## **Electronic supplementary information**

## Nitrogen-doped carbon nanotube confined CuCo alloy nanocatalysts for the one-

## pot conversion of levulinic acid to 1,4-pentanediol

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#### **Materials and Methods**

#### Synthesis of Co@CN

3.49 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 3.94 g 2-methylimidazole were dissolved in 60 mL methanol, respectively. Then the 2-methylimidazole methanol solution was quickly poured into the methanol solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and stirred at room temperature for 20 h. After stirring, solids were separated by centrifugation and washed with anhydrous ethanol for 4 times and dried at 60 °C for 24 h. The obtained purple powder was ZIF-67 precursor. The ZIF-67 precursor was heated to 400 °C in 10%H<sub>2</sub>/Ar atmosphere at a rate of 2 °C/min and maintained for 2 h. Heating to 700 °C for 1 h with the same heating rate and cooling to room temperature, the samples obtained were recorded as Co@CN.

### Synthesis of CuCo@N-CNT

The 0.1 g Co@CN was dispersed into 7.5 mL n-hexane with 10 min ultrasonic treatment. 200  $\mu$ L of 1.39 M Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O aqueous solution was added into n-hexane. The solid sample was dispersed by 120 min powerful ultrasonic treatment. After centrifuge, dried in a vacuum oven at 60 °C for 24 h and the powder sample was labeled as 0.5Cu<sup>2+</sup>/Co@CN. In addition, the same method was used to prepare 0.2Cu<sup>2+</sup>/Co@CN, 1.0Cu<sup>2+</sup>/Co@CN, and 2.0Cu<sup>2+</sup>/Co@CN with 0.56 M, 2.79 M, and 5.58 M Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O aqueous solution, respectively.

The obtained catalyst precursor 0.5  $Cu^{2+}/Co@CN$  was reduced at 300 °C for 2 h at a rate of 2 °C·min<sup>-1</sup> in 10% H<sub>2</sub>/Ar atmosphere, and the samples obtained was labeled as 0.5CuCo@N-CNT. The catalyst 0.2CuCo@N-CNT, 1.0CuCo@N-CNT, and

2.0CuCo@N-CNT was obtained by using the same method.

# Synthesis of Cu/CN

0.5Cu/CN was obtained by the following processing: 0.6 g Co@CN catalyst was added into 120 mL 6 M HNO<sub>3</sub> solution, and reflux at 120 °C for 6 h, black solid was collected by centrifugation. The black solid was washed with deionized water and anhydrous ethanol for several times, and dried at 60 °C for 24 h. The black solid powder finally obtained was recorded as CN. 0.5Cu/CN catalyst was obtained using the same immerse method as 0.5CuCo@N-CNT.

#### **Instruments and measurements**

TEM (Transmission Electron Microscopy) was used to characterize the morphology and structure of catalyst by the Hitachi H-9500. XRD (X-ray diffraction) was used to analyze the crystal structure of the samples by the D8 Advance instrument of Brock Company in Germany, and used Cu K $\alpha$  ray ( $\lambda$ =0.15418 nm) as the radiation source. The pore structure and surface parameters of the samples were measured by Micromeritics ASAP 2020 physical adsorption instrument. Before sample measurement, samples were pretreated at 300 °C vacuum degassing for 5 h. NH<sub>3</sub>-TPD (NH<sub>3</sub>-temperature programmed desorption) analysis was performed by Micromeritics AutoChem 2920 chemisorption equipped with TCD detector. XRF (X-ray fluorescence) was used to analyze the elemental composition on the surface of samples by shimadzu XRF-1800. XPS (X-ray photoelectron spectrometer) was used for qualitative analysis of chemical composition and chemical states on the surface of samples with ESCALAB Xi+ XPS produced by Thermo Phillips Technology Co..

#### Catalyst tests

The activity evaluation experiment of catalysts was carried out in a stainless steel autoclave with an effective volume of 35 mL PCF0035-15 produced by Yantai Keri Chemical Equipment Co., LTD. 80 mg LA, catalyst and 20 mL 1,4-dioxane were introduced into autoclave, and then the autoclave was installed and its air tightness was tested,  $N_2$  was used to purge the air for three times, then  $H_2$  with a certain pressure was filled into the autoclave. Start stirring at 500 rpm and heating, after heating to the setting temperature, start timing. After keeping a certain reaction time under the reaction conditions, stop heating and quickly cool down with ice bath to end the reaction. After the reactor was cooled to room temperature, the reaction liquid was collected. The collected reaction liquid was filtered by a 0.22 µL organic filter for chromatographic analysis. The reaction liquid was analyzed subsequently with Aglient GC7820A equipped with HP-FFAP column.

Using a recycle experiment to evaluate the stability of the catalyst. Every time after the reaction, catalyst was collected by magnet and washed several times with reaction solvent, and then dried at 70 °C overnight, applied directly to the next cycle experiment without further roasting or reduction.



Fig. S1 The  $N_2$  adsorption-desorption isotherms (a) and pore size distribution (b) of

the

different

catalysts.



Fig. S2 SEM images of ZIF-67 (a) and Co700@NC (b), TEM images of 0.5CuCo@N-

CNT (c), TEM images of Co@CN (d-f) and TEM images of Cu/CN.



Fig. S3 TEM mapping of 0.5CuCo@N-CNT.



Fig. S4 raman spectra of 0.5CuCo@N-CNT (a), XRD patterns of ZIF-67 (b) and bimetallic CuCo@N-CNT catalysts with different Cu/Co ratios (c).



Fig. S5 The survey XPS spectra (a), Cu LMM profiles (b), C 1s(c) and N 1s(d) of the different catalysts.

Samples	Content of different elements (at.%) <sup>a</sup>					Content of different Cu types (at.%) <sup>b</sup>		
	С	N	0	Co	Cu	$\mathrm{Cu}^0$	Cu <sup>+</sup>	
Co@CN	88.0	1.0	8.5	2.5	-	-	-	
0.5CuCo@N-CNT	79.8	0.8	15.6	2.3	1.5	57.6	42.4	
Cu/CN	87.2	2.7	8.6	-	1.5	63.8	36.2	

# Table S1 The results of XPS analysis

<sup>a</sup> Determined by XPS.

<sup>b</sup> Determined by Cu LMM.



**Fig. S6** NH<sub>3</sub>-TPD profiles of bimetallic CuCo@N-CNT catalysts with different Cu/Co ratios.

Catalysts	Cu/Co molar ratio <sup>a</sup>	$S_{BET}$ $(m^2/g)^b$	$V_p$ $(m^{3/g})^b$	D <sub>p</sub> (nm) <sup>b</sup>	Total (mmol NH <sub>3</sub> /g)°
Co@CN	-	286.1	0.48	6.7	0.4
0.2CuCo@ N-CNT	0.2	215.1	0.38	7.0	2.3
0.5CuCo@ N-CNT	0.5	189.4	0.33	7.0	2.9
1.0CuCo@ N-CNT	1.0	160.2	0.28	7.0	2.2
2.0CuCo@ N-CNT	1.8	132.5	0.20	6.1	2.4
Cu/CN	-	224.7	0.24	4.2	0.1

 Table S2 Physicochemical properties of the different catalysts

<sup>a</sup> Determined by XRF.

 $^{\rm b}$  Determined by  $N_2$  adsorption.

<sup>c</sup> Determined by NH<sub>3</sub> chemisorption



Fig. S7 The time-dependence experiment results (a), the effect of reaction temperature (b),  $H_2$  pressure (c) and catalyst loading (d) on the catalytic performance of 0.5CuCo@N-CNT.



Scheme 1 The possible reaction pathway for one-pot conversion of LA to 1,4-PDO.



Fig. S8 Reusability of 0.5CuCo@N-CNT (Reaction conditions: 80 mg LA, 20 mg catalyst, 20 mL 1,4-dioxane, 160 °C, 5 MPa H<sub>2</sub>)



Fig. S9 The XRD patterns (a) and NH<sub>3</sub>-TPD profiles (b) of the fresh and used 0.5CuCo@N-CNT.





Fig. S10 GC spectrum of standard compound with internal standard hexyl alcohol dissolved in isopropanol: Levulinic acid (a),  $\gamma$ -valerolactone (b), 1,4-pentanediol (c), 2-methyltetrahydrofuran (d) and valeric acid (e).