Electronic Supporting Information (ESI)

CIS QDs Nucleated on Oxygen Vacancy rich BOI Microplates: A Hybrid Photocatalyst with Enhanced Green Energy Production via Mediator free Z-scheme Dynamic

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Experimental section

Chemicals Requirement

Copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 99%), Thioglycolic acid (TGA, 79%), Potassium iodide (KI, >99.5%), sodium hydroxide (NaOH, 97%), NBT (nitro blue tetrazolium chloride), Methanol, Nafion, Na_2SO_4, TA (Terepthalic Acid) were purchased from Merck and Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, 98%), Indium chloride ($InCl_3$, 98%), sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 58%), $AgNO_3$, $FeCl_3.6H_2O$ from Himedia chemical company. All reagents are in analytical grade and are used in reaction without further purification.

Synthetic Method

**Synthesis of Bismuth Oxyiodide Micro-Plate (BOI MP)**

2D BOI MPs were fabricated via hydrolysis method at ambient temperature. Herewith, 0.0028 mol of $Bi(NO_3)_3 \cdot 5H_2O$ was added into 20.0 mL (0.140 mol/L) of aqueous KI solution with stirring. After 2 min of sonication, the suspension undergoes 5h of constant stirring. A brick-red colorization was attained, which was filtered along with washing frequently by ethanol and water. Afterward, it was dried for 8 h at 60°C to obtain BOI MPs. The overall synthetic method is represented schematically in scheme 1.

Synthesis of $CuInS_2$ Quantum dot (CIS QD)

The $CuInS_2$ ternary QD was synthesized in a single pot reflux method. In a two-necked round-bottom-flask, appropriate amount of $CuCl_2 \cdot 2H_2O$, $InCl_3 \cdot 4H_2O$ as copper, indium precursors respectively and TGA as capping ligand were taken and dissolved into water. The pH of the above solution was accustomed to 8.5 by adding 1M NaOH solution. Aqueous solution of $Na_2S \cdot 9H_2O$ as a sulfur source was introduced into the round-bottom-flask and the entire solution was refluxed for 4 h at 100°C. Then after 4 h, the solution was precipitated by adding ethanol and was dehydrated at 40°C under vacuum to obtain ternary CIS QD.

Synthesis of CuInS$_2$-BiOI (CIS-BOI) Composite

 The CuInS$_2$-BOI hybrid was synthesized *via.* reflux strategy by in-situ insertion of the as-prepared

BOI MP. In a two-necked round-bottom-flask, appropriate amount of CuCl$_2$·2H$_2$O, InCl$_3$·4H$_2$O as

copper, indium precursors respectively and TGA as capping ligand were taken and dissolved into

water. The pH of the above solution was accustomed to 8.5 by adding 1M NaOH solution. Aqueous

solution of Na$_2$S·9H$_2$O as a sulfur source was introduced into the round-bottom-flask. A certain

amount of as-prepared BOI was inserted with constant stirring and the entire solution was refluxed

for 4 h at 100°C. Then after 4 h, the solution was precipitated by adding ethanol and was

dehydrated at 40°C under vacuum to obtain CIS-BOI binary hybrid. Likewise, CIS-BOI

composites at various weight percentages were synthesized by following the same procedure. The

overall synthesis process is represented in Scheme. S1.
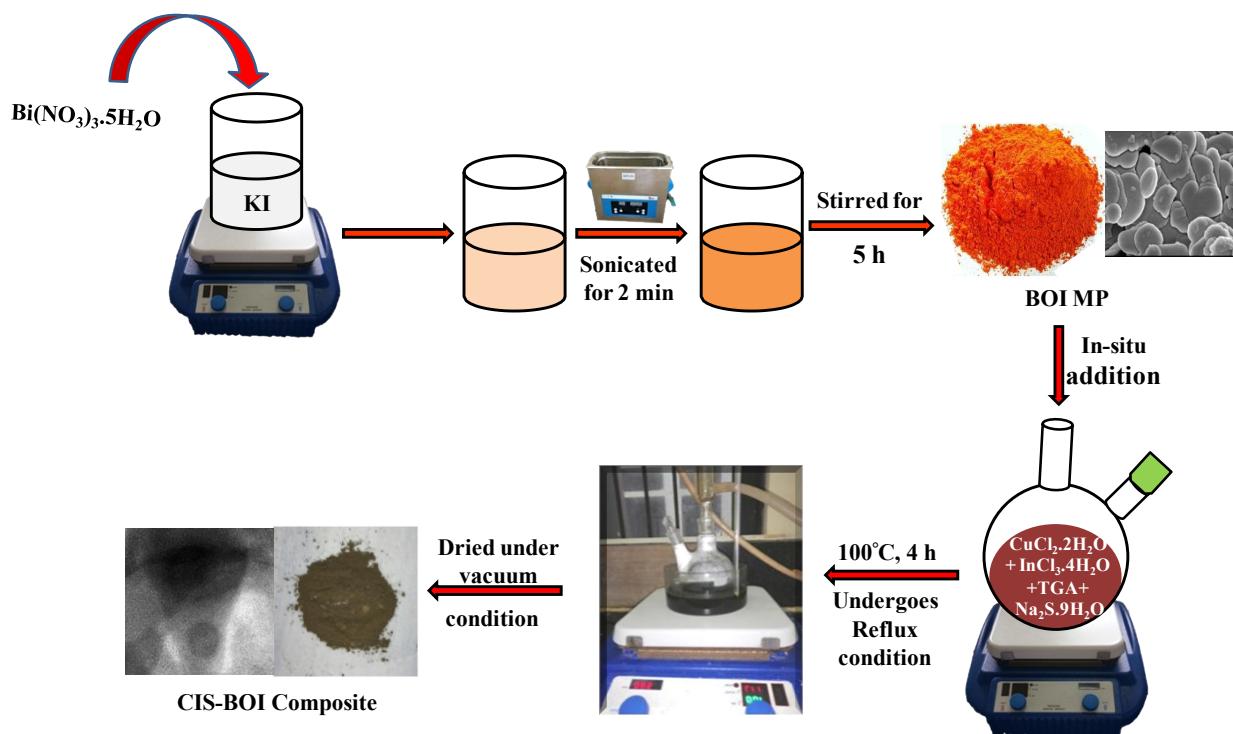
Scheme. S1: Overall in-situ synthesis scheme for CIS-BOI composite.

Characterization techniques

Structural characterization of the as-prepared samples was analyzed by XRD (X-Ray Diffraction), FESEM (Field-Emission-Scanning-Electron-Microscopy), HRTEM (High-Resolution-Transmission-Electron-Microscopy), XPS (X-ray photoelectron-spectroscopy) and Raman analysis. The crystalinity nature and phase purity of the photocatalysts were anticipated by powder XRD technique with a RigakuUltima-IV X-ray diffractometer (40 KV/40 mA), outfitted with Cu Kα radiation ($\lambda = 1.54$ Å) at a 2θ range of 10-60°. XPS was executed with VG Microtech Multilab ESCA 3000 spectrometer via non-monochromatic Kα Mg X-ray supply to analyze surface elemental states and chemical composition of the sample. C 1s with binding energy 284.8 eV is taken reference for spectral calibration. The morphology of CIS QD on BOI MP surface was studied by FESEM analysis (FEI Quanta 400FEG_SEM). The internal structure and particle size of the as synthesized materials were analyzed by 200 kV HRTEM (analyzer JEOL-2100 JEOL). Raman spectrometer is used to know the composite formation and oxygen vacancy of the material. Here we used a laser of 332 nm RENISHAW via Raman spectrometer. The optical property of the as-prepared samples was carried out by UV-Vis DRS (UV- visible diffuse reflectance spectroscopy) and PL (Photoluminescence) spectroscopy. The UV-Vis DRS spectra of the prepared samples were deliberated by JASCO-V-750 UV-Vis spectrophotometer in a wavelength range of 200-800 nm ($BaSO_4$ as reference), to study the absorbance and bandgap energy of the pristine and composite materials. The Photoluminescence (PL) excitation and emission spectra were analyzed with a JASCO-FP-8300 fluorescence spectrometer where Xe- lamp is used as excitation source. The excitation and emission spectra were recorded in a range of 500- 640 nm and 420- 500 nm respectively. The electrochemical measurement were carried out via multi-channel-Iviumpotentiostat analyzer with a three electrode system which consists of Ag/AgCl as reference electrode, platinum as counter electrode and the as-prepared sample as a working

electrode. A solution of 0.1 M Na_2SO_4 with a pH of 6.8 was used as electrolyte for electrochemical measurements. Light illumination can be carried out by taking 300 W Xenon lamps fitted with 400 nm cut-off filter.

Photocatalytic H_2 Evolution

Furthermore, the photocatalytic activity of the as-synthesized samples was deliberated for hydrogen generation. The photocatalytic reaction was executed in a 100 mL quartz-set reactor. Typically, 20mg of catalyst was put into the reactor containing 20 mL of 10 volume percent aqueous methanol solution (as hole scavenger). 125W Xe-lamp of wavelength larger than 420nm was used as a source of visible-light in photo-reactor and was placed at 1.5 cm distance away from the catalyst. Then, the solution was constantly stirred throughout the reaction to avoid settling of catalyst. Before the light-irradiation, the catalytic mixed suspension undergoes nitrogen gas purging for 30mins to eliminate all the dissolved-oxygen and then for another 30mins in dark condition for the establishment of adsorption-desorption equilibrium. After light irradiation for 1h, the evolved gas was collected by water displacement technique. Afterward, the gas was identified by using GC-7890B coupled with TCD (thermal conductivity detector) and 5 Å molecular sieves. As blank experiment, no hydrogen gas evolution was observed in absence of light and catalyst; authenticate the significance of catalyst and light in a photo-catalytic reaction.

Photocatalytic O_2 Evolution

More to the point, the photocatalytic O_2 evolution ability of pristine BOI, CIS QD and the best composite material (15% CIS-BOI) was studied by using the same light source with different electron scavengers. Here, 20 mg of photocatalyst was taken in the photo-reactor containing 20 mL of 0.05M aqueous $AgNO_3$ and $FeCl_3$ solution differently. After light illumination of 1 h, the generated gas was accumulated by water displacement method. Subsequently the gas was collected

by using GC-7890B coupled with TCD (thermal conductivity detector) and 5 Å molecular sieves. As blank experiment, no oxygen gas evolution was observed in absence of light illumination and catalyst; validate the importance of light and catalyst in photo-catalytic reaction.

Fabrication of working electrodes:

Working electrodes were fabricated through dropcast technique by taking 0.5 mg of the as-prepared materials. The synthesized material was dispersed into 0.7 mL ethanol with 40 μL nafion solution. Then the suspension was sonicated for 7min to obtain a homogeneous mixture. After that the solution was dropcasted on the conducting side of a FTO (Fluorine Doped Tin Oxide) of area 1 cm². Then the catalyst loaded FTO was dried in a vacuum-oven overnight at room temperature for electrochemical study.
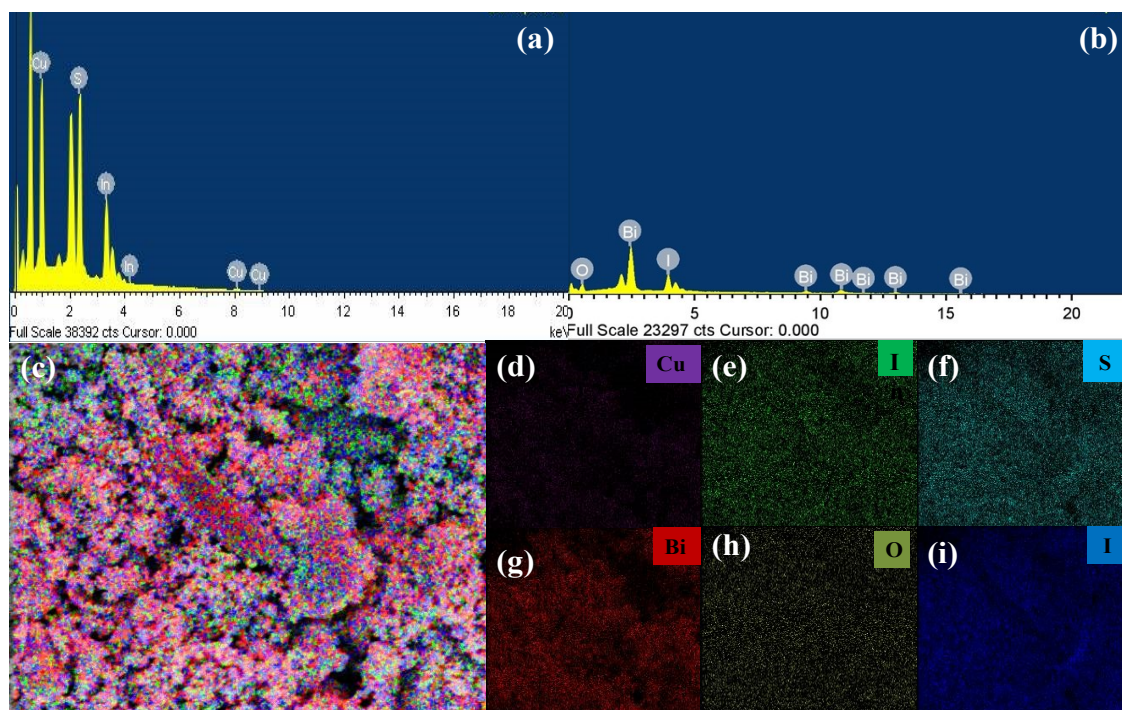

Fig. S1: EDX pattern of (a) CIS, (b) BOI; Elemental color-mapping image of (c) 15%CIS-BOI composite, (d) Cu, (e) In, (f) S, (g) Bi, (h) O, and (i) I elements.
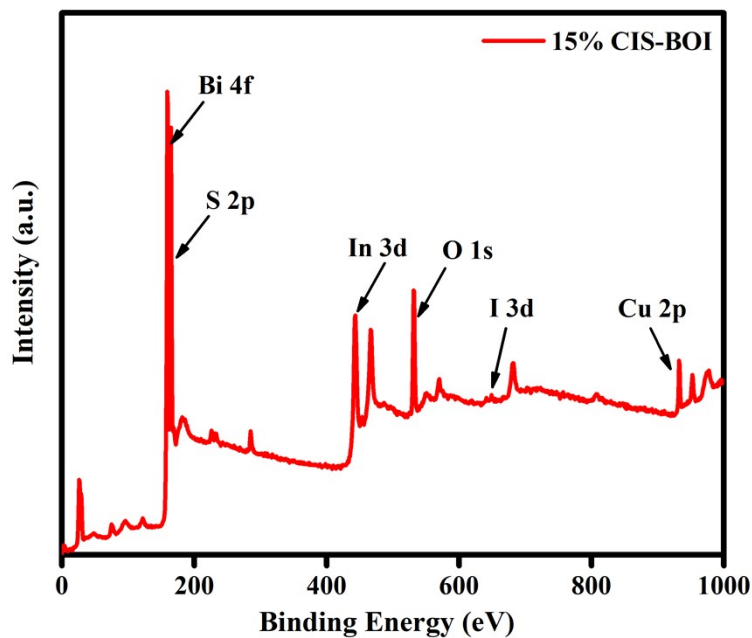
Fig. S2: XPS Survey of 15%CIS-BOI Composite.

Table: S1 comparison in binding energy of the elements in (a) neat BOI and 15%CIS-BOI, (b) neat CIS and 15%CIS-BOI

(a)

Elements	Binding energy in BOI	Binding energy In 15%CIS-BOI
Bi	159.2 eV	159.4 eV
	164.0 eV	164.6 eV
O	528.9 eV	529.1 eV
	531.4 eV	531.6 eV
	532.6 eV	532.8 eV
I	618.7 eV	618.9 eV
	630.2 eV	630.4 eV

(b)

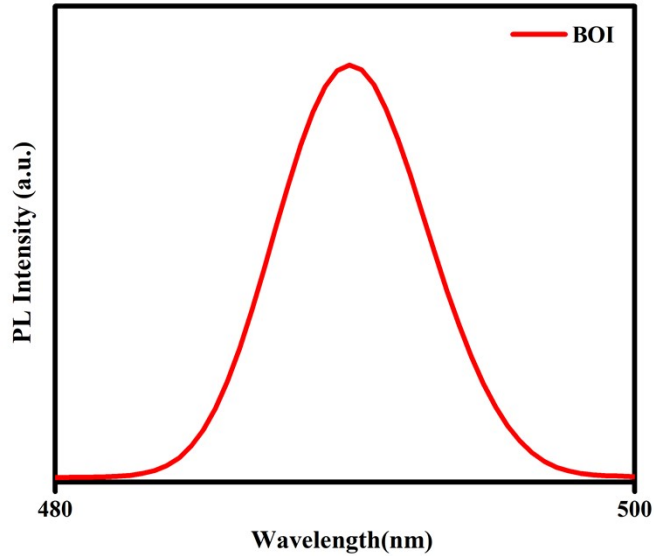| Elements	Binding energy in CIS	Binding energy in 15%CIS-BOI
Cu	932.7 eV	932.3 eV
	952.6 eV	952.2 eV
In	445.1 eV	444.6 eV
	452.8 Ev	452.6 eV
S	158.6 eV	158.1 eV
	164.0 eV	163.6 eV

Fig. S3: PL emission spectra of pristine BOI.

H$_2$ Evolution

Calculation of Apparent Conversion Efficiency (ACE) of 15%CIS-BOI composite [1]

$$\text{ACE} = \frac{Stored\ chemical\ energy}{Incident\ light\ intensity} \times 100$$

$\Rightarrow$ Stored chemical energy $=$ moles of H$_2$ produced $\times \Delta$Hc

$= 0.1709 \times 10^{-6}$ µmols$^{-1} \times 285.8$ KJmol$^{-1} = 0.0487$ Js^{-1} or W

$\Rightarrow$ Incident light intensity $= 70$ mW cm^{-2}

$\times$ (Area of the spherical surface where light falls)

$= 70$ mW cm$^{-2} \times 3.141 \times 1.5$ cm $\times 1.5$ cm $= 0.4947$ W

$\Rightarrow$ ACE $= \dfrac{0.0487\ W}{0.4947\ W} \times 100 = 9.84\%$

Where, ΔHc = Heat of combustion of hydrogen = 285.8 kJ/mol.

Calculation of ACE of pristine CIS QD

$$\text{ACE} = \frac{Stored\ chemical\ energy}{Incident\ light\ intensity} \times 100$$

$\Rightarrow$ Stored chemical energy $=$ moles of H_2 produced $\times \Delta Hc$

$= 0.0644\ \mu mols^{-1} \times 285.8\ kJmol^{-1} = 0.0184\ Js^{-1}$ or W

$\Rightarrow$ Incident light intensity $= 70\ mW\ cm^{-2}$

$\times$ (Area of the spherical surface where light falls)

$= 70\ mW\ cm^{-2} \times 3.141 \times 1.5\ cm \times 1.5\ cm = 0.4947\ W$

$\Rightarrow$ ACE $= \dfrac{0.0184\ W}{0.4947\ W} \times 100 = 3.72\%$

Where, ΔHc = Enthalpy of combustion of H_2 = 285.8 kJmol^{-1}.

Calculation of number of H_2 molecule of CIS-BOI composite [1]

Volume of H_2 gas liberated in reaction = 13.2 mL = 0.013 L

Standard gas equation is PV= nRT

(Where n= no. of moles, P= pressure at standard condition= 1 atm, V= volume of gas, R= gas constant= 0.082 L.atm mol^{-1} K^{-1}, T= standard temperature= 298 K)

$\Rightarrow$ n = (0.0138 L $\times$ 1 atm) / (0.082 L.atm mol-1 K^{-1} $\times$ 298 K)

$\Rightarrow$ n = 0.0005647 moles h^{-1}

1 mole H_2 gas = 6.023 $\times$ 10^{23} molecules

0.0005647 moles H_2 gas = 6.023 $\times$ 10^{23} $\times$ 0.0005647

Number of H_2 molecule (*per s*) = (6.023 $\times$ 10^{23} $\times$ 0.0005647) / (60 min $\times$ 60 s)

= **9.44 $\times$ 10^{16} per sec**

Calculation of number of H_2 molecule of pristine CIS QD

Volume of H_2 gas liberated in reaction = 5.2 mL = 0.00521 L

Standard gas equation is PV= nRT

$\Rightarrow$ n = (0.00521 L $\times$ 1 atm) / (0.082 L.atm mol^{-1} K^{-1} $\times$ 298 K)

$\Rightarrow$ n = 0.0002132 moles h^{-1}

1 mole H_2 gas = 6.023 $\times$ 10^{23} molecules

0.0002132 moles H_2 gas = 6.023 $\times$ 10^{23} $\times$ 0.0002132

Number of H_2 molecule (*per s*) = (6.023 $\times$ 10^{23} $\times$ 0.0001686) / (60 min $\times$ 60 s)

= **3.56 $\times$ 10^{16} per sec**

O_2 Evolution

Calculation of ACE of 15%CIS-BOI composite

$$ACE = \frac{Stored\ chemical\ energy}{Incident\ light\ intensity} \times 100$$

$\Rightarrow$ Stored chemical energy = moles of O_2 produced $\times \Delta Hc$

= 0.1585 $\times$ 10^{-6} μmols^{-1} $\times$ 285.8 KJmol^{-1} = 0.0453 Js^{-1} or W

$\Rightarrow$ Incident light intensity = 70 mW cm^{-2}

$\times$ (Area of the spherical surface where light falls)

= 70 mW cm^{-2} $\times$ 3.141 $\times$ 1.5 cm $\times$ 1.5 cm = 0.4947 W

$\Rightarrow$ ACE = $\frac{0.0453\ W}{0.4947\ W} \times 100$ = 9.16%

Where, ΔHc = Heat of combustion of H_2 = 285.8 kJ/mol.

Calculation of ACE of pristine BOI MP

$$ACE = \frac{Stored\ chemical\ energy}{Incident\ light\ intensity} \times 100$$

$\Rightarrow$ Stored chemical energy = moles of O_2 produced $\times \Delta Hc$

= 0.0531 μmols^{-1} $\times$ 285.8 kJmol^{-1} = 0.0151 Js^{-1} or W

⇒ Incident light intensity $= 70$ mW cm^{-2}

$\times$ (Area of the spherical surface where light falls)

$= 70$ mW cm^{-2} $\times$ 3.141 $\times$ 1.5 cm $\times$ 1.5 cm $= 0.4947$ W

⇒ ACE $= \dfrac{0.0151\ W}{0.4947\ W} \times 100 = 3.06\%$

Where, ΔHc = Enthalpy of combustion of H_2 = 285.8 kJmol^{-1}.

Calculation of number of O_2 molecule of 15%CIS-BOI composite

Volume of O_2 gas liberated in reaction = 12.8 mL = 0.0128 L

Standard gas equation is PV= nRT

(Where n= no. of moles, P= pressure at standard condition= 1 atm, V= volume of gas, R= gas constant= 0.082 L.atm mol^{-1} K^{-1}, T= standard temperature= 298 K)

⇒ n = (0.0128 L $\times$ 1 atm) / (0.082 L.atm mol-1 K^{-1} $\times$ 298 K)

⇒ n = 0.0005238 moles h^{-1}

1 mole O_2 gas = 6.023 $\times$ 10^{23} molecules

0.0005238 moles O_2 gas = 6.023 $\times$ 10^{23} $\times$ 0.0005238

Number of O_2 molecule (*per s*) = (6.023 $\times$ 10^{23} $\times$ 0.0005647) / (60 min $\times$ 60 s)

= **8.76 $\times$ 10^{16} per sec**

Calculation of number of O_2 molecule of pristine BOI MP

Volume of O_2 gas liberated in reaction = 4.28 mL = 0.00428 L

Standard gas equation is PV= nRT

⇒ n = (0.00428 L $\times$ 1 atm) / (0.082 L.atm mol^{-1} K^{-1} $\times$ 298 K)

⇒ n = 0.0001751 moles h^{-1}

1 mole O_2 gas = 6.023 $\times$ 10^{23} molecules

0.0001751 moles O_2 gas = $6.023 \times 10^{23} \times 0.0001751$

Number of O_2 molecule (*per s*) = $(6.023 \times 10^{23} \times 0.0001751) / (60\ min \times 60\ s)$

= **2.93×10^{16} per sec**

Table: S2 Comparison table for photocatalytic H_2 generation of CIS based composites and photocatalytic O_2 evolution of BOI based composites.

Sl. No	Type of catalytic reaction	Photocatalysts	Light Source/ Scavenger	Hydrogen Evolution ($\mu mol g^{-1} h^{-1}$)	Reference
1		CuInS$_2$-CN	-----	192	2
2		CuInS$_2$- ZnIn$_2$S$_4$	300 W Xenon lamp ($\lambda \geq 420$ nm) 0.25 mol/L Na$_2$S and 0.35 mol/L Na$_2$SO$_3$	292	3
3	CIS-Based Photocatalysts Towards H$_2$ Evolution	ZnIn$_2$S$_4$-rGO-CuInS$_2$	150 W Xenon lamp ($\lambda \geq 420$ nm) 50 mL Na$_2$S/Na$_2$SO$_3$ (10 volume %)	506.2	4
4		CuInS$_2$/TiO$_2$/MoS$_2$	300 W Xenon lamp ($\lambda > 420$ nm), 250 mL of 0.1 M Na2S/ Na2SO3	$10.34*10^2$	5
5		ZnIn$_2$S$_4$ /CuInS$_2$ –QD-Pt	1000 W Xenon lamp ($\lambda > 420$ nm), 80 mL of 0.35 M Na2S/0.25 M Na2SO3	411.17	6
6		CuInS$_2$ QD/ZnS	3 mW LED ($\lambda = 405$ nm), 1	$16.45*10^2$	7

			mL of 0.2M ascorbic acid solution (pH = 5)		
7		$CuInS_2/TiO_2$	300 W Xe lamp, 100 mL of 0.55 M Na_2S /0.25 M Na_2SO_3	785.4	8
8		$CuInS_2$ QD/ZnS	150 W xenon lamp (λ=400-700 nm), 5 mL of 0.5 M sodium ascorbate/ascorbic acid	$15.90*10^2$	9
9		Zn dopped-$CuInS_2$ QD	300 W Xe-lamp (λ=400–780 nm), 0.2 M Ascorbic Acid at pH=5	$14.4*10^3$	10
10		Ni-catalyzed Cu_xIn_yS	3 W LED light (λ = 470 nm), 0.5 M H_2A/NaHA	$11.6*10^3$	11
11		$Cu_{0.75}In_{0.25}S$-BOI MF	125 W Xe-lamp (λ > 420 nm), Methanol (10 volume %)	$29.436*10^3$	12
12		$CuInS_2$ QD-BOI	125 W Xe-lamp (λ > 420 nm), Methanol (10 volume %)	$30.774*10^3$	This work

13		BiOI-CeO$_2$	125 W Hg-lamp (λ>420 nm), 20mL of 0.05M AgNO$_3$	8075	13
14		RuO$_2$-loaded BiOI	300 W Xenon lamp (λ>420 nm), 0.05M AgNO$_3$	2730	14
15		CuInS$_2$ QD/BOI MP	125 W Xe-lamp (λ > 420 nm), Methanol (10 volume %)	28.544*10^3	This work

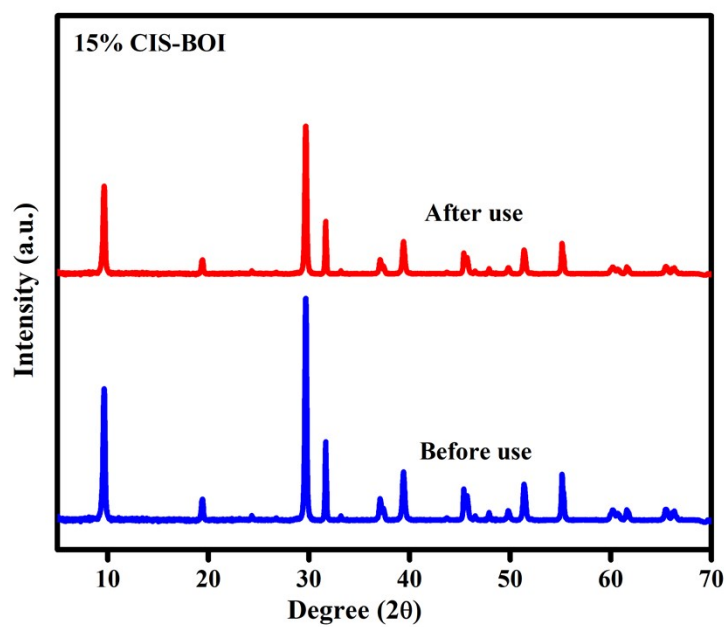(Left column spanning rows: **BOI-Based Photocatalysts Towards O$_2$ Evolution**)

Fig. S4: XRD of 15%CIS-BOI before and after used.

Reference

1. S. Mansingh, S. Subudhi, S. Sultana, G. Swain, and K. Parida, *ACS Appl. Nano.,* 2021, **4**, 9635-9652.

2. Y. Zheng, Y. Chen, B. Gao, J. Chen, Z. Du, and B. Lin, *Mater. Lett.,* 2019, **254**, 81–84.

3. X. Guo, Y. Peng, G. Liu, G. Xie, Y. Guo, Y. Zhang, and J. Yu, *J. Phys. Chem. C,* 2020, **124**, 5934–5943.

4. A. Raja, N. Son, M. Swaminathan and M. Kang, *J. Colloid Interface Sci.,* 2021*,* **602**, 669–679.

5. Y.-J. Yuan, G. Fang, D. Chen, Y. Huang, L.-X. Yang, *et al.Dalton Trans.,* 2018, **47**, 5652-5659.

6. O. Cavdar, A. Malankowska, D. Amgar, P. Mazierski, J. Luczak, *et al. Int. J. Hydrog. Energ.,* 2021,**46**, 486-498

7. W. Hu, S. Yang, and J. Huang, *J. Chem. Phys.,* 2019, **151**, 214705.

8. Y. Yana, M. Yanga, H. Shia, C. Wanga, J. Fanb, E. Liua, and X. Hu, *Ceram. Int.* 2019, **45**, 6093-6101.

9. M. Sandroni, R. Gueret, K. D. Wegner, P. Reiss, J. Fortage, D. Aldakov, and M.-N. Collomb, *Energy Environ. Sci.* **2018**,*11*, 1752-1761.

10. X.-Y. Liu, G. Zhang, H. Chen, Haowen. Li, J. Jiang, Y.-T. Long, and Z. Ning, *Nano Research,* 2018, **11**, 1379–1388.

11. X.-B. Fan, S. Yu, F. Zhan, Z.-J. Li, and Y.-J. Gao, *Chem. Sus. Chem.***,** 2017, **10**, 1–7.

12. D. Prusty, S. Mansingh, L. Acharya, and L. Paramanik, K. M. Parida, *RSC Adv.* 2022, **12**, 1265.

13. S. Sultana, S. Mansingh, and K. M. Parida, *J. Phys. Chem. C,* 2018, **122**, 808–819.

14. T.-H. Chen, M. Yoshida, S. Tsunekawa, J.-H. Wu, K. L. Andrew, and Hu, C. *Catal. Sci. Technol.* 2020, **10**, 3223-3231.