Supporting Information

Aggrandized Photocatalytic H_2O_2 and H_2 Production by TiO_2/Ti_3C_2-TiC/Mixed Metal Ce-Zr MOF Composite: An Interfacial Engineered Solid-State Mediator Based Z-Scheme Heterostructure

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1. Characterizations and Experimental Methods:

1.1. Characterization Techniques:

Powder X-ray Diffraction (XRD) were conducted with a Rigaku Miniflex X-ray diffractometer having a monochromator outfitted with Cu K $\propto$ radiation ($\lambda = 0.154\ nm$, 30 KV/50 mA) was utilized to analyzed the crystallographic structure and phase purity of and phase purity of prepared sample. Fourier transform infrared spectroscopy (FTIR) measurement was used to give a more complete characterization of the surface structure. FTIR spectra were obtained with a frequency range between 400 to 4000 cm^{-1} using a JASCO-FT-IR-4600 spectrometer (with KBr as a reference). X-ray photoelectron spectroscopy (XPS) was carried with a VG Microtech Multilab ESCA-3000 spectrometer using Mg-Kα as an X-ray source, to examine the chemical state of the produced samples. The morphological analysis was done by using FEIN Quanta-400 FEG-SEM (FESEM), whereas the internal structure of the as-synthesized sample was analyzed by JEOL-JEM-2100 transmission electron microscope (HRTEM). To determine the absorbance and bandgap of the obtained sample, UV-Vis DRS spectra were investigated by JASCO-V-750 UV-Vis. spectrometer by using $BaSO_4$ as reference with a range of 200-800 nm. The excitation and emission spectra of photoluminescence (PL) were studied by using a JASCO FP-8300 fluorescence spectrometer having an excitation wavelength 325 nm along with a Xenon lamp as the light source.

1.2. Photoelectrochemical Measurements:

The multi-channel-Ivium potentiostat-galvanostat (IVIUM-n-STAT) electrochemical workstation was used to perform all photo electrochemical measurements, with three electrode configurations consisting of reference (Ag/AgCl), counter (Pt foil) and working electrode (fluorine doped Tin Oxide (FTO)), respectively. The hole workstation was supplied with a 300 W Xenon lamp as visible light source with 400 nm cut-off. 0.1 M Na_2SO_4 aqueous solution was utilized as electrolyte. Furthermore, working electrode was papered with 10 mg of the sample, 0.7 ml of ethanol, and 1% Nafion (20 μL), and the resulting slurry was then dropped-cast onto the conducting surface of the FTO substrate. The FTO was given for oven dry at 90 °C for 12 hours to make the functioning electrode. Light source can be performed by using 300 W Xenon lamps equipped with a 400 nm cut-off filter.

1.3. Photocatalytic Applications:

The photocatalytic activities of pure materials (TiO_2/Ti_3C_2-TiC, ZUNH and CZUNH) and TiO_2/Ti_3C_2-TiC/CZUNH-X composites were confirmed by (i) photocatalytic H_2O_2 and (ii) photocatalytic hydrogen generation.

1.3.1. Photocatalytic H_2O_2 Production:

In an O_2-saturated environment, photocatalytic H_2O_2 generation was carried out using pristine TiO_2/Ti_3C_2-TiC, ZUNH, CZUNH and ternary TiO_2/Ti_3C_2-TiC/CZUNH-X photocatalysts. For thorough dispersion, 0.02 g of photocatalysts were ultrasonicated for 10 minutes in a mixed solution of 19 mL DI water and 1 mL ethanol. Afterward the sample was bubbled with O_2 gas for 30 min to achieve O_2 equilibrated environment followed by irradiation with 250 W Xe lamp. After 2h of light illumination the photocatalysts were separated from the solution through centrifugation and filtration. Then 1 mL of resultant solution was mixed with 2 mL of KI (0.1 M) solution followed by the addition of 0.05 mL of ammonium molybdate (0.01 M) solution to achieve a light-yellow colour. After the addition, the concentration of the H_2O_2 was measured by a UV-Vis spectrophotometer at a wavelength of 350 nm.

1.3.2. Photocatalytic H_2 Production:

The photocatalytic water splitting reaction was implemented in a Pyrex quartz glass photo reactor containing 20 mg of catalysts (TiO_2/Ti_3C_2-TiC, ZUNH, CZUNH and TiO_2/Ti_3C_2-TiC/ CZUNH-X -X (X= 10, 20 and 30 wt % of CZUNH) along with 20 mL of 10 vol% Methanol solution used as sacrificial agent for hole. For this reaction to happen, a visible light source of 125 W Xenon lamp with 1 M $NaNO_2$ cut off filter connected to the reactor with water circulation. Then the sample was kept on stirring to prevent the catalysts from settling down at the bottom of the reactor followed by purging of N_2 gas for 30 mins. Then the distance between the light source and the suspension solution mixture was measured which was found to be 8.7 cm and the intensity of incident light on the sample surface is measured to be 70 $mWcm^{-2}$. After 1 h of light irradiation, the evolved hydrogen gas was collected via water displacement technique. Then the amount of H_2 evolution was measured by GC-7890B (Agilent technology) supplied with thermal conductivity detector (TCD) and a 5 Å molecular sieve packed column. The apparent conversion efficiency (ACE) was calculated by using the formula.

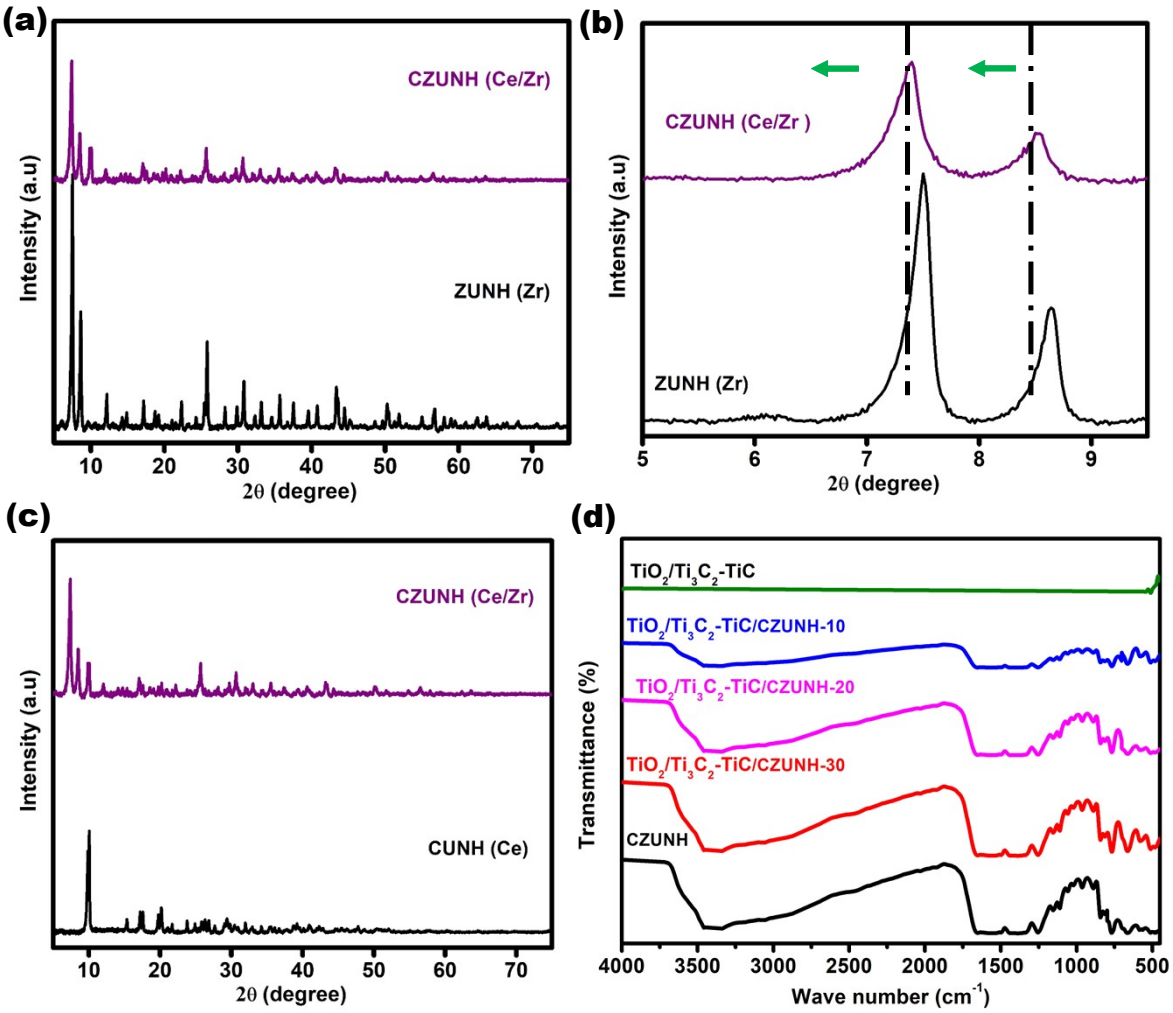

Figure S1. (a) XRD patterns of CZUNH and ZUNH (b) Zoom image of XRD patterns of CZUNH and ZUNH (c) XRD patterns of CUNH (d) FTIR spectra of all as-synthesized heterostructures.

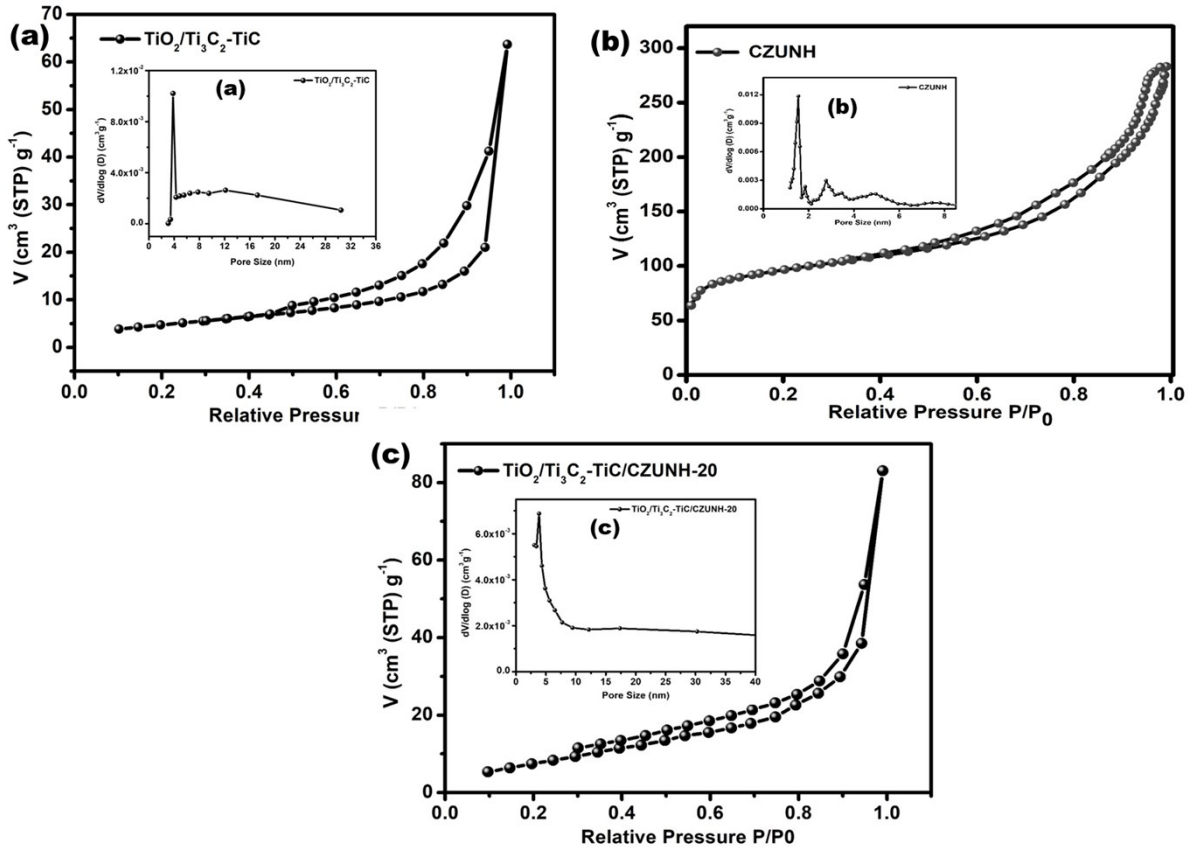

Figure S2. BET surface area (a) TiO_2/Ti_3C_2-TiC (b)CZUNH (c) TiO_2/Ti_3C_2-TiC/CZUNH-20 and insert image represented pore size distribution of (a) TiO_2/Ti_3C_2-TiC (b)CZUNH (c) TiO_2/Ti_3C_2-TiC/CZUNH-20.

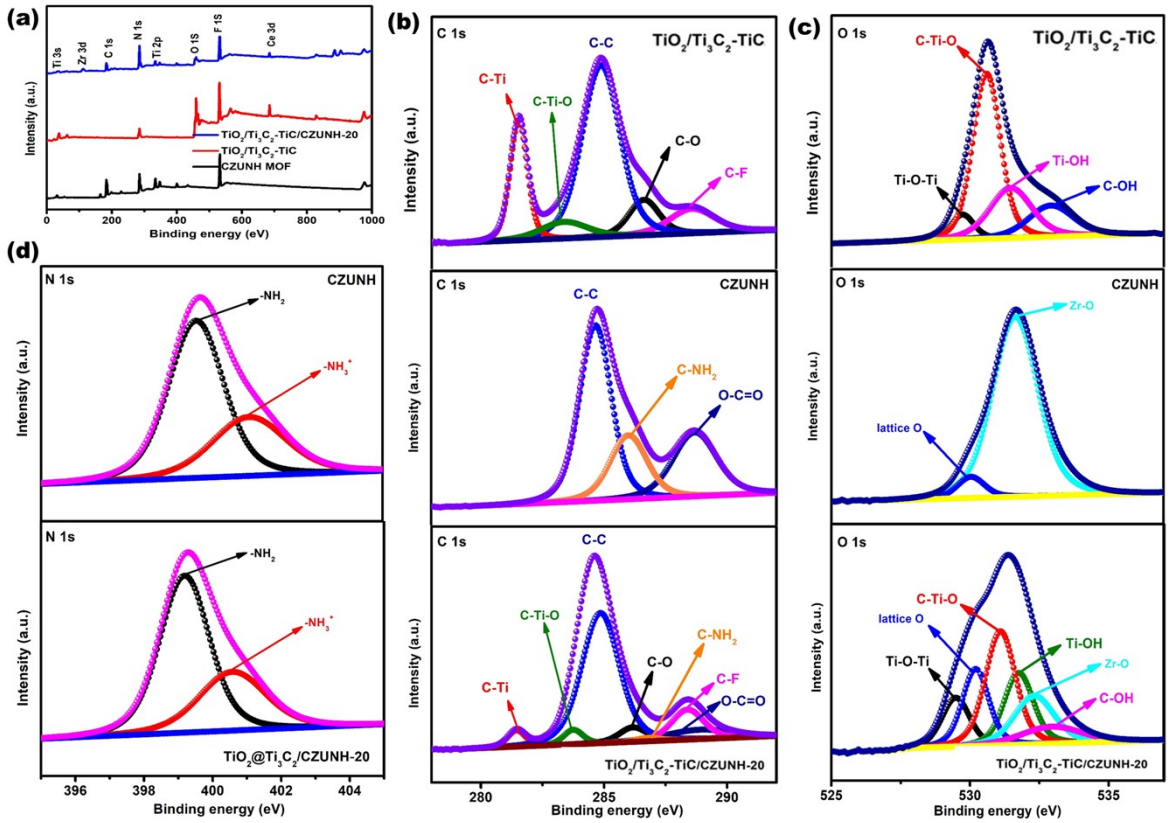

Figure S3. (a) XPS survey scan of CZUNH, TiO_2/Ti_3C_2-TiC and TiO_2/Ti_3C_2-TiC/CZUNH-20 composite, XPS spectra of (b) C 1s, (c) O 1s and (d) N 1s for TiO_2/Ti_3C_2-TiC, CZUNH and TiO_2/Ti_3C_2-TiC/CZUNH-20 composite.

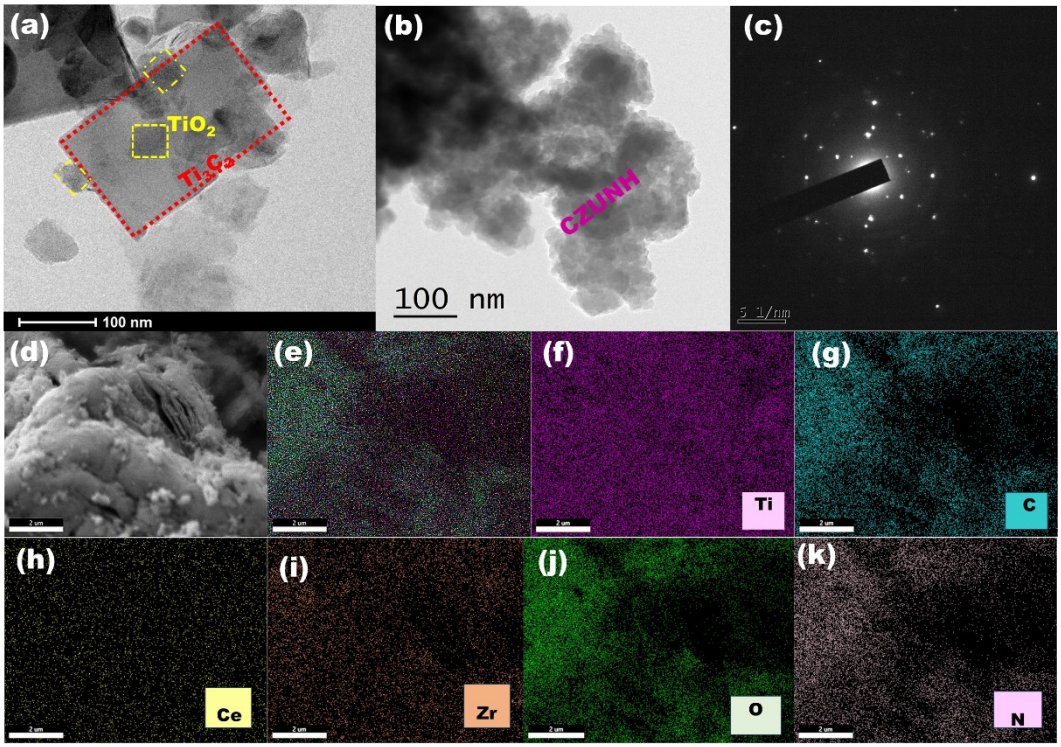

Figure S4. HRTEM image (a) TiO_2/Ti_3C_2-TiC (b)CZUNH (c) SAED patterns of TiO_2/Ti_3C_2-TiC/CZUNH-20 composite and (d-e) EDX colour mapping images of Ti, C, Zr, Ce, O and N elements (f-k) of the TiO_2/Ti_3C_2-TiC/CZUNH-20 composite.

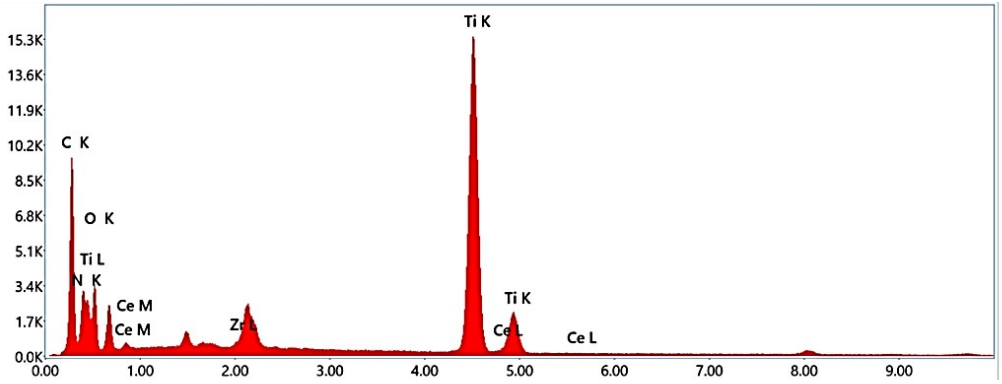

Figure S5. EDX spectra of TiO_2/Ti_3C_2-TiC/CZUNH-20.

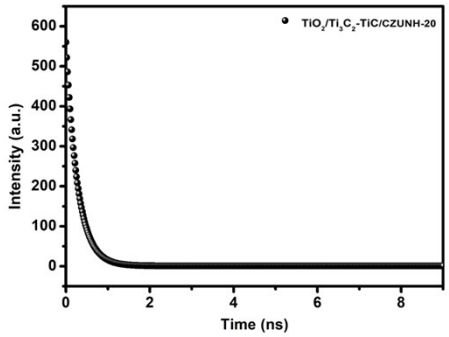

Figure S6. TRPL spectra of TiO_2/Ti_3C_2-TiC/CZUNH-20.

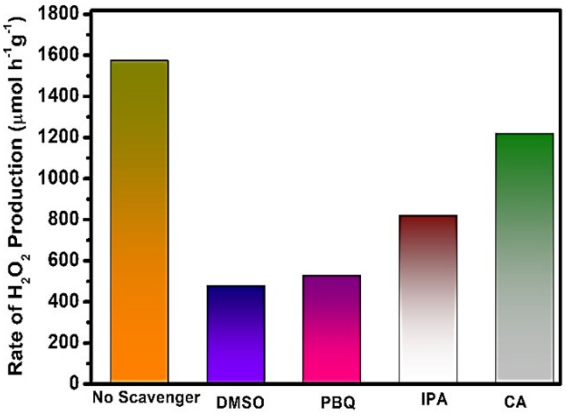

Figure S7. Influence of scavenging agent (PBQ for $\bullet O_2^-$; IPA for •OH; CA for h^+; DMSO for e^-) on photocatalytic H_2O_2 production ability over ternary composite TiO_2/Ti_3C_2-TiC/CZUNH-20.

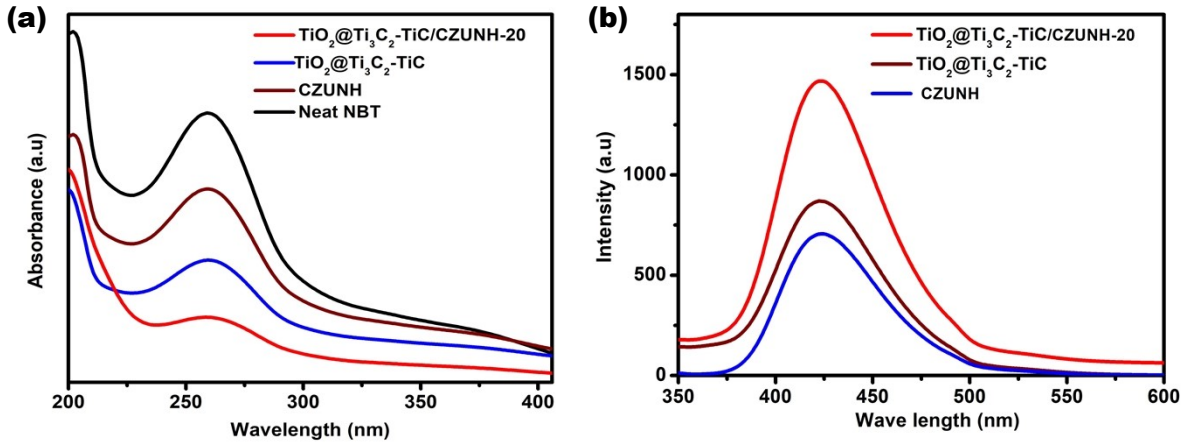

Fig. S8 (a) NBT (b) TA test for CZUNH, TiO_2/Ti_3C_2-TiC and TiO_2/Ti_3C_2-TiC/CZUNH-20 composite.

Table S1. Comparison table for Photocatalytic H_2O_2 production by various photocatalyst

Sl. No.	**Materials**	**Amount of catalysts (mg)**	**Sacrificial reagent**	**Light source**	**H_2O_2 production rate**	**Reference**
1	TiO_2/Ti_3C_2-TiC/CZUNH-20	20	Ethanol/ H_2O (20 mL)	125 W Xe lamp (> 400 nm)	1575	This work
2	Ti_3C_2/g-C_3N_4 /BiOCl	50	5 vol% IPA/ H_2O (50 mL)	300 W Xenon lamp	1275 µM	1
3	Ti_3C_2/g-C_3N_4 TC–pCN	50	10 vol% IPA/ H_2O (50 mL)	Visible light source (≥400 nm)	2.20 µmol L^{-1} min^{-1}	2
4	Pt@b-CD/g-C_3N_4-MXene	60	Water (60 mL)	Visible light source (≥400 nm)	147.1 mM L^{-1}	3
5	TiO_2@MXene/ B g C_3N_4	20	Ethanol/ H_2O (20 mL)	Visible light source	1480.1 µmol h^{-1} g^{-1}	4

				300 W Xe lamp (≥400 nm)		

Table S2. Comparison table for photocatalytic H_2 evolution by various photocatalyst

Sl. No.	**Materials**	**Amount of catalysts (mg)**	**Sacrificial reagent**	**Light source**	**H_2 production rate (μmol.g^{-1}h^{-1})**	**Reference**
1	TiO_2/Ti_3C_2-TiC/CZUNH-20	20	Methanol	125 W Xe lamp (> 400 nm)	570	This work
2	MoS_2 @Ti3C_2 @TiO_2	10	TEOA	300 W Xe arc lamp (> 400 nm)	6425.297	5
3	1 T-MoS_2 nanopatch/Ti_3C_2/ TiO_2	10	TEOA and aqueous acetone	300 W Xe lamp (≥ 420 nm)	9738	6
4	Ti_3C_2/TiO_2/Ui O-66- NH	20	Na_2S and Na_2SO_3	300 W Xe lamp	1980	7
5	Cu/TiO_2/Ti_3C_2 T_x	20	Methanol	300 W Xe lamp	1892	8
6	$ZnIn_2S_4$/TiO_2/ Ti_3C_2	15	Na_2S and Na_2SO_3	300 W Xe lamp	1185.8	9

7	$CuIn_2S_4/TiO_2/Ti_3C_2$	10	Methanol	300 W Xe lamp	356.27	10
8	Ru/MXene/TiO_2	10	Methanol	300 W Xe lamp	235.3	11
9	$TiO_2@Ti_3C_2$/MIS	20	Methanol	125 W Xe lamp (> 400 nm)	520.3	12

Calculation of Apparent Conversion Efficiency (ACE) of TiO_2/Ti_3C_2-TiC/CZUNH-20 Composite:

$$\textbf{ACE} = \frac{Stored\ chemical\ energy}{incident\ photon\ energy} \times 100 \quad \text{(S1)}$$

⇒ Stored chemical energy = moles of H_2 evolution $\times$ ΔH_c

= 0.1445μmol/s $\times$ 285.8 kJ/mol = 0.041 J/s or W

⇒ Incident photon energy = 70 mWcm^{-2} $\times$ (Area of spherical surface on which light falls)

=70 mWcm^{-2} $\times$ 3.141 $\times$ (1.5 cm)^2 = 0.4947 W

$$\Rightarrow \text{ACE} = \frac{0.041\ W}{0.4947 W} \times 100 = \textbf{9.1}\ \%$$

Where, ΔH_c = Enthalpy of combustion of H_2 = 285.8 kJ mol^{-1}

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