

Supporting Information

Thermocatalytic and Photocatalytic Chemoselective Reduction of Cinnamaldehyde to Cinnamyl Alcohol and Hydrocinnamaldehyde over Ru@ZnO/CN

Arzoo Chauhan^{a*}, Rajat Ghalta^{a*}, Rajaram Bal^b, and Rajendra Srivastava^{a*}

^a*Catalysis Research Laboratory, Department of Chemistry, Indian Institute of Technology
Ropar, Rupnagar, Punjab-140001, India*

^b*Nanocatalysis Area Conversion and Catalysis Division, CSIR-Indian Institute of Petroleum,
Dehradun-248005, India*

*Equal contribution.

*Email: rajendra@iitrpr.ac.in

*Phone: +91-1881-232064

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Materials

Cinnamaldehyde (99 %) and Ruthenium chloride were purchased from Sigma-Aldrich. Formic acid (88%) and tertiary butyl alcohol from Tokyo Chemical Industry Co., Ltd, and urea and zinc acetate were purchased from Loba-chemie. All other chemicals and solvents were obtained from Merck. All the chemicals were used without any further purification.

Catalyst preparation

Synthesis of CN

A crucible was charged with 16 g of urea and was covered with a lid. The material was annealed at 550 °C in a muffle furnace with a ramp rate of 2.5 °C min⁻¹ for 3 h. The resulting yellow material was grounded into a powder using a mortar pestle and was designated g-C₃N₄ (CN).

Synthesis of ZnO

2 g of Zn(OAc)₂·2H₂O was crushed and mounted in an alumina crucible. The material was calcined at 400 °C for 3 h with a ramping rate of 5 °C min⁻¹. Around 400 mg of ZnO was obtained as the final material.

Preparation of (Y%)Ni@ZnO(1.5)/CN and (Y%)Co@ZnO(1.5)/CN nanocomposites

The ZnO(1.5)/CN was dispersed in 50 ml of ethanol and subjected to sonication for a duration of 30 minutes. Subsequently, a predetermined quantity of Ni(CH₃CO₂)₂·4H₂O or Co(CH₃CO₂)₂·4 H₂O was dissolved in 10 ml of ethanol and added dropwise to the ZnO(1.5)/CN composite solution under continuous stirring conditions. The resulting solution was stirred at 80 °C until the complete evaporation of ethanol. The synthesized materials were then dried at 75 °C in an oven overnight. The synthesized materials were reduced in a tube furnace at 450 °C for 3 h with a ramp rate of 5 °C/min, in a 10% H₂/Ar to yield Y%Ni@ZnO(1.5)/CN and (Y%)Co@ZnO(1.5)/CN catalysts (where Y= 1, and 3 w% of Ni and Co).

Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex III diffractometer (30 kV and 10 mA) with Cu K α radiation. FT-IR spectra were recorded using Bruker Tensor 27 spectrometer. Nitrogen-sorption measurements were performed at -200 °C by Quantachrome Instruments, Autosorb-iQ volumetric adsorption analyzer, to determine the textural properties of the catalyst. Degassing was conducted at 200 °C for 3 h in the degassing port of the adsorption apparatus. Brunauer-Emmett-Teller (BET) equation was used to calculate the surface area of the material from the adsorption data points obtained for P/P₀ between 0.05-0.3, and the pore diameter was estimated using the Barret-Joyner-Halenda (BJH) model. Scanning electron microscopy (SEM) measurements were carried out on a Joel instrument at an accelerating voltage of 10 kV to explore the morphology. (TEM) was obtained for an in-depth study of material on (M/s JEOL JSM 2100) instrument operating at 200 kV at IIP Dehradun. The surface composition of the catalyst was investigated by the Thermofisher scientific 'Nexsa Base' X-Ray Photoelectron Spectroscopy (XPS) instrument. The metal content in the catalyst was determined by Agilent's microwave plasma atomic emission spectrometer (MP-AES). TGA/DSC 1 STARe SYSTEM from Mettler Toledo instrument with a temperature increment of 10 °C min⁻¹ under a nitrogen atmosphere from 27 °C to 600 °C was utilized for TGA analysis. The basicity of the materials was analyzed using the temperature-programmed desorption (CO₂-TPD) technique on a Quantachrome Autosorb-iQ2-TPX, CHEMBETTM TPR/TPD instrument. Before the analysis, the samples were outgassed at 500 °C with a heating ramp of 10 °C min⁻¹ under continuous He gas flow for 30 min. After cooling to room temperature, the probe gas (CO₂) was adsorbed for 30 min, and the physically adsorbed gas was removed by flowing He gas for 30 min. Finally, the desorbed gases were analyzed on thermal conductivity (TCD) detector against temperature with a ramp rate of 10 °C min⁻¹ in the

temperature range from 50 °C – 600 °C. Similarly, acidity was calculated using NH₃-TPD analysis.

Catalytic reaction procedure

Selective reduction of cinnamaldehyde in thermal conditions

20 mg of catalyst, 0.5 mmol of cinnamaldehyde (CAL), 4.5 mmol of formic acid, and 3 mL of water were charged in a Teflon liner secured with a stainless-steel jacket, and the reactions were conducted at a desired temperature, for example, 140 °C, in an oil bath for 6 h. After the reaction, the reaction mixture was centrifuged, and the catalyst was separated. The organic phase of the reaction was carefully extracted with ethyl acetate for CAL conversion and product selectivity determination, which were monitored using gas chromatography (given below). The products were confirmed by GC-MS and ¹H NMR.

Selective reduction of cinnamaldehyde in photochemical conditions

The selective hydrogenation of CAL was conducted in a homemade photoreactor using a 150 W LED (Fig. S1). The reactor was charged with 0.5 mmol of CAL, 20 mg catalyst, and 5 mL solvent, followed by H₂ purging thrice. Finally, the reactor was filled with 2 bar H₂, and the reaction was conducted for varied reaction intervals. The CAL conversion and product selectivity were determined using gas chromatography (given below). The product was confirmed by GC-MS and ¹H NMR.

The conversion and product selectivity were monitored by gas chromatography (GC, Yonglin 6100; BP-5; 30 m × 0.25 mm × 0.25 mm) using the following equations.

$$\text{Substrate conversion (\%)} = \frac{\text{Moles of substrate reacted}}{\text{Initial moles of substrate}} \times 100 \quad (\text{S1})$$

$$\text{Product selectivity (\%)} = \frac{\text{Moles of specific product formed}}{\text{Moles of substrate converted}} \times 100 \quad (\text{S2})$$

The product was confirmed using GC-MS (Shimadzu GCMS-QP 2010 Ultra Rtx-5 Sil Ms; 30 m × 0.25 mm × 0.25 mm). The reactant conversion and product selectivity were determined by calculating the response factor obtained from the GC calibration using a standard addition method. The standards containing a fixed concentration of n-decane with different

concentrations of reactants were prepared in ethyl acetate for the thermal condition and in IPA for the reactions conducted in photochemical conditions. Solutions were injected in GC (triplicate injection), and the areas were recorded. After the analysis, the calibration curve was plotted with concentration (g/L) vs peak area, and the reactant conversion and its corresponding product selectivity were determined using the above expression.

The response factors for reactant and product were calculated using the following equation. For the calculation of the response factor, n-decane was used as an internal standard in the reaction mixture.

$$\frac{Area(x)}{[x]} = F \times \frac{Area(s)}{[s]} \quad (S3)$$

Where F is the response factor, Area(x) and Area(s) are areas under the peaks for analyte and n-decane, respectively. [x] and [s] are the concentrations of analyte and n-decane, respectively.

Procedure for the detection of H₂ and CO₂ generated from FA

The experimental verification of hydrogen and carbon dioxide generation from formic acid was evaluated using GC and GC-MS. 20 mg of catalyst, 0.5 mmol of cinnamaldehyde (CAL), 4.5 mmol of formic acid, and 3 mL of water were charged in a stainless-steel reactor. The reaction was conducted at 140 °C for 2 h. The gas generated during the reaction was collected and injected into the GC using a gas-tight syringe and monitored using TCD detector. A GC report is provided in Fig. S13, containing the chromatograph and the method used for the analysis.

Turn Over Frequency (TOF) Calculation

TOF of the reaction was calculated by equation S4. The moles of the catalyst used was calculated by considering the whole mass of the catalyst. The moles of CN, ZnO, and Ru NPs were calculated and considered to calculate the total moles used to convert the substrate.

$$Turn\ over\ frequency\ (TOF) = \frac{Moles\ of\ cinnamaldehyde\ converted}{Moles\ of\ catalyst\ used \times reaction\ time} \quad (S4)$$

Apparent Quantum Yield (ϕ) Calculation

The quantum yield of the reaction was calculated using eq S5, which gives the ratio between the electron involved in the reaction and the molar flow of photons introduced into the reactor. The apparent wavelength (λ) of photons was estimated from the band gap of the catalyst, determined from Tauc plots. The quantum yield calculated in this manner was not the exact value but served as a reference to compare the photo efficiency of the photocatalytic system.

$$\text{Apparent Quantum Yield } (\phi) = \frac{\text{Number of reacted electron} \times 100}{\text{Number of incident photon}} \quad (\text{S5})$$

$$\text{Number of reacted electron} = \text{Reactant conversion } (\text{mol}^{-1}) \times N_A (\text{mol}) \quad (\text{S6})$$

$$\text{Number of incident photon} = \frac{\text{Light intensity } (\text{Wm}^{-2}) \times \text{Area } (\text{m}^2) \times \text{Time } (\text{s})}{\frac{h (\text{Js}) c (\text{ms}^{-1})}{\lambda (\text{m})}} \quad (\text{S7})$$

$$\phi = \frac{\text{Reactant conversion } (\text{mol}^{-1}) \times N_A (\text{mol}) \times h (\text{Js}) c (\text{ms}^{-1}) \times 100}{\text{Light intensity } (\text{Js}^{-1}\text{m}^{-2}) \times \text{Area } (\text{m}^2) \times \text{Time } (\text{s}) \times \lambda (\text{m})} \quad (\text{S8})$$

Photoelectrochemical measurement

The photoelectrochemical analyses were performed with PGSTAT302N Autolab electrochemical workstation using standard three-electrode grouping in Pyrex cell with a 0.5 M aqueous sodium sulphate 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 μ l of Nafion. 20 ml of the photocatalyst was added in the binder solution and sonicated for 10 min. The binder solution was casted dropwise over the glass surface using a dropper and hotplate with a temperature of 45 °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) with a cut-off filter ($\lambda > 420$ nm and intensity of 100 mW.cm^{-2}).

Nitro blue tetrazolium (NBT) test

10 mL of 2.5×10^{-5} M aqueous solution of NBT was mixed with the 5 mg of the catalyst. The mixture was illuminated with light under continuous stirring. After 10 min, the catalyst was separated from the solution using a centrifuge. The solution was monitored using a UV-visible spectrophotometer, and its absorbance for NBT was compared with the neat stock solution. A decreased absorbance peak of NBT after light illumination confirms the capability of the photocatalyst for the generation of $\text{O}_2^{\cdot-}$.

Terephthalic acid (THA) test

The 5×10^{-3} M aqueous solution of THA was prepared with a small amount of NaOH to make THA soluble in an aqueous medium. 20 mg of catalyst was mixed with the 20 ml of THA solution and exposed to light for 30 min. Then catalyst was separated from the solution using a centrifuge. The clear solution was monitored using a fluorescence spectrophotometer with an excitation wavelength of 330 nm. The emission peak at 425 nm confirms 2-hydroxyl terephthalic acid in the reaction mixture. The OH radicals react with THA (non-fluorescent) and convert it into 2-hydroxyl terephthalic acid (fluorescent). The emission peak of the reaction mixture was compared with the stock solution.

Table S1 Surface elemental composition, determined from XPS analysis.

S.N.	Catalyst	Atomic (%)				
		Ru (283.9 eV)	Zn (1021.3 eV)	C (286.9 eV)	N (398.3 eV)	O (531.0 eV)
1	1%Ru@ZnO(1.5)/CN	0.50	6.3	48.52	32.4	12.3

2	3%Ru@ZnO(1.5)/CN	0.89	6.24	53.1	24.9	12.6
3	1%Ru@ZnO(1.5)/CN(spent)	0.48	6.0	48.4	32.9	12.1
4	3%Ru@ZnO(1.5)/CN(spent)	0.85	5.9	52.7	24.7	12.0

Table S2 Surface area and total pore volume derived from N₂-sorption analysis.

S.N.	Catalyst	S _{BET} (m ² g ⁻¹)	Total pore vol. (cm ³ g ⁻¹)
1	ZnO	7	0.0265
2	CN	45	0.25
3	ZnO(1)/CN	65	0.23
4	ZnO(1.5)/CN	64	0.23
5	ZnO(2)/CN	63	0.22
6	1%Ru@ ZnO(1.5)/CN	67	0.23
7	3%Ru@ ZnO(1.5)/CN	70	0.24

S_{BET} = BET Surface area, TPV= Total pore volume.

Table S3 Band gap of the synthesized catalysts calculated from tauc plot.

Entry	Catalyst	Band gap
1	ZnO	3.13
2	CN	2.83
3	ZnO(1.5)/CN	2.80
4	1% Ru@ ZnO(1.5)/CN	2.78
5	2% Ru@ ZnO(1.5)/CN	2.73
6	3% Ru@ ZnO(1.5)/CN	2.72

Entry	Catalyst	Pre-exponential functions			Decay lifetimes (ns)				Fractional contribution		
		α_1	α_2	α_3	τ_1	τ_2	τ_3	$\langle\tau\rangle$	f_1	f_2	f_3
1	ZnO	29	8	63	6.40E-10	2.52E-09	1.24E-10	1.37	0.39	0.44E	0.17
2	CN	29	13	58	6.52E-10	3.51E-09	1.23E-10	2.42	0.26	0.64	0.1
3	CN(1.5)/ZnO	19	11	70	1.12E-09	4.96E-09	2.52E-10	3.20	0.23	0.59	0.19
4	3%Ru@CN(1.5)/ZnO	39	12	49	1.78E-09	6.97E-09	4.21E-10	4.11	0.4	0.48	0.12

Table S4 Best fitted parameters of multiexponential components for decay curve.

Table S5 Selective hydrogenation of cinnamaldehyde over various metal oxide catalysts with formic acid.

S.N.	Catalyst	^a Conversion (%)	^a Selectivity (%)		
			COL	HCAL	HCOL
1	TiO ₂	5	43	57	0
2	Al ₂ O ₃	9	50	50	0
3	MgO	2.5	0	100	0
4	ZnO	17	100	0	0
5	In ₂ O ₃	12	0	100	0
6	SnO ₂	15	50	13	37

Reaction conditions: Cinnamaldehyde (0.5 mmol), FA (4.5 mmol), catalyst amount (20 mg), water (3 mL), temperature (140 °C), time (6 h). ^aAverage of three measurements presented as integer.

Table S6 Comparative activity data of transition metal decorated catalysts in thermal and photocatalytic hydrogenation of CAL.

Entry	Catalyst	Condition	Conversion (%)	Selectivity (%)		
				COL	HCAL	HCOL
1	1%Co@ZnO(1.5)/CN	^a Thermal	32	27	21	52
2	1%Ni@ZnO(1.5)/CN	^a Thermal	29	34	20	46
3	1%Ru@ZnO(1.5)/CN	^a Thermal	96	85	0	15
4	3%Co@ZnO(1.5)/CN	^b Photocatalytic	~1	-	>99	-
5	3%Ni@ZnO(1.5)/CN	^b Photocatalytic	~6	-	>99	-
6	3%Ru@ZnO(1.5)/CN	^b Photocatalytic	96	-	>99	-

Reaction conditions: ^aCAL (0.5 mmol), FA (4.5 mmol), catalyst (20 mg), water (3 mL), temperature (140 °C), time (6 h). ^bCAL (0.5 mmol), catalyst amount (20 mg), IPA (5 mL), 150 W LED, room temperature, H₂ (2 bar), time (5 h).

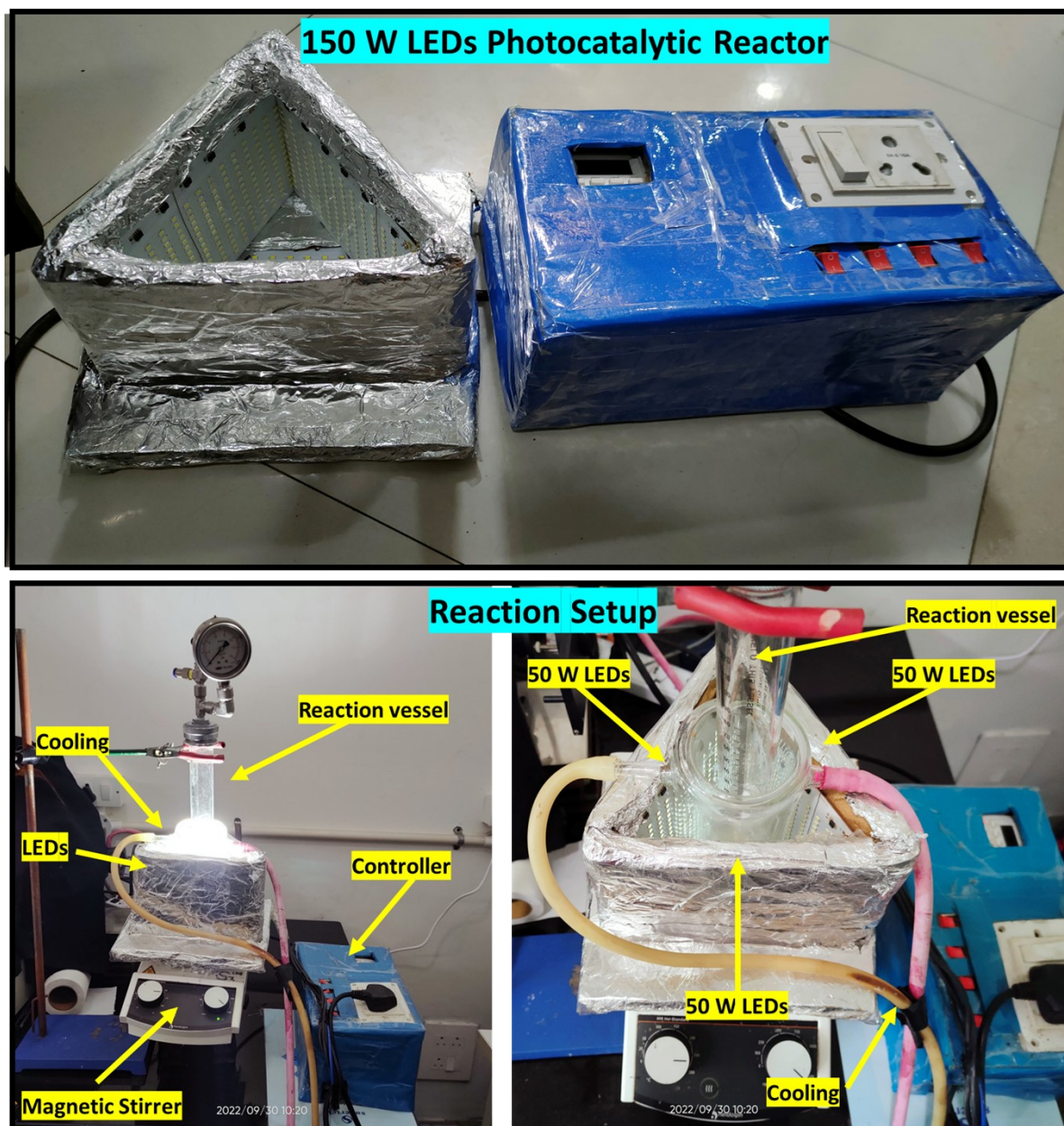


Fig. S1 The photograph of photocatalytic reactor and reaction setup for the photocatalytic reduction.

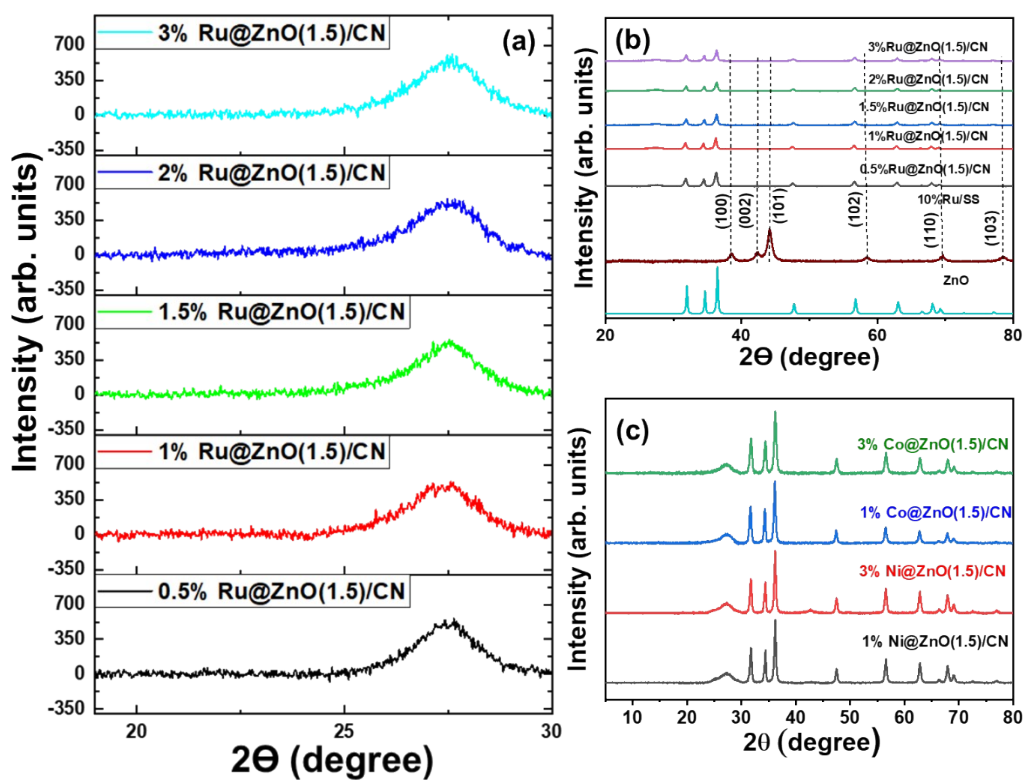


Fig. S2 XRD patterns of (a) RuNPs decorated ZnO(1.5)CN by keeping the intensity at the same scale, (b) ZnO and Ru NPs decorated ZnO(X)CN catalysts comparing peaks of Ru NPs originating from 10%Ru/SS catalyst, and (c) Ni NPs decorated ZnO(1.5)CN and Co NPs decorated ZnO(1.5)CN catalysts.

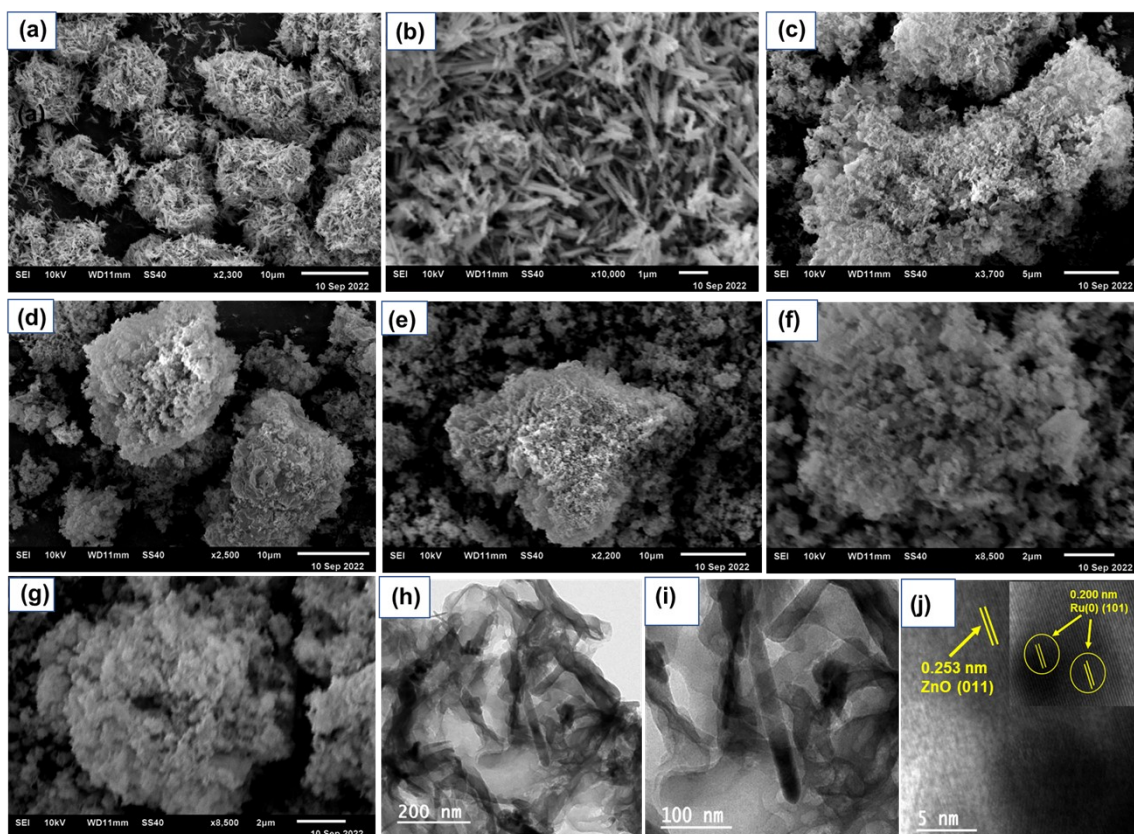


Fig. S3 SEM images of (a) ZnO, (b) magnified image of ZnO, (c) ZnO(1)/CN, (d) ZnO(1.5)/CN, (e) ZnO(2)/CN, (f) 1%Ru@ZnO(1.5)/CN, (g) 3%Ru@ZnO(1.5)/CN, and (h-j) HRTEM images of 3%Ru@ZnO(1.5)/CN of different magnifications.

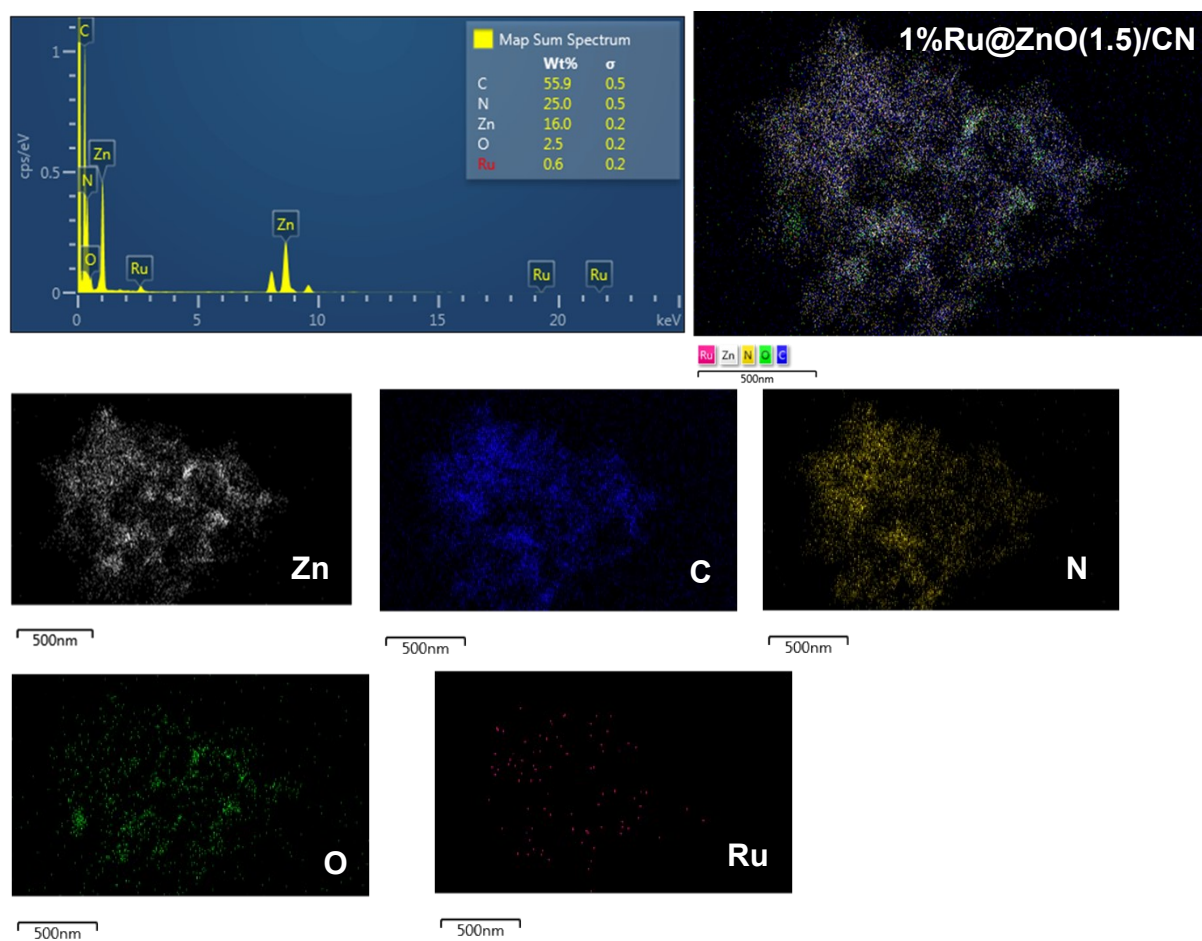


Fig. S4 EDS and elemental mapping of 1%Ru@ZnO(1.5)/CN.

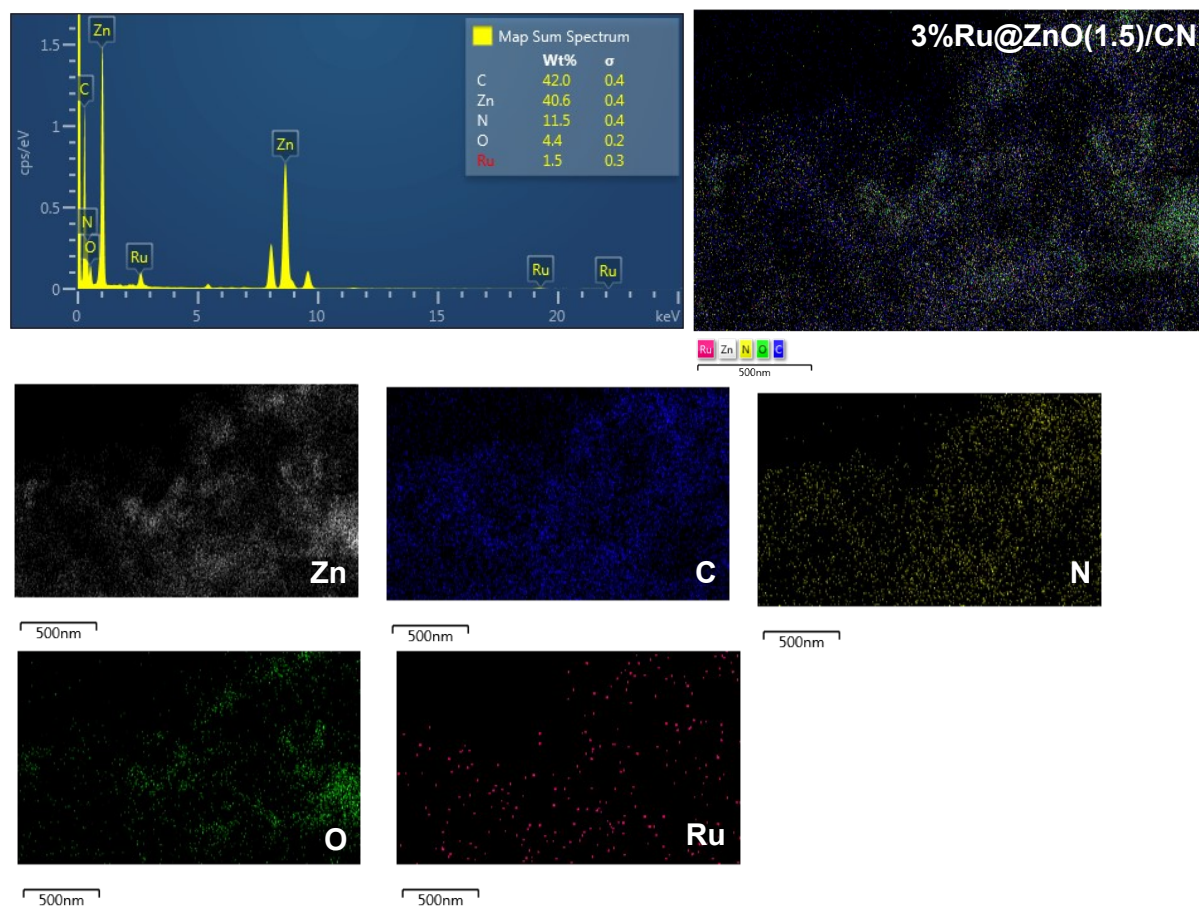


Fig. S5 EDS and elemental mapping of 3%Ru@ZnO(1.5)/CN.

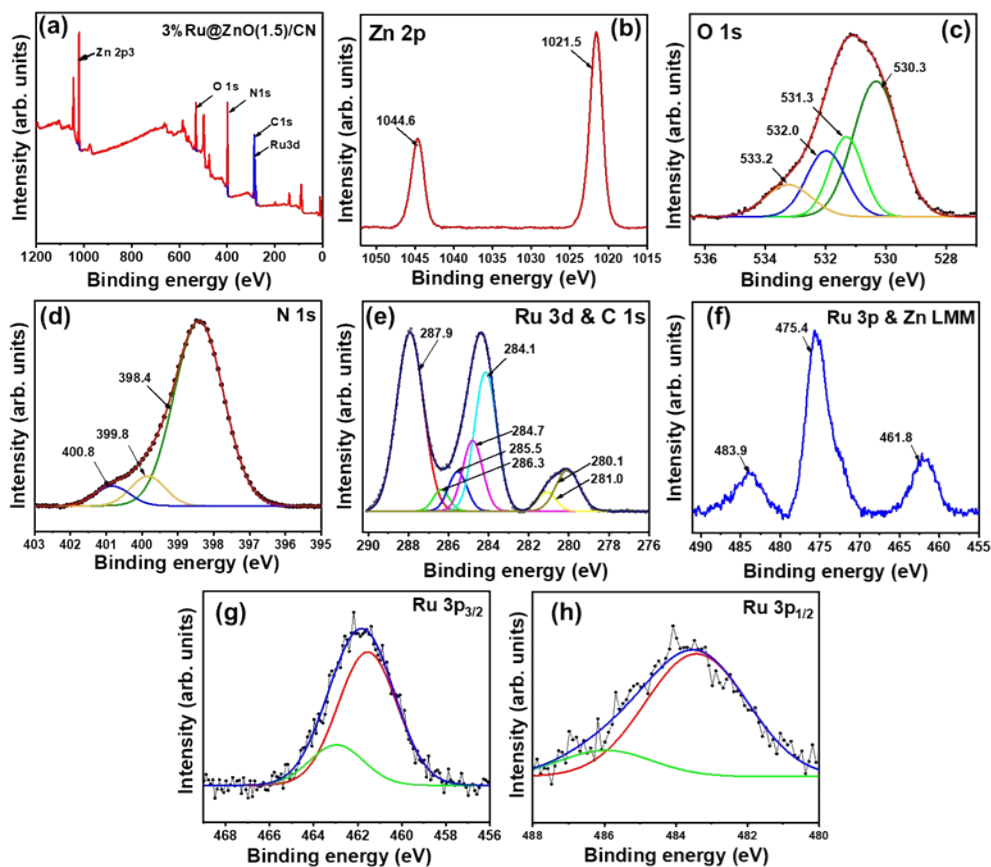


Fig. S6 (a) XPS surface survey of 3%Ru@ZnO(1.5)/CN, (b) Zn 2p, (c) O 1s, (d) N 1s, (e) Ru 3d and C 1s, (f) Ru 3p and Zn LMM, (g) Ru 3p_{3/2}, and (h) Ru 3p_{1/2}.

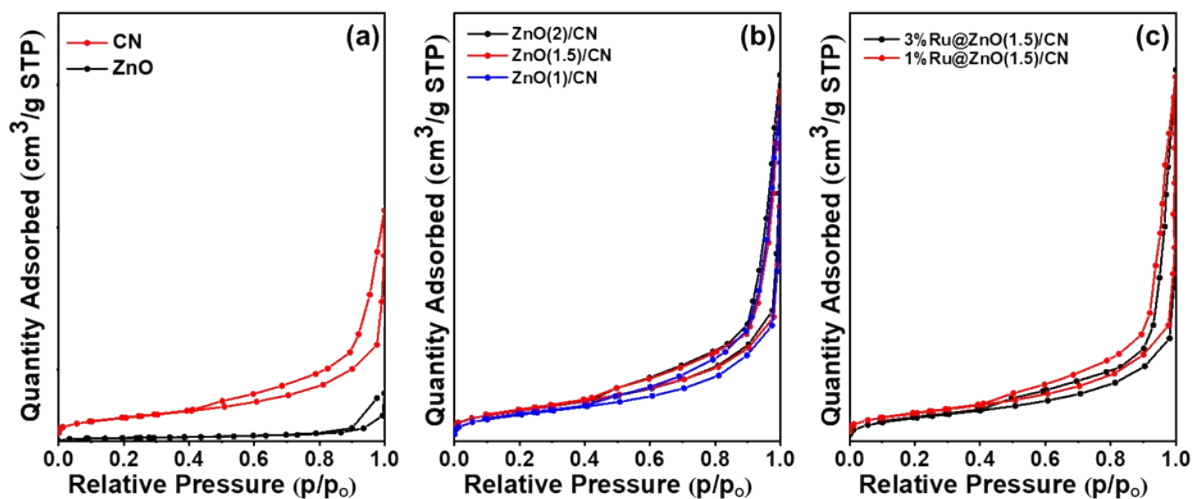


Fig. S7 N₂-adsorption/desorption isotherms of (a) CN and ZnO, (b) ZnO/CN composites, and (c) 1%Ru@ZnO(1.5)/CN and 3%Ru@ZnO(1.5)/CN.

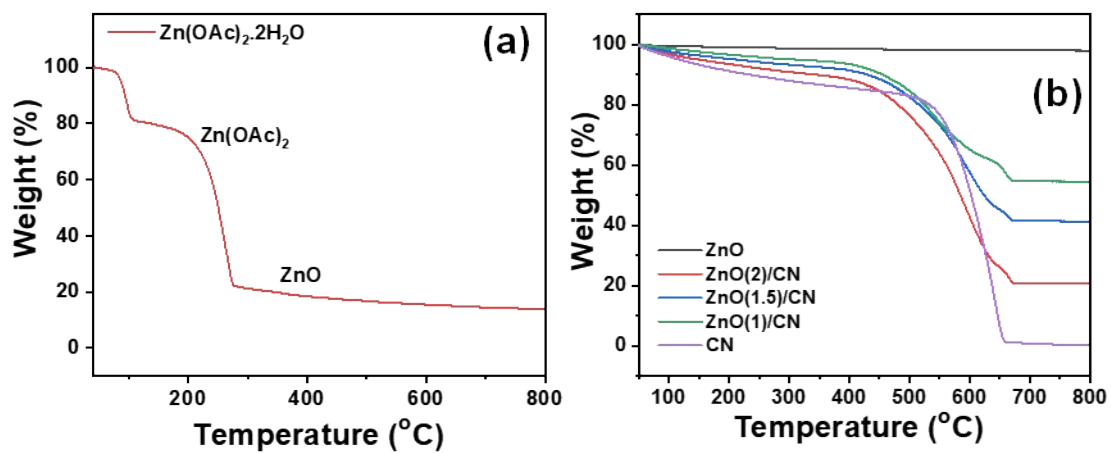


Fig. S8 TGA profiles for (a) $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$, and (b) ZnO , CN , and ZnO(X)/CN composites.

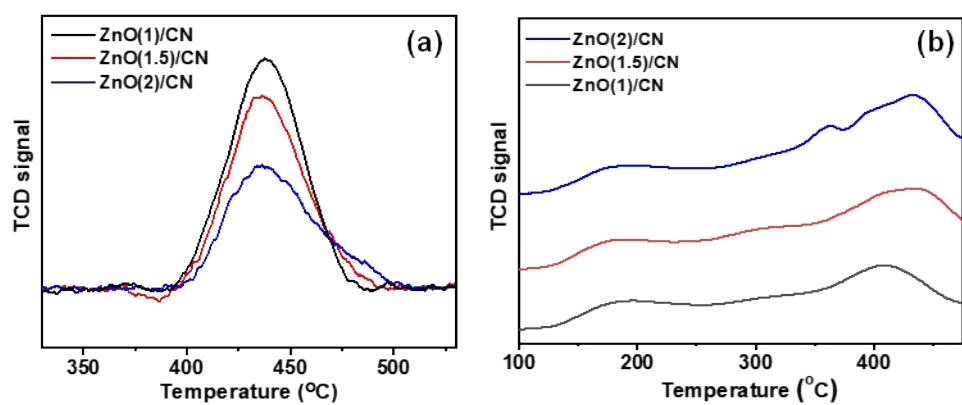


Fig. S9 (a) CO₂ temperature-programmed desorption profiles, and (b) NH₃ temperature-programmed desorption profiles of all the ZnO(X)/CN composites.

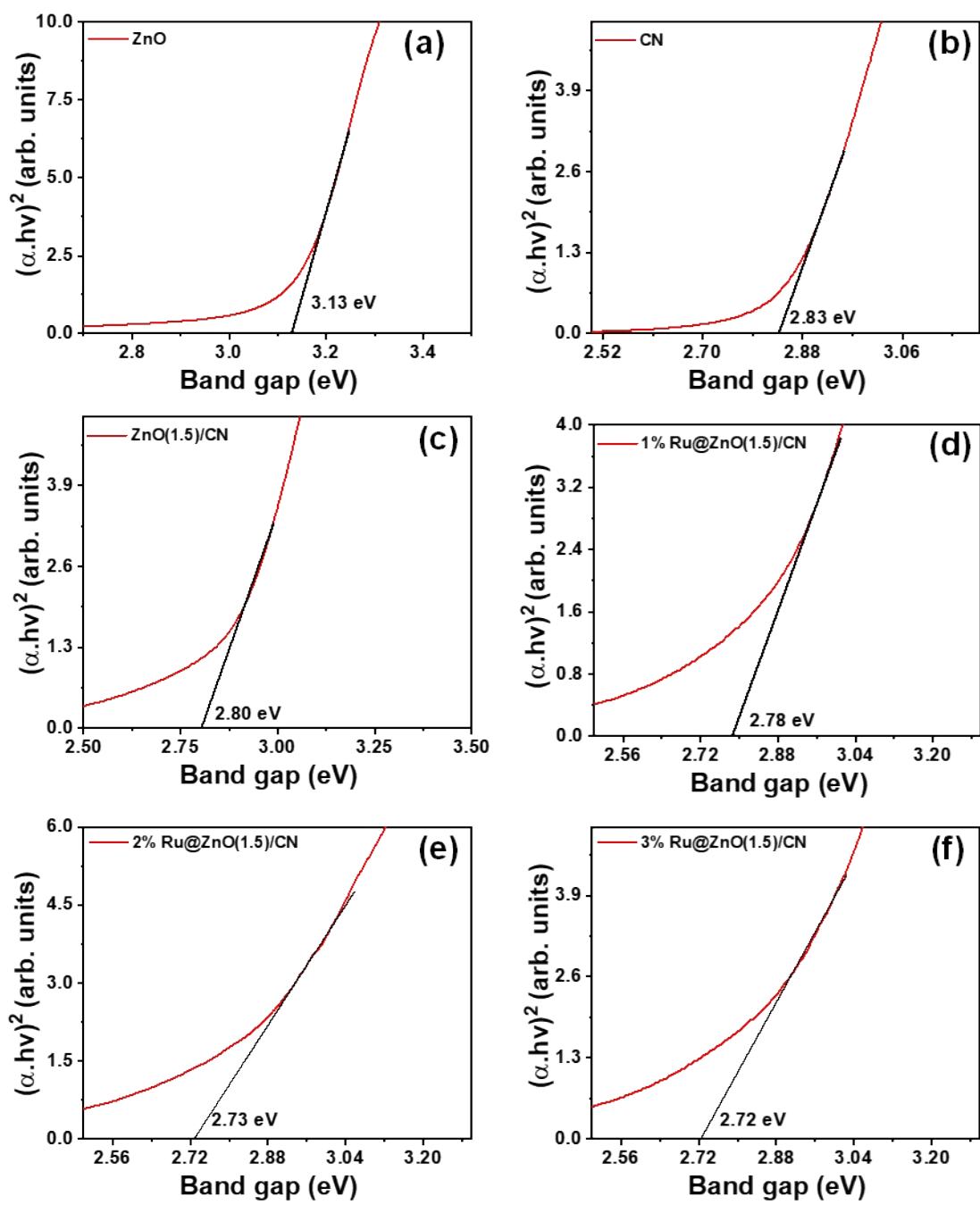


Fig. S10 Tauc plots of all synthesized photocatalyst.

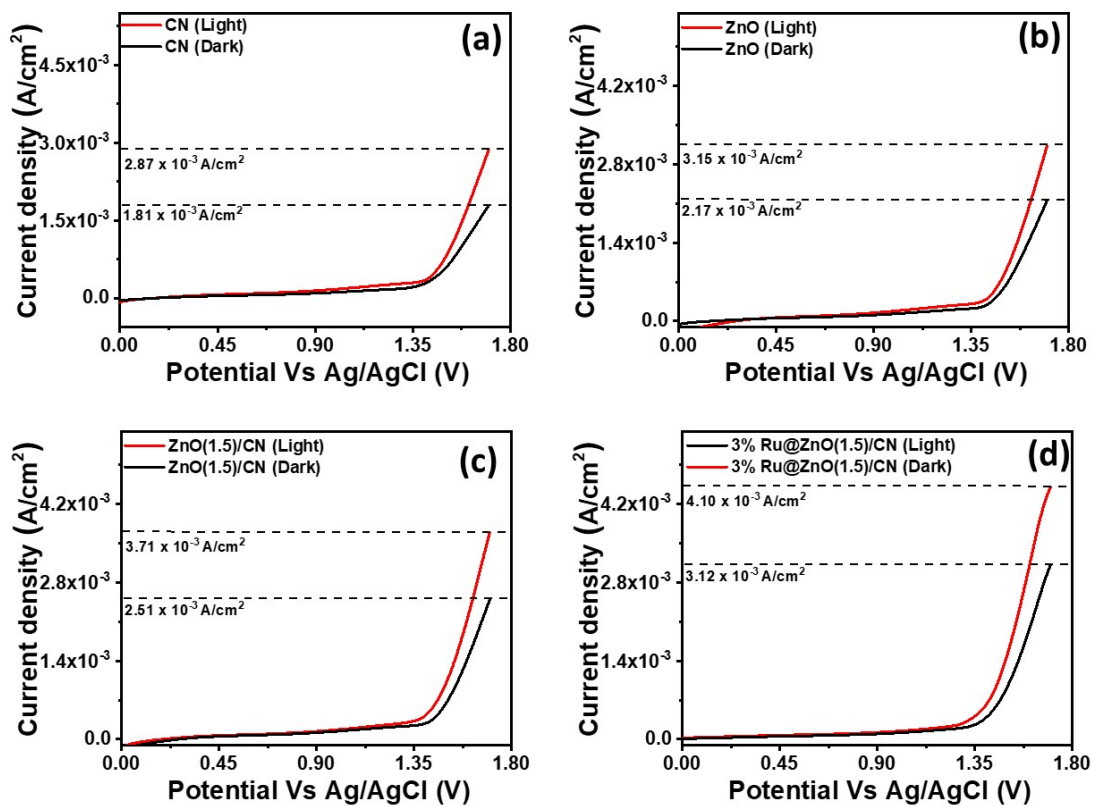


Fig. S11 LSV spectra of pristine in dark and light for (a) CN, (b) ZnO, (c) ZnO(1.5)/CN and (d) 3%RuZnO(1.5)/CN.

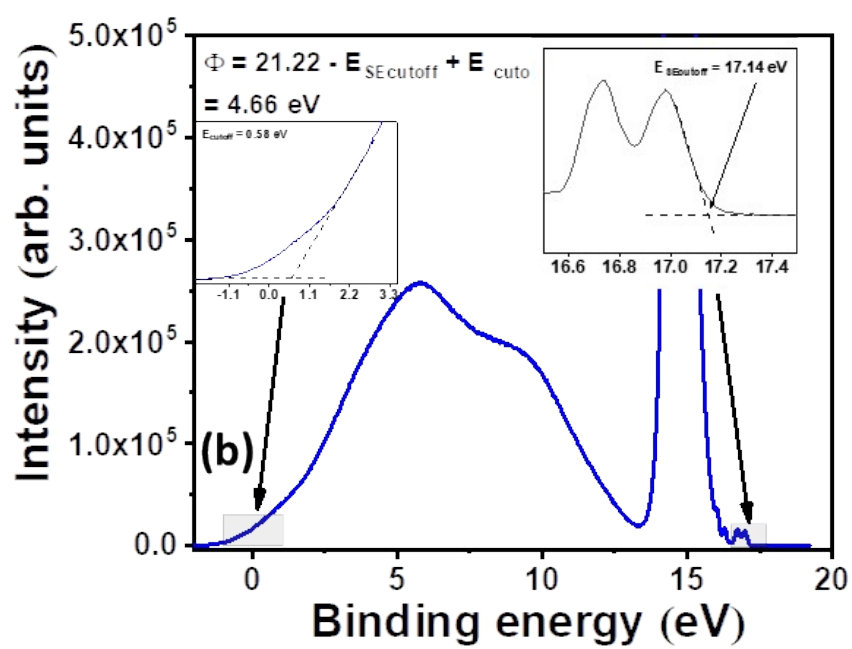
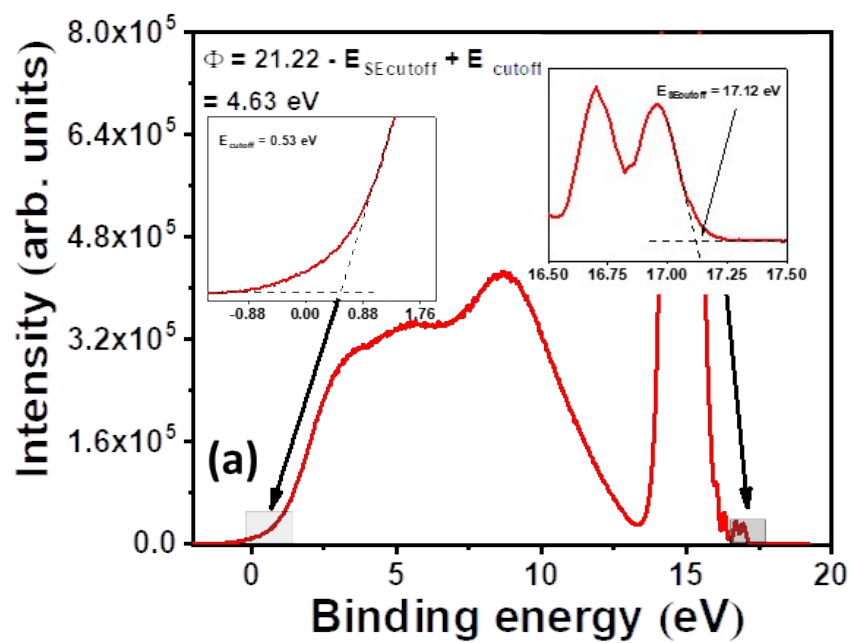
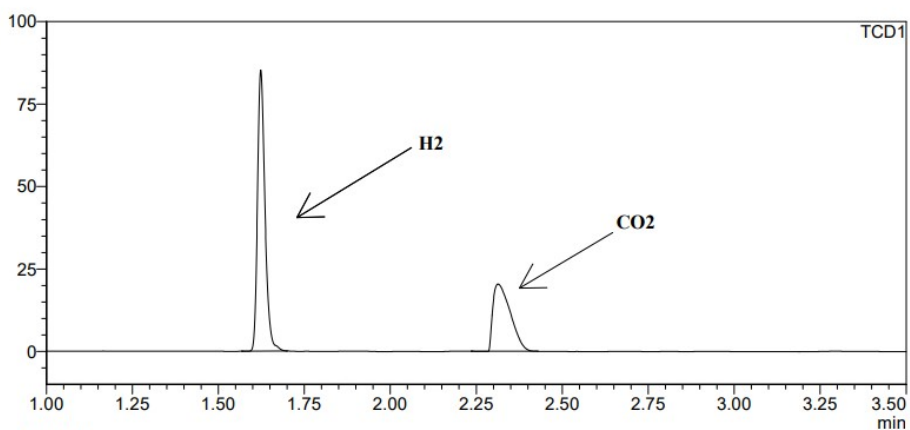


Fig. S12 UPS spectra of (a) CN(1.5)/ZnO, and (b) 3% Ru@CN(1.5)/ZnO.



<Peak Table>

TCD1

Peak#	Name	Ret. Time	Area	Height	Conc.	Unit	Mark
1	H2	1.624	128210	83285	64.130		M
2	CO2	2.314	71713	20345	35.870		M
Total			199923	103630			

Method

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 Modified : 21-04-2023 13:29:52
 ModifiedBy : IIT ROPAR

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 Temperature : 45.0 C
 Carrier Gas : N2
 Flow Control Mode : Velocity
 Pressure : 73.8 kPa
 Total Flow : 64.1 mL/min
 Column Flow : 1.20 mL/min
 Linear Velocity : 27.9 cm/sec
 Purge Flow : 3.0 mL/min
 Split Ratio : 50.0
 High Pressure Injection : Off
 Carrier Gas Saver : Off

Fig. S13 GC-TCD chromatogram showing the composition of gas generated from the formic acid mediated thermal hydrogenation of CAL. Reaction conditions: (CAL (0.5 mmol), FA (4.5 mmol), catalyst (20 mg), water (3 mL), temperature (140 °C), time (3 h)).

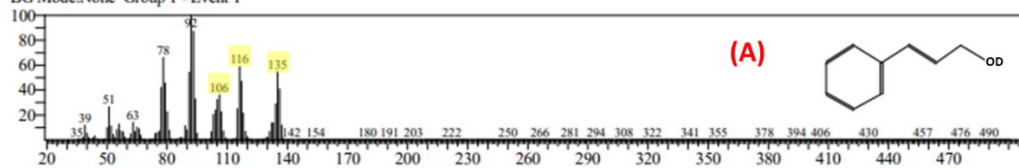
Library Search

<< Target >>

Line#:1 R.Time:13.625(Scan#:2526) MassPeaks:464

RawMode:Single 13.625(2526) BasePeak:92.05(10000)

BG Mode:None Group 1 - Event 1



Hit#:1 Entry:16922 Library:NIST17.lib

SI:80 Formula:C9H10O CAS:104-54-1 MolWeight:134 RetIndex:1243

CompName:2-Propen-1-ol, 3-phenyl-

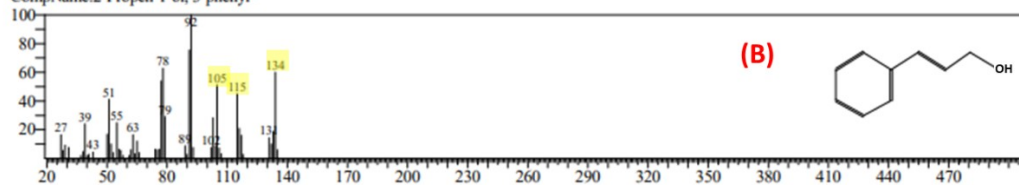
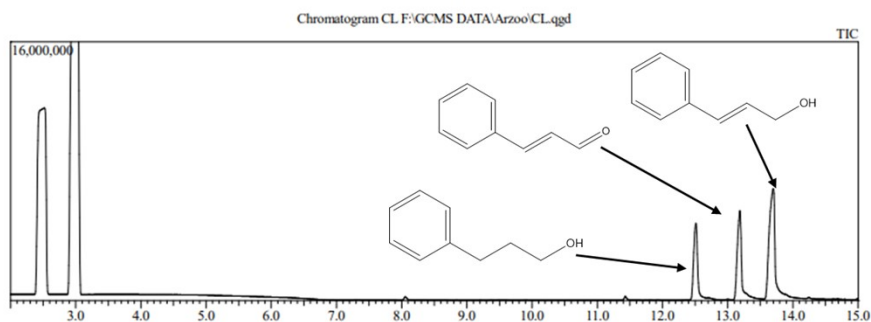
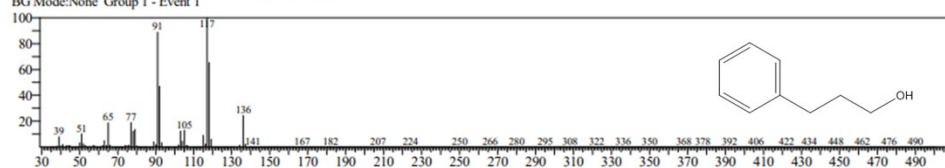


Fig. S14 GC-MS spectrum of (A) Deuterated cinnamyl alcohol, obtained by using D₂O as a solvent, and (B) cinnamyl alcohol, obtained by using H₂O as a solvent. Reaction condition: CAL (0.5 mmol), FA (4.5 mmol), catalyst (20 mg), solvent (3 mL), temperature (140 °C), time (6 h).



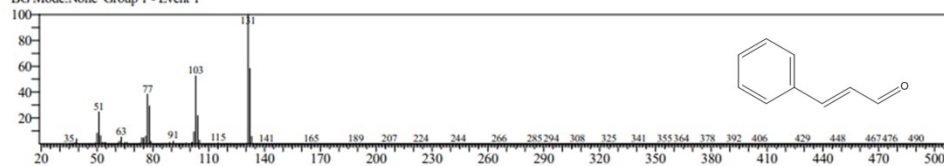
Spectrum Comparison

Spectrum1 #Data# THERMAL.qgd R.Time:12.480(Scan#:2297)
 MassPeaks:466
 RawMode:Single 12.480(2297) BasePeak:117.10(10000)
 BG Mode:None Group 1 - Event 1



Spectrum Comparison

Spectrum1 #Data# THERMAL.qgd R.Time:13.170(Scan#:2435)
 MassPeaks:466
 RawMode:Single 13.170(2435) BasePeak:131.10(10000)
 BG Mode:None Group 1 - Event 1



Spectrum Comparison

Spectrum1 #Data# THERMAL.qgd R.Time:13.645(Scan#:2530)
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 RawMode:Single 13.645(2530) BasePeak:92.05(10000)
 BG Mode:None Group 1 - Event 1

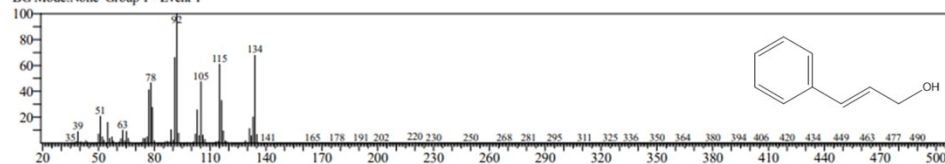


Fig. S15 GC-MS chromatograph of the reaction mixture recovered after 3 h in thermal hydrogenation of CAL. (Reaction conditions: (CAL (0.5 mmol), FA (4.5 mmol), catalyst (20 mg), water (3 mL), temperature (140 °C), time (3 h)).

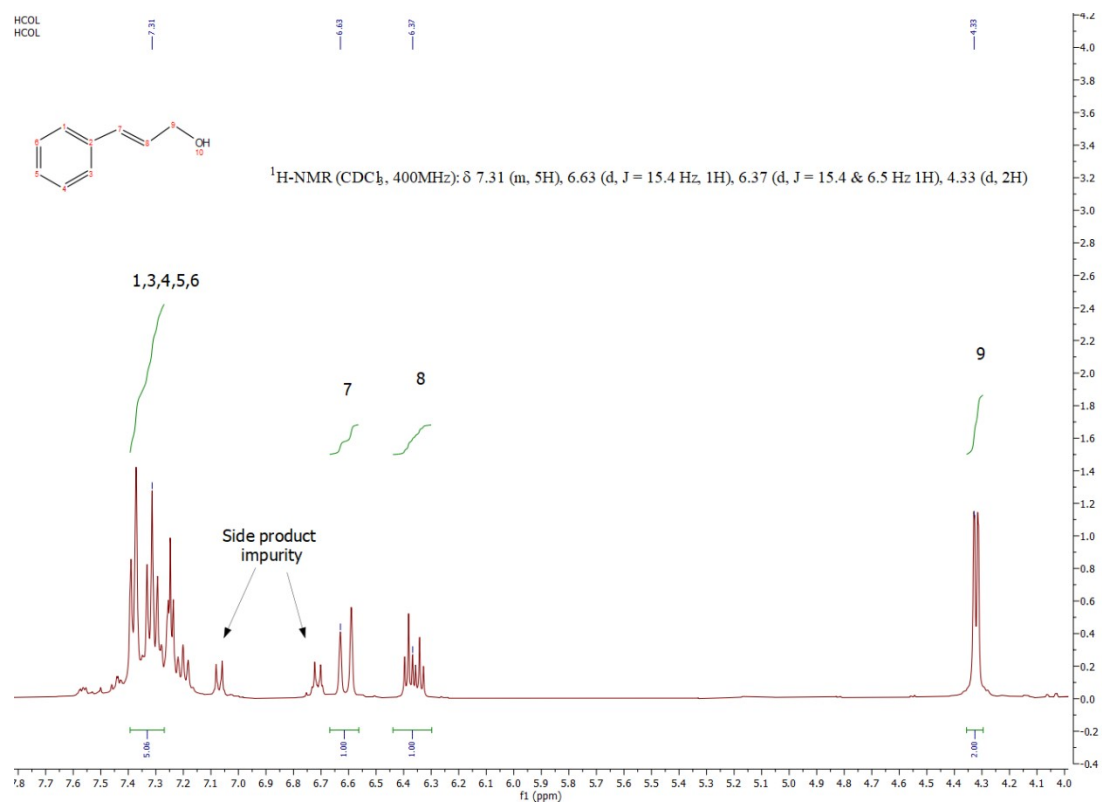


Fig. S16 ^1H NMR of COL in the reaction mixture of thermal hydrogenation of CAL.

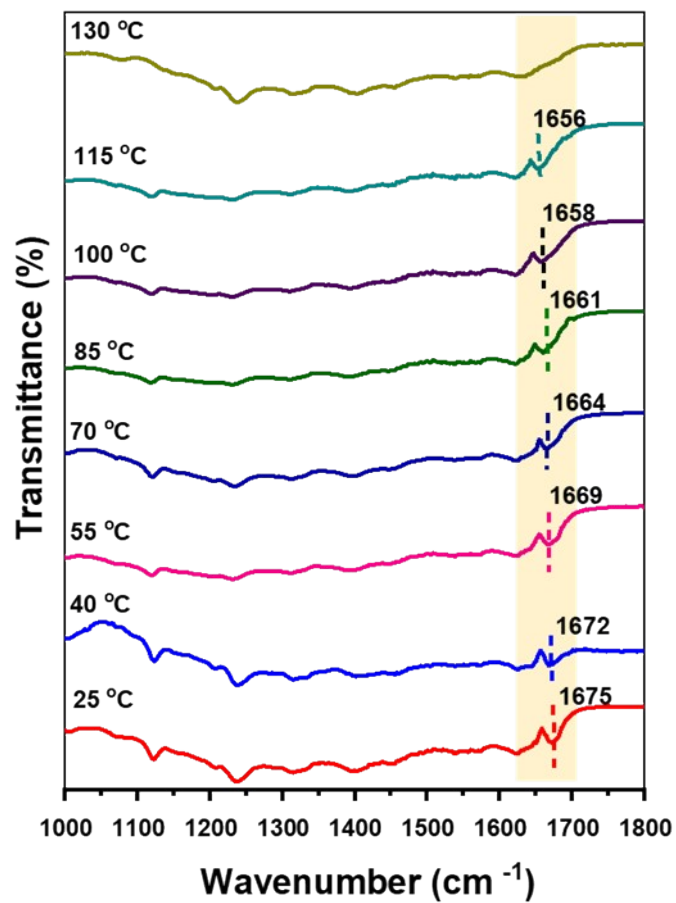
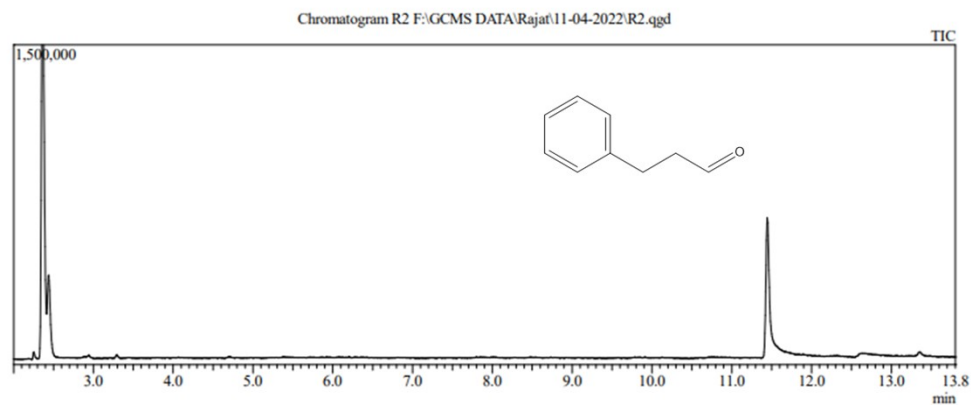


Fig. S17 Temperature-dependent FT-IR spectra of cinnamaldehyde adsorbed over 1%Ru@ZnO(1.5)/CN.



Spectrum Comparison

Spectrum1 #Data# PHOTO.qgd R.Time:11.465(Scan#:2094)
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RawMode:Single 11.465(2094) BasePeak:91.05(10000)
BG Mode:None Group 1 - Event 1

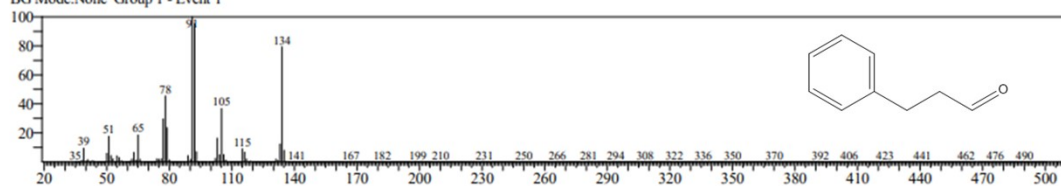


Fig. S18 GC-MS chromatograph of reaction mixture recovered after 5.5 h in photocatalytic hydrogenation of CAL. (Reaction conditions: substrate (0.5 mmol), catalyst amount (20 mg), IPA (5 mL), 150 W LED, room temperature, H₂ (2 bar), time (5.5 h).

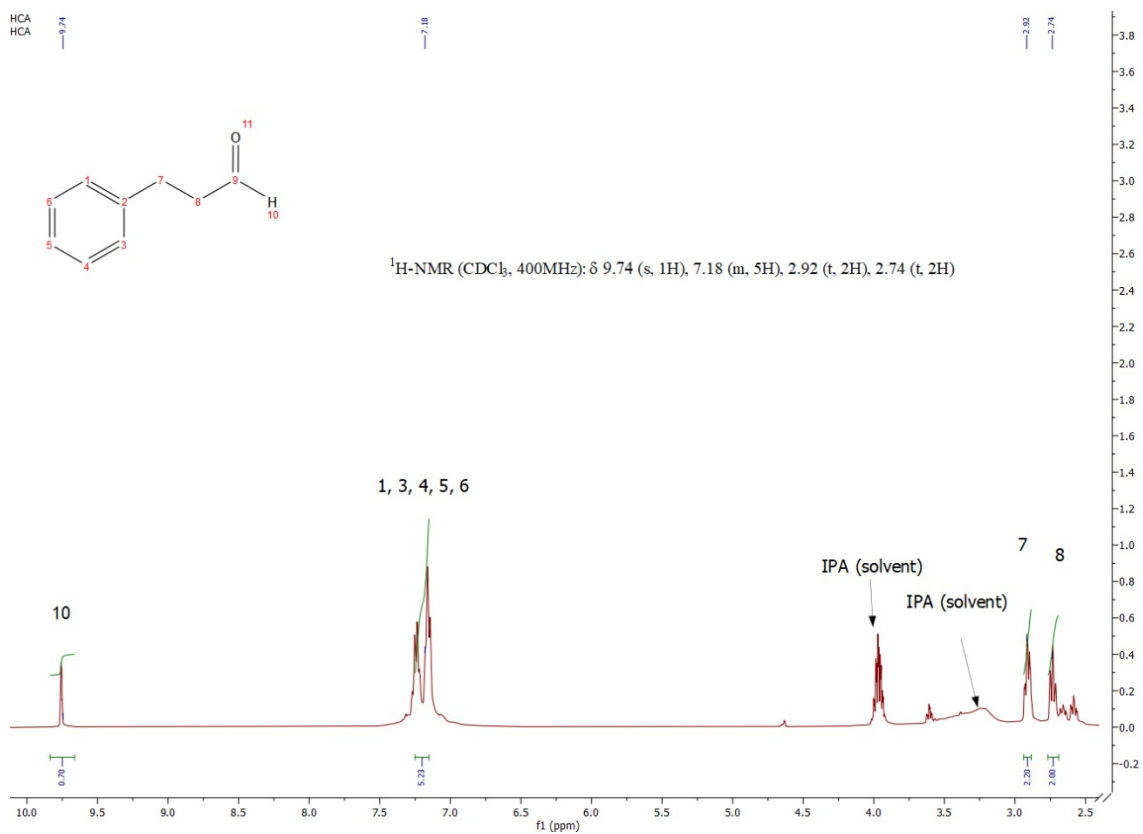


Fig. S19 $^1\text{H NMR}$ of HCAL in reaction mixture of photocatalytic hydrogenation of CAL.

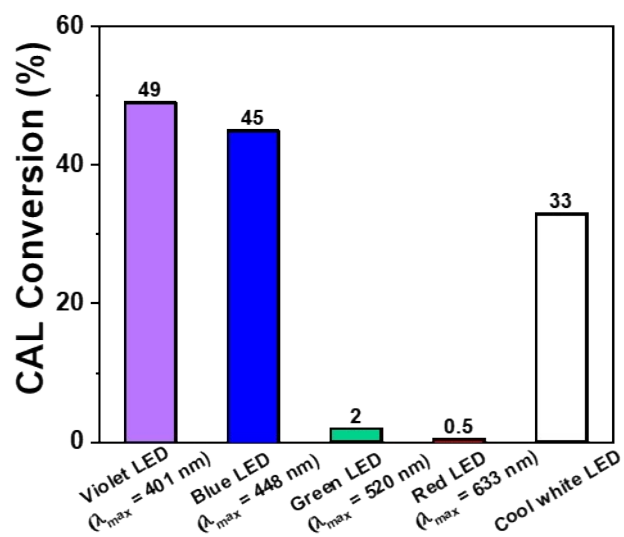


Fig. S20 Spectral response of 3%Ru@ZnO(1.5)/CN in different LEDs. (Reaction conditions: substrate (0.5 mmol), catalyst amount (20 mg), IPA (5 mL), 9W LEDs, room temperature, H₂ (2 bar), time (4 h).

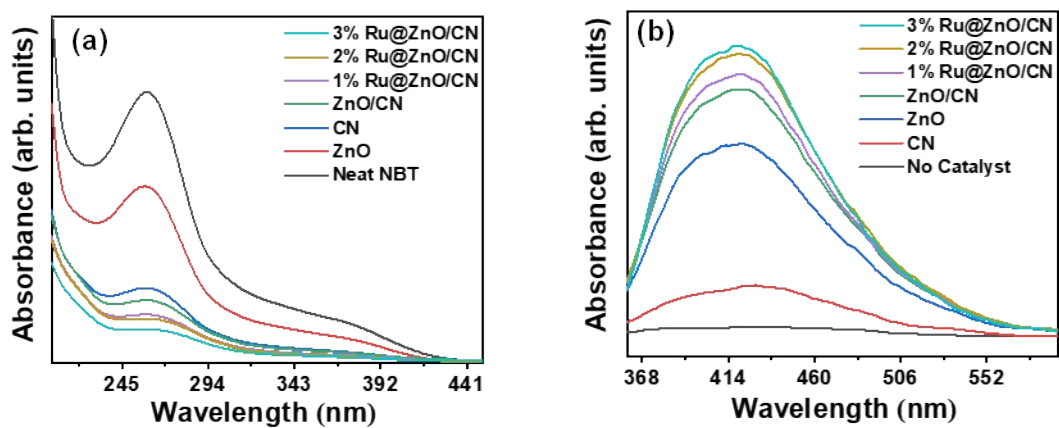


Fig. S21 (a) Comparative absorption spectra of NBT solution after light illumination for 10 min over various photocatalysts, and (b) comparative fluorescence spectra of THA solution after light illumination for 30 min over various photocatalysts.

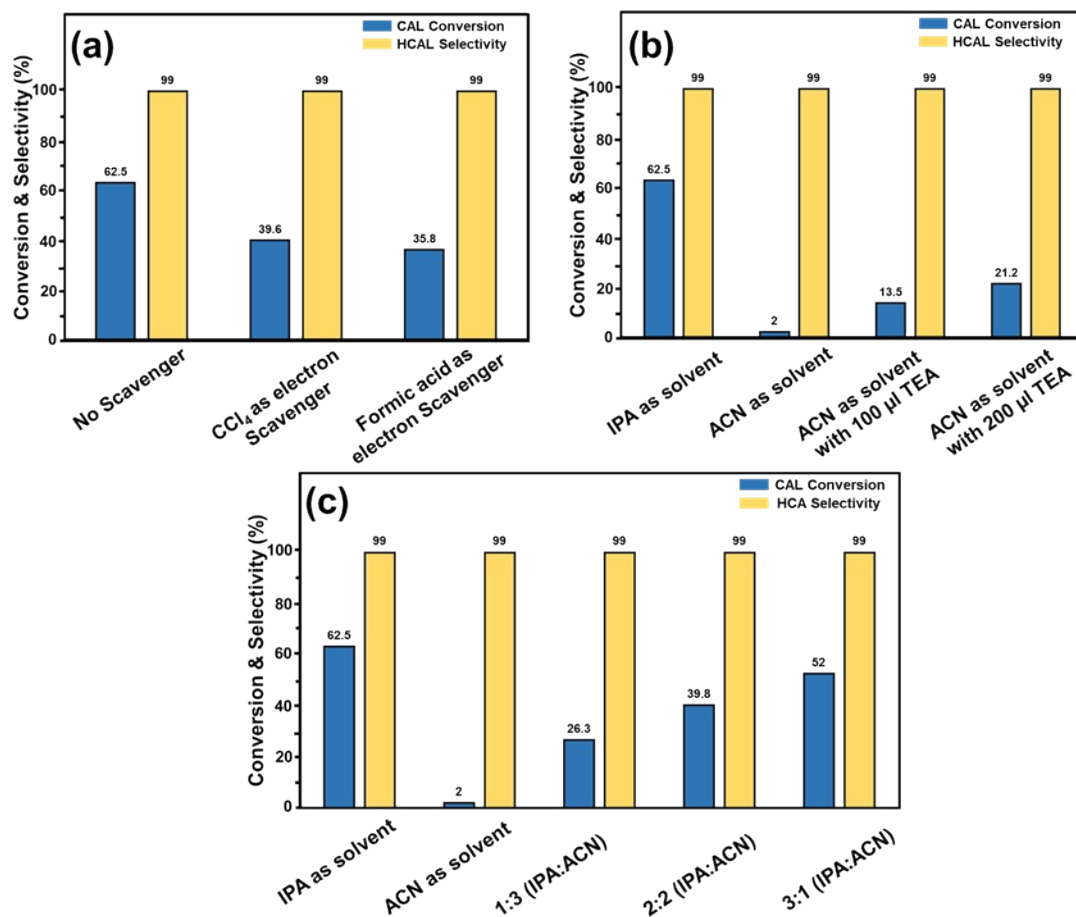


Fig. S22 Control experiments during CAL reduction (a) with using 1.5 mmol of electron scavenger, (b) in IPA, ACN and ACN + TEA, (c) in mixture of different ratio of IPA and ACN [Reaction conditions: 3%Ru@ZnO(1.5)/CN (20 mg), light source (150W LED), CAL (0.5 mmol), solvent (5 ml), time (1 h), and H₂ (2 bars)].

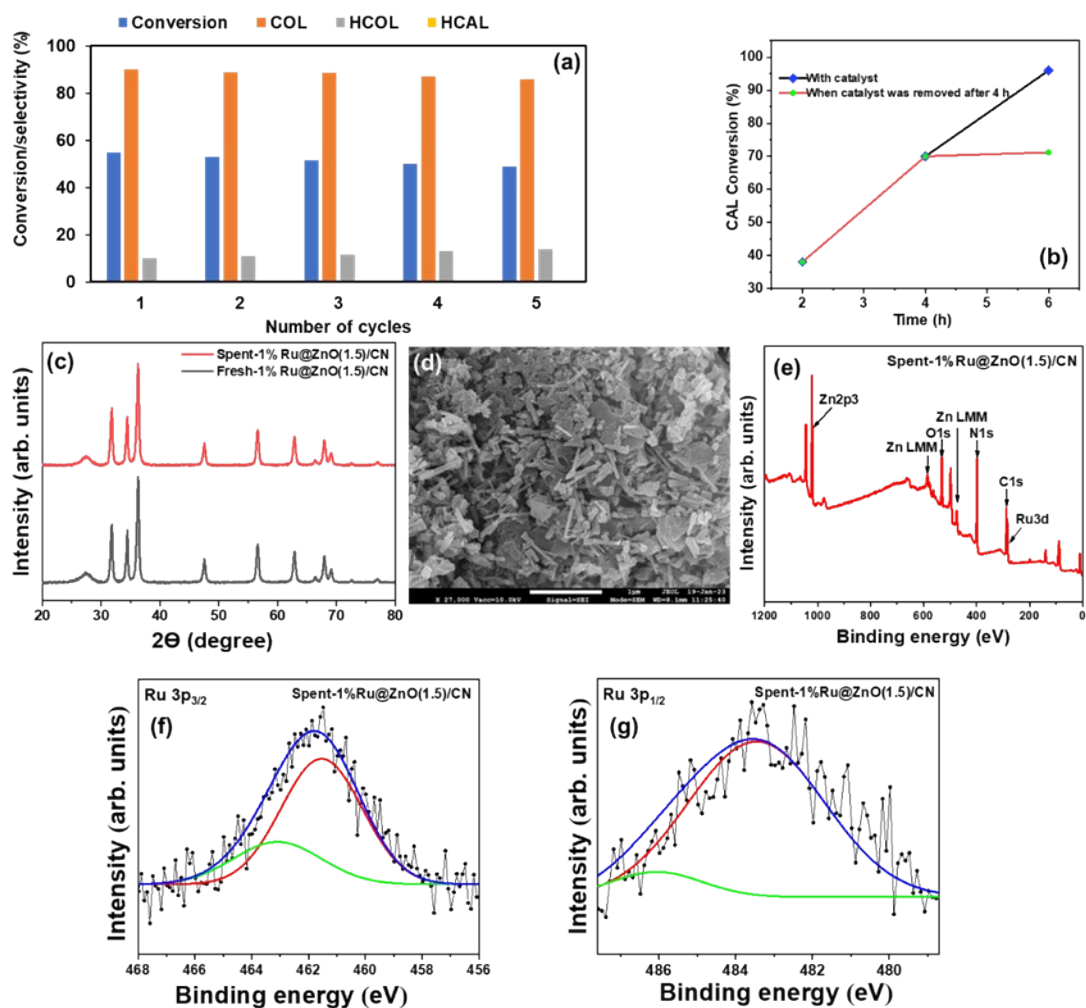


Fig. S23 (a) Catalyst recyclability conducted at half reaction starting from 55% conversion [Reaction conditions: CAL (1.5 mmol), FA (13.5 mmol), catalyst (60 mg), water (9 mL), temperature (140 °C)], (b) Hot filtration test [Reaction conditions: CAL (0.5 mmol), FA (4.5 mmol), catalyst (20 mg), water (3 mL), temperature (140 °C)], (c) XRD, (d) FESEM image of spent catalyst (e) XPS survey scan, (f-g) Deconvoluted Ru 3p of the spent catalyst.

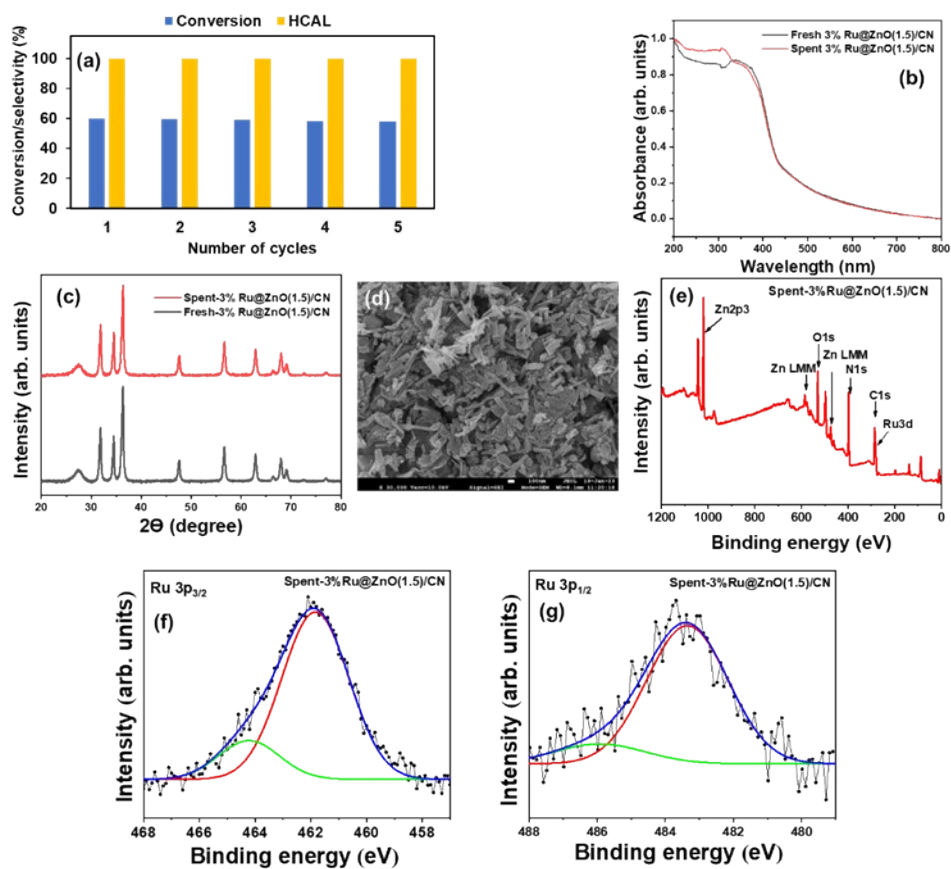


Fig. S24 (a) Catalyst recyclability conducted at half reaction starting from ~58% conversion [Reaction conditions: substrate (1 mmol), catalyst amount (40 mg), IPA (10 mL), 150 W LED, room temperature, H₂ (4 bar)], (b) DRUV-vis spectra, (c) XRD, (d) FESEM image of spent catalyst (e) XPS survey scan, (f-g) Deconvoluted Ru 3p of spent catalyst.