Supporting Information for

Conversion of levulinic acid to γ-valerolactone over ultra-thin TiO2 nanosheets decorated with ultrasmall Ru nanoparticle catalysts under mild condition

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1. Experimental

1.1 Chemicals

Material： The reagents Tetra-n-butyl titanate (Ti(OBu)$_4$·(TBOT)) (99.0%, AR grade), hydrofluoric acid solution (HF, 40 wt %, AR grade), NaOH (99.9%, AR grade), P25(Degusai, >99%), ethanol (99.8%, AR grade), RuCl$_3$(99.9%, Across Chemicals), and ammonium carbonate (99.9%, AR grade) were bought from Beijing Chemical Reagent Factory. H$_2$(>99.99%) and Ar(>99.99%) were supplied by Beijing Analytical Instrument Company. All the chemicals were used as received without further purification.

1.2 Preparation of the catalysts

Synthesis of TiO$_2$ nanosheets (TiO$_2$-n)

   TiO$_2$ nanosheets with exposed different ratios (001) facets were prepared by the hydrothermal method similar to that reported by Xie.[1] In a typical experimental procedure, 25 mL of Ti(OC$_4$H$_9$)$_4$ and 4 mL of hydrofluoric acid solution (with a concentration ca. 40 wt %) were mixed in a dried Teflon autoclave with a capacity of 100 mL at ambient temperature, followed by hydrothermal treatment of the mixture at 180 °C for 24 h. After being cooled to room temperature, the white precipitate was separated by high-speed centrifugation, washed with ethanol and distilled water for three times, and then dried in an oven at 70 °C for 6 h. 1 g of the TiO$_2$ was dispersed in 10 mL of 0.5 M NaOH aqueous solution under vigorous shaking for 30 min in an ultrasonic cleaner and then by high-speed centrifugation, washed with ethanol and distilled water for three times, and then dried in an oven at 70 °C for 6 h.

Synthesis of TiO$_2$ decanedron (TiO$_2$-d)

   Firstly, potassium titanate nanowires(PTNWS) were prepared at 200 °C over 24 h under hydrothermal conditions with a high concentration KOH solution and P25 and according to the literature method. Then TiO$_2$ decanedron were prepared by means of a facial hydrothermal route and by using potassium titanate nanowires as a precursor and hexamethylenetetramine as a shape regulator. In a typical experiment, 10 mg potassium titanate nanowires and 133 mg hexamethylenetetramine were dispersed in distilled water under intense ultrasonic treatment.

The resulting solution was then transferred into a 25 mL Teflon-lined stainless-steel autoclave and was kept at 200 °C for 12 h. After being cooled to room temperature, the white precipitate was separated by high-speed centrifugation, washed with ethanol and distilled water for three times, and then dried in an oven at 70 °C for 6 h.

Synthesis of TiO_2 octahedron (TiO_2-o)

The preparation method of TiO_2-o was similar to TiO_2-d, in a typical experiment, 10 mg potassium titanate nanowires was dispersed in distilled water under intense ultrasonic treatment. The resulting solution was then transferred into a 25 mL Teflon-lined stainless-steel autoclave and was kept at 200 °C for 12 h. After being cooled to room temperature, the white precipitate was separated by high-speed centrifugation, washed with ethanol and distilled water for three times, and then dried in an oven at 70 °C for 6 h.

Synthesis of Ru/TiO_2-x

The Ru/TiO_2-x(Ru/TiO_2-n, Ru/TiO_2-d and Ru/TiO_2-o) catalysts were prepared by impregnation reduction of the above-prepared TiO_2 powders (200 mg) into a clean beaker, which contained 50 mL of deionized water were mixed with appropriate amount of $RuCl_3$ solution, vigorously stirred and ultrasonic for another 1 h to disperse them completely. Under the ice bath, the $NaBH_4$ (freshly prepared) was added drop-wise into the solution with a continuous magnetic stirring, the reaction solution kept on stirring for 3 h to complete the reduction reaction. The obtained black granules washed with deionized water and dried in a vacuum oven at 70 °C for 6 h. For comparison, the commercial TiO_2(Ru/TiO_2-com.) was also prepared using the same method.

1.3 Characterizations

The scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4800 scanning electron microscope operated at 15 kV. The TEM and EDS images of the catalysts were obtained using a JEOL-2100F electron microscope operated at 120 kV. The XPS spectra were obtained using an ESCALab 220I-XL electron spectrometer (VG Scientific) using 300 W Al Kα radiation with a hemispherical energy analyser. The binding energies were calibrated with the

C1s level of adventitious carbon at 284.8 eV as the internal standard reference. Identification of the products was conducted GC/MS analysis on Agilent 7890B GC+5977 MSD. The quantitative analysis of the samples was carried out using an Agilent 4890 gas chromatography equipped with a flame ionization detector (FID) and a HP-5 capillary column (30 m × 0.25 mm × 0.25 μm), Agilent Technologies Singapore (Sales) Pte Ltd., Singapore. The contents of Ru in the catalysts were analysed by ICP-AES (VISTA-MPX), rf power 1.15 kw, coolant gas flow rate 15 L/min, nebulizer gas flow rate 0.75 L/min, sampling depth 12 mm, auxiliary gas flow rate 1.5 L/min.

1.4 Activity tests

The reaction was carried out in a Teflon-lined stainless steel reactor of 16 mL, which was similar to that used previously. In a typical experiment, 1.0 mmol substrate, 2 mL solvent and the desired amount of catalyst were added into the reactor. The air in the reactor was purged with H_2 for 3 times. Then, the reactor was placed in an air bath of desired temperature, and H_2 was charged to desired pressure. After a certain reaction time, the autoclave was placed in an ice-water mixture and the reaction solution was centrifuged using n-propanol as an internal standard.
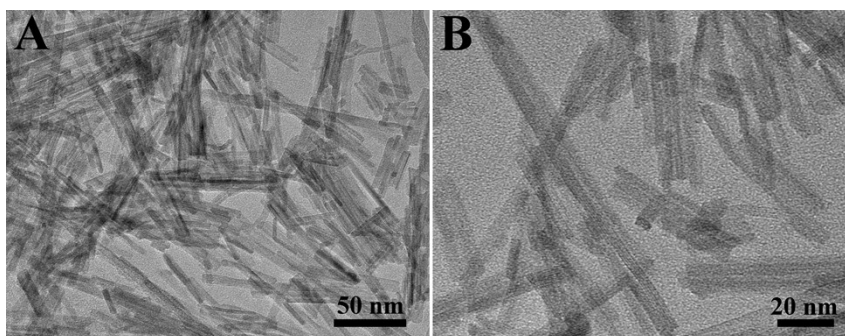
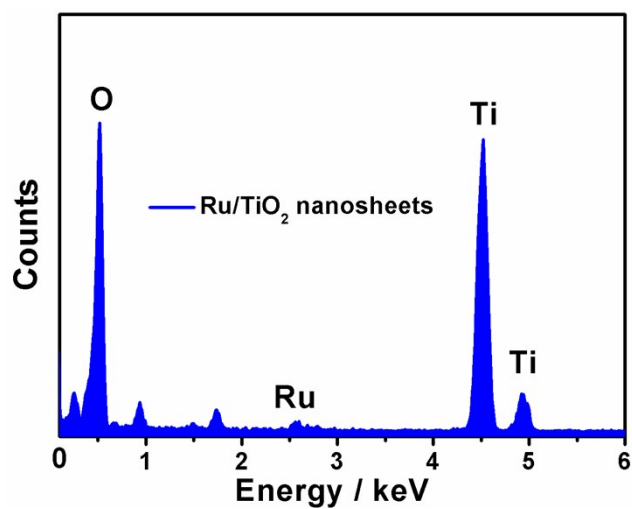**Fig. S1** (A, B) TEM images with different magnifications of PTNWS.
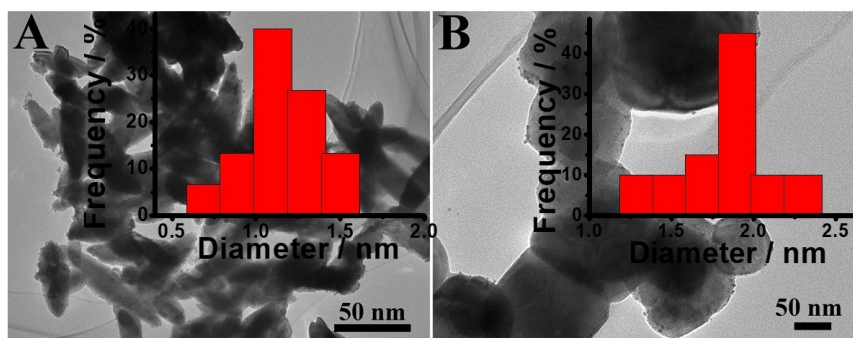

Fig. S2 EDX patterns of as-prepared Ru/TiO$_2$ nanosheets.

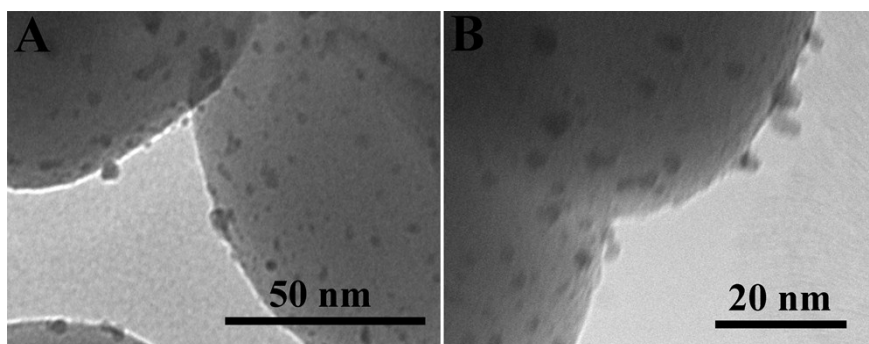**Fig. S3** (A) TEM images of Ru/TiO$_2$-o; (B) TEM images of Ru/TiO$_2$-d.

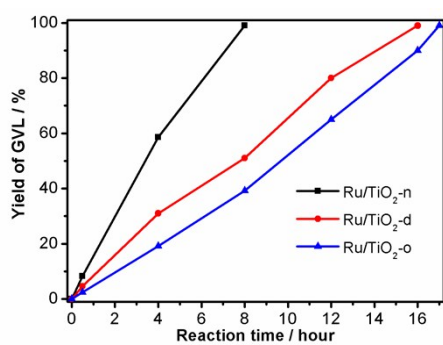**Fig. S4** (A, B) TEM images of Ru/TiO$_2$-com. with different magnifications.

Fig. S5 Plots of yield of LA toward GVL against reaction time with Ru/TiO$_2$-x (Ru/TiO$_2$-n, Ru/TiO$_2$-d and Ru/TiO$_2$-o)

as the catalyst

Table S1. The inductively coupled plasma mass spectrometry of

Ru/TiO$_2$-x (TiO$_2$-n, TiO$_2$-d and TiO$_2$-o)

Entry	Sample	Ru content
1	Ru/TiO$_2$-n	2.02%
2	Ru/TiO$_2$-d	1.98%
3	Ru/TiO$_2$-o	1.90%

References:

1. X. Han, Q. Kuang, M. Jin, Z. Xie and L. Zheng, *Journal of the American Chemical Society*, 2009, **131**, 3152-3153.