

# Supplementary Information

## Catalytic Hydrogenation of Levulinic Acid for the Preparation of $\gamma$ -

### Valerolactone by CuAgZrO<sub>2</sub>-graphene Nanocomposite

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## 1 Experimental

### 1.1 Chemicals

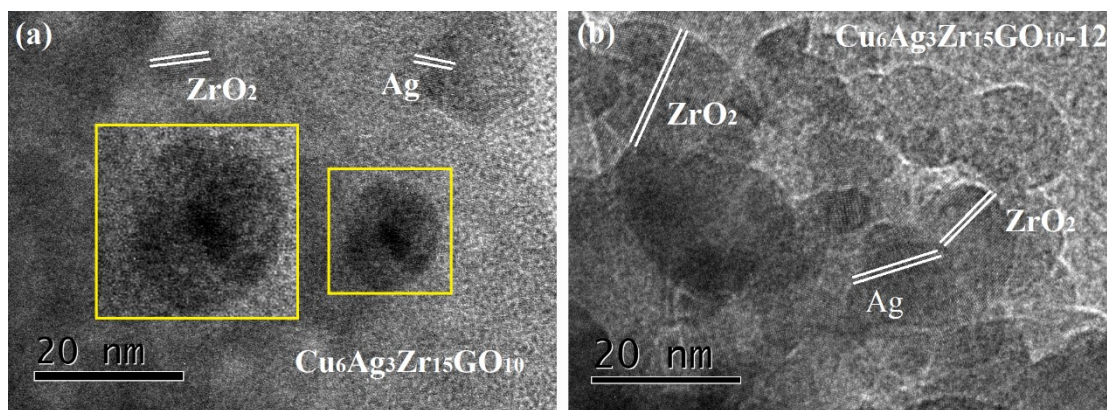
LA (98%), GVL (98%), and triethylene glycol dimethyl ether (TGDE, 99.8%) were purchased from Beijing Bailingwei Technology Co., Ltd. Graphite (99.95%, Z325 mesh) was obtained from Aladdin Chemical Reagent Co., Ltd (China). AgNO<sub>3</sub> (AR), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (AR), Zr(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O (AR), NaOH (AR), and ethanol (99.7%) were supplied by Tianjin Kermel Chemical Reagent Co., Ltd (China).

### 1.2 Characterization

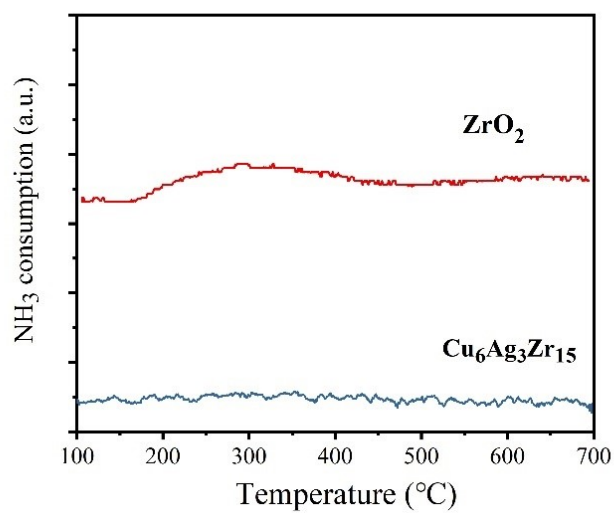
The particle size and morphology of the catalyst were characterized by using transmission electron microscopy (TEM, Tecnai F30 system at 300 kV) and high-resolution TEM (HRTEM) analyses. X-ray photoelectron spectroscopy (XPS) was conducted with an ESCALAB-250 photoelectron spectrometer using an Al K $\alpha$  monochromatic X-ray source. The spectra were calibrated with the C 1s peak at 284.6 eV and mathematically analyzed by using the XPSPEAK41 software. X-ray diffraction (XRD) analysis of the catalysts was performed on an X-ray diffractometer (M/s. Rigaku Corporation, Japan) at 30 kV and 15 mA with Ni-filtered Cu-K $\alpha$  radiation. Metal-leaching analysis was carried out using an inductively coupled plasma-optical emission spectroscopy (ICP-OES) instrument (Optima 7000 DV, PerkinElmer Ltd) to measure the metal content in the solution. The reduced properties of the metal oxides on the catalysts were analyzed by on an AutoChem II 2920 chemisorption analyzer. For each test, 50 mg of the sample was dried in Ar and reduced in 5 vol.% H<sub>2</sub>/Ar gas mixture (30 mL/min) at a linear heating rate of 10 °C/min. The acidic sites in the catalysts were determined on an AutoChem II 2920 chemisorption analyzer, too. The samples were saturated with NH<sub>3</sub>, and the excess was purged at 100 °C, after which the temperature was ramped up to 800 °C at a rate of 10 °C/min, and the amount of desorbed NH<sub>3</sub> was determined using a TCD detector.

### 1.3 Performance measurement

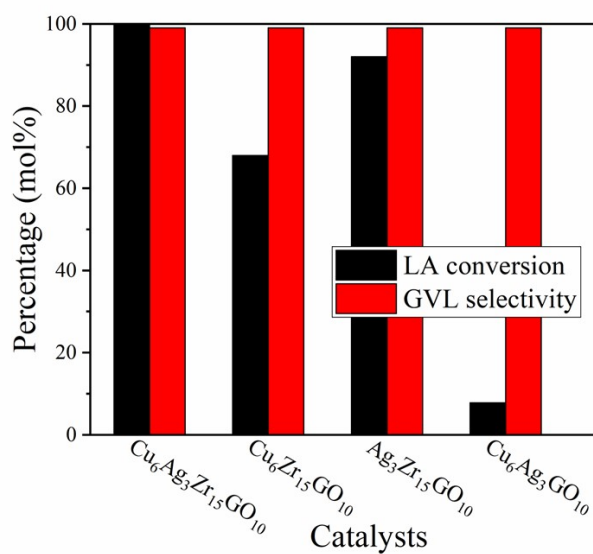
The products were analyzed by a gas chromatograph (Agilent GC7820) with a flame ionization detector (FID) using a PEG2W capillary column and H<sub>2</sub> as a carrier gas. The results were quantified as LA conversion ( $C_{LA}$ ), GVL selectivity ( $S_{GVL}$ ), and yield ( $Y_{GVL}$ ) in mol% on the basis of the initial molar amount of LA. Repeated runs showed that data variation was in the range of  $\pm 2\%$  (relative value). Overall carbon balance in the products was  $> 98\%$ .



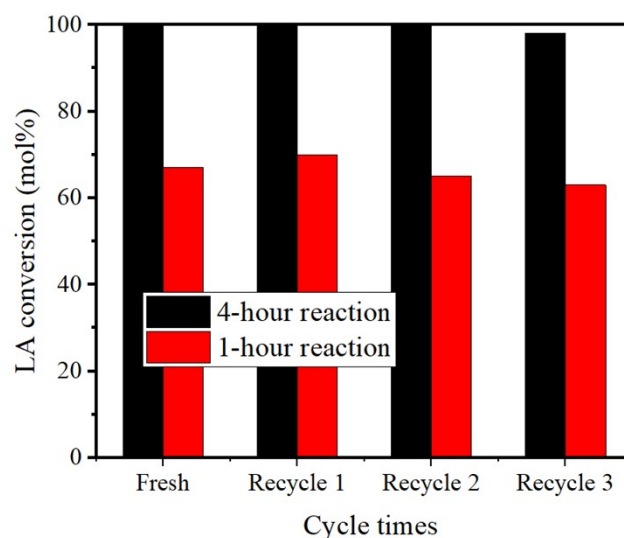
**Fig. S1** HRTEM images of  $\text{Cu}_6\text{Ag}_3\text{Zr}_{15}\text{GO}_{10}$  and  $\text{Cu}_6\text{Ag}_3\text{Zr}_{15}\text{GO}_{10-12}$ .



**Fig. S2**  $\text{NH}_3$ -TPD analysis of  $\text{ZrO}_2$  and  $\text{Cu}_6\text{Ag}_3\text{Zr}_{15}$ .



**Fig. S3** Results of LA hydrogenation over different catalysts (Reaction conditions: 200 mg LA in 8 mL water, catalyst loading = 100 mg, 3MPa  $\text{H}_2$ , 200  $^\circ\text{C}$ , 4h.)



**Fig. S4** Results of cyclic reaction of the  $\text{Cu}_6\text{Ag}_3\text{Zr}_{15}\text{GO}_{10}$  catalyst (Reaction conditions: 200 mg of LA in 8 mL water, catalyst loading = 100 mg, 3 MPa  $\text{H}_2$ , 200 °C, with black stripes corresponding to 4-hour batch reactions and red stripes corresponding to 1-hour batch reactions).

Table S1 Crystallite sizes of the  $\text{Cu}_6\text{Ag}_3\text{Zr}_{15}\text{GO}_{10}$  catalyst calculated by Scherrer equation from X-ray powder diffraction measurement <sup>a</sup>

Component	FWHM (rad)	$\theta$ (°)	D (nm)
Ag	0.0113	19.04	12
ZrO <sub>2</sub>	0.0124	15.12	11

$$D = \frac{K\lambda}{FWHM * \cos\theta} \quad (\text{Equ. S1})$$

D — crystallite size, nm ;

FWHM — full width at half-maximum of the diffraction peak, rad ;

K — a parameter, 0.9;

$\lambda$  — wavelength of the radiation , 0.15406 nm;

$\theta$  — Bragg angle, °.