

Supporting Information

1. Materials

Fluorine doped tin oxide (FTO, Nippon Sheet Glass, Japan, 2.2 mm thick, 14 Ω) substrates were purchased from Wu Han Jinge-solar Energy Technology Co., Ltd. The FTO glasses were sonicated sequentially in acetone, ethanol, and distilled water for 30 minutes, respectively. Indium trichloride (InCl₃, metals basis, 99.99%), bismuth chloride (BiCl₃, AR, ≥ 99%), thioacetamide (CH₃CSNH₂, metals basis, 99.999%), ethylene glycol ((CH₂OH)₂, AR, 99.9%), sodium sulfate (Na₂SO₄, AR, 99.5%), and sodium sulphite (Na₂SO₃, AR, 99.5%) were purchased from Aladdin and all chemicals were used without any further purification. Deionized water was used for preparation of solutions and washing.

2. Physical characterization

The X-ray diffraction (XRD) was detected on a Shimadzu ZD-3AX diffractometer with Cu Kα radiation (λ = 1.5418 Å). The 2θ scanning angular range was from 10° to 90° with rate of 2° per minute. Raman spectra of these samples were conducted by using LabRAM HR Evolution (λexc = 532 nm). The morphologies and high-resolution microstructure images were recorded though a field emission scanning electron microscope (FE-SEM, Nova 400 Nano-SEM) and transmission electron microscope (TEM, Talos F200S, 200kV). The surface composition and chemical state was carried out by the X-ray photoelectron spectroscopy (XPS,
ESCALab250) technique, all spectra were calibrated by using the C 1s peak at 284.8 eV. The optical properties of as-prepared samples were performed by a spectrophotometer (UV-3600, Shimadzu) in the region of 300 - 900 nm, room temperature photoluminescence (PL) measurement were carried out with a fluorescence spectrometer (Cary eclipse) with an excitation wavelength of 365 nm; the measured powder was scraped from the FTO substrate.

3. Photoelectrochemical measurements

Electrochemical tests were carried out by using a Zahner Zennium electrochemical workstation (Zennium and PP211, Germany) in a standard three-electrode configuration, a photoanode (1 cm²) used as the working electrode. Meanwhile, a Pt coil (diameter is about 1 mm, length is about 5 cm) served as the counter electrode, an Ag/AgCl electrode (saturated KCl) used as the reference electrode. The photo-response of the synthesized electrodes were measured under front-side illumination by a 300 W Xenon arc lamp (NBet HSX-F300, China) equipped with an AM 1.5G filter (Ceaulight). The intensity of the light source was calibrated with a UV enhanced silicon photo-detector (Newport, Models 1916C and 818-UV) to simulate one solar illumination (100 mW cm⁻²). The applied potential versus Ag/AgCl was converted to RHE by the Nernst equation:

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \mathrm{pH} + E^{\circ}_{\text{Ag/AgCl}} \]  

(1)

\[ E^{\circ}_{\text{Ag/AgCl}} \] is 0.1976 V vs. RHE at 25 °C. In a typical experiment, 0.2 M Na₂SO₄ (pH 6.8) with/without 0.5 M Na₂SO₃ as a hole scavenger was used as the
electrolyte. For all samples, a positive scan rate of 25 mV s⁻¹ was used for the photocurrent-voltage (J-V) measurements. Photocurrent stability tests were performed at a fixed bias potential of 0.90 V vs. RHE and the incident photo to current efficiency (IPCE) performance was performed at 1.23 V vs. RHE under illumination. The IPCE is expressed by the following equation:

\[
\text{IPCE} = \frac{(J \times 1240)}{(P_{\text{light}} \times \lambda)} \tag{2}
\]

where \(J\) is the measured photocurrent density at a specific wavelength (mA cm⁻²), \(\lambda\) is the incident light wavelength (nm), and \(P_{\text{light}}\) is the recorded irradiance intensity at a specific wavelength (mW cm⁻²). The photovoltages of various photoanodes were estimated by the onset potential (E) shift of the anodic current in dark and under illumination. The controlled intensity modulated photo spectroscopy (CIMPS) was conducted with the frequency range from 10k to 1 Hz with water oxidation, which was conducted by a constant power density (\(\lambda = 365\) nm, 5 mW cm⁻²) under different potential. The charge transport time (\(\tau\)) could be calculated by the following equation,

\[
\tau = \frac{1}{2\pi f} \tag{3}
\]

where \(\tau\) and \(f\) are electron transport time across the film and the minimum characteristic frequency. Mott-Schottky plots were obtained in 0.2 M Na₂SO₄ at an ac frequency of 500 and 1000 Hz. The carrier concentration and the flat band potential can be estimated by the following equation:

\[
(A_s / C_{\text{bulk}})^2 = \left( \frac{2}{\varepsilon \varepsilon_0 N_d} \right)[V - V_{fb} - k_B T / e] \tag{4}
\]

where \(A_s\) is the efficient area of electrode, \(C_{\text{bulk}}\) is the space charge capacitance, \(\varepsilon\) is
the dielectric constant of the samples, \( \varepsilon_0 \) is the permittivity under vacuum (8.85 \( \times 10^{-12} \) C\(^2\) J\(^{-1}\)m\(^{-2}\)), \( N_d \) is the carrier density of the samples, \( V \) is the applied potential, \( V_{fb} \) is the flat band potential, \( k_B \) is the Boltzmann constant (1.38 \( \times 10^{-23} \) J K\(^{-1}\)), \( T \) (298 K) is the absolute temperature, and \( e \) is the electron charge (1.602 \( \times 10^{-19} \) C).

4. Calculations for the efficiencies of charge separation and oxidation kinetics

The photocurrent density arising from PEC performance (\( J_{\text{water}} \)) can be described as follows:

\[
J_{\text{water}} = J_{\text{abs}} \times \eta_{\text{sep}} \times \eta_{\text{ox}} \tag{5}
\]

where \( J_{\text{abs}} \) is the photocurrent density when completely converting the absorbed photons into current (i.e., APCE = 100%). \( \eta_{\text{sep}} \) is the efficiency of charge separation and \( \eta_{\text{ox}} \) is the efficiency of surface oxidation kinetics. Adding 0.5 M Na\(_2\)SO\(_3\) to the electrolyte can completely suppress the surface recombination of charge carriers without influencing the charge separation in the electrode bulk (i.e., \( \eta_{\text{ox}} = 100\% \)). Therefore, \( \eta_{\text{sep}} \) and \( \eta_{\text{ox}} \) can be expressed as follows:

\[
\eta_{\text{sep}} = \frac{J_{\text{sulfite}}}{J_{\text{abs}}} \tag{6}
\]

\[
\eta_{\text{ox}} = \frac{J_{\text{water}}}{J_{\text{sulfite}}} \tag{7}
\]

where \( J_{\text{water}} \) is the photocurrent density for water oxidation; \( J_{\text{sulfite}} \) is the photocurrent density for sulfite oxidation. By estimating the overlapped areas between the AM 1.5G illumination, assuming APCE = 100\%, the \( J_{\text{abs}} \) of Bi\(_2\)S\(_3\), In\(_2\)S\(_3\), and In\(_2\)S\(_3@\)Bi\(_2\)S\(_3\) photoanodes are derived to be around 5.6, 4.2, and 6.5 mA cm\(^{-2}\).
Fig. S1. SEM images of In$_2$S$_3$ synthesized by different concentrations of indium trichloride in ethylene glycol solvothermal process, including (a) 3 mM, (b) 6 mM, (c) 12 mM, and (d) 20 mM. SEM images of typical In$_2$S$_3$@Bi$_2$S$_3$ structures by using different concentrations of indium trichloride, including (e) 3 mM, (f) 6 mM, (g) 12 mM, and (h) 20 mM of indium trichloride. For the optimized structure of In$_2$S$_3$@Bi$_2$S$_3$, the inner layer Bi$_2$S$_3$ was fabricated by using 20 mM bismuth chloride and 35 mM thioacetamide, and then served as the substrate for growing the In$_2$S$_3$@Bi$_2$S$_3$ heterostructures.
Fig. S2. The XRD patterns of In$_2$S$_3$, Bi$_2$S$_3$, and In$_2$S$_3$@Bi$_2$S$_3$. The mismatched lattice parameters of In$_2$S$_3$ (a = 7.691, b = 7.691, and c = 32.329 Å) and Bi$_2$S$_3$ (a = 11.149, b = 11.304, and c = 3.981 Å) in crystalline structure will lead to lattice strain when the two structures grow together. Moreover, the diffraction peaks situated at 24.93°, 28.61°, 31.79°, 46.46° and 52.62° are consistent with the planes of (130), (211), (221), (431), and (351) with Bi$_2$S$_3$, while the diffraction peaks located at 27.43°, 33.23°, 43.60°, and 47.70° agree well with the planes of (109), (0012), (1015), and (2212) by pure In$_2$S$_3$. 
Fig. S3. XPS spectra of (a) Bi 4f and S 2p orbitals for Bi$_2$S$_3$, (b) In 3d and (c) S 2p orbitals for In$_2$S$_3$, and (d) the In 3d orbitals for In$_2$S$_3$@Bi$_2$S$_3$.

The characteristic Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$ peaks appeared at 158.3 and 163.6 eV, which is consistent with the standard Bi$^{3+}$ peaks of Bi$_2$S$_3$. The signals located between Bi 4f$_{5/2}$ and Bi 4f$_{7/2}$ could be attributed to the S 2p$_{3/2}$ at 162.3 eV and the S 2p$_{1/2}$ at 161.1 eV.

The In 3d$_{5/2}$ and In 3d$_{3/2}$ are located at 444.9 and 452.4 eV with a $\Delta E$ of 7.5 eV, demonstrating the typically In$^{3+}$. The two strong peaks at 161.7 and 162.9 eV are corresponding to the S 2p$_{3/2}$ and S 2p$_{1/2}$. The In 3d spectrum consists of In 3d$_{5/2}$ (444.8 eV) and In 3d$_{3/2}$ (452.3 eV) for In$_2$S$_3$@Bi$_2$S$_3$. The lower binding energies of In$^{3+}$ suggests the change of chemical bonding energy with interfacial electronic interaction in In$_2$S$_3$@Bi$_2$S$_3$ heterostructures.
Fig. S4. (a) The UV-vis absorption spectra for Bi$_2$S$_3$, In$_2$S$_3$, and In$_2$S$_3$@Bi$_2$S$_3$, and the inset is the Tauc’s plots of these semiconductors, indicating the bandgap of Bi$_2$S$_3$ and In$_2$S$_3$ is nearly 1.4 and 2.1 eV. The UV-vis absorption spectra reveal the absorption edge of In$_2$S$_3$@Bi$_2$S$_3$ heterostructure has a red-shift compared with In$_2$S$_3$ and Bi$_2$S$_3$. (b) The Photoluminescence (PL) spectra of different samples under excitation ($\lambda_{ex} = 365$ nm).
Fig. S5. Raman spectra of (a) bare Bi$_2$S$_3$, (b) bare In$_2$S$_3$, and (c) In$_2$S$_3$@Bi$_2$S$_3$ composite.
**Fig. S6.** The simulated band structure of (a) Bi$_2$S$_3$, (b) In$_2$S$_3$, and (c) In$_2$S$_3$@Bi$_2$S$_3$. In detail, Bi$_2$S$_3$ has a direct bandgap (1.41 eV) where the valance band maximum (VBM) and the conduction band minimum (CBM) both lie at general points between G and Z point. A large bandgap of 1.97 eV is observed for In$_2$S$_3$, where the VBM locates between G and F while the CBM locates at G point. Specifically, the slab model of In$_2$S$_3$ is obtained from the bulk structures on (001) direction with vacuum (10 Å), and the Bi$_2$S$_3$ (010) direction has been established with vacuum (10 Å).
Fig. S7. J-V plots of various samples for sulfite oxidation in 0.2 M Na$_2$SO$_4$ with 0.5 M Na$_2$SO$_3$ under AM 1.5G illumination.
Fig. S8. (a) IPCE for different samples at 1.23 V vs. RHE, and (b) photocurrent density versus time at 0.9 V vs. RHE in 0.2 M Na$_2$SO$_4$ solution. The IPCE value of In$_2$S$_3$@Bi$_2$S$_3$ varies between 32%-45% at 500-350 nm and maintains a relative high value under broadband-light irradiation, suggesting the PEC performance of In$_2$S$_3$@Bi$_2$S$_3$ is higher than Bi$_2$S$_3$ nanorods and In$_2$S$_3$ nanosheets. During stability test for 2 hours, the results exhibit In$_2$S$_3$@Bi$_2$S$_3$ possess around 90% of its initial photocurrent, confirming the good stability of 2D/1D In$_2$S$_3$@Bi$_2$S$_3$ heterostructures under continuous water oxidation.
Fig. S9. SEM images of typical (a) Bi$_2$S$_3$ nanorods, (b) In$_2$S$_3$ nanosheets, and (c) In$_2$S$_3$@Bi$_2$S$_3$ heterostructure after stability test for 2 hours.
Fig. S10. Plots of CIMPS complex plane of (a) Bi$_2$S$_3$, (b) In$_2$S$_3$, and (c) In$_2$S$_3$@Bi$_2$S$_3$ with water oxidation at different applied potential (1.5, 0.9, and 0.3 V vs. RHE) with constant power density (5 mW cm$^{-2}$). (d) The electrons’ transport time ($\tau$) originated from CIMPS complex plane at different potential in 0.2 M Na$_2$SO$_4$ solution (pH 6.8).
Fig. S11. The photovoltage ($V_{ph}$) for various photoanodes, which estimated by the onset potential ($E$) shift of anodic current in dark and under illumination. The $V_{ph}$ could be written as: $V_{ph} = |E_{dark} - E_{light}|$. 
Table S1 The PEC performances of In$_2$S$_3$-based compounds compared with this study.

<table>
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<tr>
<th>Photocatalyst</th>
<th>Electrolyte</th>
<th>Applied bias</th>
<th>$J$ ($\mu$A/cm$^2$) Original</th>
<th>$J$ ($\mu$A/cm$^2$) Improved</th>
<th>Multiple</th>
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<td>700 (In$_2$O$_3$/</td>
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<td>In$_2$S$_3$/CdS</td>
<td>In$_2$S$_3$/CdS</td>
<td>In$_2$S$_3$/CdS</td>
<td>1.4 V vs.</td>
<td>137 (Pure In$_2$S$_3$)</td>
<td>1570 (In$_2$O$_3$/</td>
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<td>(In$_2$S$_3$/MoS$_2$/</td>
<td>Cds)</td>
<td>(In$_2$S$_3$/MoS$_2$/</td>
<td>Cds)</td>
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<td>In$_2$S$_3$-CNT</td>
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<td>0.7 Blank In$_2$S$_3$</td>
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<td>Titania@β-In$_2$S$_3$</td>
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<td>TiO$_2$/In$_2$S$_3$</td>
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<td>MoS$_2$/In$_2$S$_3$</td>
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Notes and references


