

Supporting Information

Levulinic Acid Hydrogenation to γ -Valerolactone over Single Ru Atoms on TiO₂@Nitrogen Doped Carbon Support

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1. Experimental

1.1 Chemicals

The Tetra-*n*-butyl-titanate (TBOT)(98.0%, AR grade), *N,N*-Dimethylformamide (DMF)(99.5%, AR grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. MeOH (>99.9%, HPLC grade) was obtained from Energy Chemical, 2-aminoterephthalic acid (99%, AR grade) was provided Alfa Aesar. RuCl₃ (99%, AR grade), **Terephthalic acid (99%, AR grade)** and **Titanium oxide (99%, AR grade)** were obtained from Beijing InnoChem Science & Technology Co., Ltd. H₂ and N₂ were purchased from Shanghai Chemical Industry Park Pujiang Special Gas Co., Ltd. All the chemicals were used as received without further purification.

1.2 Catalyst preparation

Ru@NH₂-MIL-125 (Ti): Tetra-*n*-butyl-titanate (1.4 g, 4 mmol), 2-aminoterephthalic acid (1.1 g, 6 mmol) and RuCl₃ (10.2 mg, 0.04 mmol) were dissolved in 100 mL of DMF/MeOH (V/V, 9/1). The mixture was stirred at room temperature for 2 h and was placed in an oil bath and heated to 393 K for 48 h. A yellow powder of Ru/NH₂-MIL-125 (Ti) was isolated by centrifugation. Then the powder was washed three times with DMF and dried under vacuum at 373 K overnight.

Ru@MIL-125 (Ti): **A gray powder of Ru@MIL-125 (Ti) was synthesized in accordance with the synthesis of Ru@NH₂-MIL-125 (Ti), expect that the same molar amount of terephthalic acid was used instead of 2-aminoterephthalic acid.**

Ru/TiO₂@CN: The powder of Ru/NH₂-MIL-125 (Ti) was placed in a tube furnace and then heated to 973 K at a heating rate of 2 °C/min, and then kept for 2 h under a flowing nitrogen atmosphere. After cooling to room temperature, the black powder was collected for future use. **For comparison, the catalysts of Ru/TiO₂@CN-500 and Ru/TiO₂@CN-900 were prepared by the same procedures for preparing the Ru/TiO₂@CN catalyst except the calcination temperature was 773K and 1173K.**

Ru/TiO₂@C: The black powder of Ru/TiO₂@C was obtained by calcining Ru@MIL-125 (Ti) powder, and the heating program was the same as synthesize Ru/TiO₂@CN.

TiO₂@CN: The black powder of TiO₂@CN was synthesized following the same procedures to synthesize Ru/TiO₂@CN, the main difference was that RuCl₃ was not added.

Ru(0.14wt%)/TiO₂: Anatase TiO₂ (0.5 g) was added into 10 mL deionized water, RuCl₃ (1.77 mg) was dissolved in 10 mL deionized water. While stirring. The RuCl₃ aqueous solution was added dropwise to the titanium oxide suspension. After stirring for 24 h at room temperature, the excess water was evaporated at 60 °C under vacuum to collect the gray powder. The catalyst was reduced at 400 °C for 2 h in 10% H₂/Ar flow.

1.3 Catalytic reaction

The hydrogenation of levulinic acid (LA) was carried out in a Teflon-lined stainless steel reactor of 16 mL with mechanical stirring at approximately 800 rpm. In a typical experiment, 10 mg of catalyst, 58 mg (0.5 mmol) LA and 1 mL of deionized water were added into the reactor. The reactor was purged with H₂ three times, and finally sealed at a H₂ pressure of 6 MPa. After suitable reaction time, the stirring was stopped. The liquid phase was separated from the catalyst by filtration through a Nylon membrane (Whatman, Φ13 mm×0.45 μm). The combined liquid mixture was then analyzed on a HPLC (Waters 2695) equipped with an Aminex HPX-87H column, with a UV/Visible detector (Waters 2489) and a Refractive Index Detector (Waters 2414), and the mobile phase was 5 mM sulfuric acid at a flow rate of 0.7 mL/min. Identification of the products were conducted on GC/MS (Agilent 7890B GC+ 5977A MSD).

In the recycle experiment, the catalyst was separated from solution by filtrate through a Nylon membrane (Φ50mm×0.2 μm). The catalyst was washed by ethanol several times, and then dried at 333 K overnight. The recovered catalyst was used for the next cycle.

1.4 Characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using Cu K α radiation at 35 kV and 25 mA ($\lambda = 1.5405 \text{ \AA}$) over a 2θ ranging from 5 °C to 90 °C at a scanning speed of 5°/min. The crystal morphology and size were determined by scanning electron microscopy (SEM) on a Hitachi S-4800 microscope and transmission electron microscopy (TEM) on a JEOL JEM-2100 microscope at an accelerating voltage of 200 kV. The high angle annular dark-field scanning TEM (HAADF-STEM) were operated at 300 kV by a JEOL Grand ARM 300F. The Ru and Ti contents were quantified by inductively coupled plasma emission spectrometer (ICP-OES) on an Optima 8300. X-ray photoelectron spectroscopy (XPS) was worked with Al K_{α} ($h\nu = 1486.36 \text{ eV}$) radiation with a Thermo Scientific K-Alpha spectrometer. Nitrogen sorption isotherms were obtained at 77K by using a BEL-SORP-MAX instrument after degassing the samples for 8 h under vacuum at 473 K. The surface areas were calculated by the BET method. ¹H NMR spectroscopy was acquired on a Bruker Advance 500MHz spectrometer. Raman spectroscopy was collected by using Shimadzu LabRAM HR Evolution with laser excitation at 633 nm. Fourier Transform Infrared Spectra (FT-IR) was performed on a Thermo Scientific Nicolet NEXUS670 FT-IR microscope. XAFS spectra at the Ru K-edge (22117 eV) were measured at the beamline 1W1B station of Beijing Synchrotron Radiation Facility (BSRF, 2.5 GeV, 250 mA, monochromatized with Si(111) double-crystals). The resulting spectra were energy-calibrated, background corrected, and normalized at the height of the edge step using the Athena program from the iFeffit® software suite (B. Ravel, M. Newville, J. Synchrotron Radiat. 2005, 12, 537). Fourier transformations were performed from 3 to 14 \AA^{-1} .

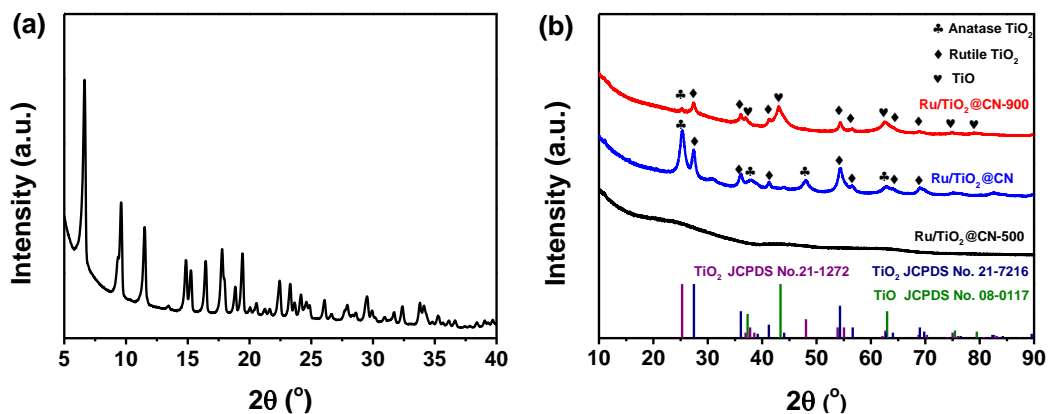


Figure S1. XRD pattern of (a) Ru/NH₂-MIL-125(Ti) and (b) Ru/TiO₂@CN-500 and Ru/TiO₂@CN-900.

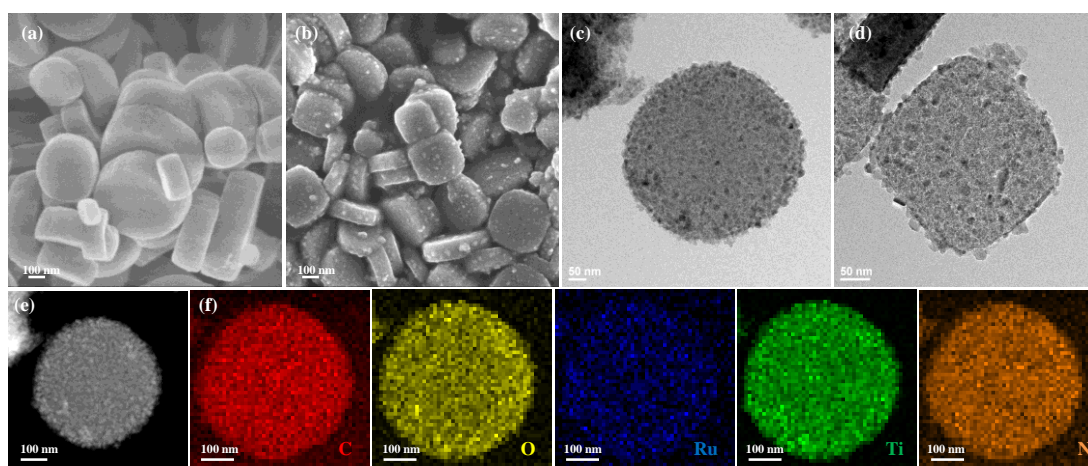


Figure S2. SEM and TEM images of the samples. SEM images of (a) Ru/NH₂-MIL-125(Ti) and (b) TiO₂@CN, TEM images of (c) Ru/TiO₂@CN and (d) TiO₂@CN. (e) HAADF-STEM and (f) elemental mapping results of Ru/TiO₂@CN.

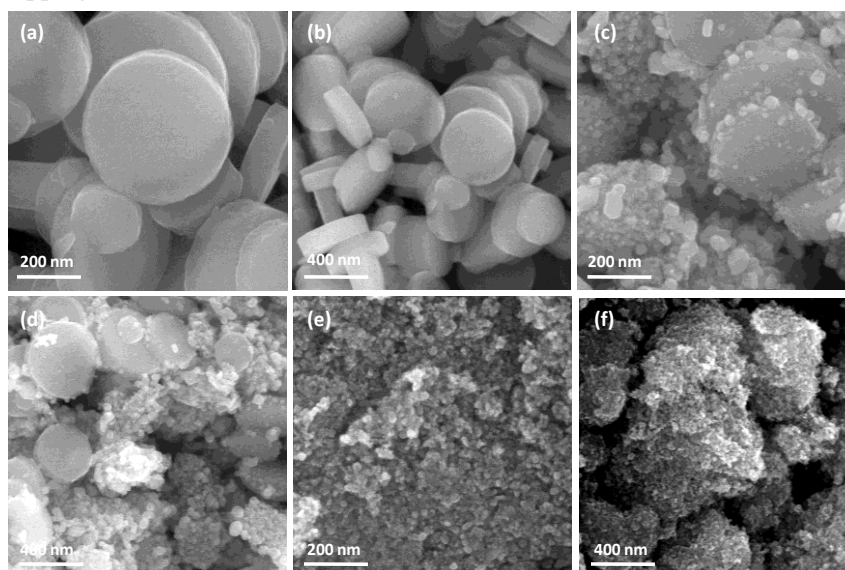


Figure S3. SEM images of (a and b) Ru/TiO₂@CN-500, (c and d) Ru/TiO₂@CN-900 and (e, f) Ru/TiO₂@C.

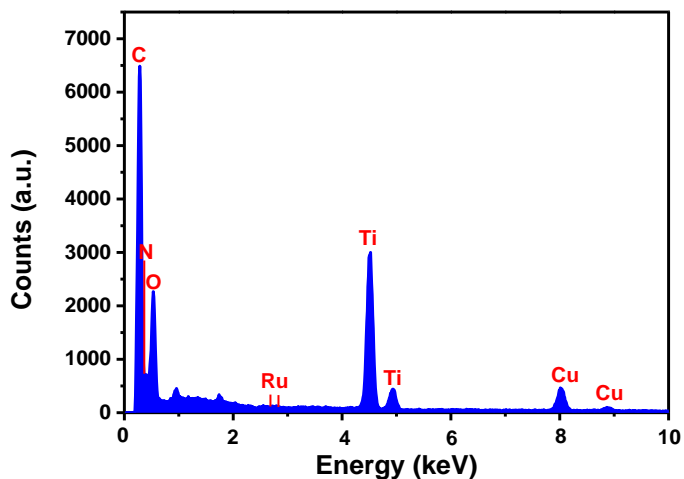


Figure S4. The EDX images of the Ru/TiO₂@CN catalyst.

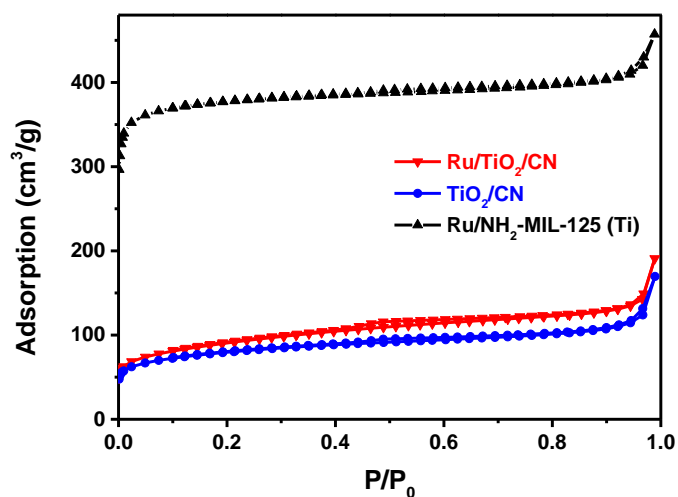


Figure S5. N₂ adsorption–desorption isotherms of different materials.

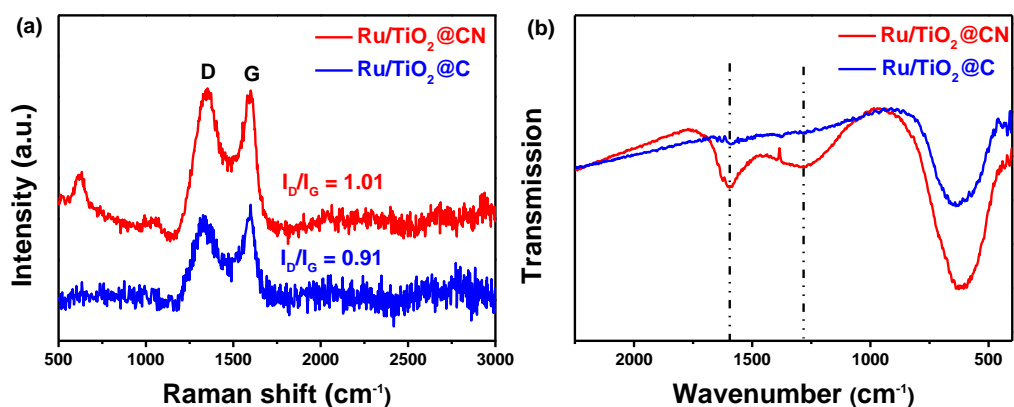


Figure S6. Raman spectra for Ru/TiO₂@CN and Ru/TiO₂@C. (b) FT-IR spectra of Ru/TiO₂@CN and Ru/TiO₂@C.

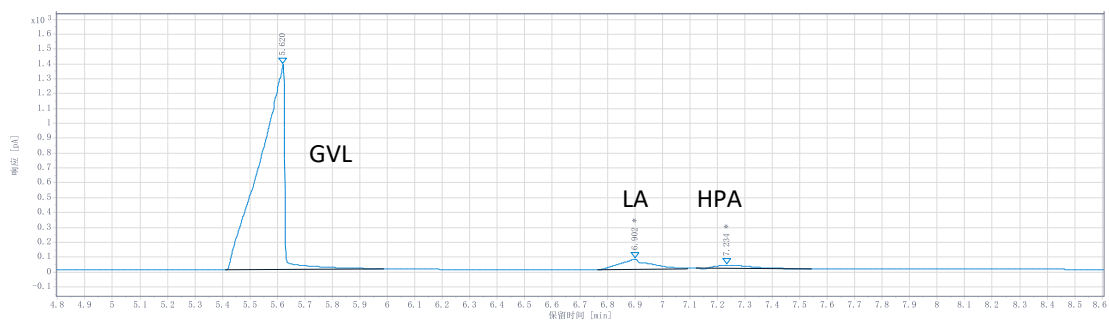


Figure S7. Gas chromatogram result of the transformation of LA at 10 h.
Reaction conditions: LA (0.5 mmol), Ru/TiO₂@CN (10 mg), D₂O (1 mL), 30 °C, H₂ (6 MPa).

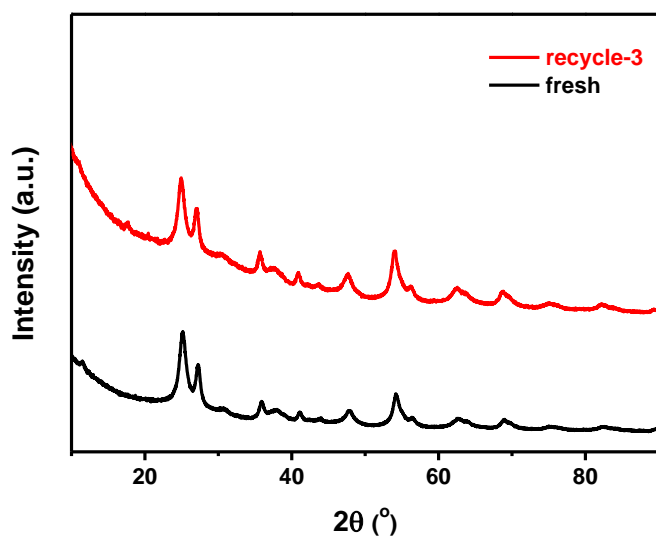


Figure S8. XRD patterns of fresh and reused (3 cycles) Ru/TiO₂@CN.

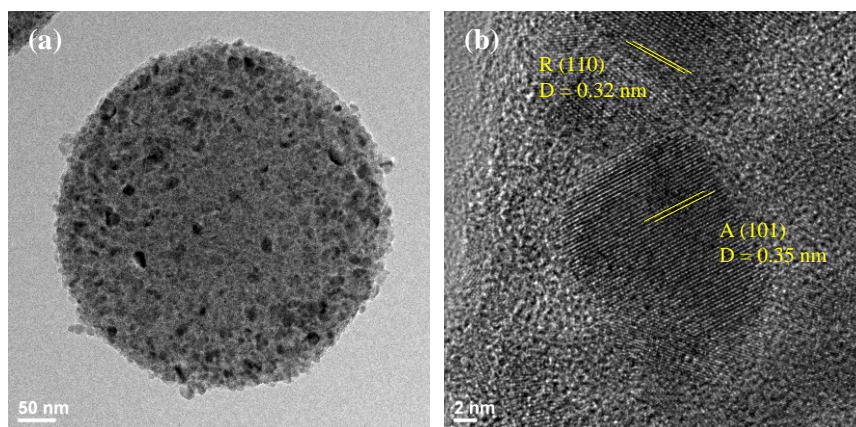


Figure S9. TEM images of (a, b) Ru/TiO₂@CN after reused 3 cycles.

Table S1. EDX analysis of the Ru/TiO₂@CN catalyst.

Catalyst	EDX analysis (wt%)				
	C (K)	N (K)	O (K)	Ti(K)	Ru (K)
Ru/TiO ₂ @CN	62.55	6.15	11.83	18.8	0.83

Table S2. Summary of the results from N₂ adsorption - desorption.

Entry	catalyst	S _{BET} (m ² g ⁻¹) ^a	Micropore surface area ^b (m ² g ⁻¹)	External surface area ^b (m ² g ⁻¹)	Micropore volume ^b (cm ³ g ⁻¹)
1	Ru/NH ₂ -MIL-125(Ti)	1316.1	1234.9	81.2	0.551
2	Ru/TiO ₂ @CN	319.9	167	153	0.075
3	TiO ₂ @CN	281.5	186	96	0.083

^aP/P₀ = 0.01-0.2.

^bP/P₀ = 0.24-0.4, obtained by the t-plot method.

Table S3. ICP – OES analysis of different catalysts and used Ru/TiO₂@CN catalysts.

Entry	Catalyst	Ru (wt%)	Ti (wt%)
1	RuTiO ₂ /CN	0.14	21
2	RuTiO ₂ /C	0.25	11
3	RuTiO ₂ /CN-500	0.13	20
4	RuTiO ₂ /CN-900	0.23	6
5	Ru/TiO ₂	0.12	59
6	RuTiO ₂ /CN(1 cycle)	0.14	19