

Electronic Supporting Information

Robust Direct Z-scheme Exciton Transfer dynamics via. Architecting 3D BiOI MF Supported Non-stoichiometric $\text{Cu}_{0.75}\text{In}_{0.25}\text{S}$ NCs Nanocomposite For Co-catalyst free Photocatalytic Hydrogen Evolution

Experimental section

Chemicals Requirement

Copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 99%), Thioglycolic acid (TGA, 79%), Potassium iodide (KI, >99.5%), sodium hydroxide (NaOH, 97%), Ethylene glycol (EG, >99%), NBT (nitro blue tetrazolium chloride), Methanol, Nafion, Na_2SO_4 , TA (Terephthalic Acid) were purchased from Merck and Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 98%), Indium chloride (InCl_3 , 98%), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 58%), from Himedia chemical company. All reagents are in analytical grade and are used in reaction without further purification.

Synthetic Method

Synthesis of Bismuth Oxyiodide Microflower (BOI MF)

BOI MFs were synthesized via hydrolysis method in presence of EG (as a structure directing group) at a room temperature. For this, 10.0 mL EG with 0.0028 mol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was added drop wise into 10.0 mL (0.280 mol/L) of aqueous KI solution with constant stirring for 5 h. A brick red colorization was obtained, which was filtered along with washing frequently with ethanol and water. Then it was dried for 8 h at 60°C to get BOI MFs. The overall synthetic method is represented schematically in scheme 1.¹⁻³

Synthesis of $\text{Cu}_{0.75}\text{In}_{0.25}\text{S}$ NC

The $\text{Cu}_{0.75}\text{In}_{0.25}\text{S}$ composite was synthesized in a single pot reflux method. In a two-necked round bottom flask, suitable amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and TGA were taken as copper, indium precursors and capping ligand respectively and was dissolved into water. The pH of the mixture solution was adjusted to 8.5 by adding 1M NaOH solution. Aqueous solution of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ as sulfur source was injected into the round bottom flask and the entire solution was refluxed for 4h at 100°C . The above solution was precipitated by adding ethanol and was dehydrated at 40°C under vacuum. Here the molar ratios of Cu and In was taken to 0.75:0.25.

Characterization techniques

Structural characterization of the synthesized samples was illustrated by XRD (X-Ray Diffraction), XPS (X-ray photoelectron spectroscopy) and FESEM (Field Emission Scanning Electron Microscopy) analysis. The crystallinity and phase purity of the catalysts were anticipated by powder XRD technique with a RigakuUltima-IV X-ray diffractometer (40 KV/40 mA), outfitted with Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) at a 2θ range of $10\text{-}60^\circ$. XPS was executed with VG Microtech Multilab ESCA 3000 spectrometer via non-monochromatic $K\alpha$ 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 NCs on BOI MF surface was studied by FESEM analysis (FEI Quanta 400FEG_SEM). 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 synthesized 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-Ivium potentiostat 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 Na₂SO₄ 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 H₂ Evolution

Besides, the photocatalytic ability of the synthesized materials (CIS, BIO and CIS-BIO) was studied for hydrogen production. The reaction was performed in a 100 mL sealed quartz-set reactor. Usually, 20 mg of photocatalyst was taken in the reactor containing 20 ml of 10 volume % aqueous methanol solution. 125 W Xenon-lamp of wavelength greater than 420 nm was used as the source of visible-light in the photo-reactor, which was placed at 1.5 cm distance away from the catalyst. The above solution was stirred constantly during the entire reaction to prevent settling of the catalyst. Before light irradiation the above catalyst mixed suspension was purged with Nitrogen gas for 30 mins to remove all dissolved oxygen and then for another ½ h in dark for establishment of adsorption-desorption equilibrium. After light illumination of 1h, the generated gas was accumulated by water displacement method. Subsequently the gas was detected by using GC-7890B coupled with TCD (thermal conductivity detector) and 5 Å molecular sieve. As blank experiment, no hydrogen gas evolution was observed in absence of light illumination and catalyst; validate the importance of light and catalyst in photo-catalytic reaction.

Preparation of working electrodes:

The working electrodes are prepared via dropcast method by taking the as prepared materials of 2 mg. The catalyst then dispersed in 1.4ml ethanol with 40 μ L nafion solution. The suspension then sonicated for 7 min to form a uniform mixture. Then the solution was drop casted on a FTO (Fluorine Doped Tin Oxide) of area 1 cm². The catalyst loaded area then dried in a vacuum oven overnight at a room temperature for electrochemical study.

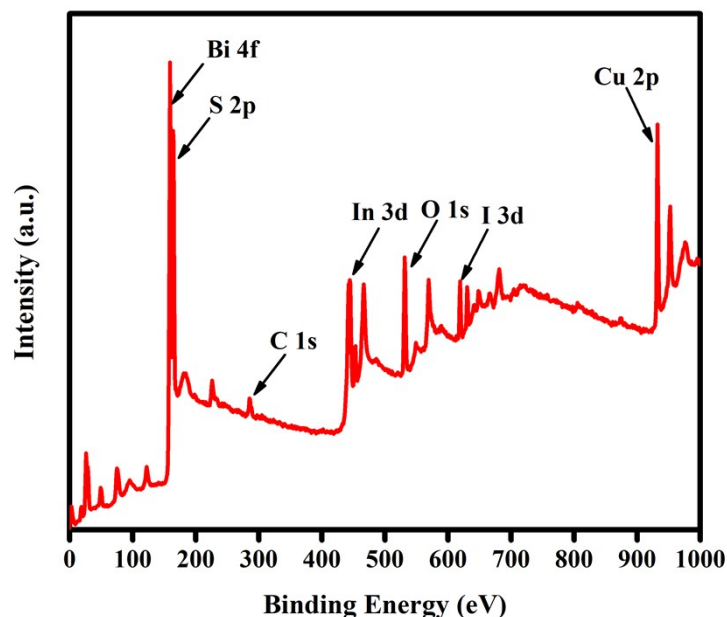


Fig. S1 XPS Survey of CIS-BOI Composite.

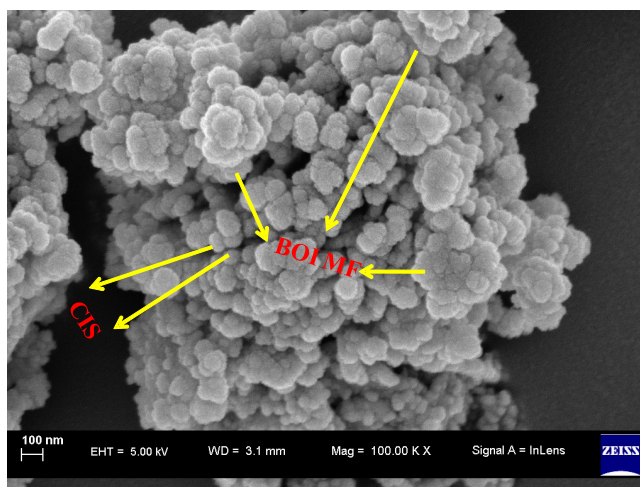


Fig. S2 FESEM image of CIS-BOI composite from a different angle.

Calculation of Apparent Conversion Efficiency (ACE) of CIS-BOI composite ⁴

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

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

$$= 0.1635 \mu\text{mols}^{-1} \times 285.8 \text{ kJmol}^{-1} = 0.0467 \text{ Js}^{-1} \text{ or W}$$

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

$$\times (\text{area of the spherical surface where light falls})$$

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

$$\Rightarrow \text{ACE} = \frac{0.0467 \text{ W}}{0.4947 \text{ W}} \times 100 = 9.44\%$$

where, ΔHc = heat of combustion of hydrogen = 285.8 kJ/mol.

Calculation of ACE of pristine CIS

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

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

$$= 0.0511 \mu\text{mols}^{-1} \times 285.8 \text{ kJmol}^{-1} = 0.0146 \text{ Js}^{-1} \text{ or W}$$

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

$$\times (\text{area of the spherical surface where light falls})$$

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

$$\Rightarrow \text{ACE} = \frac{0.0146 \text{ W}}{0.4947 \text{ W}} \times 100 = 2.95\%$$

where, ΔHc = enthalpy of combustion of H_2 = 285.8 kJmol⁻¹.

Calculation of number of H₂ molecule of CIS-BOI composite ⁵

Volume of H₂ 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)

$$\Rightarrow n = (0.013 \text{ L} \times 1 \text{ atm}) / (0.082 \text{ L.atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K})$$

$$\Rightarrow n = 0.0005321 \text{ moles h}^{-1}$$

1 mole H₂ gas = 6.023 x 10²³ molecules

$$0.0005321 \text{ moles H}_2 \text{ gas} = 6.023 \times 10^{23} \times 0.0005321$$

$$\begin{aligned} \text{Number of H}_2 \text{ molecule (per s)} &= (6.023 \times 10^{23} \times 0.0005321) / (60 \text{ min} \times 60 \text{ s}) \\ &= \mathbf{8.90 \times 10^{16} \text{ per sec}} \end{aligned}$$

Calculation of number of H₂ molecule of pristine CIS NC

Volume of H₂ gas liberated in reaction = 4.12 ml = 0.00412 L

Standard gas equation is $PV = nRT$

$$\Rightarrow n = (0.00412 \text{ L} \times 1 \text{ atm}) / (0.082 \text{ L.atm mol}^{-1} \text{ K}^{-1} \times 298 \text{ K})$$

$$\Rightarrow n = 0.0001686 \text{ moles h}^{-1}$$

1 mole H₂ gas = 6.023 x 10²³ molecules

$$0.0001686 \text{ moles H}_2 \text{ gas} = 6.023 \times 10^{23} \times 0.0001686$$

$$\begin{aligned} \text{Number of H}_2 \text{ molecule (per s)} &= (6.023 \times 10^{23} \times 0.0001686) / (60 \text{ min} \times 60 \text{ s}) \\ &= \mathbf{2.82 \times 10^{16} \text{ per sec}} \end{aligned}$$

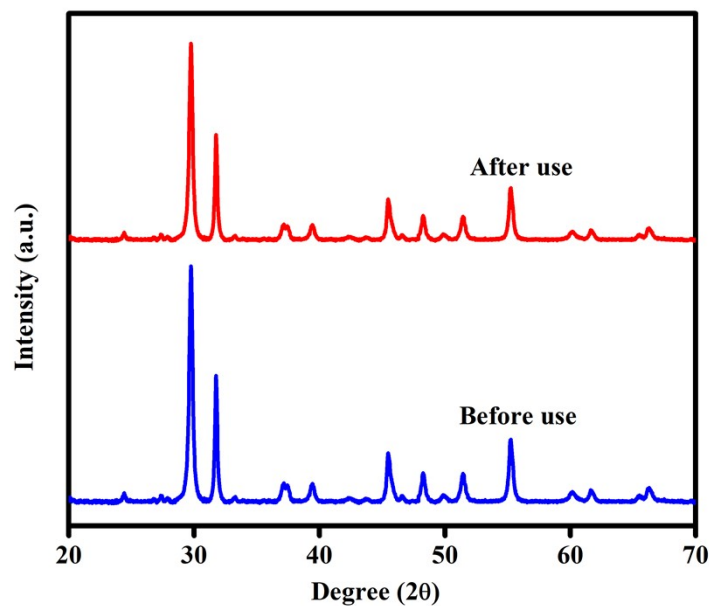


Fig. S3 XRD of CIS-BOI composite before and after use.

Confirmatory test for $\bullet\text{O}_2^-$ and $\text{OH}\bullet$ Radicals

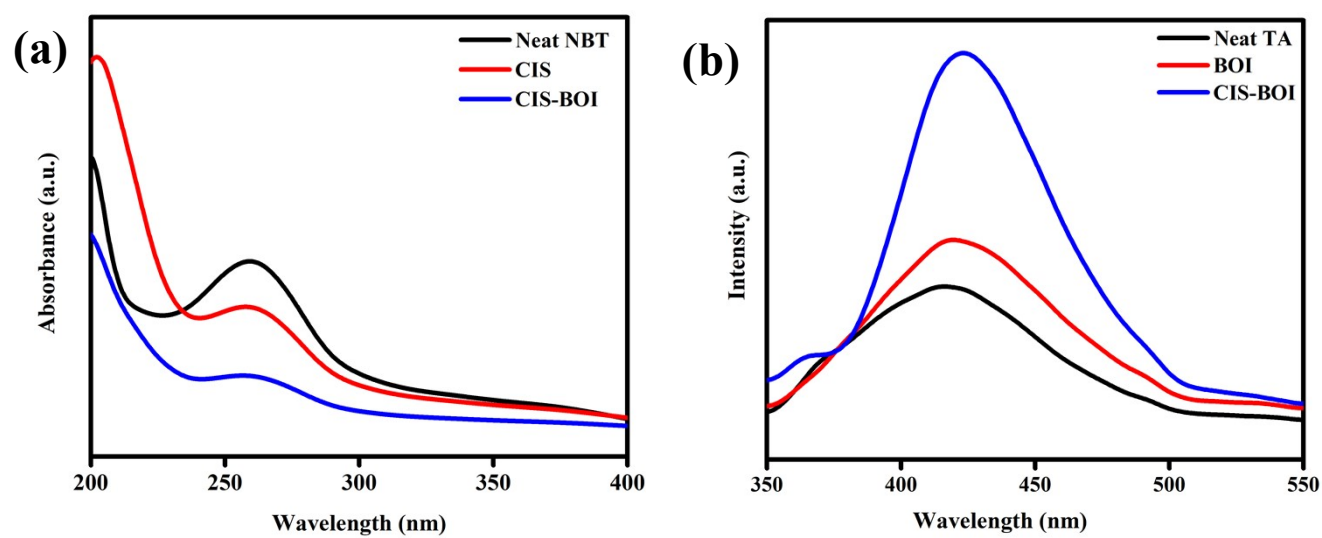


Fig. S4 (a) UV-Vis spectra of neat NBT, CIS, and CIS-BOI, and (b) PL spectra of neat TA, BOI, CIS-BOI.

References

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