Electronic Supplementary Information

Unravelling the Transformation from type-I to type-II $MA_3Bi_2I_9$ based heterostructure photocatalyst via energy band engineering

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Materials:

Ammonium molybdate tetrahydrate, Sodium hypophosphite monohydrate, Bismuth iodide, HI (57 wt.% in H_2O), thiourea, anhydrous DMSO, anhydrous toluene were purchased from Sigma-Aldrich. Methylammonium iodide was purchased from Great cell solar. All chemicals were used as received.

Preparation of amorphous MoS_2 and P doped MoS_2

In a conventional synthesis procedure, 20 mL of ethylene diamine was solubilized in 10 mL of distilled water. Subsequently, 1 mmol of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was incorporated while stirring. Following complete dissolution, 4 mmol of thiourea was introduced and the mixture was agitated for a duration of 30 minutes. As a phosphorus precursor, varying amounts of $NaH_2PO_2\cdot H_2O$ (specifically, 50 mg and 100 mg) were incorporated into the precursor solution. The resultant solution was then transferred into a 50 mL Teflon-lined stainless-steel autoclave and subjected to heating at 200 °C for a period of 12 hours, after which it was allowed to cool to ambient temperature spontaneously. The resultant black precipitate was isolated via centrifugation and subjected to multiple washings with deionized water and ethanol to eliminate any residual ions, followed by drying at 50 °C for 6 hours in preparation for subsequent characterization. Three distinct variants of MoS_2 were synthesized, denoted as MoS_2, P50_MoS_2, and P100_MoS_2.

Preparation of MoS_2/MABI composites powder:

MABI was synthesized by dissolving MAI and BiI_3 in molar ratio of 3:2. Specifically, 1176.38 mg BiI_3 was dissolved in 5 ml of anhydrous DMSO at 80°C, then 476.88 mg MAI was slowly added into the solution with vigorous stirring. A saturated bright orange solution was formed used for further preparation. 165 mg of 3 variants of MoS_2 (≈ 10 wt.% with respect to

total MABI formed) were added separately into three different solutions. Under stirring condition, anhydrous toluene was added dropwise in the solution. Precipitate would start to appear. Addition of anhydrous toluene was continued till the complete precipitation appeared with constant stirring at 90°C for 3 hours. The reaction mixture was centrifuged with dry ethyl acetate and the precipitate was collected after 3 washes. The precipitate was dried in vacuum oven at 80°C for 12 hours and stored inside the glove box for further use.

Characterization

Powder X-ray diffractogram was obtained from Rigaku Micromax-007HF diffractometer equipped with Cu Kα1 irradiation (λ = 1.54184 Å) at scan rate of 5°/min. Morphology studies were conducted using ZEISS, SIGMA FESEM and microscope (TEM) (JEOL-JEM 2010 operated at 200 kV). X-ray photoelectron spectroscopy (XPS) measurement was executed using a PHI 5000 Versa Probe III automated photoelectron spectrometer (ULVAC-PHI, Japan) with an Al Kα X-ray beam (1486.7 eV) at 20 kV, 84 W for the analysis of the chemical compositions. Solid state UV-vis spectra were recorded on a PerkinElmer Lambda-750 UV-vis-near-IR spectrometer equipped with an integrating sphere and BaSO4 powders were used as a reflectance standard. Photoluminescence spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer spectrometer. Energy-dispersive X-ray (EDX) spectroscopy (Sigma 300, Zeiss) was used for surface elemental analysis. CH Instruments 760D were used for Electrochemical measurements.

Photocatalytic measurement

The photocatalytic hydrogen evolution experiments were carried out in a glass vessel coupled with gas chromatograph (Agilent 7820A GC System). A typical process consists: (a) 50 mg of photocatalyst dispersed in 15 mL of MABI saturated HI solution under constant stirring at 25°C, (b) degassing the photocatalytic chamber for 30 min, (c) using online gas chromatography to confirm no H_2 was being generated in the reaction chamber in absence of

light irradiation and (d) turning on the light source to start the photocatalytic HI splitting reaction with continuous monitoring of the hydrogen generation by gas chromatograph.

Photoelectrochemical measurement

The electrochemical impedance spectroscopy (EIS), transient photocurrent response curves were performed on the electrochemical workstation (CH Instruments Ins.) in a three-electrode configuration with the assembled photoelectrodes (photocatalysts coated on 1 cm^2 of carbon paper) as the working electrode, the Ag/AgCl as the reference electrode and the Pt wire as the counter electrode. The EIS experiments were performed in MABI saturated aqueous HI solution under scan rate of 10 mV s^{-1}.

Visible light source for photocatalytic measurements

The visible light source used here for the experiments is a 50 W with power density of 150 mW/cm^2 white LED bought from Ledvance Osram. The spectrum of this light source is 420 - 790 nm.

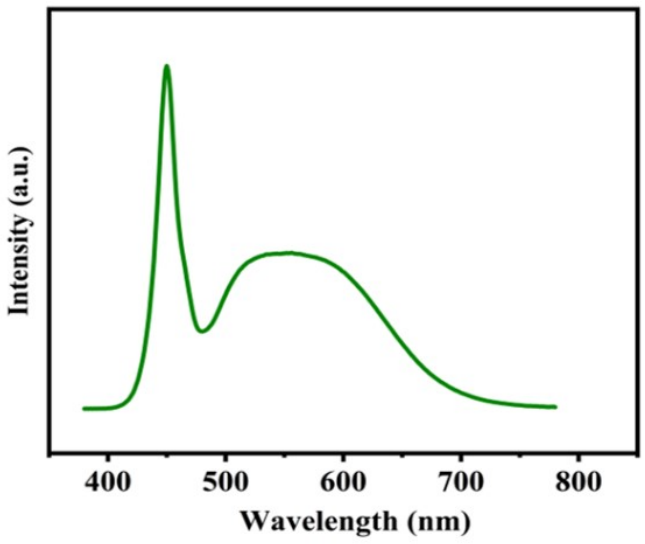

Figure S1- Electroluminescence of LED light source.

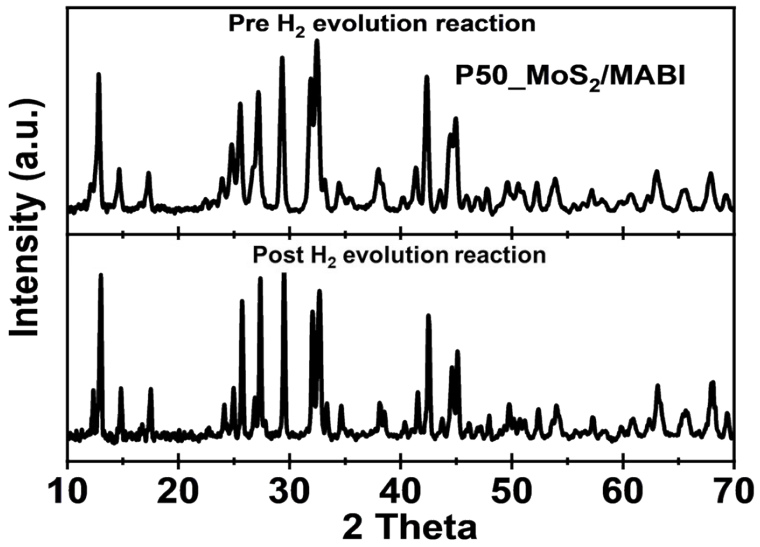

Figure S2- Stability study of P50_MoS_2/MABI composites through XRD.

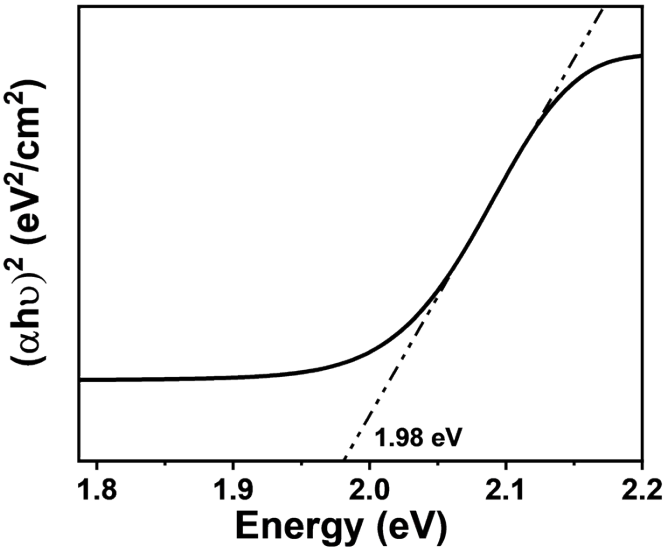

Figure S3- Band gap of MABI.

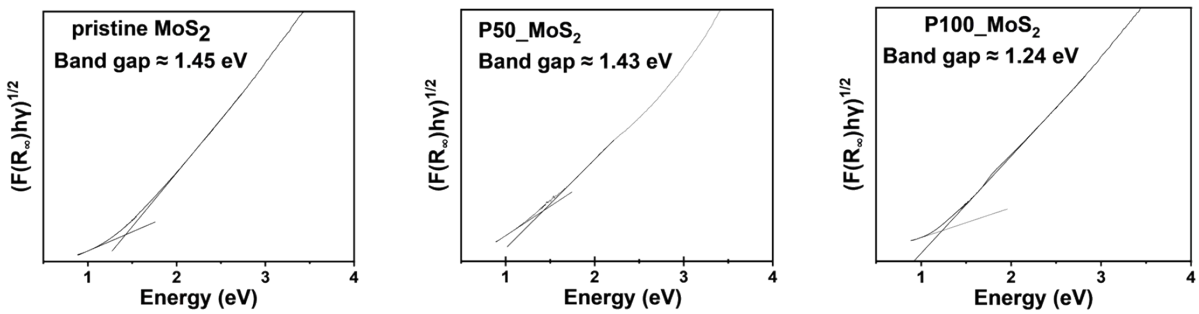

Figure S4- Band gap of 3 variants of MoS_2.

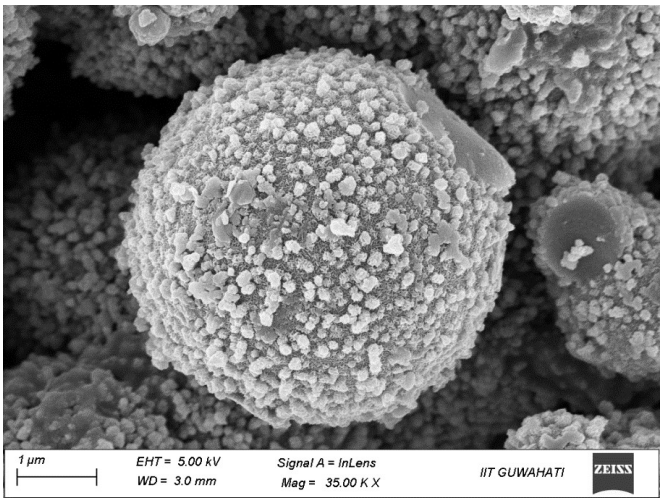

Figure S5- High resolution FESEM image of amorphous MoS_2.

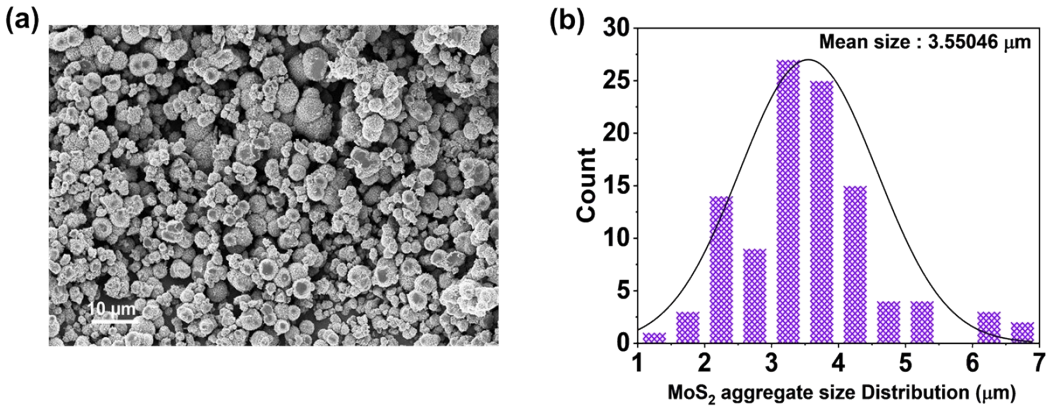

Figure S6- SEM images of synthesized amorphous MoS_2 aggregates (a) and (b) their size distributions.

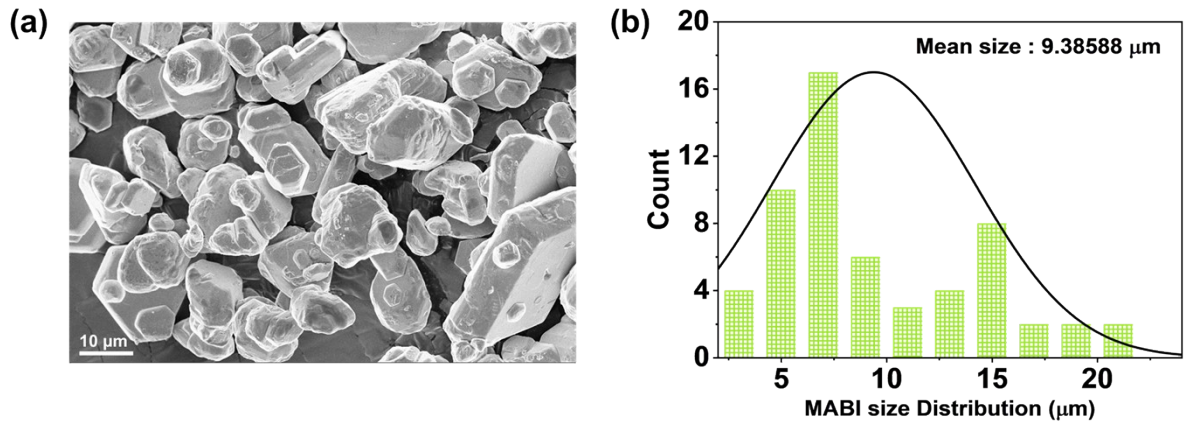

Figure S7- SEM images of synthesized MABI microcrystals (a) and (b) their size distributions.

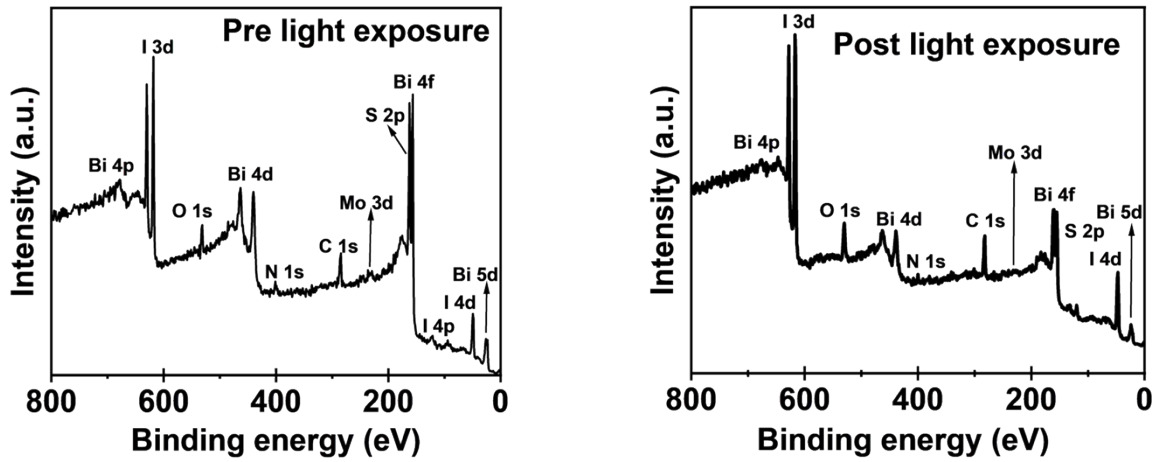

Figure S8- XPS **of** P50_MoS_2/MABI, post hydrogen evolution reaction.

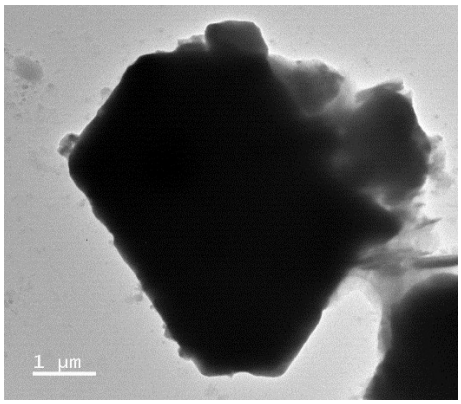

Figure S9- TEM image of P50_MoS_2/MABI, post hydrogen evolution reaction.

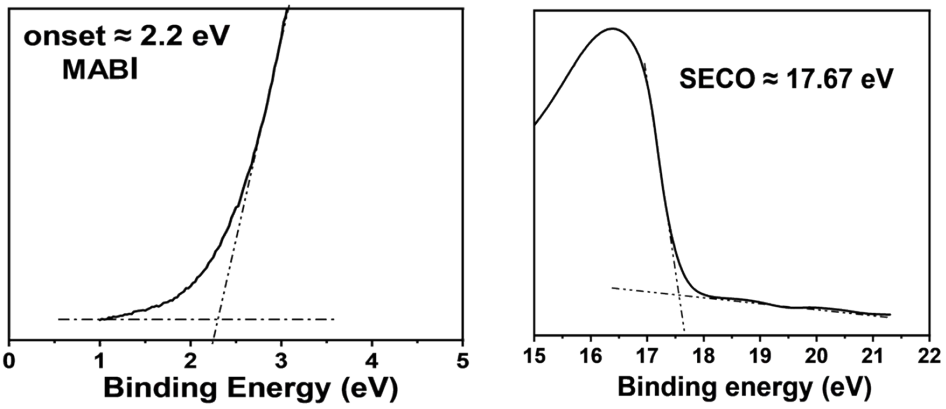

Figure S10- UPS analysis of MABI.

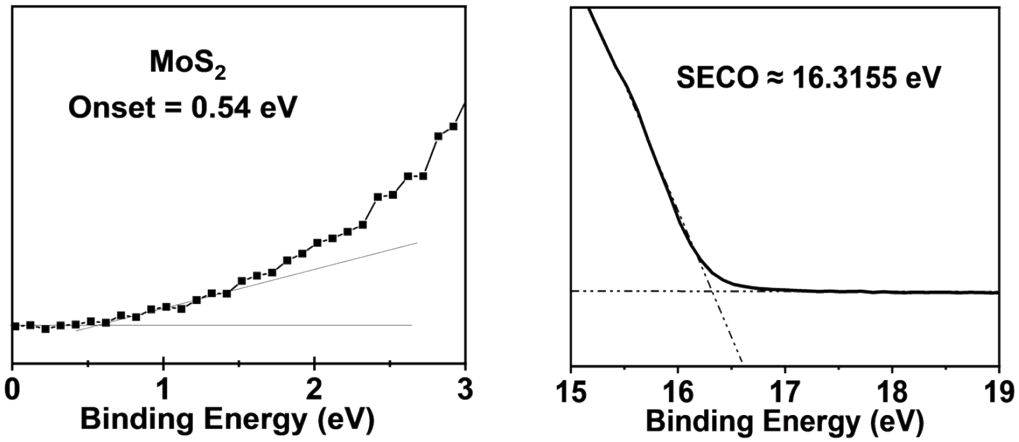

Figure S11- UPS analysis of MoS_2.

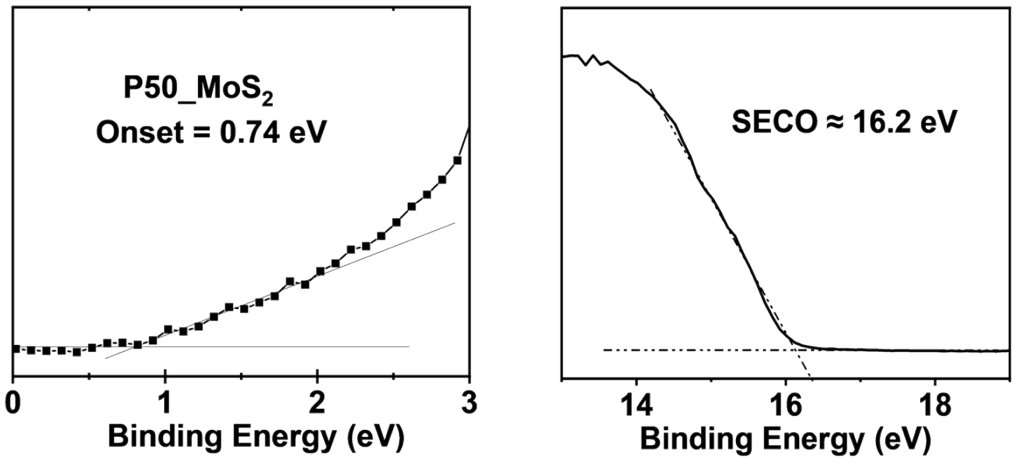

Figure S12- UPS analysis of P50_MoS_2.

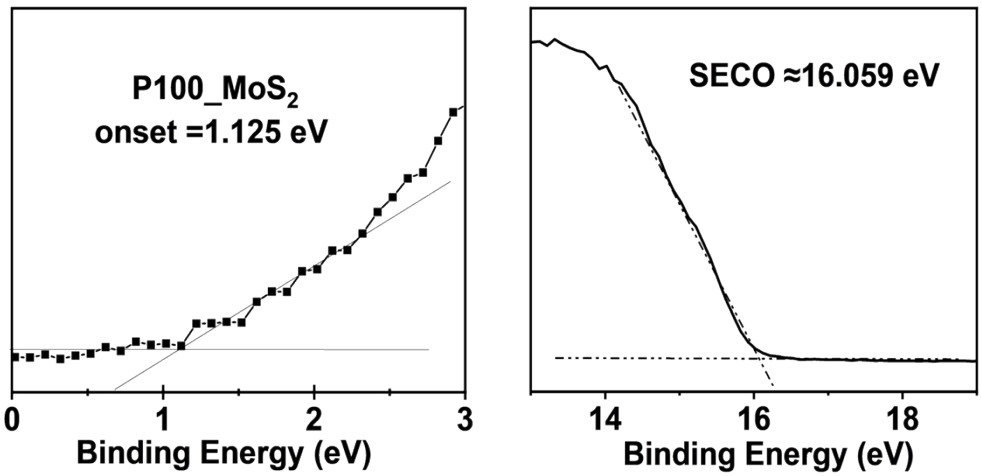

Figure S13- UPS analysis of P100_ MoS_2.

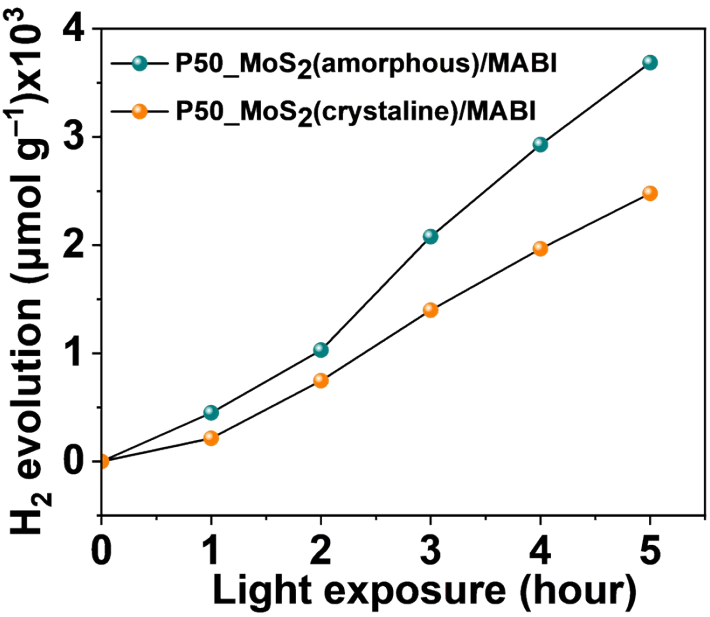

Figure S14- Comparison in HER activity between P50_MoS_2(amorphous)/MABI and P50_MoS_2(crystalline)/MABI.

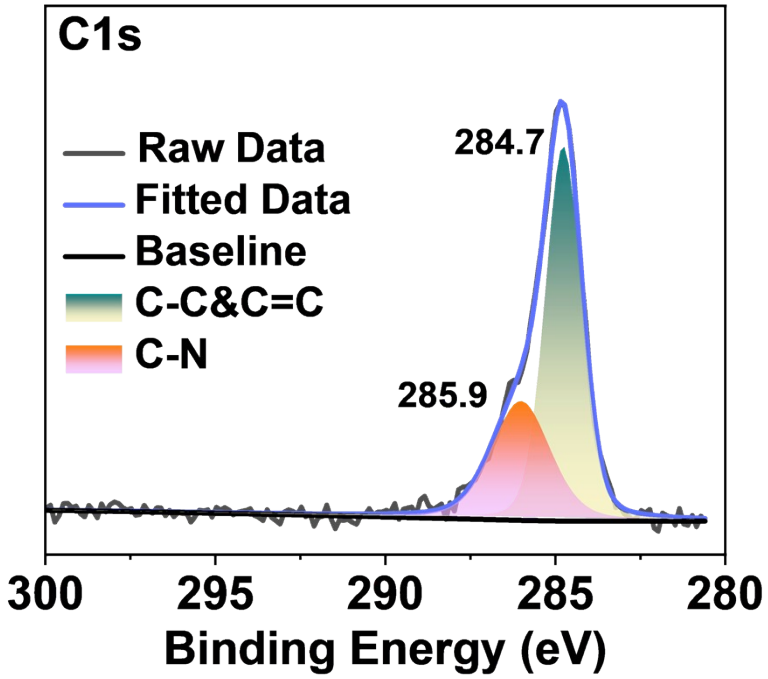

Figure S15- Deconvoluted C1s XPS spectra of MABI.

Table S1. Table for parameters of TRPL decays

	A_1	t_1 (ns)	A_2	t_2 (ns)	Average lifetime (Tav)
MABI	0.49569	0.86823	0.40312	9.05049	8.187 ns
P500_MoS_2/MABI	0.5647	0.83559	0.432	4.45275	4.2 ns
P100_MoS_2/MABI	0.5647	0.8355	0.432	4.45275	3.740 ns
MoS_2/MABI	0.93866	0.74021	0.20732	4.53447	2.921 ns

Table S2. performance and experimental parameters of reported halide perovskite photocatalysts for H_2 evolution.

Material	**Light source**	**H_2 production ($\mu mol\ g^{-1}h^{-1}$)**	**References**
$MA_3Bi_2I_9$	300 W Xe-lamp with a 400 nm cutoff filter	12.9	1
$MA_3Bi_2I_9$/Pt	300 W Xe-lamp with a 400 nm cutoff filter	169.21	1
P50_MoS_2/$MA_3Bi_2I_9$	50 W white LED with power density of 150 mW/cm^2	1176	This work

Reference-

(1) Guo, Y.; Liu, G.; Li, Z.; Lou, Y.; Chen, J.; Zhao, Y. Stable Lead-Free $(CH_3NH_3)_3Bi_2I_9$ Perovskite for Photocatalytic Hydrogen Generation. *ACS Sustain. Chem. Eng.* **2019**, *7*, 15080–15085.