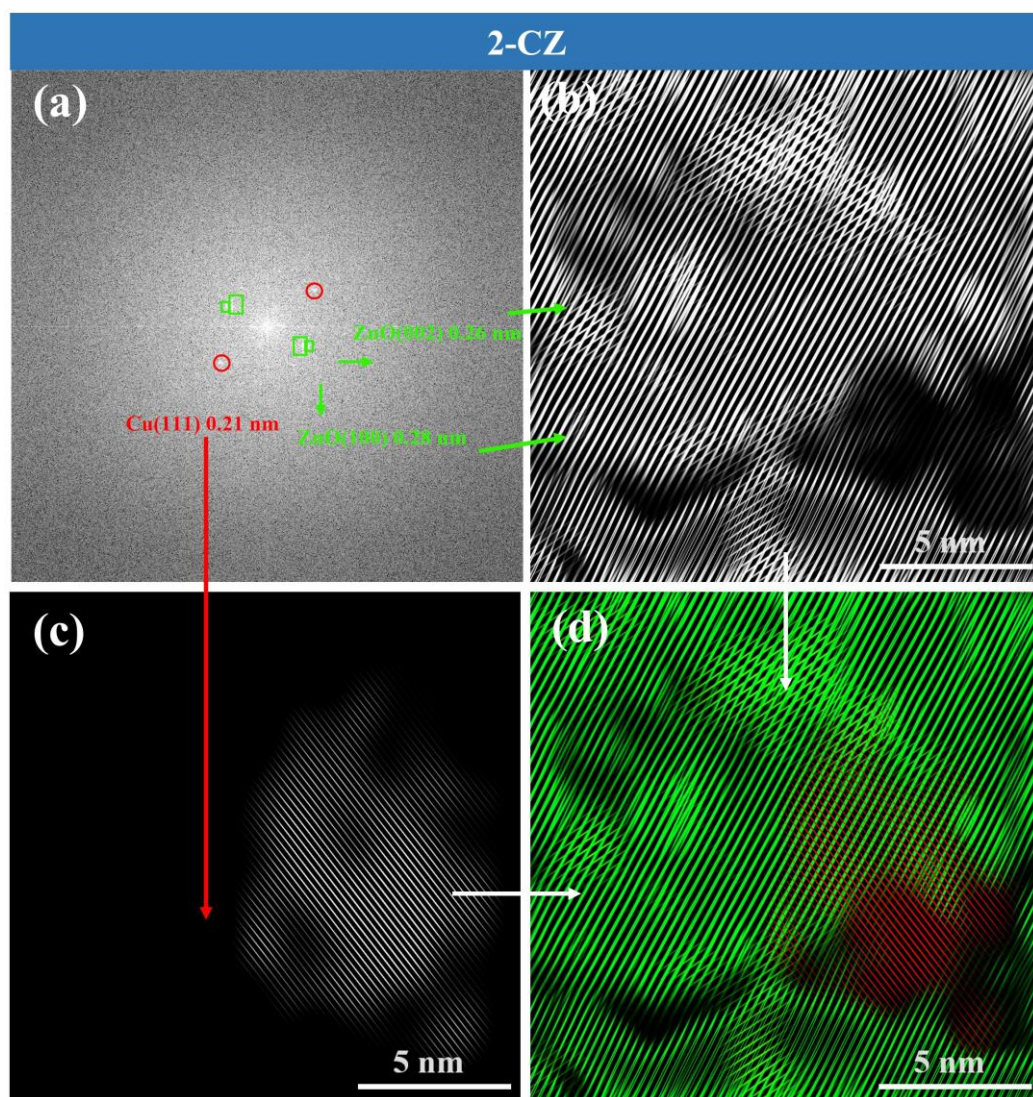


**Figure S2.** SEM images of calcined (a) 0.5-CZ, (b) 2-CZ and (c) 5-CZ catalysts.

### HR-TEM Images of Reduced Catalysts.

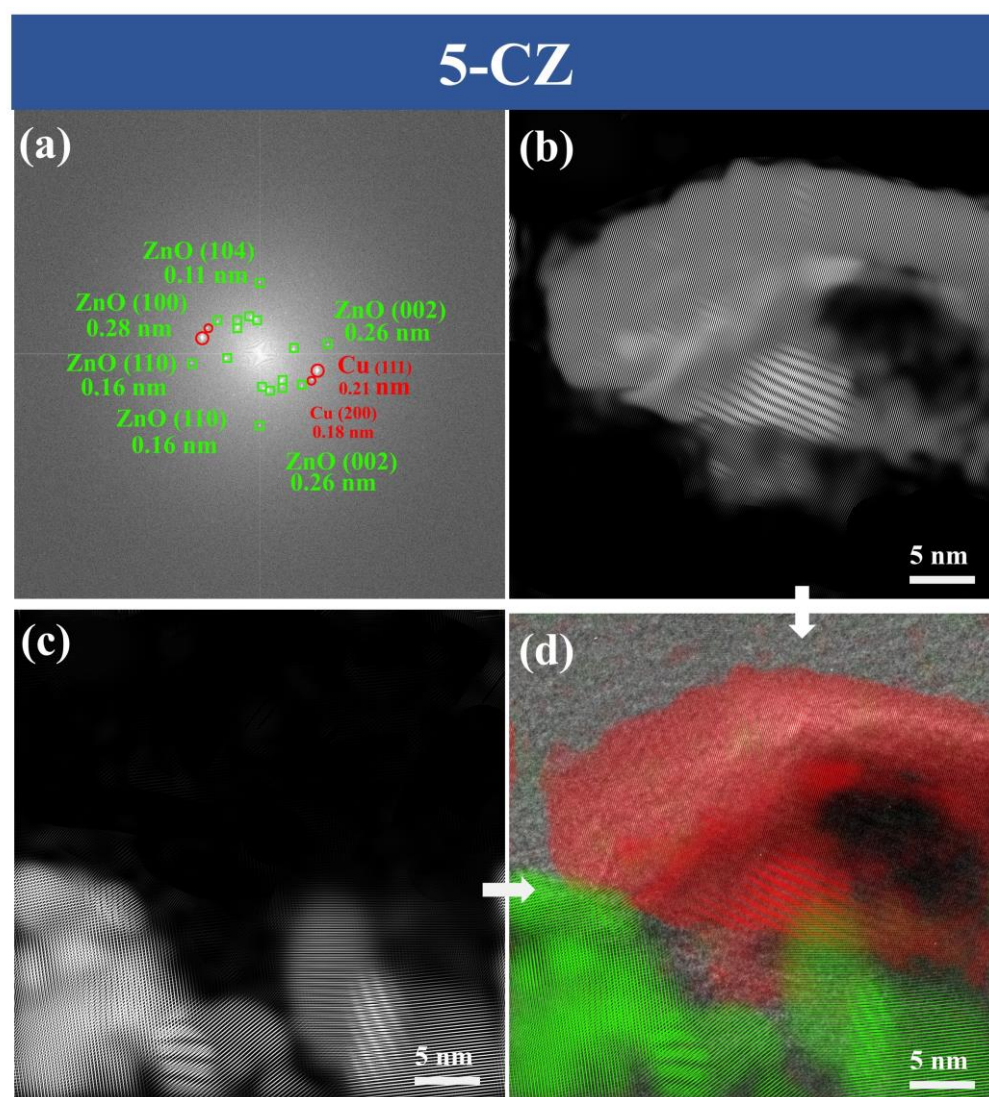


**Figure S3.** Extracted lattice features of HR-TEM Figure 4a. (a) Corresponding FFT patterns. (b-c) Fourier filtered lattice features of (b) ZnO species and (c) Cu species. (d) lattice features stained (ZnO-green, Cu-red).

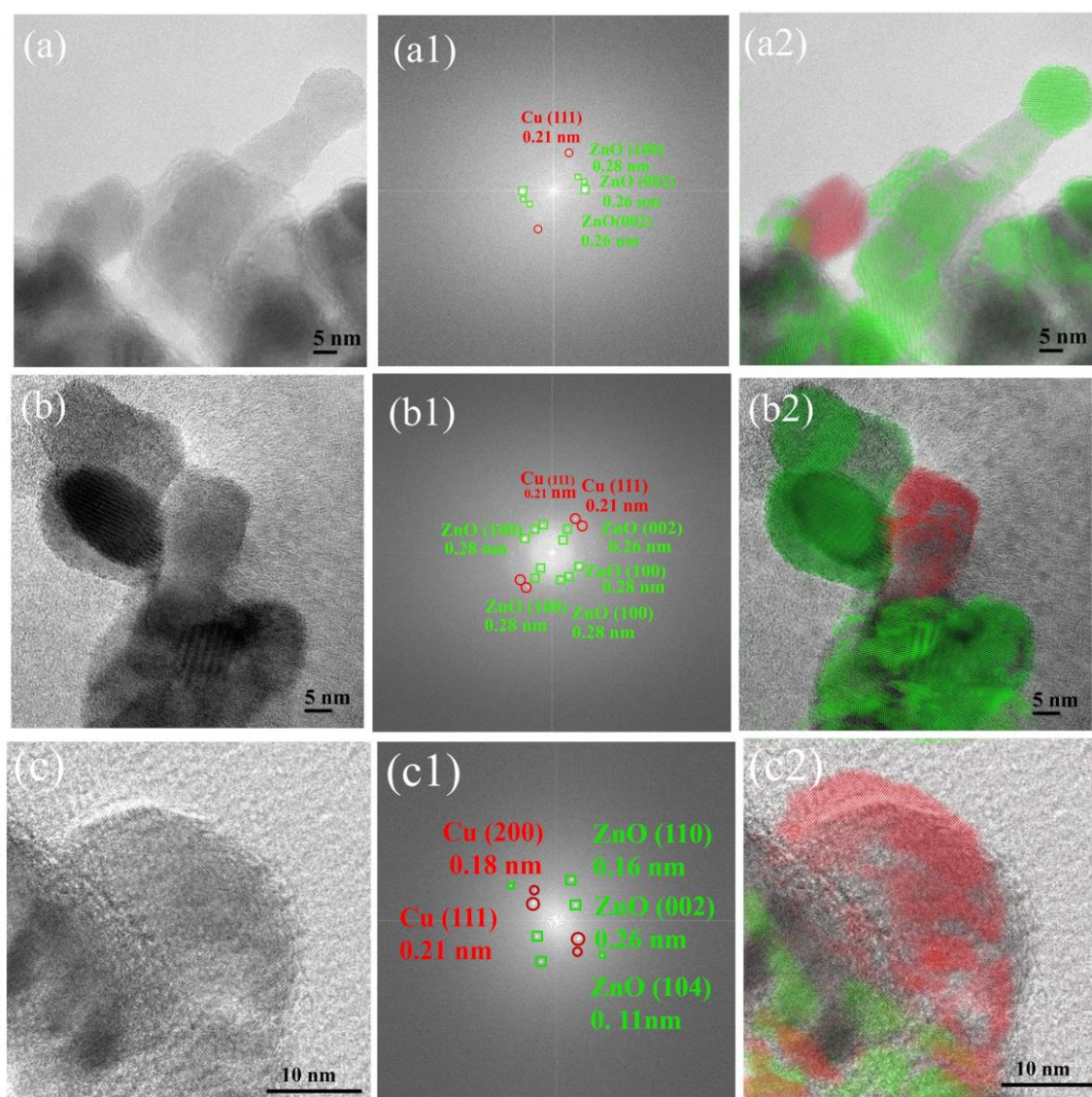


**Figure S4.** Extracted lattice features of HR-TEM Figure 4b. (a) Corresponding FFT patterns. (b-c) Fourier filtered lattice features of (b) ZnO species and (c) Cu species. (d) lattice features stained (ZnO-green, Cu-red)

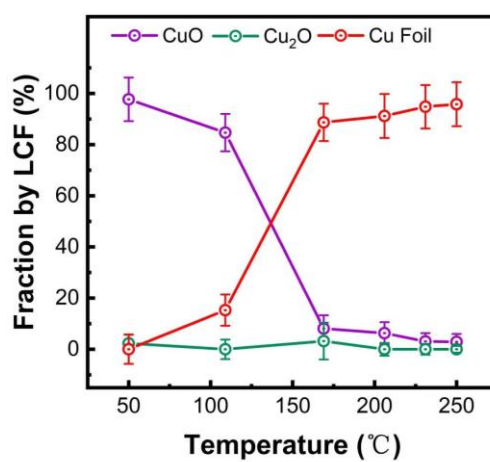




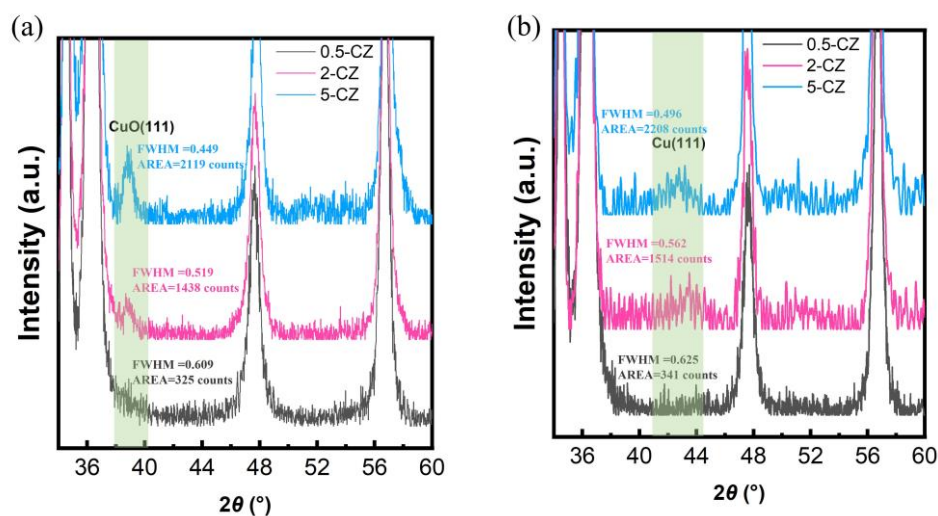
**Figure S5.** Extracted lattice features of HR-TEM Figure 4c. (a) Corresponding FFT patterns. (b-c) Fourier filtered lattice features of (b) ZnO species and (c) Cu species. (d) lattice features stained (ZnO-green, Cu-red).



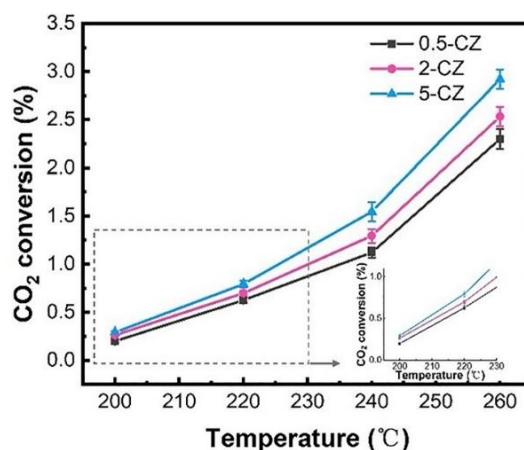
**Figure S6.** HR-TEM images for reduced Cu/ZnO catalysts (a) 0.5-CZ, (b) 2-CZ, (c) 5-CZ. (a1–c1) Corresponding FFT patterns and (a2–c2) Fourier-filtered Cu, ZnO lattice features stained (ZnO-green, Cu-red).



**Figure S7.** Comparison of the LCF (Linear Combination Fitting) results at Cu K-edge over the catalyst with 2 wt% Cu loading.



**Figure S8.** (a) XRD patterns of calcined catalysts with different Cu-loadings. (b) XRD patterns of reduced catalysts with different Cu-loadings. Each value was the standard deviation determined on the basis of at least three individual tests obtained by JADE.



**Figure S9.** CO<sub>2</sub> conversion ( $X_{\text{CO}_2}$ ) of Cu/ZnO catalysts. Error bars for the activity represent the standard deviation from at least three parallel measurements.

**Table S1.** Carbon balance of the reaction. Catalyst 50 mg, H<sub>2</sub>/CO<sub>2</sub> = 3, GHSV = 12000 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, 1 MPa.

Temperature/°C	Carbon balance of samples/%		
	0.5-CZ	2-CZ	5-CZ
200	96.5	93.7	96.6
220	92.5	96.3	96.8
240	94.2	95.0	94.2
260	93.4	97.1	98.7