Supplementary information

Cu_2NiSnS_4/g-C_3N_4 S-scheme Photocatalysts: Interfacial Surface Trap States vs Hydrogen Production

Rugma T P[a], Rishi Krishna B S[†,a], K. Priyanga Kangeyan[†,a], Neppolian Bernaurdshaw [b], *Abdullah Saad AlArifi*[c], Sandeep Kumar Lakhera[a*]

[a]*Department of Physics and Nanotechnology, SRM IST, Kattankulathur, Chennai- 603203, Tamil Nadu, India*

[b]*Department of Chemistry, SRM IST, Kattankulathur, Chennai- 603203, Tamil Nadu, India*

[c]*Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia*

[*]Corresponding author: sandeepl@srmist.edu.in; space1lakhera@gmail.com

[†] Equal contribution

Chemicals and characterization techniques used

The melamine and lead chloride utilized in this study were bought from Sigma Aldrich. Copper chloride, Nickel acetate, Thiourea, and Methanol were supplied by SRL Chemicals, India. The crystalline structure in the 2 range from 10-90° was investigated using a Powder X-ray diffraction (X' port Powder X-ray system). Fourier transform infrared spectroscopy (ATR mode), with a scanning range of 400–4000 cm^{-1}, was used to examine the chemical bonding and infrared characteristics. Morphological studies were conducted using HR-SEM (Thermofisher-scientific) and HR-TEM (JEOL, Japan) instruments. A UV-vis spectrometer was used to determine the materials' UV-vis diffuse reflectance spectra (UV-vis DRS, Thermo Scientific). The PL measurements were conducted using a Fluorescence spectrophotometer (F96pro) with a 370 nm excitation wavelength. Fluorescence spectroscopy (FL3-TCSPC), with a laser excitation of 380 nm, was used to perform the Time-Resolved Photoluminescence measurement. Utilizing a device made by Thermo Scientific ((Shimadzu ESCA 3100)), the XPS measurements were made. Using a Micromeritics ASAP 2420 surface area analyzer at liquid nitrogen temperature, the BET surface area measurements were performed.

Photocatalytic activity test

A suspension of the photocatalyst (5 mg) was prepared in a 50 mL mixture of water and methanol (used as the sacrificial agent) within a glass reactor. To prevent any leakage, the reactor was sealed with a rubber septum, and the mixture was stirred in the dark while being

purged with N_2 gas for 30 minutes. The reactor was then exposed to direct sunlight and continuously stirred using a magnetic stirrer. The experiments were conducted outdoors under natural sunlight conditions with a peak intensity of 65,000 lux ±15%. The light intensity was measured with lux meter. All the samples were placed under sunlight at the same time for comparison and measurements were taken between 10 am and 2 pm to ensure consistent light exposure during peak sunlight hours. The average ambient temperature during the experiments was 35°C. Gases evolved during the reaction were collected every hour using a 250 µL microsyringe and analysed with an offline gas chromatograph (Shimadzu GC-2014, using N_2 as the carrier gas).

Electrochemical measurements

Photocurrent and impedance responses of the samples were measured using a three-electrode system (comprising a glassy carbon working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode) in a 0.1 M Na_2SO_4 electrolyte solution. The measurements were conducted on an electrochemical workstation (CHI760E, Chenhua, China). For illumination, a solar simulator equipped with a 300 W Xenon lamp (300WSS-EM) was employed, providing 20-second on-off light pulses.

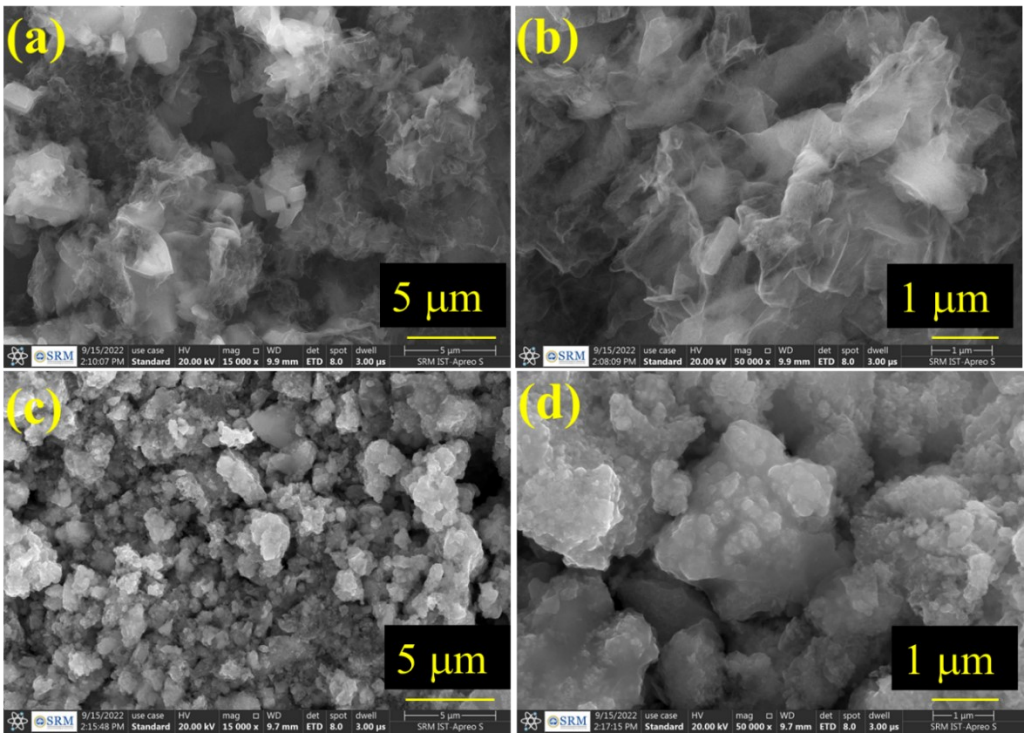

Figure S1: HR-SEM images of (a–b) PCN and (c-d) CNTS particles

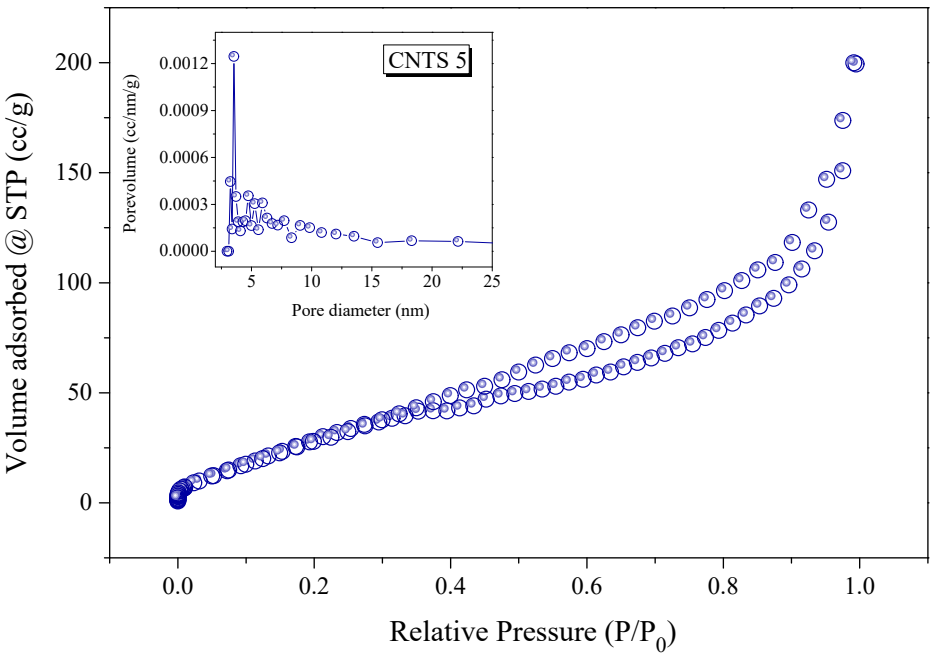

Figure S2: The adsorption-desorption isotherms of CNTS 5 samples.

Table S1: The specific surface area (SSA) and pore size distribution of PCN and CNTS 5 samples

Sample Name	Pore size (nm)	Pore volume (cc/g)	Surface area (m^2/g)
PCN	1.745	0.377	214.3
CNTS 5	1.617	0.284	140.3

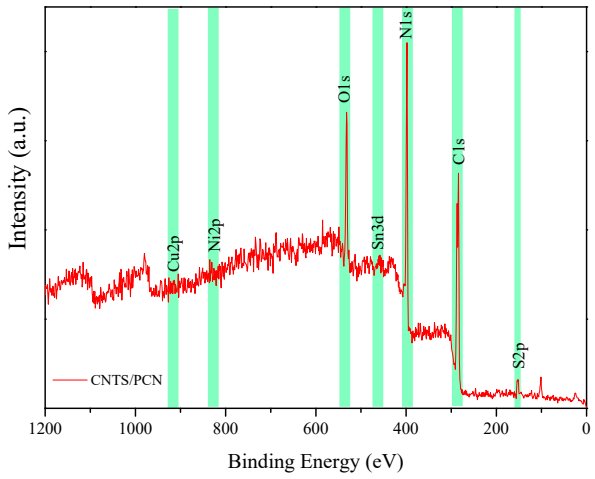

Figure S3: XPS survey spectra of CNTS composite photocatalyst

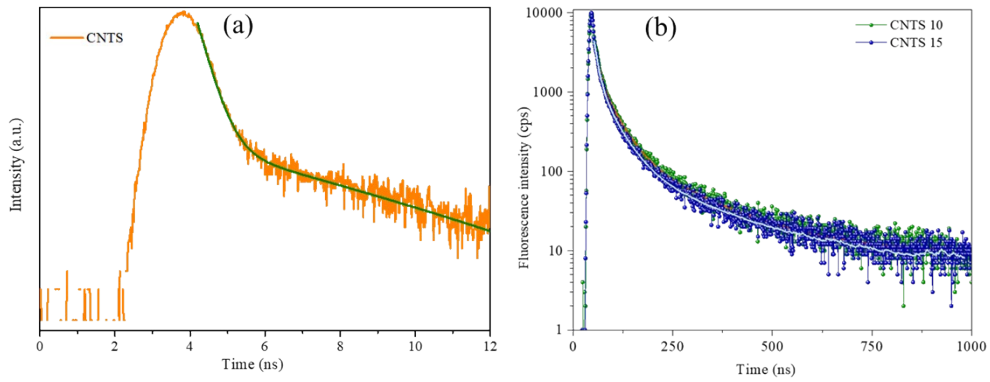

Figure S4: (a) TRPL spectra of CNTS photocatalyst, (b) TRPL spectra of CNTS10 and CNTS 15 photocatalysts

Table S2: Time constants and lifetimes of the PCN, CNTS and CNTS/PCN photocatalysts

Samples	**B_1**	**τ_1 (ns)**	**B_2**	**τ_2 (ns)**	**τ_{avg} (ns)**	**χ^2**	**k_{NT} (ns^{-1})**	**k_{ET} (ns^{-1}) w.r.t. PCN**
PCN	787.38	2.50	164.91	10	6.24	1.16		
CNTS	771.54	0.32	51.68	4.50	2.34	1.12		
CNTS 3	555.53	2.00	219.93	8.00	5.68	1.17	0.38	0.02
CNTS 5	650.24	1.85	195.76	8.56	5.76	1.16	0.43	0.02
CNTS 10	0.0179	4.83	0.0576	1.03	2.94	1.18	-0.763	0.19
CNTS 15	0.4076	1.10	0.0016	20.70	2.53	1.13	0.86	0.24

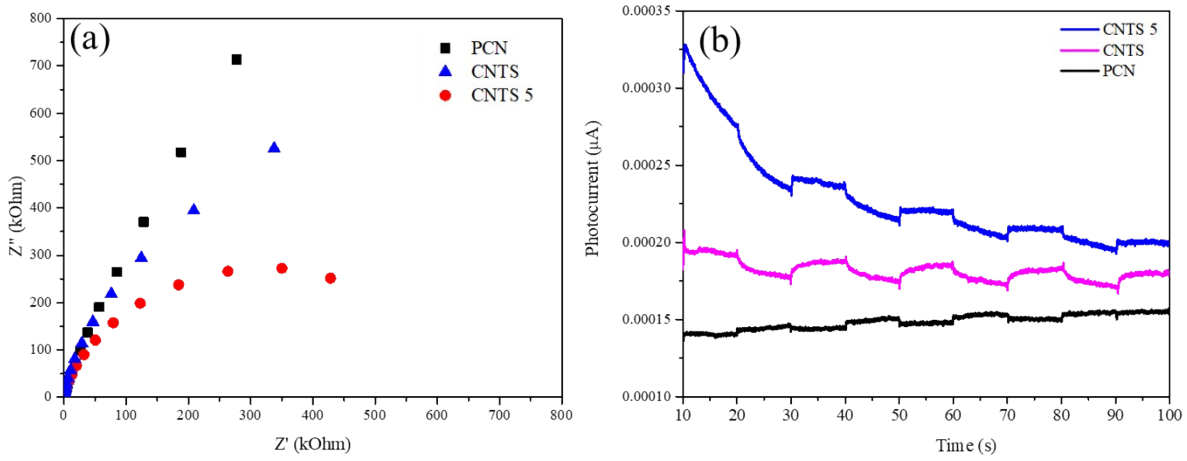

Figure S5: (a) EIS and (b) Photocurrent measurements of PCN, CNTS and CNTS 5 photocatalysts

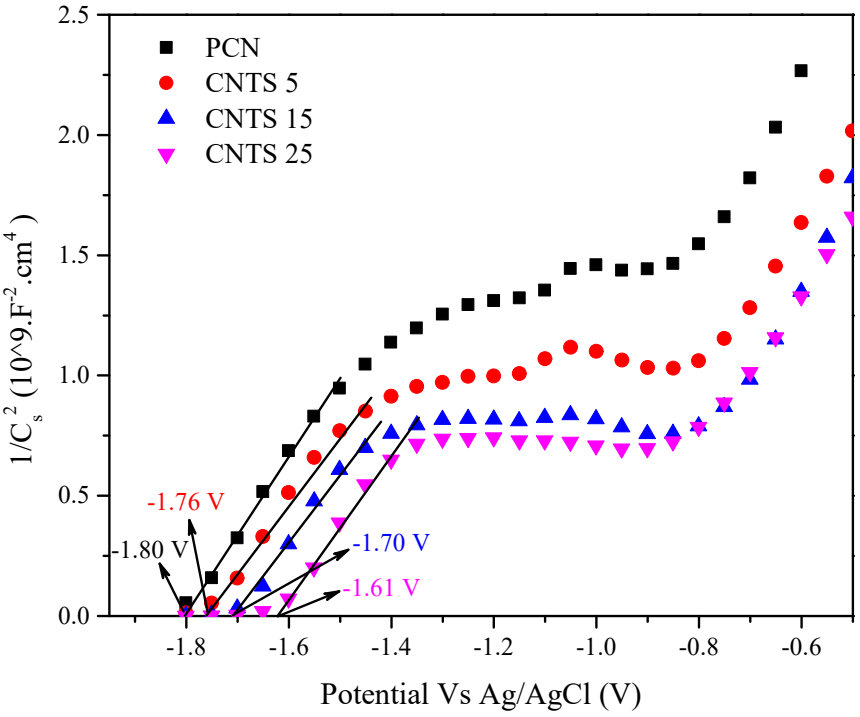

Figure S6: Mott–Schottky plot of the CNTS/PCN photocatalysts

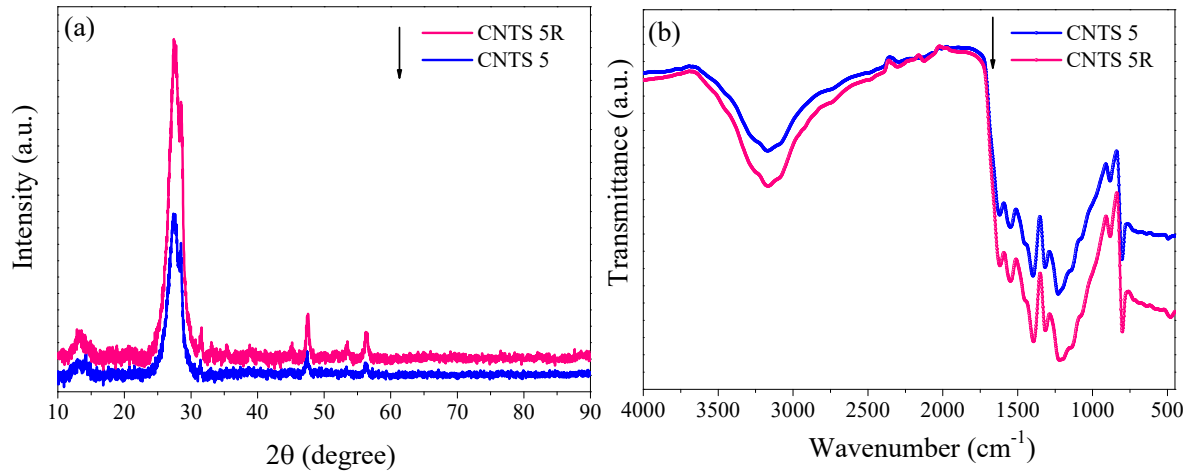

Figure S7: (a) X-ray Diffraction patterns and (b) FTIR spectra of PCN and CNTS/PCN photocatalysts before and after the reactions

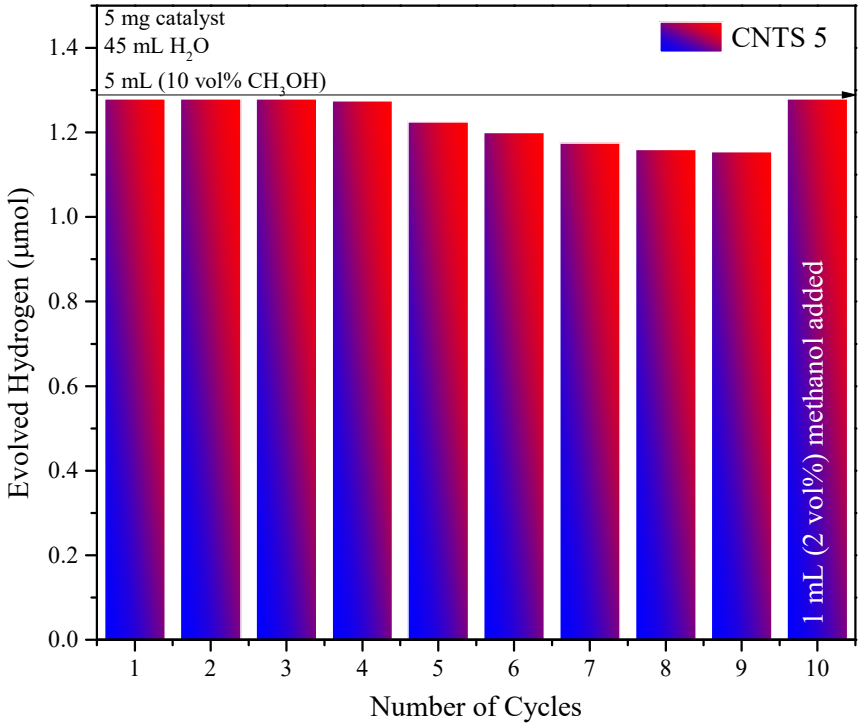

Figure S8: Reusability reaction of the CNTS 5 photocatalysts under Xenon lamp (300W) for 4h per cycle

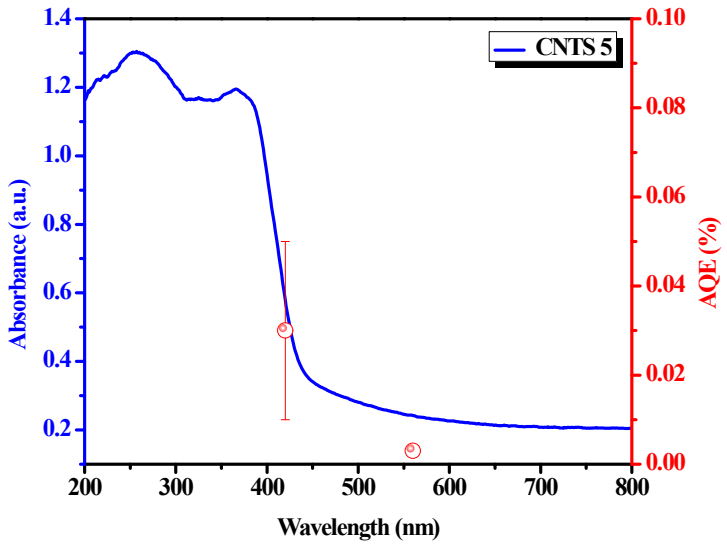

Fig. S9: The UV-vis absorption spectra and apparent quantum efficiency (AQE) measurements of CNTS-5 photocatalyst

Table S3: Photocatalytic hydrogen evolution activity of Cu_2MSnS_4 -based photocatalysts

S. No	Catalyst	Co-Catalyst/Dye sensitizer	Light source	Amount of H_2 produced ($\mu mol\ h^{-1}\ g^{-1}$)	Scavenger	Ref.
1	Cu_2NiSnS_4	EY	solar simulator (Solar Light XPS 300TM)	2028	TEOA (-)	[1]
2	Cu_2FeSnS_4	EY	solar simulator (Solar Light XPS 300TM)	1870	TEOA (-)	[1]
3	Cu_2CoSnS_4	EY	solar simulator (Solar Light XPS 300TM)	1926	TEOA (-)	[1]
4	Cu_2ZnSnS_4	EY	solar simulator (Solar Light XPS 300TM)	1420	TEOA (-)	[1]

5	Cu_2MnSnS_4	EY	solar simulator (Solar Light XPS 300TM)	389	TEOA (-)	[1]
6	TiO_2	Cu_2NiSnS_4	Sunlight	1786	Glycerol (5 Vol%)	[2]
7	g-C_3N_4	Pt/ Cu_2ZnSnS_4	400W Xenon lamp	147.2	-	[3]
8	**g-C_3N_4**	**Cu_2NiSnS_4**	**Direct Sunlight**	**230.3**	**Methanol (10 Vol%)**	**Current Work**

References

1. Gonce, M.K., et al., Dye-Sensitized Cu_2XSnS_4 (X=Zn, Ni, Fe, Co, and Mn) Nanofibers for Efficient Photocatalytic Hydrogen Evolution. ChemSusChem, 2016. **9**(6): p. 600-605
2. Dhileepan MD, Lakhera SK, Neppolian B. Interface engineering of 0D–1D Cu_2NiSnS_4/TiO_2 (B) p–n heterojunction nanowires for efficient photocatalytic hydrogen evolution. Catalysis Today. 2023, **423**:p.114006.
3. Raza, A., H. Shen, and A.A. Haidry, Novel Cu_2ZnSnS_4/Pt/g-C_3N_4 heterojunction photocatalyst with straddling band configuration for enhanced solar to fuel conversion. Applied Catalysis B: Environmental, 2020. **277**: p. 119239.