

UiO-66(-NH₂) crystal decorated Cu₇S₄ snowflake nanoarchitecture with synergistic charge migration for enhanced photocatalytic H₂ evolution and N₂ fixation

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Materials and methods

Zirconium chloride (ZrCl₄), copper (I) chloride (CuCl), thiourea, 2-amino terephthalic acid (NH₂-H₂BDC), sodium sulphite (Na₂SO₃), sodium sulphide (Na₂S), triethanol amine (TEOA) and lactic acid were purchased from Merck India pvt. Ltd. N, N-dimethyl formamide (DMF), ethylene diamine (ED), dichloro methane (DCM), and ethanol were procured from Hi Media laboratories pvt. Ltd. All the chemicals used in this work were of analytical reagent grade, which were used directly without further purification.

Synthesis of pure UiO-66(-NH₂) MOF

The UiO-66-NH₂ (UN) MOF nanocrystals were prepared by a facile reflux method. In the typical reaction, zirconium chloride (ZrCl₄) (0.5 mmol), 2-amino terephthalic acid (ATA) (0.5 mmol) were dissolved in a round-bottom flask containing 60 ml of dimethyl formamide (DMF) and vigorously stirred for 1 h. The resulting homogeneous solution was placed in a preheated oil bath at 120 °C for 24 h. After the completion of reaction, the resulting grey solid was separated by centrifugation at 5000 rpm and repeatedly washed with DMF and dichloromethane (DCM). The obtained solid product was vacuum dried at 90 °C for 24 h to obtained grey coloured crystalline UiO-66(-NH₂) powder.

Synthesis of pristine Cu₇S₄

Typically, the CuCl (0.5 mmol) and thiourea (0.5 mmol) was dissolved in 60 ml of ethylene diamine and stirred for 1 h. The prepared solution was transferred into 100 ml Teflon line autoclave and placed in a preheated oven at 80 °C for 6 h. The resulting solid product was separated by centrifugation and washed with distilled water and ethanol. Finally, the obtained black solid product was vacuum dried at 60 °C for 12 h.

Characterization techniques

The binary UiO-66(-NH₂)/Cu₇S₄ heterostructures together with pristine Cu₇S₄ and UiO-66(-NH₂) materials were characterized using XRD, FESEM, TEM, XPS, N₂ adsorption-desorption, FTIR, UV-Vis-DRS, Photoluminescence (PL) and time resolved photoluminescence (TRPL) techniques. The crystalline character and phase detection of the as prepared photocatalysts were investigated by X-ray diffraction method using a Rigaku Ultima IV multipurpose X-ray diffraction system supplied with Cu K α radiation ($\lambda = 0.154$ nm). The XRD analysis was performed in the 2θ range of 5-70° at a scan rate of 2° per min. The optical absorption features of all as-synthesized nanocomposites together with pristine materials were measured by a Jasco V-650 UV-Vis spectrometer in the spectral range of 200-800 nm by taking BaSO₄ as reference material. A WITec alpha 300R spectrometer was used to record the Raman spectra of the composites by using a 532 nm LASER source. The surface morphology of pristine CS, UN66 and UNCS(X) nanocomposites were accessed using a Nova Nano FESEM microscope model FEI working at an acceleration voltage of 10 kV. The inner microstructural character of the UNCS20 heterostructure material was examined by transmission electron microscopy (TEM) using a TECNAI 300 kV instrument. The electronic state and coordination environment of the as prepared UNCS20 nanocomposite was explored by XPS technique using a SPECS spectrophotometer (Germany) equipped with a 150 mm hemispherical analyser and Al K α radiation (1486.74 eV) as the X-ray source. Adjustments of binding energy were formulated relative to C1s peak at 284.6 eV. N₂ sorption and Brunauer-Emmett-Teller (BET) surface areas of the photocatalytic materials were determined by a Quantachrome Autosorb-iQMP apparatus. The recombination rate of photo-excited charge carriers of UNCS20 photocatalyst as compared to its pristine materials was analyzed by steady state photoluminescence (PL) technique using a Horiba Scientific Fluoromax-4 spectrometer at an excitation wavelength 325 nm. The time resolved photoluminescence (TRPL) analysis was carried out using Edinburg Spectrofluorometric FS-5 instruments with SC-10 and SC-30 integrating sphere module at an excitation wavelength of 325 nm for various photocatalytic materials.

Photo-electrochemical measurements

Photo-electrochemical measurements of the photocatalyst were performed by using a CHI660C electrochemical workstation having a standard three electrode system. The measurements were

carried out by using Ag/AgCl as reference electrode, Pt wire as counter electrode and UNCS20 as working electrode using a 300W Xe lamp as light source. The working electrode was prepared by drop casting of UNCS20 aqueous suspension on fluorinated tin oxide (FTO) glass. 0.5 M Na₂SO₄ solution was used as electrolyte for the electrochemical measurement. The impedance measurements were conducted in the frequency range of 1 Hz to 100 kHz with 10 mV amplitude. Linear sweep voltammetry measurements were performed in the range of -1.5 to 1 V at a scan rate of 10 mVs⁻¹. Further, Mott-Schottky measurements were carried out at 1 kHz frequency. Photocurrent response was recorded *w.r.t.* time in presence and absence of light with approximately 30 s time interval of light on and off mode. The photocurrent measurement for pure semiconductors and heterostructure materials was conducted using a Kiteley 2400 source meter incorporated with AM 1.5G filter fitted solar simulator.

Photocatalytic experiment

Photocatalytic H₂ production

To explore the photocatalytic activity of UNCS(X) hybrid material, hydrogen evolution reaction was performed by using Na₂S and Na₂SO₃ as sacrificial agent. In a typical photocatalytic experiment, 30 mg of UNCS(X) hybrid photocatalyst was finely dispersed in 100 ml of aqueous solution containing 0.5 M each of Na₂S and Na₂SO₃ sacrificial agent by ultrasonication. The resulting mixture was transferred into a 250 ml quartz photoreactor and nitrogen gas was purged for 30 min to maintain inert atmosphere inside the photoreactor. The catalytic suspension was stirred for 30 min under dark condition to attain better sorption. The photocatalytic solution was irradiated with a 250 W xenon lamp ($\lambda \geq 420\text{nm}$) for 5 h. The amount of H₂ gas evolved was quantified at different time interval by using gas chromatography attached with a thermal conductivity detector (TCD). Further, the recyclability test is carried to investigate the stability of the UNCS photocatalyst. After each catalytic cycle, the photocatalyst suspension is centrifuged to separate the catalyst particles. The recovered photocatalyst is thoroughly washed three times each with water and ethanol and then vacuum dried at 60 °C overnight for use in subsequent cycle. After completion of the catalytic cycle experiments, the recovered photocatalyst is examined using XRD, XPS and FESEM techniques to investigate its structural, chemical and morphological stability.

Photocatalytic N₂ reduction reaction (NRR)

The visible light assisted photocatalytic N₂ fixation reaction was performed by using a quartz photo-reactor equipped with 250 W xenon lamp. Prior to photocatalytic reaction, the prepared UNCS(X) photocatalyst was vacuum dried overnight at 80 °C. Typically, 30 mg of UNCS(X) photocatalyst was dispersed in 100 ml of aqueous solution containing 10 vol% MeOH under ultrasonic treatment for 30 min. The photocatalytic suspension was transferred into the photo reactor and was bubbled with high purity N₂ gas (99.99 %) for 1 h under dark condition to attain better sorption equilibrium. The suspension was irradiated by using a 250 W xenon lamp for 5 h. The N₂ gas was continuously passed through the reaction mixture at a rate of 30 ml/min during the photocatalytic study. In a regular time, interval, 5 ml of aliquots was taken out and filtered in a nylon syringe filter to remove the photocatalyst. To quantify the concentration of NH₃ in the aqueous solution, the supernatant was analysed spectrophotometrically using indophenol blue method.¹

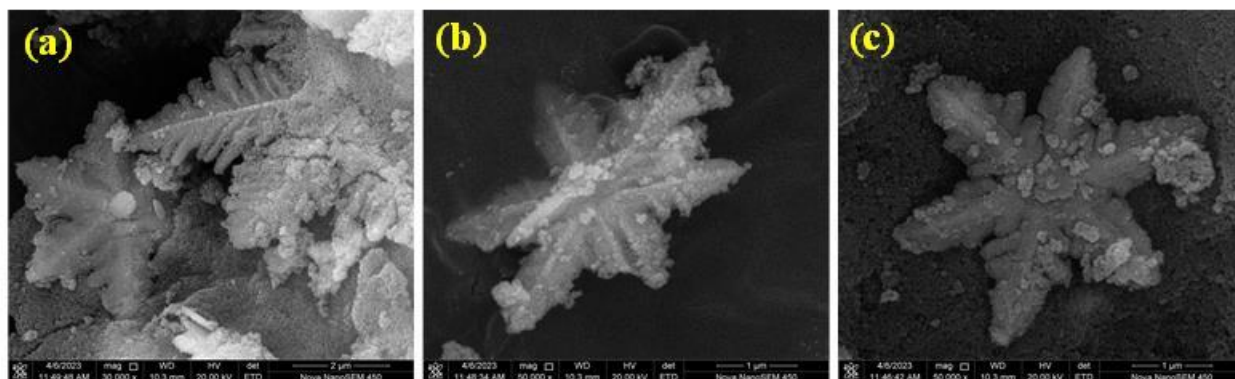


Figure S1. FESEM images of (a) UNCS5, (b) UNCS10 and (c) UNCS30 heterostructures.

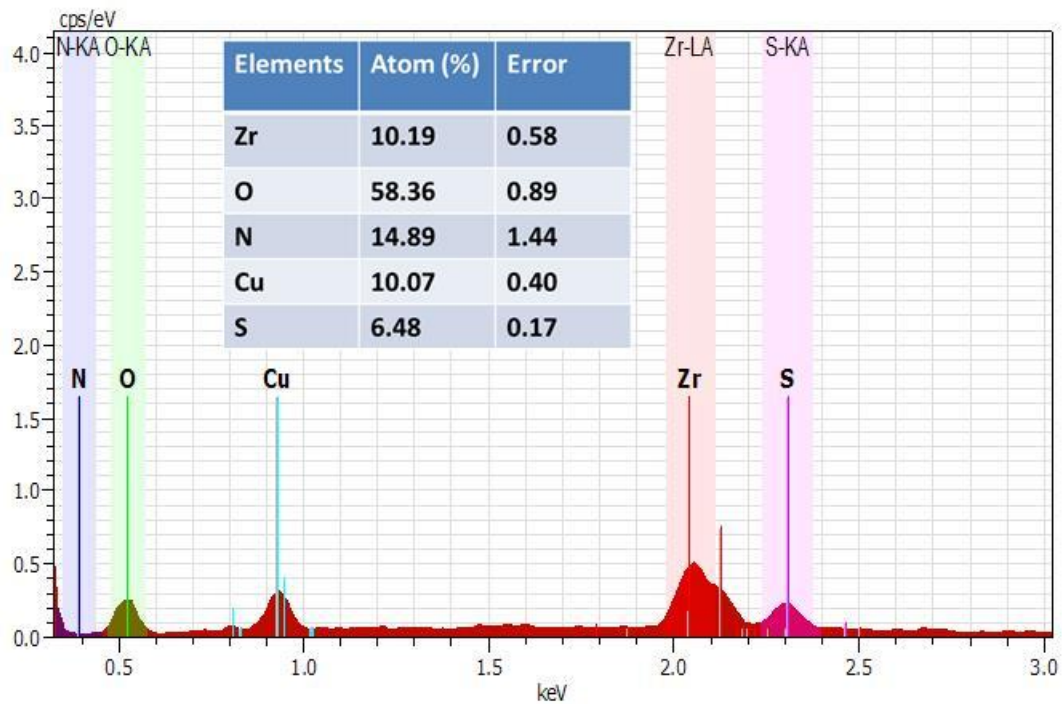


Figure S2. EDX spectrum of UNCS20 heterostructure.

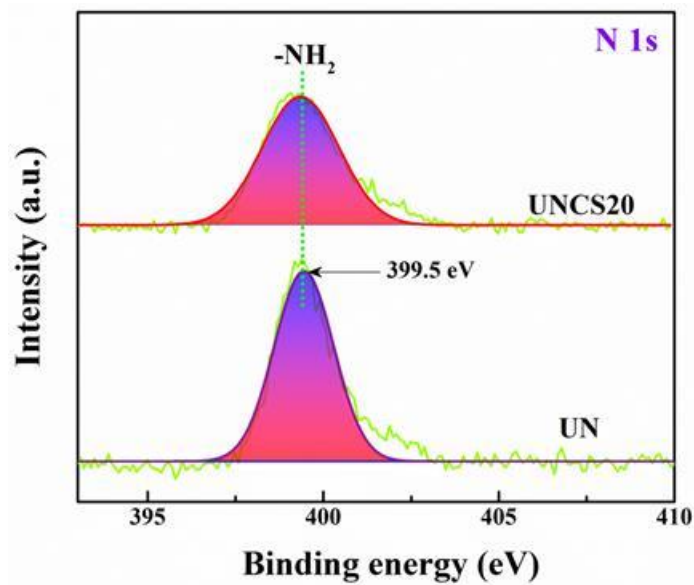


Figure S3. High resolution XPS spectra of N1s in pure UN and UNCS20 heterostructure.

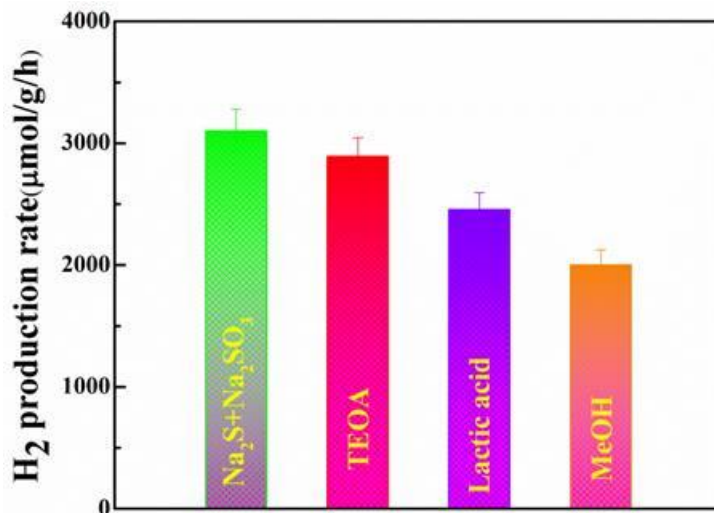


Figure S4. Effect of different scavengers towards PHE over UNCS20 photocatalyst.

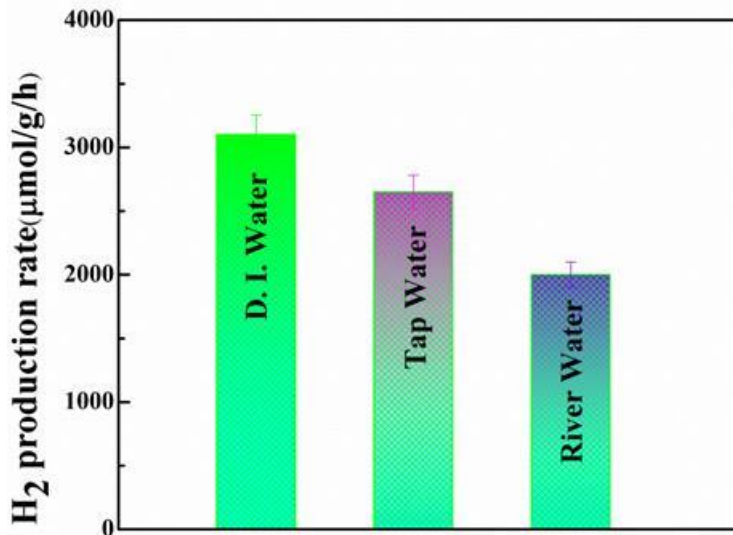


Figure S5. Effect of different water matrices on the PHE rate of UNCS20 photocatalyst.

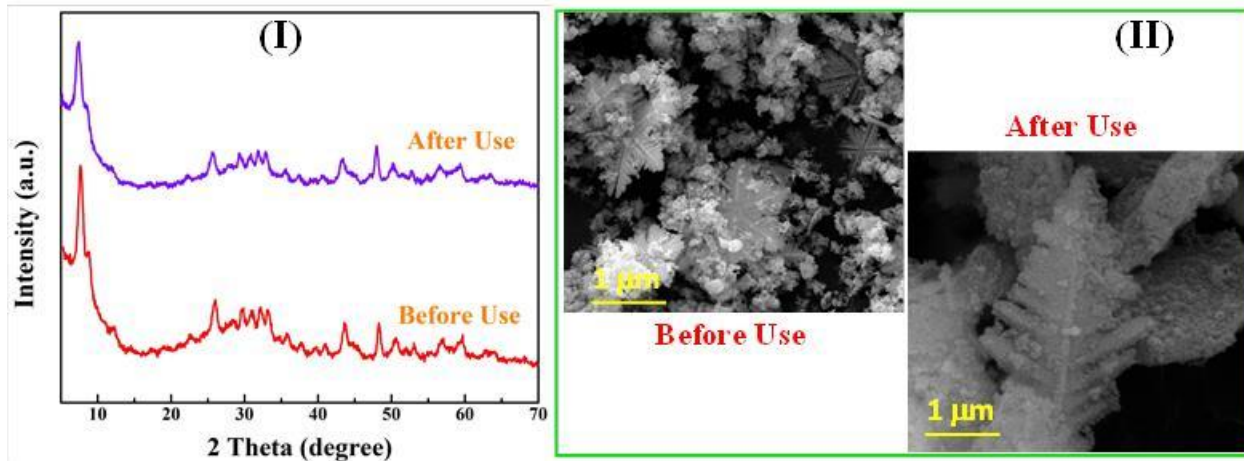


Figure S6. (I) XRD patterns and (II) FESEM images of UNCS20 heterojunction photocatalyst before and after H₂ evolution reaction.

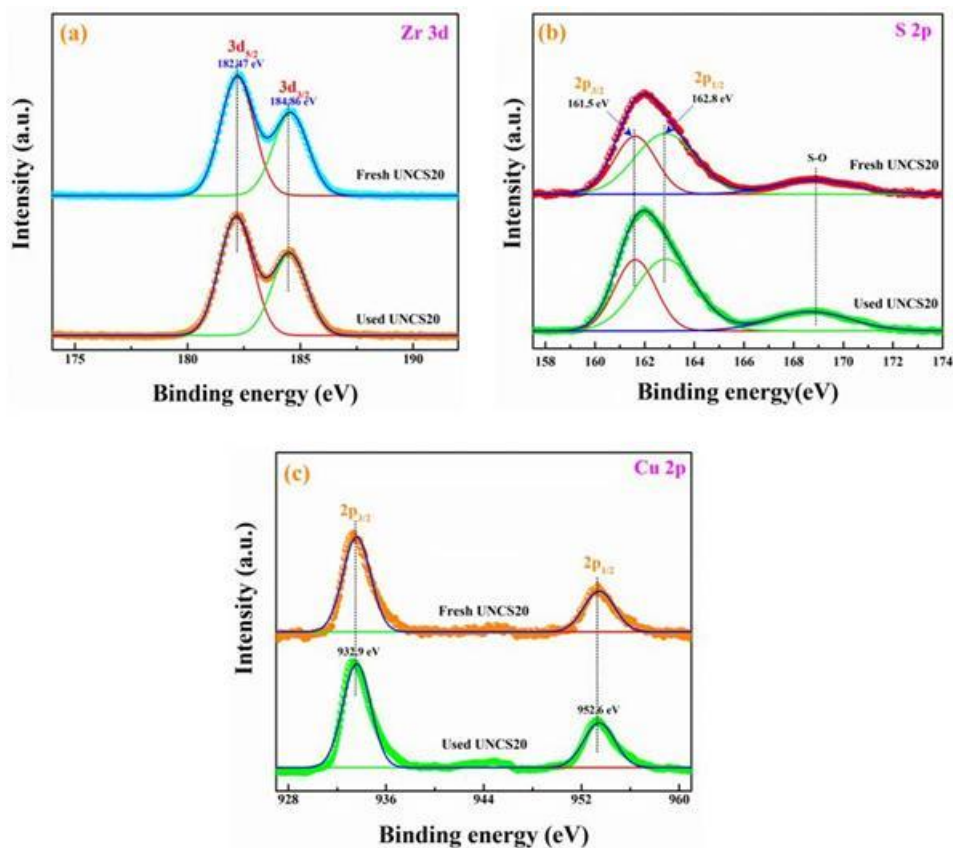


Figure S7. Comparison of the high resolution XPS spectra of fresh and regenerated UNCS20 photocatalyst in (a) Zr 3d, (b) S 2p and (c) Cu 2p regions.

Detection of NH_4^+ ions by Colorimetric Method.

Indophenol blue (IB) method is utilized to measure the production of NH_4^+ ion during the photocatalytic N_2 reduction.² Typically, 3 mL of reaction mixture is extracted out and filtered in a nylon syringe filter to remove the photocatalyst. Then 2 mL NaOH solution (1 M) containing salicylic acid (5 wt%) and sodium citrate (5 wt%) was added to the above supernatant followed by addition of 1 mL NaOCl (0.05 M) and 0.1 mL sodium nitroprusside ($\text{C}_5\text{FeN}_6\text{Na}_2\text{O}$) (1 wt%). The resulting supernatant is stored in dark under ambient temperature for 3 h for colour improvement. The absorption spectra of the obtained coloured solution are analysed using an UV-Vis spectrometer. The concentration of indophenol blue dye is quantified from its absorbance maxima at a wavelength of 680 nm. The concentration-absorbance curve is obtained using standard ammonium chloride solutions with varied concentrations.

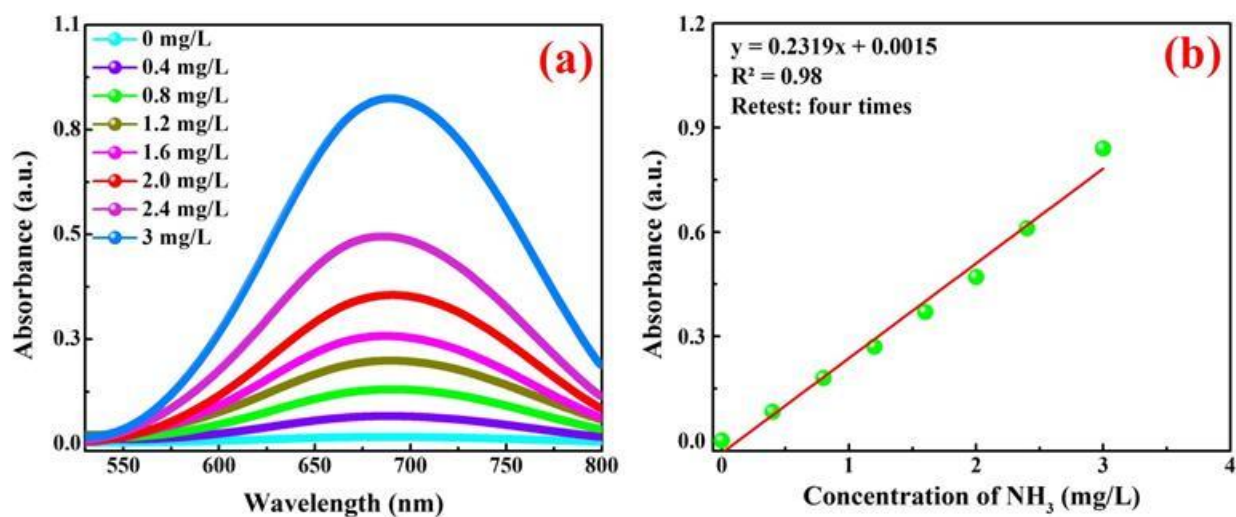


Figure S8. (a) UV-Vis absorption spectra and (b) the equivalent standard calibration curves for different concentrations of NH_4^+ using the calorimetric indophenol blue method.

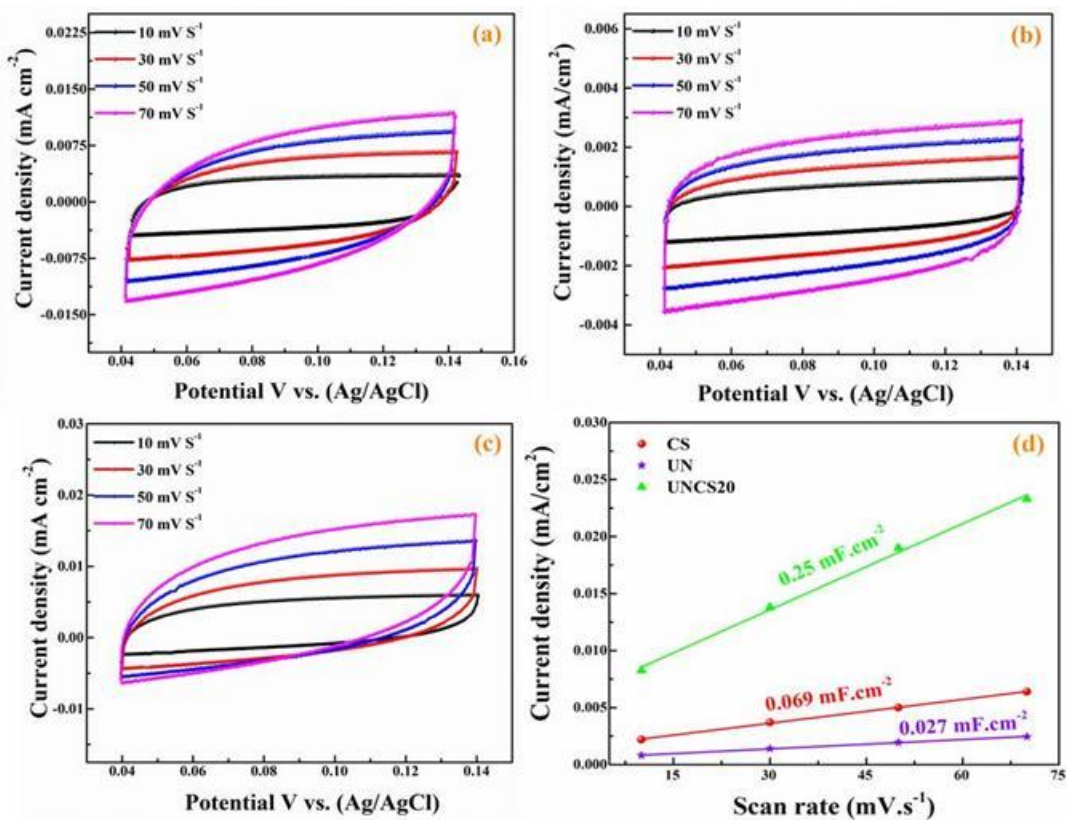


Figure S9. Cyclic voltammetry (CV) curves of (a) UN, (b) CS, (c) UNCS20 composite at different scan rates and (d) plot of current density vs scan rate for UN, CS and UNCS20 photocatalysts.

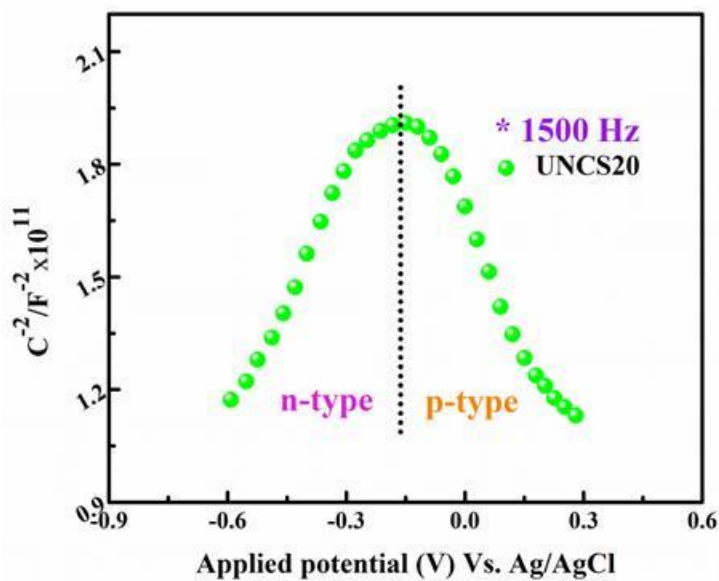


Figure S10. Mott-Schottky plot of UNCS20 n-p heterostructure.

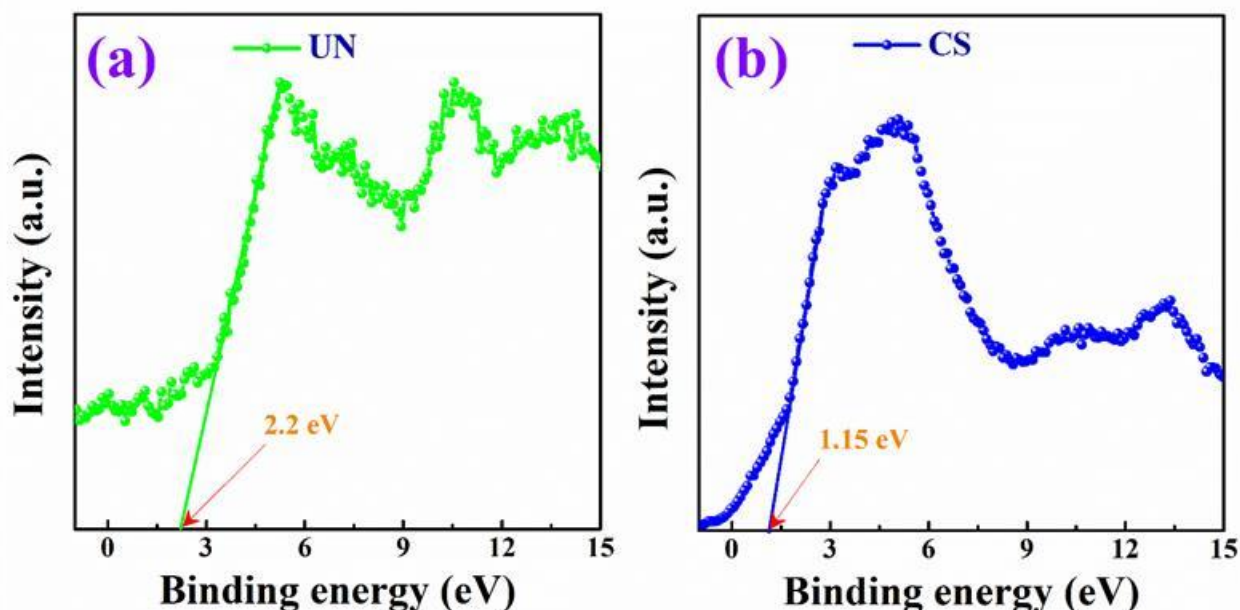


Figure S11. VB XPS spectra of (a) UN and (b) CS material.

Table S1: Comparison of PHE rate of UNCS20 n-p heterostructure photocatalyst with recently reported photocatalytic materials.

S.L. No	Photocatalyst	Light Source	Reaction condition	PHE ($\mu\text{mol. g}^{-1} \cdot \text{h}^{-1}$)	Ref.
1	UNCS20	250 W Xe lamp	Na_2S and Na_2SO_3	3110	This work
2	$\text{ZnIn}_2\text{S}_4/\text{UiO-66}$	300 W Xe lamp	0.25 M Na_2SO_3 and 0.35 M Na_2S	1860	3
3	$\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}/\text{UiO-66-NH}_2$	300 W Xe lamp	0.1 M Na_2S and 0.1 M Na_2SO_3	5846.5	4
4	$\text{CdS}/\text{UiO-66}$	300 W Xe lamp	10 vol% lactic acid	1725	5
5	$\text{UiO-66}/\text{CdIn}_2\text{S}_4$	250 W Xe lamp	10 vol% methanol	2950	6
6	$\text{CNT}@\text{Ni}_3\text{S}_2$	300 W Xe lamp	15 vol% TEOA	5320	7
7	$\text{MoS}_2\text{-ZnS}$	100 W halogen lamp	15 vol% of TEOA	606	8
8	$\text{K}_7\text{HNb}_6\text{O}_{19}/\text{g-C}_3\text{N}_4$	300 W Xe lamp	MeOH	359.89	9
9	$\text{MoS}_2\text{QDs}@\text{ZnIn}_2\text{S}_4@\text{RGO}$	300 W Xe lamp	lactic acid	5791	10
10	$\text{TiO}_2@\text{ZIF-8}$	300 W Xe lamp	20 vol% MeOH	2459	11

Table S2: Comparison of PNR over UNCS20 n-p heterostructure photocatalyst with recent reported photocatalytic materials.

S.L. No	Photocatalyst	Light source	Reaction condition	PNR ($\mu\text{mol. g}^{-1} \cdot \text{h}^{-1}$)	Method	Ref.
1	UNCS20	250 W Xe lamp	MeOH	374	IB	This work
2	$\text{In}_2\text{O}_3/\text{ZnIn}_2\text{S}_4$	250 W Xe lamp	MeOH	870	IB	1
3	NiS/KNbO_3	300 W Xe lamp	MeOH	155.6	NR	12
4	$\text{ZnIn}_2\text{S}_4/\text{BiOCl}$	300 W Xe lamp	H_2O	14.6	NR	13
5	$\text{In}_2\text{O}_3/\text{In}_2\text{S}_3$	300 W Xe lamp	H_2O	40.04	NR	14
6	$\text{MoS}_2/\text{C-ZnO}$	300 W Xe lamp	EtOH	245.7	NR	2
7	NiO/KNbO_3	300 W Xe lamp	MeOH	470.6	NR	15
8	$\text{PANI}@/\text{ZnIn}_2\text{S}_4$	300 W Xe lamp	MeOH	290	NR	16
9	$\text{g-C}_3\text{N}_4/\text{ZnFe}_2\text{O}_4$	500 W Xelamp	H_2O	61.15	NR	17
10	$\text{MnO}_{2-x}/\text{g-C}_3\text{N}_4$	300 W Xelamp	MeOH	225	NR	18

IB: Indophenol Blue method, NR: Nessler's reagent

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