Supporting Information

Highly Efficient Ru-Decorated CeO$_2$ for Photocatalytic Hydrogenation and Cyclization of Levulinic Acid to γ-Valerolactone

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Materials

High-purity $Ce(NO_3)_2 \cdot 6H_2O$ and $RuCl_3.xH_2O$ were purchased from Sigma Aldrich India Pvt. Ltd. NaOH was purchased from Loba Chemie India Pvt. Ltd. Levulinic acid was purchased from Sigma Aldrich India Pvt. Ltd. Other substrates were purchased from Loba Chemie and BLD Pharma India Pvt. Ltd, and Sigma Aldrich India Pvt. Ltd.

Catalyst synthesis

Synthesis of CeO_2

In a typical reaction procedure, 1 g of $Ce(NO_3)_2.6H_2O$ was dissolved in 10 mL of deionized (DI) water. Concurrently, 3.6 g of NaOH was dissolved in 5 mL of DI water. The NaOH solution was then gradually added dropwise to the Ce-nitrate solution under vigorous stirring. After 10 minutes of stirring, the resulting precipitate was transferred to a Teflon-lined autoclave for hydrothermal treatment at 110 °C for 24 h. Post-treatment, the precipitate was filtered and washed with DI water until a neutral pH was achieved. Finally, the precipitate was dried overnight at 80 °C and calcined at 400 °C for 2 h.

Synthesis of Ru decorated CeO_2

The required amount of $RuCl_3$ (wt% relative to the support) was dissolved in a 10 mL mixture of DI water and ethanol (1:1 v/v). Then, 0.5 g of the prepared CeO_2 was dispersed into the Ru solution using sonication for 10 minutes. This solution was stirred for 3 h at room temperature, followed by solvent evaporation using a rotary evaporator. The resulting solid was dried at 70 °C under vacuum and then underwent treatment with 10% H_2/Ar at 400 °C in a tube furnace for 2 h, yielding the final product, Ru/CeO_2.

Catalyst characterization

The powder X-ray diffraction patterns of the synthesized materials were obtained on a RIGAKU Mini-Flex diffractometer with Cu kα ($\lambda = 0.154$ nm, 40 kV, 15 mA) radiation source in a 2θ range of 5-80°. Nitrogen-sorption measurements were conducted by using a Bellsorp-MiniX volumetric adsorption analyzer to evaluate the textural properties of the catalyst. Before measurement, degassing was carried out at 200 °C for 3 h in the degassing port of the adsorption apparatus. The surface area of the material was calculated using the Brunauer-Emmett-Teller (BET) equation based on the adsorption data points obtained for P/P_0 between 0.05 and 0.3. Additionally, the pore diameter was estimated using the Barret-Joyner-Halenda (BJH) model.

Field Emission Scanning Electron microscopy (FESEM) measurements were carried out on a Joel instrument at an accelerating voltage of 10 kV to explore the morphology. Transmission Electron Microscopy (TEM) was obtained for an in-depth study of material on (M/s JEOL JSM 2100) instrument operating at 200 kV. The surface composition of the catalyst was investigated by the Thermofisher scientific 'Nexsa Base' X-Ray Photoelectron Spectroscopy (XPS) instrument. The XPS, VB-XPS and UPS were conducted using the Thermofisher scientific 'Nexsa Base' X-Ray Photoelectron Spectroscopy (XPS) instrument. The obtained XPS data was deconvoluted using XPS Peak-41 software. Initially, the background was incorporated into the raw data. Peaks were then added at the respective positions using XPS Peak-41. Afterward, the parameters were optimized, and the peaks were fitted using a Gaussian function.

The NH_3 and CO_2 uptake capacity of materials was analyzed by using the NH_3-TPD and CO_2-TPD techniques employing Quantachrome, CHEMBETTM TPR instrument. The sample was preheated at 500 °C at a heating rate of 10 °/min under a continuous He gas flow for 30 min. Then, after cooling to 50 °C, NH_3/CO_2 gas was allowed to adsorb on the sample for 1 h. After adsorption, the excess or physically adsorbed NH_3/CO_2 was removed by flushing with He gas (50 mL/min) for 30 min. Finally, the temperature was ramped from 50-500 °C at a rate of 10 °/min, then cooled to 50 °C with a ramp rate 10 °C/min.

UV-DRS measurement was conducted on a UV-visible spectrophotometer of Shimadzu (UV-2600) using $BaSO_4$ as standard reference material. The liquid UV analysis was also conducted using a UV-visible spectrophotometer of Shimadzu (UV-2600). The fluorescence decay time was evaluated using the TCSPC instrument of DeltaFlex TCSPC Lifetime Fluorimeter

Catalytic reaction procedure

Levulinic acid (0.2 mmol), catalyst (20 mg), and H_2O (5 mL) were added to a glass reactor. The reactor was then purged with H_2 gas and pressurized to 0.2 MPa with hydrogen. The reaction was conducted using 15 W blue LED light for the required time (Fig. S4). After the reaction, the catalyst was separated by centrifugation. The reaction mixture was then extracted with ethyl acetate and analyzed using GC and GC-MS. The catalyst was separated by centrifugation and the reaction mixture was analyzed using gas chromatography by the internal standard method (GC, Shimadzu GC-2010 Plus, SH-Rtx-5 column, column temperature 80-280 °C with 10 °C/min ramp, injector temperature 250 °C, FID 300 °C). The products of the reaction were confirmed using GC-MS (Shimadzu GCMS-QP 2010 Ultra).

The following equations to determine the conversion of reactant, selectivity of product, and overall yield.

$$Conversion = \frac{C_0 - C_t}{C_0} \; x \; 100\%$$

$$\ldots\ldots \textbf{(Eq. S1)}$$

$$Selectivity = \frac{C_p}{C_0 - C_t} \; x \; 100\%$$

$$\ldots\ldots \textbf{(Eq. S2)}$$

C_0 concentration of the initial reactant, C_t concentration of reactant after time t, and C_p concentration of product at time t.

$$Yield \; of \; the \; product \; = \frac{reactant \; conversion \; x \; product \; selectivity}{100} \ldots(Eq. \; S3)$$

Apparent Quantum Yield (ϕ) Calculation

The quantum yield of the reaction was determined by calculating the ratio of electrons participating in the reaction to the molar flow of photons introduced into the reactor (Eq. S7).[31]The effective wavelength (λ) of the photons was estimated based on the catalyst's band gap, which was derived from Tauc plots. While this calculated quantum yield was not an absolute value, it provided a useful reference for comparing the photo efficiency of different photocatalytic systems.

$$Apparent \; Quantum \; Yield \; (AQY) = \frac{No. \; of \; reacted \; electrons \; x \; 100}{No. \; of \; incident \; photons} \ldots(Eq. \; S4)$$

$$No. \; of \; reacted \; electrons \; = Reactant \; conversion \; (mol^{-1}) x \; NA \; (mol) \ldots(Eq. \; S5)$$

$$Number \; of \; incident \; photon$$
$$= \frac{Light \; intensity \; (Wm^{-2}) x \; Area \; (m^2) x \; Time \; (s)}{\dfrac{h \; (Js) \; c \; (ms^{-1})}{\lambda \; (m)}} \ldots(Eq. \; S6)$$

$$AQY = \frac{Reactant\ conversion\ (mol^{-1})\ x\ NA\ (mol)\ x\ h\ (Js)\ c\ (ms^{-1})\ x\ 100}{Light\ intensity\ (Js^{-1}m^{-2})\ x\ Area\ (m^2)\ x\ Time\ (s)\ x\ \lambda\ (m)} ...(Eq.\ S7)$$

Photoelectrochemical measurement

The photoelectrochemical analyses were performed with PGSTAT302N Autolab electrochemical workstation using standard three-electrode grouping in Pyrex cell with a 0.1 M aqueous sodium sulfate solution as electrolyte. The coated photocatalyst acts as a photoanode (working electrode), Pt wire electrode as a counter electrode, and Ag/AgCl as a reference electrode. Photoanode was prepared by coating photocatalyst on glass slides containing fluorine-doped tin oxide (FTO), cleaned with acetone, rinsed with DI water, and oven-dried before use. The catalyst was coated over the FTO surface using the drop-casting method. To make a binder solution, 1.5 ml of ethanol was mixed with 1 ml of water and 40 µl of Nafion (binder). 20 mg of the photocatalyst was added to the solution and sonicated for 10 min. The binder solution was cast dropwise over the glass surface using a dropper and hotplate with a temperature of 50 °C. The electrochemical impedance measurement was conducted in the frequency range of 1 MHz to 1 Hz using a sinusoidal AC perturbation signal of 5 mV. Mott Schottky experiment was conducted at 1000 Hz constant frequency in dark conditions. LSV and transient photocurrent measurements were carried out under dark and illumination conditions using a 300 W Xenon arc lamp (Newport-R22).

Band gap calculations by using Tauc plot for

We employed the equation $((\alpha h\nu)1/r = \beta(h\nu - E_g))$ to determine the band gap. The value of r depends on the nature of the transition, with r = 1/2 being suitable for direct transitions, and r = 2 indicating indirect transitions. By plotting $(\alpha h\nu)^{1/r}$ vs. (hν) with r = 1/2, we could estimate the band gap for direct allowed transitions through straight-line extrapolation, particularly for the synthesized catalysts.

Mott-Schottky analysis

This approach involved the relationship $1/C^2 = 2\ [V-V_{fb}-(k_bT/e)]/(\varepsilon\varepsilon_0eA_2Nd)$. Plots of $1/C^2$ versus applied potential were generated. All materials exhibited a positive slope, indicating their n-type semiconducting behaviour. The x-intercepts of the Mott-Schottky plots provided

the flat-band position (E_{fb}) (Fig. S2). In n-type semiconductors, the E_{fb} is situated below the conduction band (CB) edge. These E_{fb} values were used to determine the position of the CB edge (ECB) using the relation $E_{CB} = E_{fb}$ -0.1 V. To standardize potential values, the equation ($E_{NHE} = E_{Ag/AgCl} + 0.196$) was applied, and Table S1 presents the calculated E_{CB} vs. NHE values for all materials. Finally, the valence band positions (E_{VB}) were determined using the relation $E_{VB} = E_{CB} + Eg$, where E_{CB} represents the conduction band potential and Eg is the band gap.
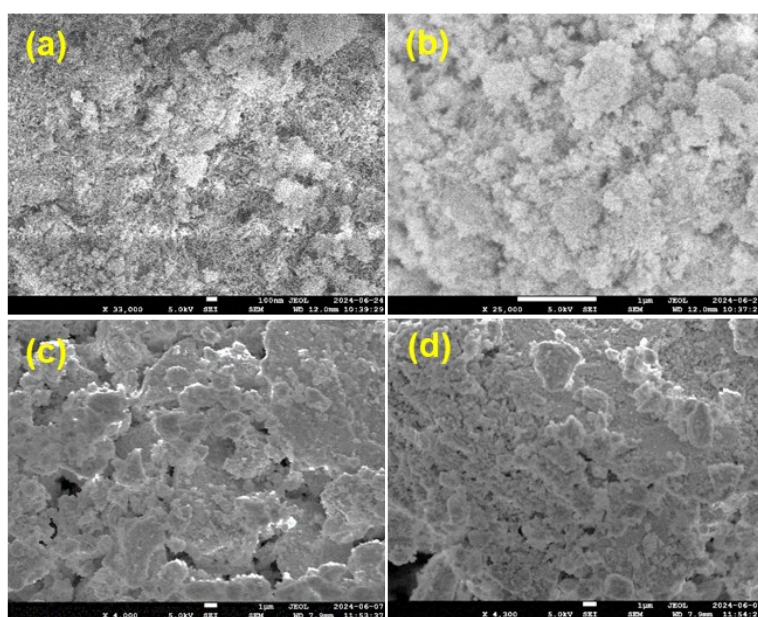
Fig. S1. FESEM images of (a-b) CeO_2 and (c-d) $1Ru/CeO_2$.
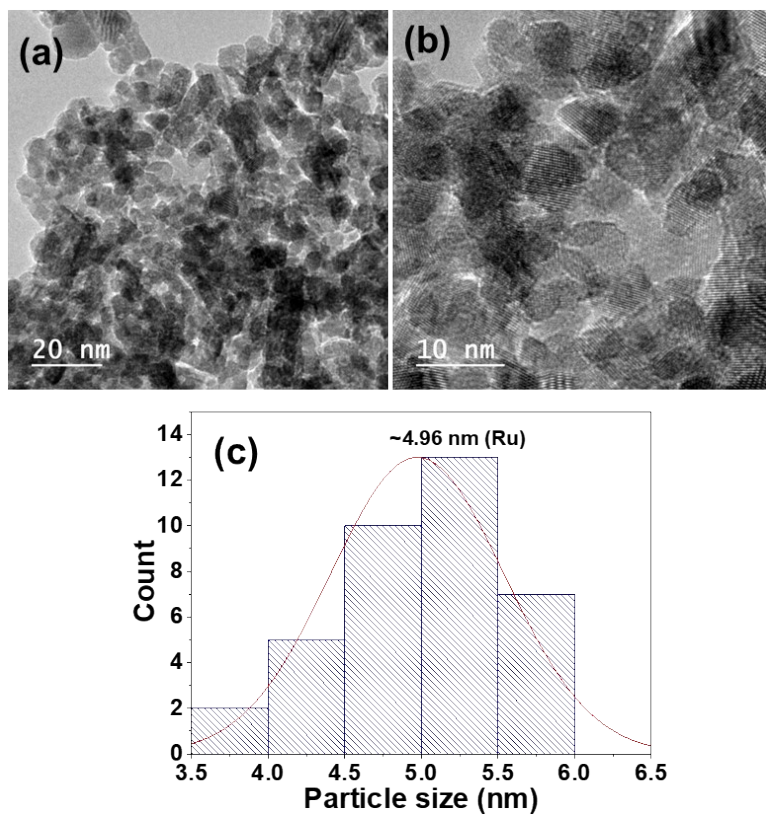
Fig. S2. (a-b) HRTEM images of 1Ru/CeO$_2$ and (c) particle size of Ru present in 1Ru/CeO$_2$
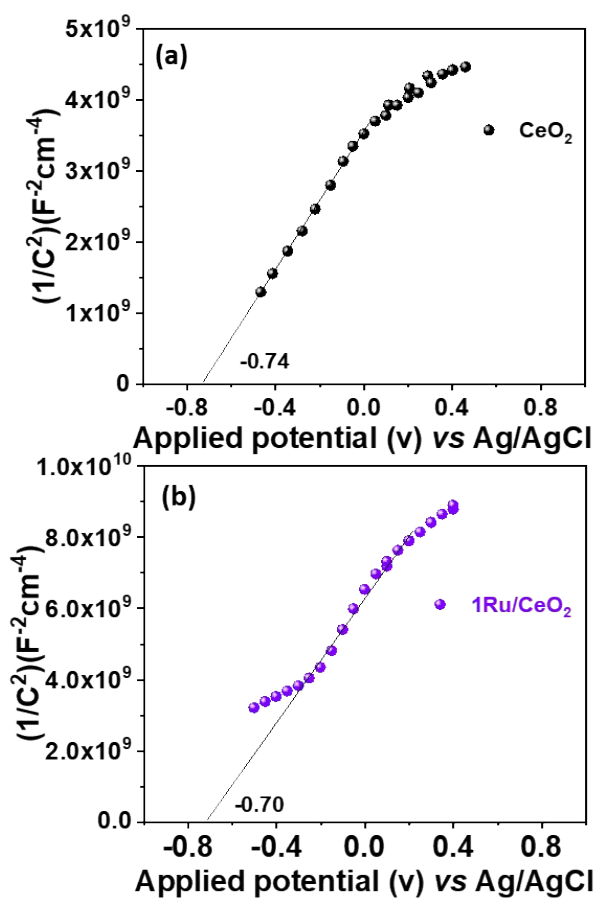
Fig. S3. Mott-Schottky (M-S) plots of (a) CeO_2 and (b) $1Ru/CeO_2$.
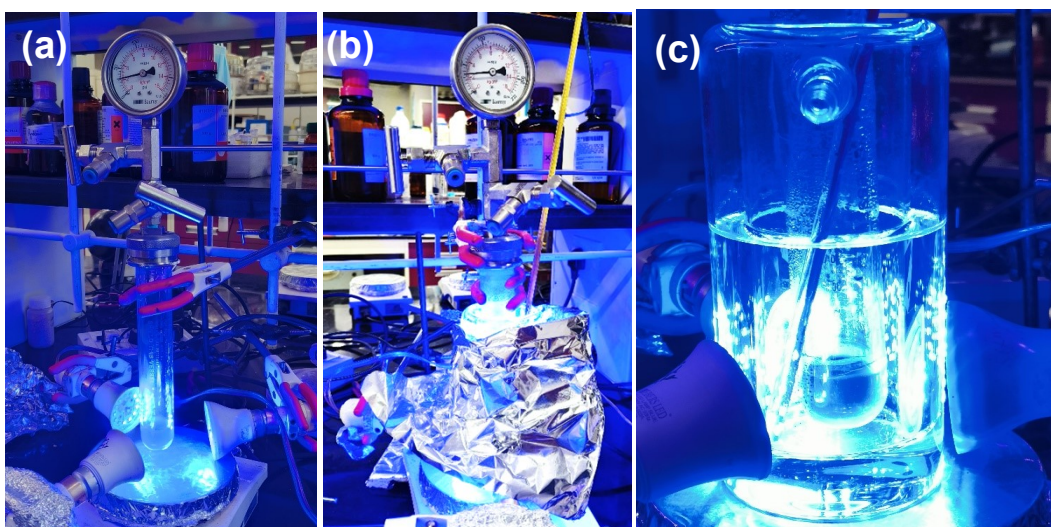
Fig. S4. (a) Reaction setup without glass jacket (15 W blue light irradiation) and (b-c) reaction setup with glass jacket and water circulation (15 W blue light irradiation).
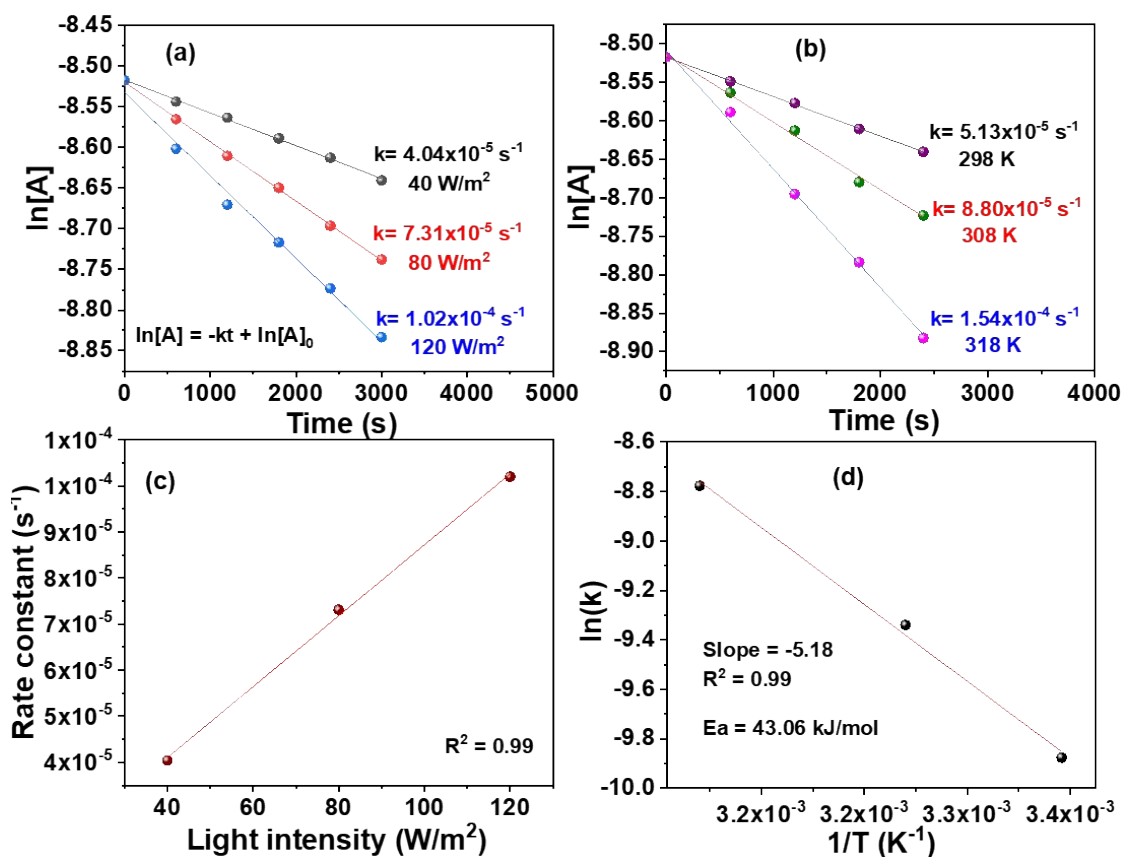
Fig. S5. Kinetics plots of reactions at various intensities of light for (a) LA reduction and cyclization using $1Ru/CeO_2$. (b) Kinetics plots of reactions at various temperatures (298 K, 308 K, and 318 K) for LA hydrogenation. (c) The dependency of rate constant (k) on the light intensity at room temperature. Arrhenius plot (d) ln(k) vs. 1/T for Ea calculation of LA hydrogenation.
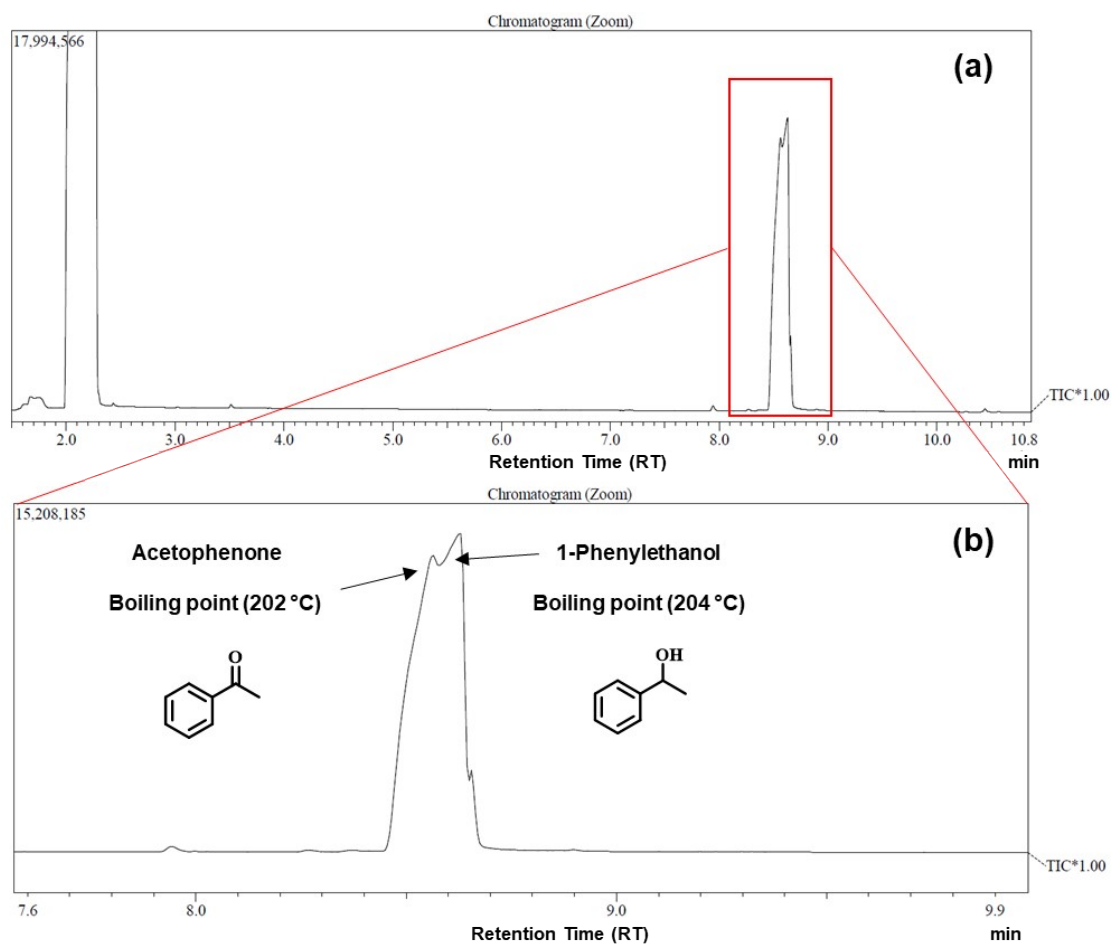
Fig. S6. (a-b) GC-MS analysis of the photocatalytic reduction of Acetophenone using electrons present in the CB of 1Ru/CeO$_2$ catalyst. [Reaction conditions: Acetophenone (60 µL), 1Ru/CeO$_2$ (20 mg), H$_2$ (0.2 MPa), time (1 h), 15 W blue LED light, H$_2$O (5 mL), TEA (60 µL)]. (TEA = Triethanolamine used as a hole scavenger to produce electrons). (The merged peak was obtained due to the close boiling point of Acetophenone and 1-Phenylethanol).
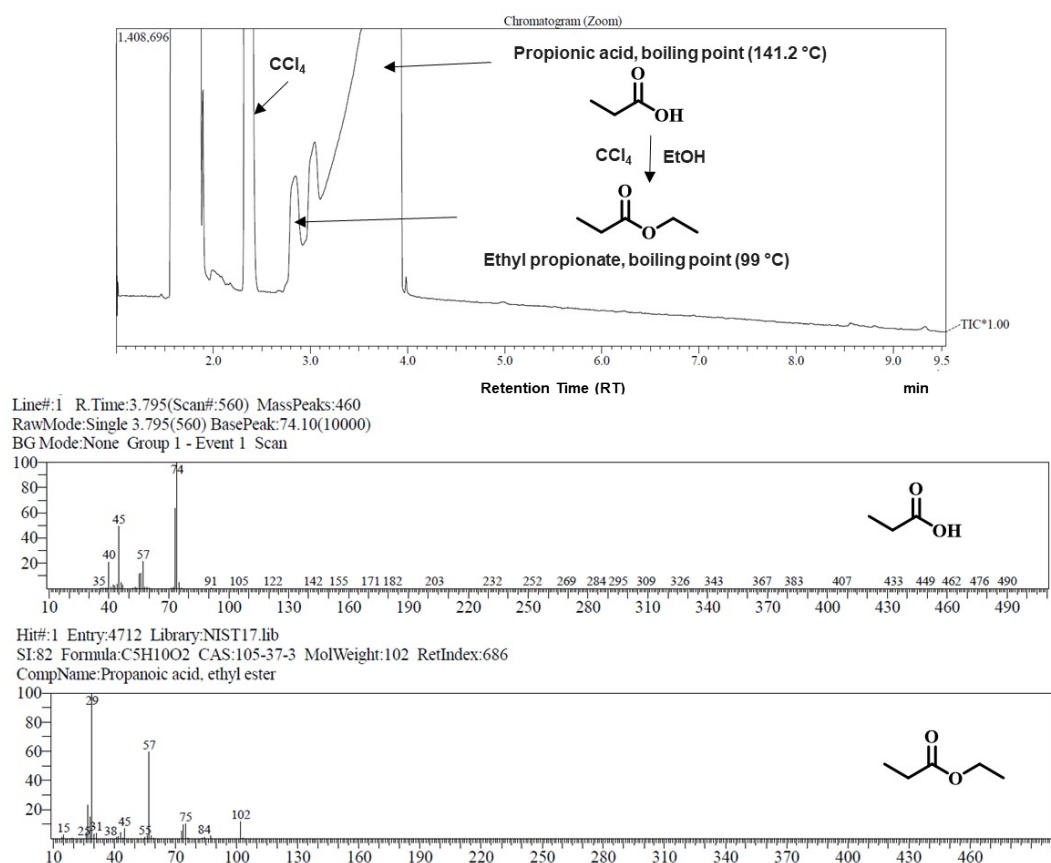
Fig. S7. GC-MS analysis of the photocatalytic reaction of Propionic acid using holes present in the VB of 1Ru/CeO$_2$ catalyst. [Reaction conditions: Propionic acid (60 μL), 1Ru/CeO$_2$ (20 mg), H$_2$ (0.2 MPa), time (1 h), 15 W blue LED light, EtOH (5 mL), CCl$_4$ (60 μL)]. (CCl$_4$ = Carbon tetrachloride used as an electron scavenger to produce holes).
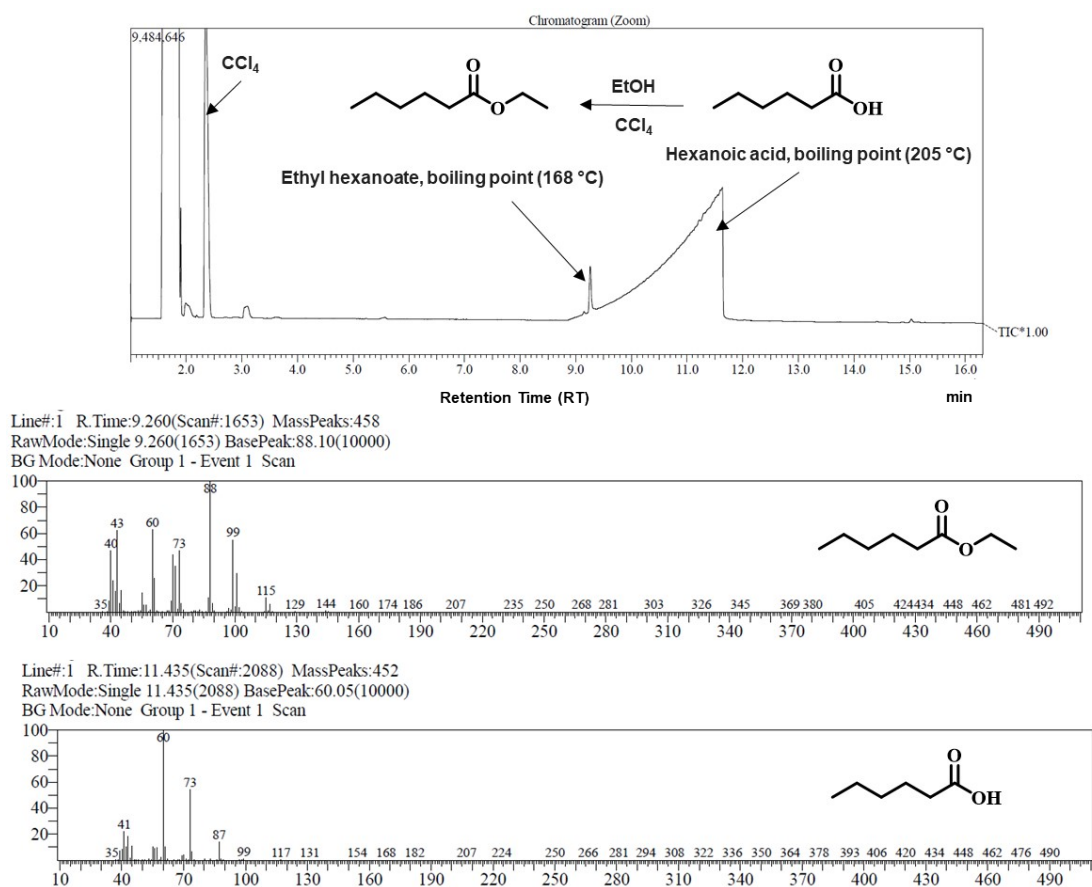
Fig. S8. GC-MS analysis of the photocatalytic reaction of Hexanoic acid using holes present in the VB of 1Ru/CeO$_2$ catalyst. [Reaction conditions: Hexanoic acid (60 μL), 1Ru/CeO$_2$ (20 mg), H$_2$ (0.2 MPa), time (1 h), 15 W blue LED light, EtOH (5 mL), CCl$_4$ (60 μL)]. (CCl$_4$ = Carbon tetrachloride used as an electron scavenger to produce holes).
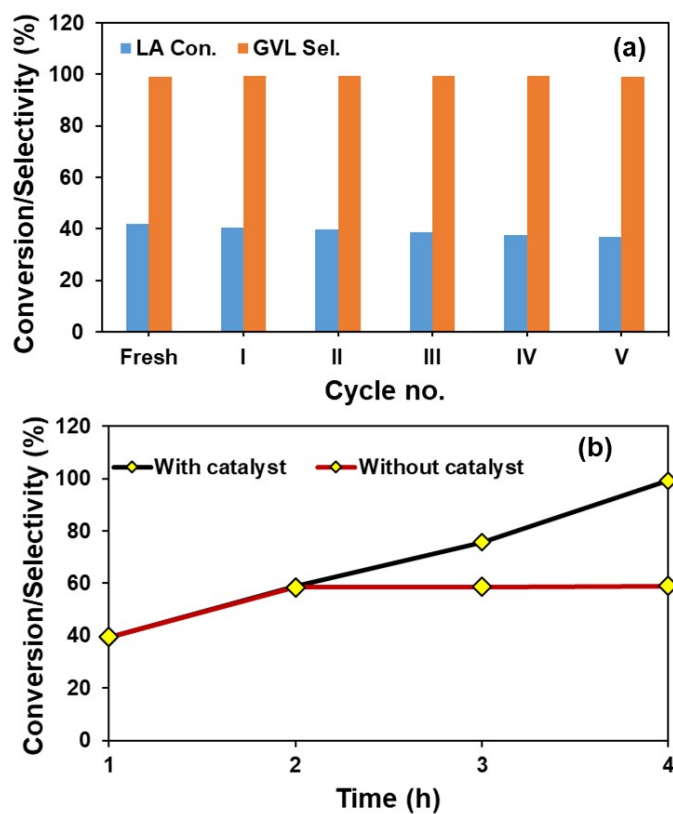
Fig. S9. (a) Recyclability test (Reaction conditions: Levulinic acid (1 mmol), 1Ru/CeO$_2$ (100 mg), H$_2$O (5 mL), time (1 h), H$_2$ (0.2 MPa), blue LED (15 W). (b) Hot filtration test with and without catalyst.
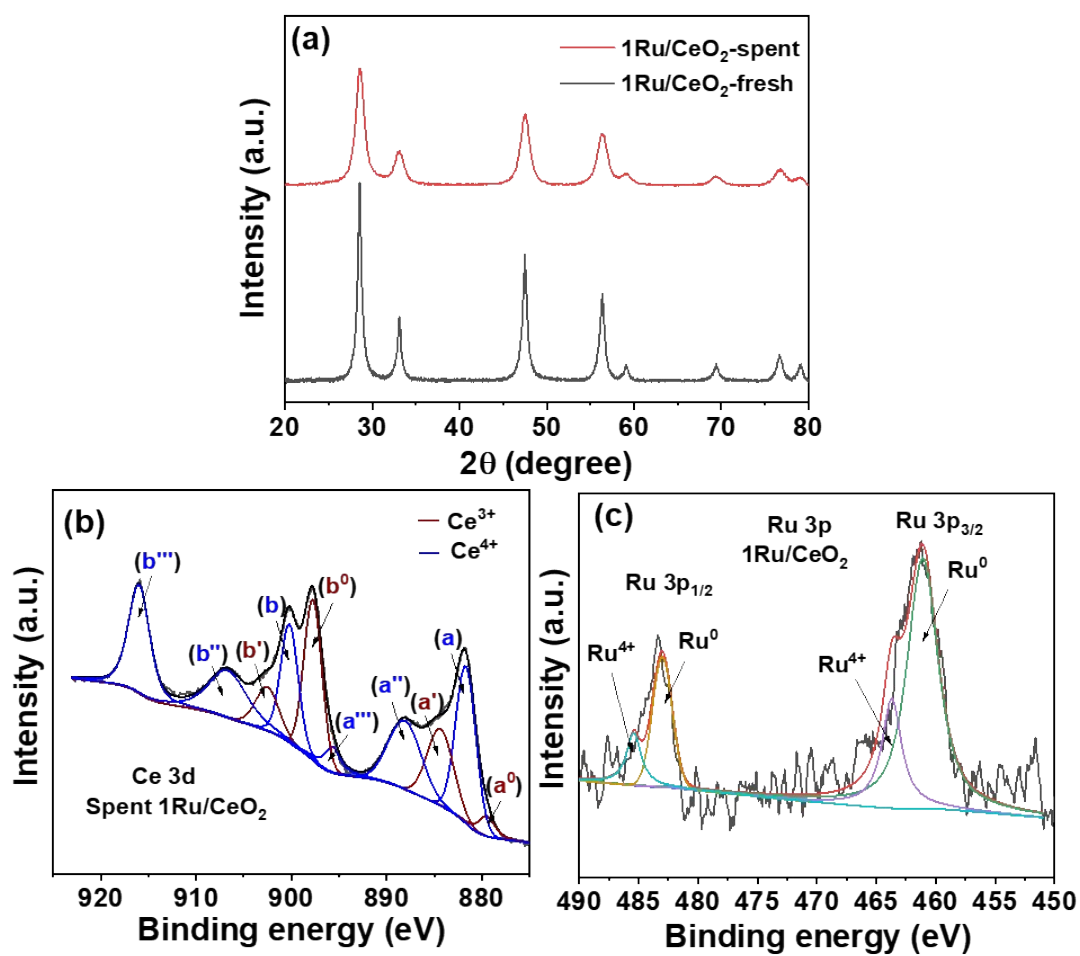
Fig. S10. (a) XRD patterns of fresh and spent $1Ru/CeO_2$. High-resolution XPS spectra of (b) Ce 3d and (c) Ru 3p present in spent $1Ru/CeO_2$.

Table S1. Calculated band gap from tauc plot and flat band potential, Ecb, Evb from Mott-Schottky and VBXPS, UPS analysis.

Entry No.	Catalyst	Band gap (eV)	Flat band potential (E_{fb} vs NHE)	[a]Conduction band (E_{cb} vs NHE)	[a]Valance band (E_{cb} vs NHE)	[b]Conduction band (E_{cb} vs NHE)	[b]Valance band (E_{cb} vs NHE)
1	CeO_2	2.94	-0.74	-0.64	2.20	-0.99	1.95
2	$1Ru/ZrO_2$	4.97	-0.70	-0.60	2.37	-0.76	2.21

[a]Calculated from Mott-Schottky plot

[b]Calculated from UPS and VB-XPS

Table S2. Comparative catalytic activity data of photocatalytic hydrogenation of LA to GVL.

Sr. No.	Catalyst	Reaction conditions	LA Con. (%)	GVL Sel. (%)	Ref.
1.	Au-decorated TiO$_2$	LA (0.02 mol), isopropanol (20 ml), catalyst (0.05 g), noble metal co-catalyst (0.5 wt%), argon atmosphere, temperature (20 °C), light source (300 W high-pressure Hg-lamp), irradiation time (9 h).	79	85.3	17
2.	commercial niobic acid (HY-340)	LA (3 mmol), EtOH (30 mL), catalyst (100 mg), time 24 h, low-pressure Hg lamp (11 W, λ_{max} =254 nm).	~30	GVL= ~15 GHV= ~17	18
3.	Niobium oxides (H3-600 °C)	LA (0.2 mmol), ethanol (2 mL), photocatalyst (20 mg), room temp, N$_2$ atmosphere, and UV irradiation time of 16 h.	43.5	GHV= ~65 GVL= ~10 GHE= ~25	19
4.	Pt/TiO$_2$, NaOH	LA (20 mg, 0.172 mmol), Pt/TiO$_2$ catalyst (10 mg), NaOH (55 mg in 0.4 mL aqueous solution, 1.376 mmol), and 2-propanol (1.6 mL), LED (18 W, 365 nm), time 12 h.	~99	~98	20
5.	Co-MoOx/PW	LA (10 µL), IPA (5 mL), catalysts (50 mg), time (18 h), 400 nm LED, 36 W	-	Yield 83.8	21
6.	1Ru/CeO$_2$	Levulinic acid (0.2 mmol), catalyst (20 mg), time (4 h), 15 W blue LED, H$_2$ (0.2 MPa).	~99	~99	**This study**

[a](Carboxyl acid functionalized ionic liquid entangled porphyrin photocatalyst), (LA= Levulinic acid, EL= Ethyl Levulinate, GVL= γ-Valerolactone, GHV= γ-hydroxyvaleric acid, GHE= γ-hydroxyethyl valerate). (Con.= Conversion, Sel. Selectivity).