

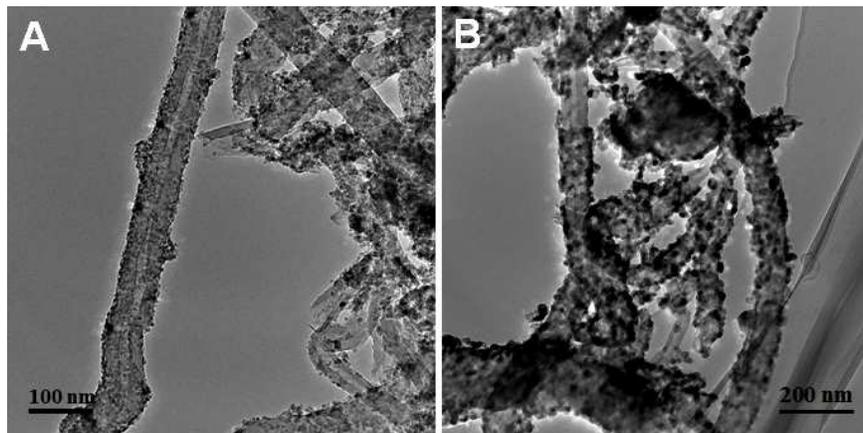
## Supporting Information

### High efficiency Cu-ZnO Hydrogenation Catalyst: the Tailoring of Cu-ZnO Interface Sites by Molecular Layer Deposition

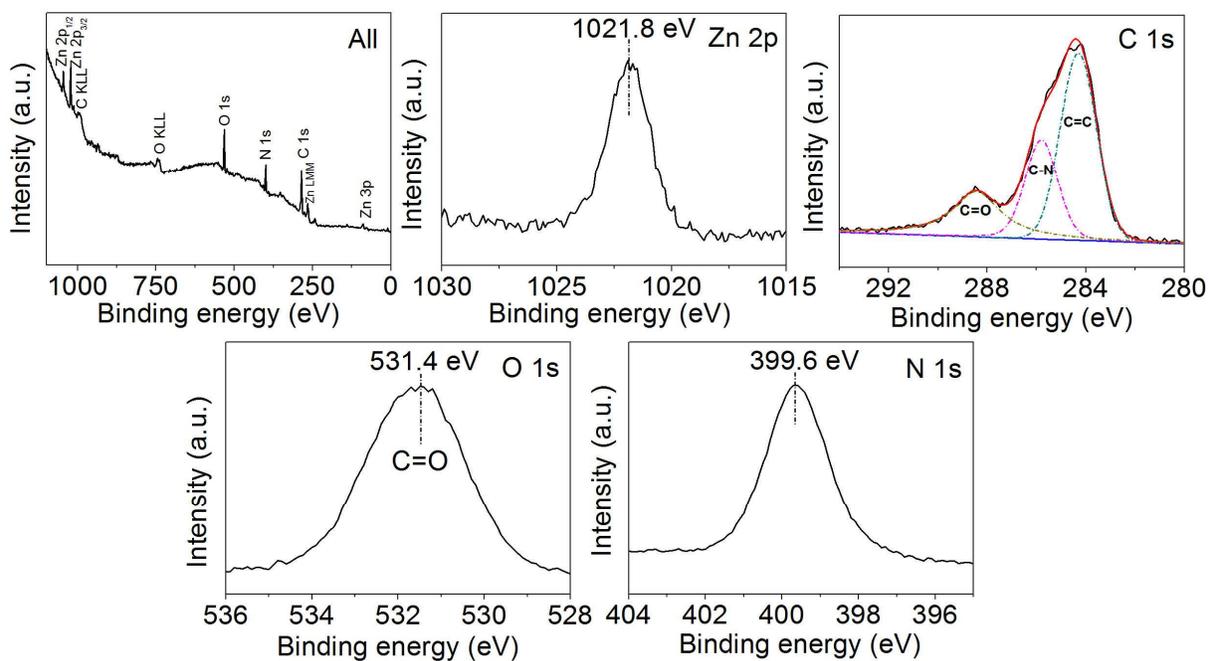
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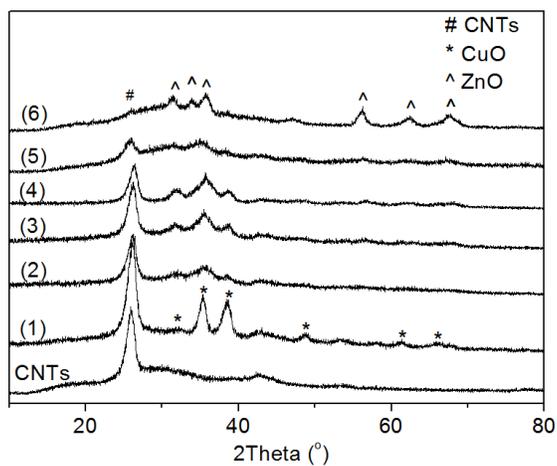
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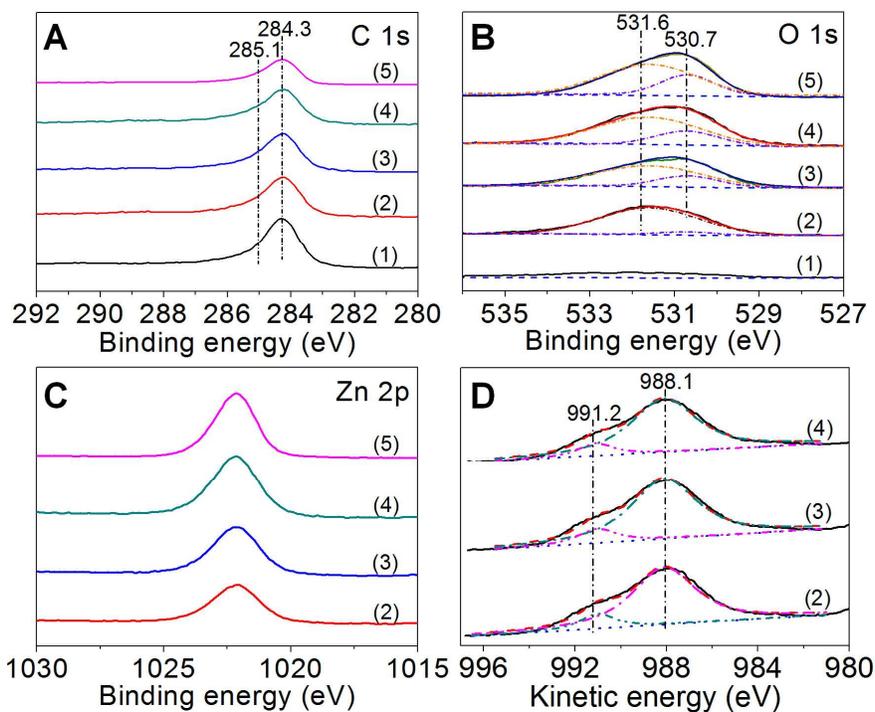
**Figure S1.** TEM images of the catalysts. (A) Cu-Zn120MLD after reductions; (B) Cu-Zn120ALD after reduction.



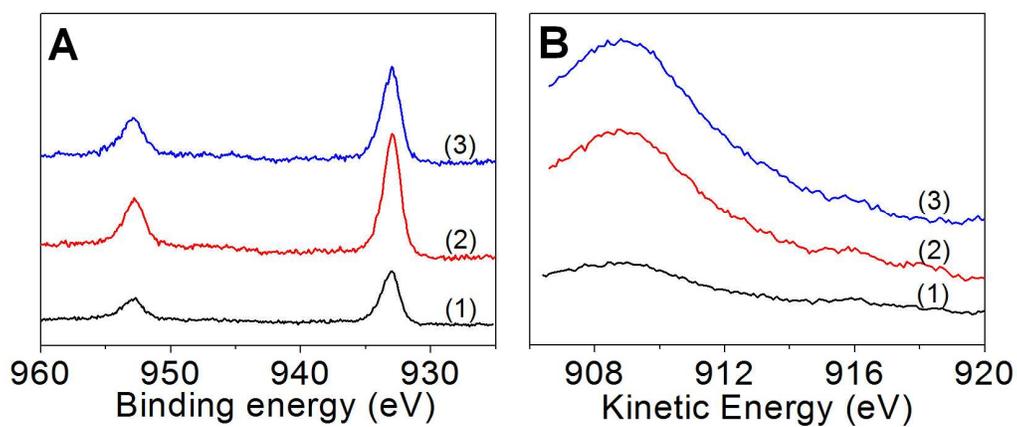
**Figure S2.** XPS spectra of Zn-hybrid film.



**Figure S3.** (A) XRD of samples after calcinations in air at 300 °C. (1) Cu/CNTs; (2) Cu-Zn40MLD; (3) Cu-Zn80MLD; (4) Cu-Zn120MLD; (5) Cu-Zn160MLD; (6) Cu-Zn120ALD.



**Figure S4.** XPS and AES of reduced catalysts: (A) XPS of C 1s; (B) XPS of O 1s; (C) XPS of Zn 2p; (D) AES of Zn LMM. (1) Cu/CNTs; (2) Cu-Zn40MLD; (3) Cu-Zn80MLD; (4) Cu-Zn120MLD; (5) Cu-Zn160MLD.



**Figure S5.** XPS and AES analysis of reduced catalysts: (A) XPS of Cu 2p, (B) AES of Cu LMM. (1) Cu-Zn40ALD; (2) Cu-Zn80ALD; (3) Cu-Zn120ALD.

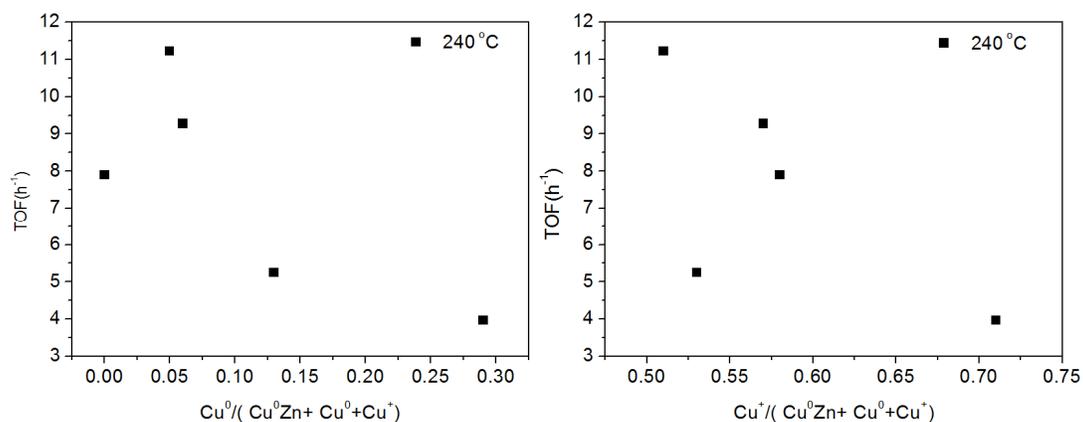


Figure S6. Correlation of the TOF of GVL yield with  $\text{Cu}^0/(\text{Cu}^0+\text{Cu}^0\text{Zn}+\text{Cu}^+)$  and  $\text{Cu}^+/(\text{Cu}^0+\text{Cu}^0\text{Zn}+\text{Cu}^+)$  for the Cu/CNTs and Cu-Zn-MLD catalysts.

**Table S1.** Physicochemical of calcinated Cu-Zn-MLD catalysts.

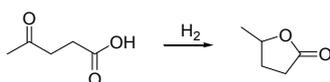
Catalyst	Composition (wt%) <sup>a</sup>	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ ) <sup>b</sup>	$V_p$ ( $\text{cm}^3/\text{g}$ ) <sup>b</sup>	$D_p$ (nm) <sup>b</sup>
	Cu			
Cu/CNTs	25.5	42.8	0.11	15.7
Cu-Zn40MLD	20.2	65.6	0.17	10.4
Cu-Zn80MLD	20.8	53.3	0.16	13.2
Cu-Zn120MLD	19.8	43.1	0.12	12.5

(a) Metal loading determined using ICP+AES; (b) BET method. The concentration of the metal in the catalyst was determined by an Induced Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Thermo iCAP 6300, USA). The BET surface area ( $S_{\text{BET}}$ ), pore volume ( $V_p$ ) and pore size distribution ( $D_p$ ) of calcined catalysts were determined via  $\text{N}_2$  physisorption at the normal boiling point of  $\text{N}_2$  ( $-196^\circ\text{C}$ ), using a Micromeritics ASAP 2020 instruments. Each sample was degassed under vacuum at  $90^\circ\text{C}$  for 1 h and  $280^\circ\text{C}$  for 6 h prior to the measurement. The pore size distribution data were obtained by fitting the DFT model for the  $\text{N}_2$  sorption isotherm. The copper composition of Cu-Zn-MLD catalysts is around 20%, while that of Cu/CNTs is 25.5%. The  $S_{\text{BET}}$  of the Cu-Zn-MLD catalysts is higher than that of Cu/CNTs, which is due to the formation of ZnO NPs on the catalyst surface.

**Table S2.** Surface composition of the reduced catalysts.<sup>a</sup>

Catalyst	Cu/Zn	Surface Composition (%)			Cu <sup>0</sup> Zn/(Cu <sup>0</sup> Zn+Cu <sup>0</sup> +Cu <sup>+</sup> ) <sup>b</sup>	Cu <sup>0</sup> /(Cu <sup>0</sup> Zn+Cu <sup>0</sup> +Cu <sup>+</sup> ) <sup>b</sup>	Cu <sup>+</sup> /(Cu <sup>0</sup> Zn+Cu <sup>0</sup> +Cu <sup>+</sup> ) <sup>b</sup>
		Cu	Zn	O			
		Cu/CNTs	—	3.4			
Cu-Zn40MLD	0.35	4.2	11.9	15.2	0.34	0.13	0.53
Cu-Zn80MLD	0.39	6.0	15.5	15.9	0.37	0.06	0.57
Cu-Zn120MLD	0.30	5.6	18.4	20.5	0.44	0.05	0.51
Cu-Zn160MLD	0.27	2.9	10.7	17.7	0.42	0.0	0.58
Cu-Zn40ALD	0.14	1.2	8.7	15.5	—	—	—
Cu-Zn80ALD	0.11	1.3	12.5	20.5	—	—	—
Cu-Zn120ALD	0.07	1.5	20.5	27.9	—	—	—

Calculated from XPS of the element; (b) Calculated from the AES results of Cu.

**Table S3.** Physicochemical properties of the catalysts and their catalytic performance for LA hydrogenation to GVL.<sup>a</sup>

Catalyst	GVL yield %	S <sub>Cu</sub> <sup>b</sup> m <sup>2</sup> /gCat.	TOF <sup>c</sup> h <sup>-1</sup>	E <sub>a</sub> <sup>d</sup> KJ/mol
Cu/CNTs	21.7	23.0	4.0	38.9
Cu-Zn40MLD	31.9	25.6	5.2	33.1
Cu-Zn80MLD	56.5	25.6	9.3	15.1
Cu-Zn120MLD	75.2	28.2	11.2	16.2
Cu-Zn160MLD	63.7	33.3	7.9	19.1
Cu-Zn40ALD	27.6	13.8	8.4	—
Cu-Zn80ALD	34.2	14.6	9.8	—
Cu-Zn120ALD	32.4	18.4	7.4	—
Cu/CNTs-Pre	46.7	41.6	4.7	—
Cu-Pre-Zn120MLD	80.7	36.5	9.3	—
Cu-Zn-Al (MWC-612) <sup>e</sup>	71.4	198.4	3.0	—

(a) Reaction conditions: 0.02g Catalyst, H<sub>2</sub>/LA=70, 240 °C, 1 MPa, P<sub>H2</sub>/P<sub>N2</sub>=0.5, catalysts were reduced at 300 °C in in H<sub>2</sub>/N<sub>2</sub> before testing; (b) surface area of Cu<sup>0</sup> determined by N<sub>2</sub>O titration; (c) Turnover frequency (TOF) was calculated as moles of GVL formation per mole of surface copper at WHSV=1.2 h<sup>-1</sup> in the initial 2 h; (d) The apparent activation energy (E<sub>a</sub>) was calculated from Arrhenius plots between 180 °C and 240 °C; (e) 0.01g Catalyst, H<sub>2</sub>/LA=70, 240 °C, 1 MPa, P<sub>H2</sub>/P<sub>N2</sub>=0.5, catalysts were reduced at 300 °C in in H<sub>2</sub>/N<sub>2</sub> before testing. Cu/CNTs-Pre was prepared by a direct precipitation method using sodium hydroxide as precipitant. Firstly, 0.150 g treated CNTs were added into the aqueous solution of copper nitrates (0.152 g) at room temperature. Then, the 1 M NaOH solution was added into the copper solution at room temperature. The final pH of the solution is 9.5. Then, the solution was stirred for 0.5 h, filtered, washed with deionized water, dried at 80 °C, and then calcined at 350 °C for 2 h. The Cu-Pre-Zn120MLD was prepared by the same pathway as Cu-Zn120MLD by using Cu/CNTs-Pre as precursor.

Table S4 Uncertainties on experimental data points of Arrhenius plot for LA hydrogenation.

Samples	Statistics
	R-Square
Cu/CNTs	0.95
Cu-Zn40MLD	0.98
Cu-Zn80MLD	0.99
Cu-Zn120MLD	0.97
Cu-Zn160MLD	0.95