

## Supporting Information

**NiFe prussian blue analogue cocatalyzed  $\text{TiO}_2/\text{In}_2\text{S}_3$  type-II heterojunction for solar water splitting**

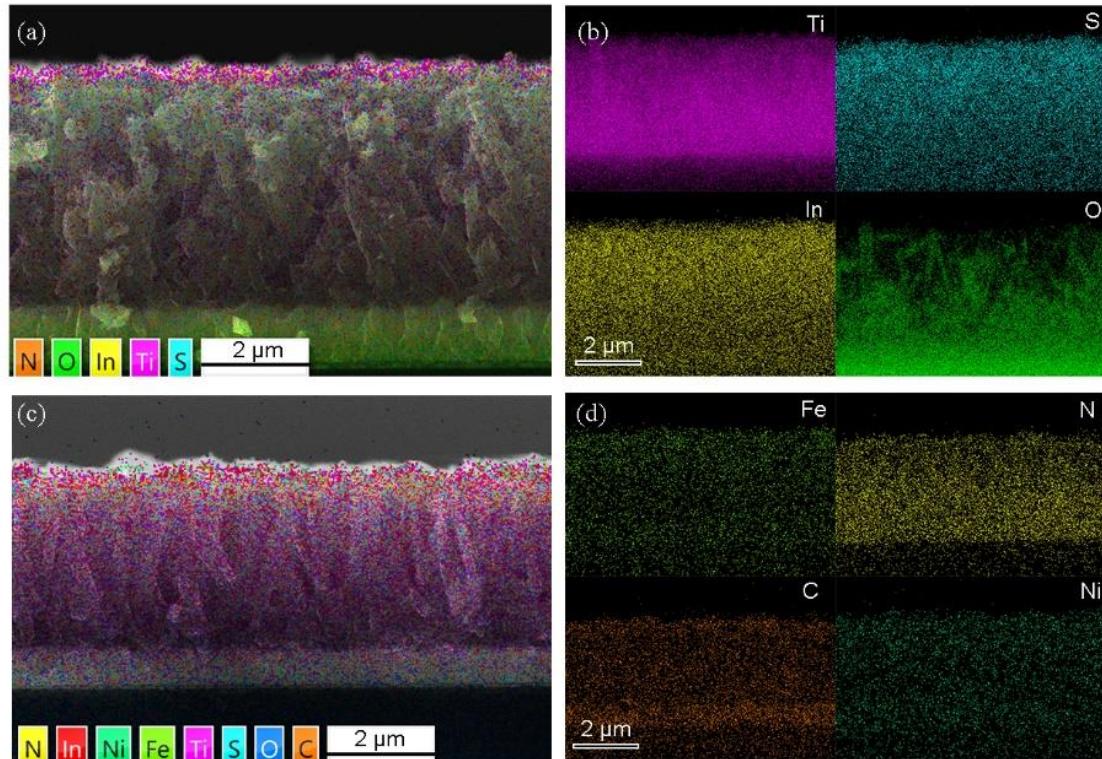
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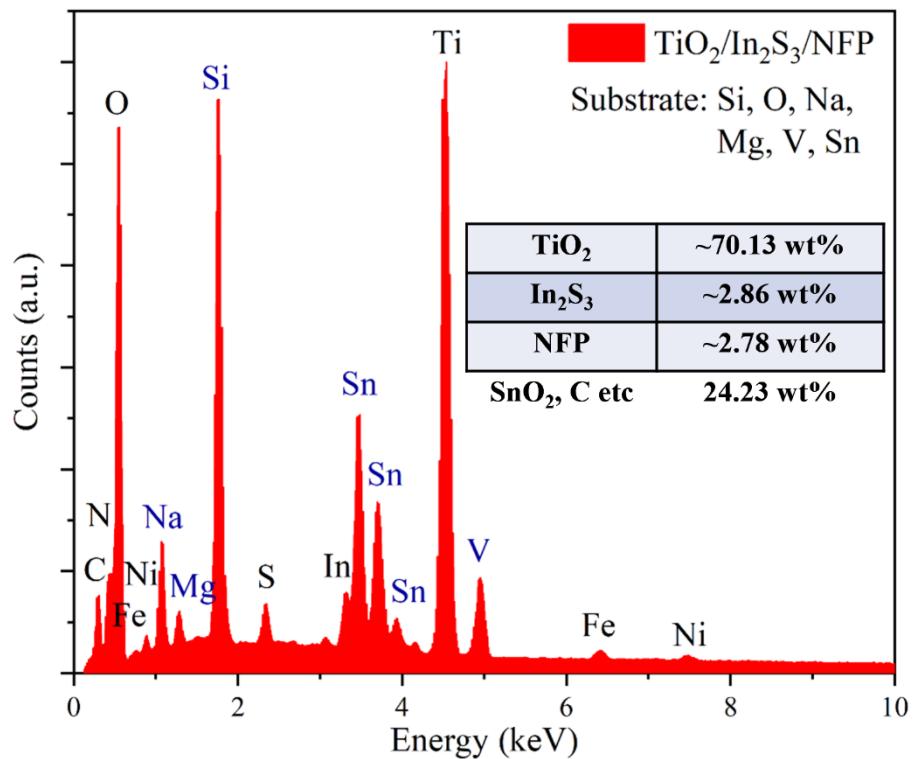
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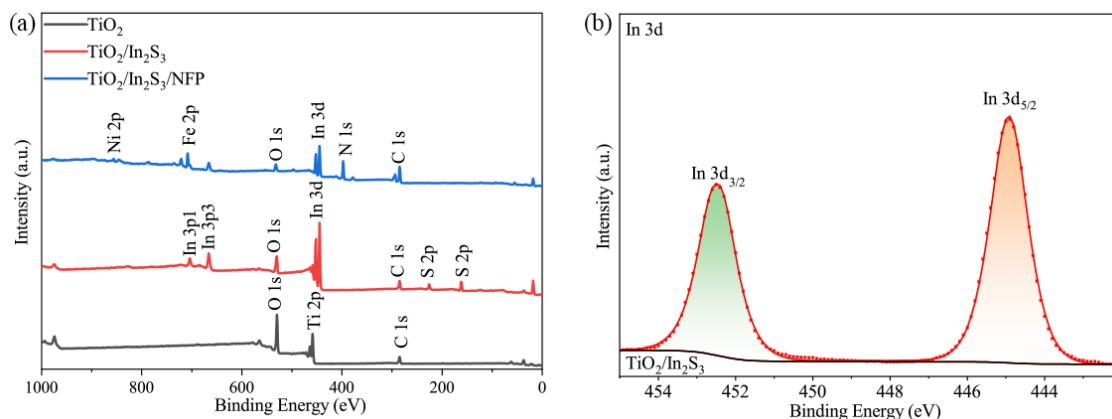
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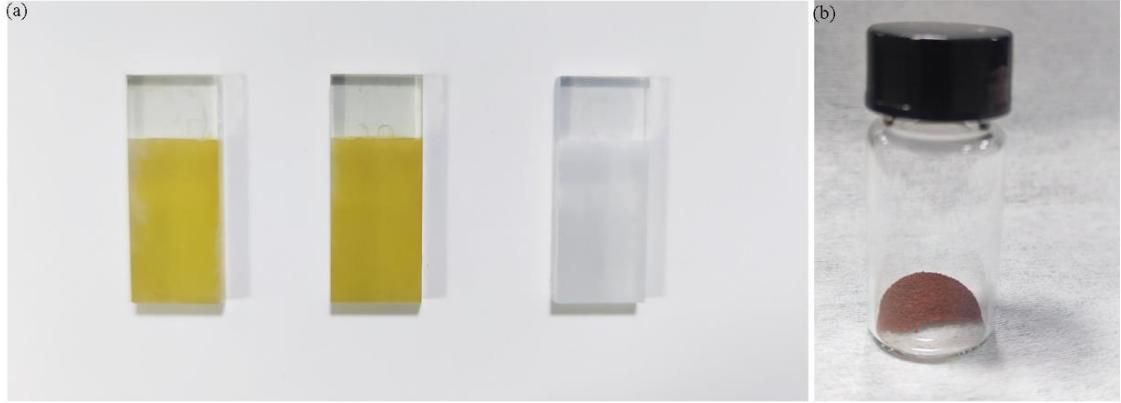
**Figure S1.** EDS images of  $\text{TiO}_2/\text{In}_2\text{S}_3$  (a, b) and  $\text{TiO}_2/\text{In}_2\text{S}_3/\text{NFP}$  (c, d).



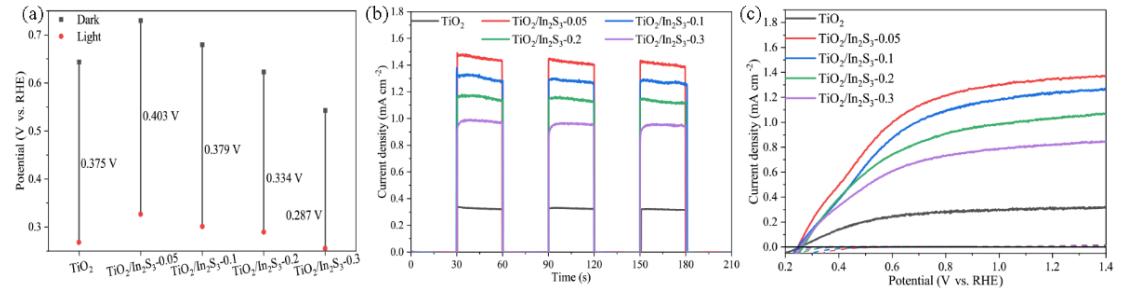
**Figure S2.** EDS pattern of  $\text{TiO}_2/\text{In}_2\text{S}_3/\text{NFP}$  photoanode.



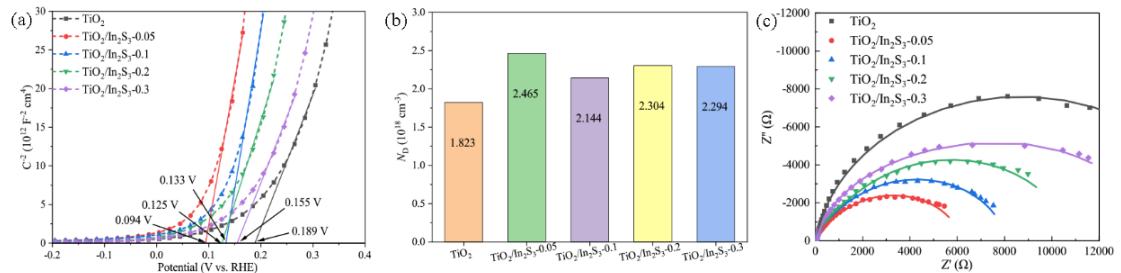
**Figure S3.** (a) XPS survey spectra of  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{In}_2\text{S}_3$ , and  $\text{TiO}_2/\text{In}_2\text{S}_3/\text{NFP}$ . (b) XPS spectra of In 3d of  $\text{TiO}_2/\text{In}_2\text{S}_3$  photoanode.



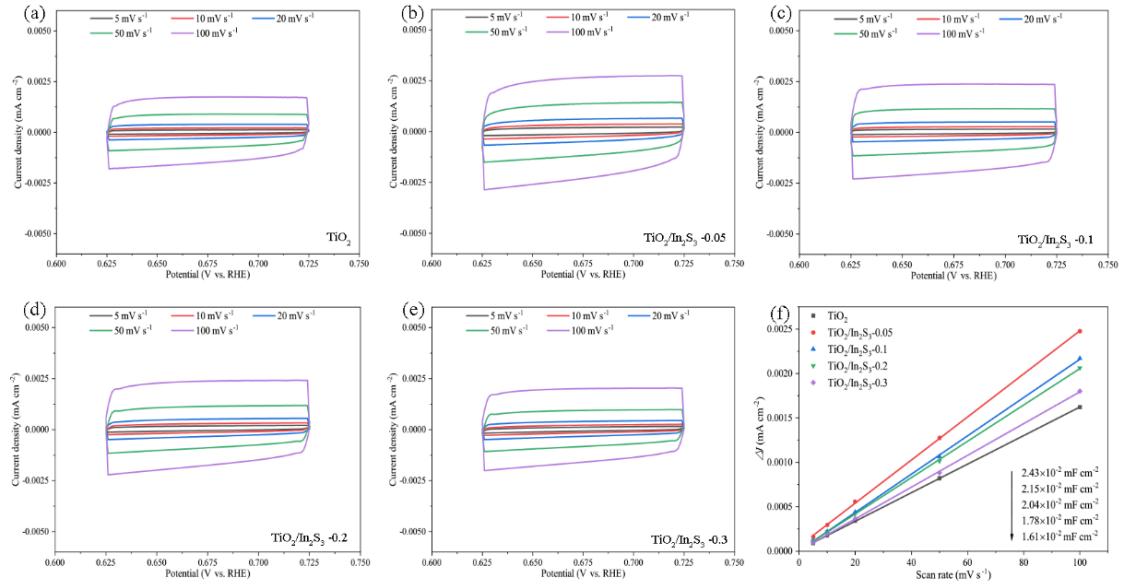
**Figure S4.** (a) Optical images of TiO<sub>2</sub> (right), TiO<sub>2</sub>/In<sub>2</sub>S<sub>3</sub> (left), and TiO<sub>2</sub>/In<sub>2</sub>S<sub>3</sub>/NFP (middle) photoanodes. (b) Optical image of as-prepared In<sub>2</sub>S<sub>3</sub> powder.



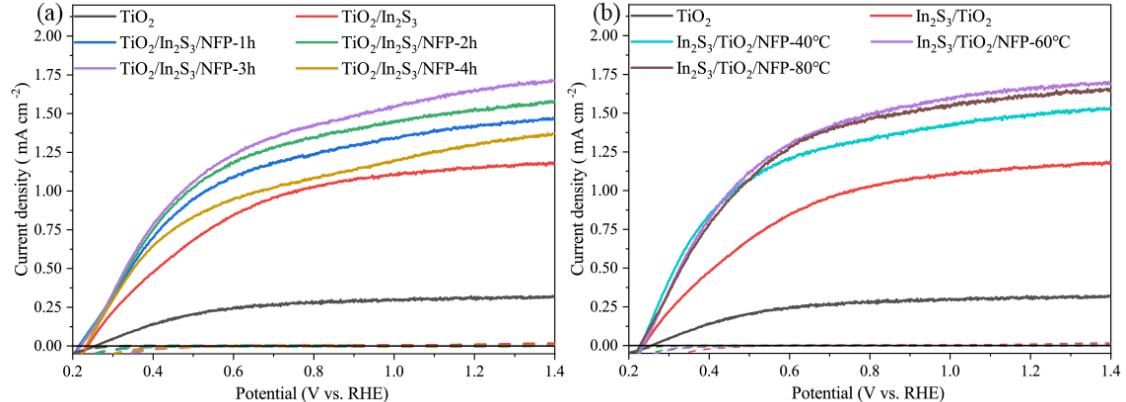
**Figure S5.** Photovoltage (a), it (b), LSV (c) curves of TiO<sub>2</sub>/In<sub>2</sub>S<sub>3</sub> with different precursor concentrations.



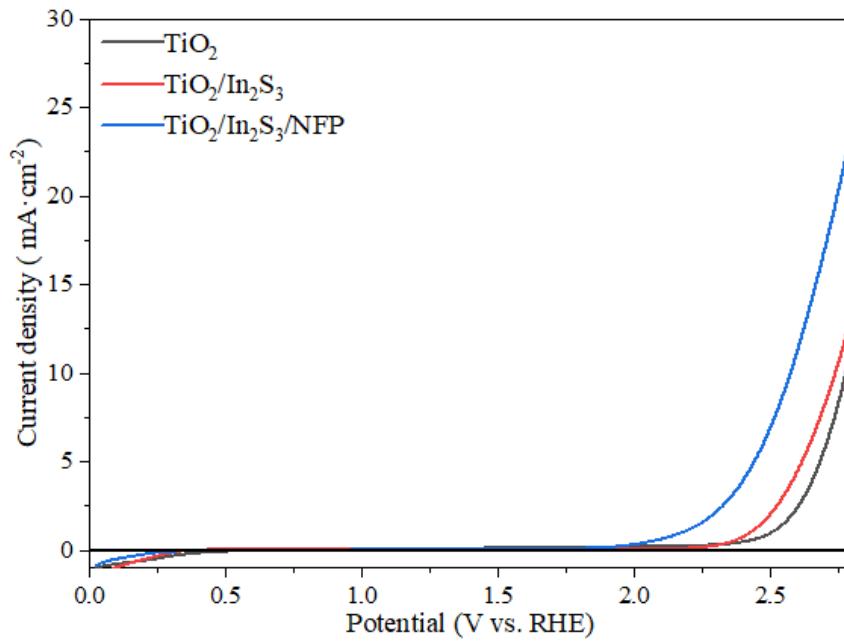
**Figure S6.** (a) M-S plots of TiO<sub>2</sub> and TiO<sub>2</sub>/In<sub>2</sub>S<sub>3</sub> photoanodes measured at 2000 Hz in the dark. (b) Histogram of the corresponding carrier concentration. (c) Nyquist plots of TiO<sub>2</sub>-based photoanodes measured at 0.47 V vs. RHE under AM1.5G illumination.



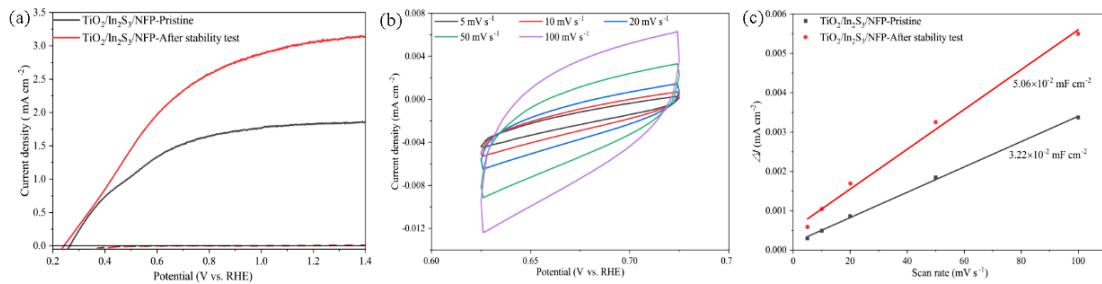
**Figure S7.** CV curves of  $\text{TiO}_2$  (a) and  $\text{TiO}_2/\text{In}_2\text{S}_3$  (b-e) prepared with different precursor concentrations in 1 M KOH at a scan rate of 5-100 mV s<sup>-1</sup>. (f) Determination of capacitance ( $C_{dl}$ ) values through  $\Delta J$  vs. scan rate plots for  $\text{TiO}_2$ -based photoanodes.



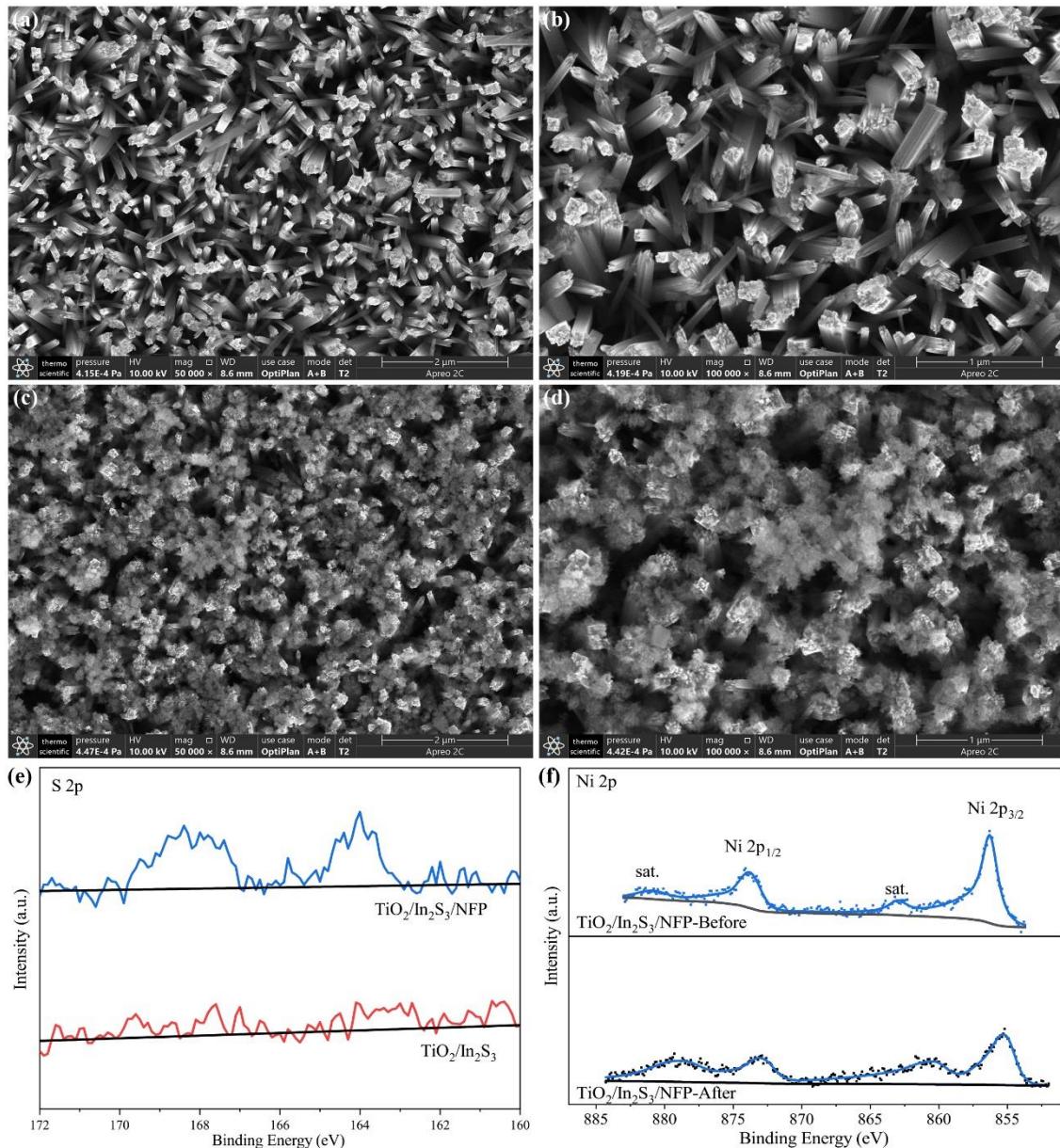
**Figure S8.** LSV curves of  $\text{TiO}_2/\text{In}_2\text{S}_3/\text{NFP}$  at different reaction times (a) and various reaction temperatures (b).



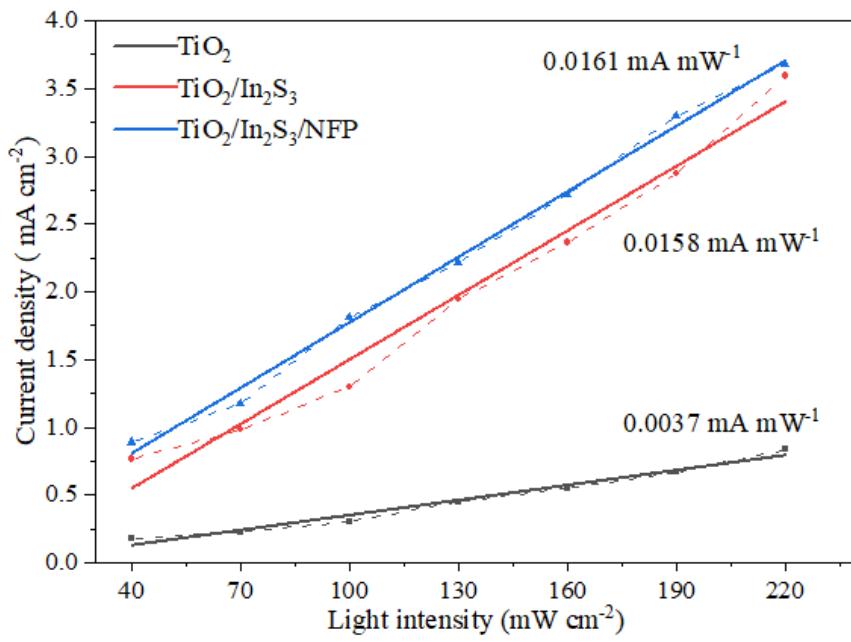
**Figure S9.** Dark LSV curves of  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{In}_2\text{S}_3$ , and  $\text{TiO}_2/\text{In}_2\text{S}_3/\text{NFP}$  electrodes measured at a scan rate of  $20 \text{ mV s}^{-1}$ .



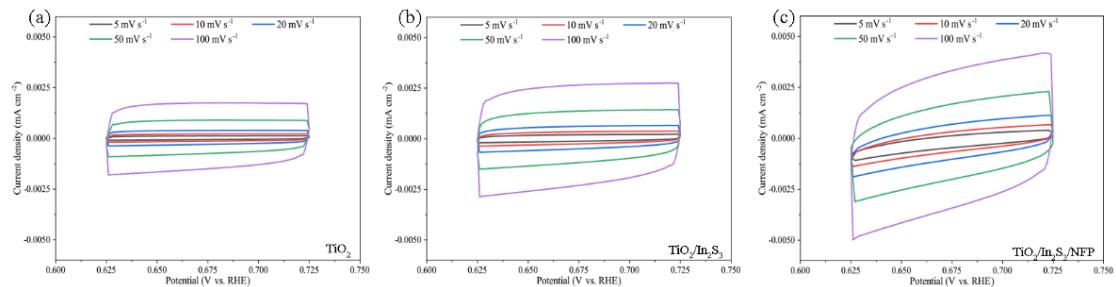
**Figure S10.** LSV (a) and CV (b) curves of  $\text{TiO}_2/\text{In}_2\text{S}_3/\text{NFP}$  photoanode before and after stability testing. (c) Determination of capacitance ( $C_{\text{dl}}$ ) values through  $\Delta J$  vs. scan rate plots for  $\text{TiO}_2/\text{In}_2\text{S}_3/\text{NFP}$  photoanode before and after stability testing.



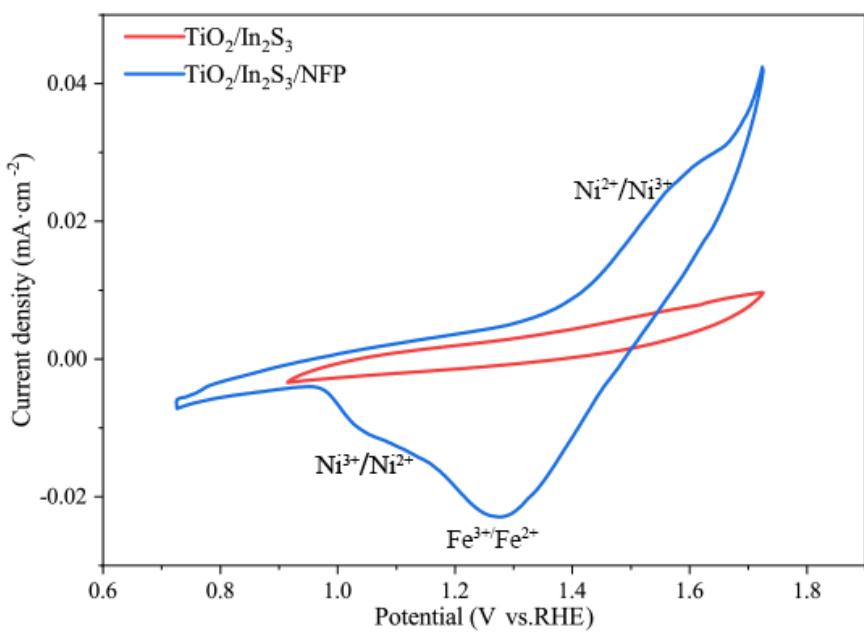
**Figure S11.** (a, b) SEM images of TiO<sub>2</sub>/In<sub>2</sub>S<sub>3</sub> photoanode after the stability test. (c, d) SEM images of TiO<sub>2</sub>/In<sub>2</sub>S<sub>3</sub>/NFP photoanode after the stability test. (e) S 2p XPS spectra of the tested TiO<sub>2</sub>/In<sub>2</sub>S<sub>3</sub> and TiO<sub>2</sub>/In<sub>2</sub>S<sub>3</sub>/NFP photoanodes. (f) Ni 2p XPS spectra of the as-prepared and tested TiO<sub>2</sub>/In<sub>2</sub>S<sub>3</sub>/NFP photoanodes.



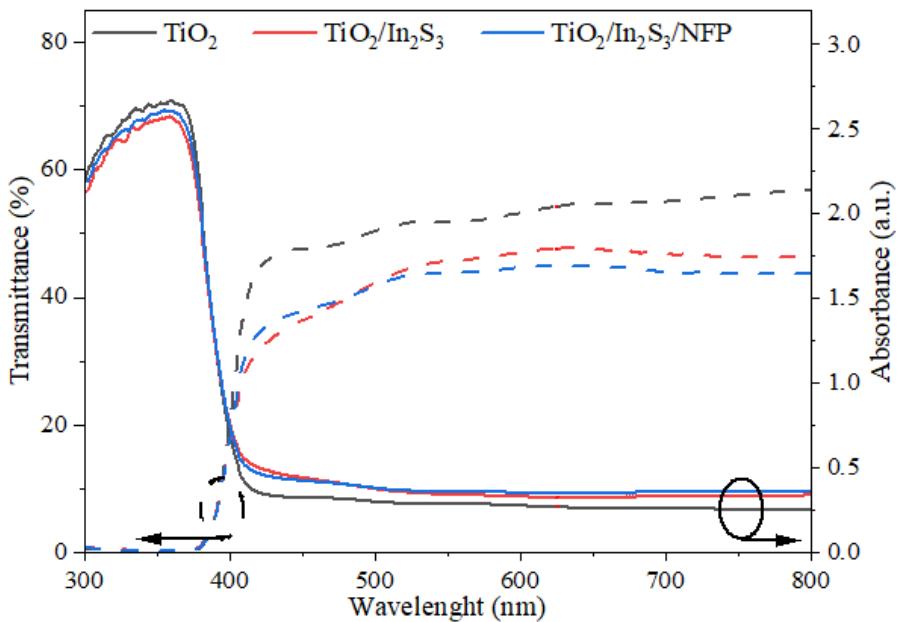
**Figure S12.** Relationship of photocurrent density vs. light intensity of  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{In}_2\text{S}_3$ , and  $\text{TiO}_2/\text{In}_2\text{S}_3/\text{NFP}$  photoanodes.



**Figure S13.** CV curves of  $\text{TiO}_2$  (a),  $\text{TiO}_2/\text{In}_2\text{S}_3$  (b), and  $\text{TiO}_2/\text{In}_2\text{S}_3/\text{NFP}$  (c) in 1 M KOH at a scan rate of 5-100  $\text{mV s}^{-1}$ .



**Figure S14.** CV curves of  $\text{TiO}_2/\text{In}_2\text{S}_3$  and  $\text{TiO}_2/\text{In}_2\text{S}_3/\text{NFP}$  electrodes measured at a scan rate of  $20 \text{ mV s}^{-1}$  and in the dark.



**Figure S15.** Transmission spectra and UV-vis absorption spectra of  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{In}_2\text{S}_3$ , and  $\text{TiO}_2/\text{In}_2\text{S}_3/\text{NFP}$  photoanodes.

The bandgap ( $E_g$ ) and the theoretical photocurrent density ( $J_{abs}$ ) of TiO<sub>2</sub>-based films are obtained by:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (\text{S1})$$

$$J_{abs} = \frac{1}{E_g} \int_{\lambda_2}^{\lambda_1} A_\lambda \Phi_\lambda d\lambda \quad (\text{S2})$$

where  $\alpha$  denotes the absorbance index,  $h$  represents the Planck constant,  $v$  signifies the frequency of light,  $A$  stands for a material-specific constant,  $E_g$  represents the band gap of the semiconductor,  $A_\lambda$  characterizes the absorption rate of the semiconductor photocathode, and  $\Phi_\lambda$  delineates the photon flux within the AM1.5G spectrum.

**Table S1.** Comparison of the performance of this work with the reported related photoanodes.

Photoanode	Electrolyte (AM 1.5G)	$J$ (mA cm <sup>-2</sup> ) (1.23 V vs. RHE)	Stability	Ref.
S,N-TiO <sub>2</sub> /In <sub>2</sub> S <sub>3</sub>	1 M NaOH	2.74 mA cm <sup>-2</sup> , 3.5 times	20 h, 80%	[1]
FTO/TiO <sub>2</sub> /In <sub>2</sub> S <sub>3</sub>	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	1.74 mA cm <sup>-2</sup> (0 V vs. Ag/AgCl)	6 h, 86.4%	[2]
TiO <sub>2</sub> /In <sub>2</sub> S <sub>3</sub>	1 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	1.1 mA cm <sup>-2</sup>	N/A	[3]
GO/In <sub>2</sub> S <sub>3</sub> /TiO <sub>2</sub>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	0.2 mA cm <sup>-2</sup> , 20 times (0 V vs. Ag/AgCl)	1000 s, ~76%	[4]
V-TiO <sub>2</sub> @β-In <sub>2</sub> S <sub>3</sub>	0.25 M Na <sub>2</sub> S + 0.35 M Na <sub>2</sub> SO <sub>3</sub>	1.42 mA cm <sup>-2</sup> , 3 times (0.5 V vs. Ag/AgCl)	2000 s	[5]
Fe <sub>2</sub> O <sub>3</sub> /Fe <sub>2</sub> TiO <sub>5</sub> /CoFe-PBA	0.1 M NaNO <sub>3</sub> + 0.1 M HNO <sub>3</sub>	1.25 mA cm <sup>-2</sup>	24 h, 80%	[6]
ZnO/BiVO <sub>4</sub> /NiFePB	0.5 M Na <sub>2</sub> SO <sub>4</sub>	1.66 mA cm <sup>-2</sup>	N/A	[7]
TiO <sub>2</sub> @FeFe-PB	0.1 M Na <sub>2</sub> SO <sub>4</sub>	1.5 mA cm <sup>-2</sup> , 2 times	2400 s, 80%	[8]
CoFe-PBA/PiH	1 M NaOH	1.24 mA cm <sup>-2</sup>	N/A	[9]
α/γ-Fe <sub>2</sub> O <sub>3</sub> /FCP	1 M KOH	3.5 mA cm <sup>-2</sup> , 7.8 times	2h, 94%	[10]
TiO <sub>2</sub> /[CoFe-JG]	0.1 M PBS, pH=7	551 μA cm <sup>-2</sup>	2 h, 80%	[11]
CoFe(OH) <sub>x</sub> @Sb-TiO <sub>2</sub>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	1.48 mA cm <sup>-2</sup>	N/A	[12]
TiO <sub>2</sub> /In <sub>2</sub> S <sub>3</sub> /NFP	1 M KOH	1.81 mA cm <sup>-2</sup> , 6 times	12 h, 95.17%	This work

## REFERENCES

1. Park J, Lee TH, Kim C et al. Hydrothermally obtained type-II heterojunction nanostructures of  $\text{In}_2\text{S}_3/\text{TiO}_2$  for remarkably enhanced photoelectrochemical water splitting. *Appl Catal B Environ.* 2021;295:120276. [DOI: 10.1016/j.apcatb.2021.120276]
2. Hsieh PY, Chiu YH, Lai TH et al.  $\text{TiO}_2$  Nanowire-Supported Sulfide Hybrid Photocatalysts for Durable Solar Hydrogen Production. *ACS Appl Mater Interfaces.* 2019;11:3006-3015. [DOI: 10.1021/acsami.8b17858]
3. Wang X, Li H, Zhang J, Liu X, Zhang X. Wedged  $\beta\text{-In}_2\text{S}_3$  sensitized  $\text{TiO}_2$  films for enhanced photoelectrochemical hydrogen generation. *J Alloys Compd.* 2020;831:154798. [DOI: 10.1016/j.jallcom.2020.154798]
4. Braiek Z, Ben Naceur J, Jrad F, Ben Assaker I, Chtourou R. Novel synthesis of graphene oxide/ $\text{In}_2\text{S}_3/\text{TiO}_2$  NRs heterojunction photoanode for enhanced photoelectrochemical (PEC) performance. *Int J Hydron Energy.* 2022;47:3655-3666. [DOI: 10.1016/j.ijhydene.2021.10.268]
5. Mumtaz A, Mohamed NM, Mazhar M, Ehsan MA, Mohamed Saheed MS. Core–Shell Vanadium Modified Titania@ $\beta\text{-In}_2\text{S}_3$  Hybrid Nanorod Arrays for Superior Interface Stability and Photochemical Activity. *ACS Appl Mater Interfaces.* 2016;8:9037-9049. [DOI: 10.1021/acsami.5b10147]
6. Tang P, Han L, Hegner FS et al. Boosting Photoelectrochemical Water Oxidation of Hematite in Acidic Electrolytes by Surface State Modification. *Adv Energy Mater.* 2019;9:1901836. [DOI: 10.1002/aenm.201901836]
7. Bai S, Jia S, Zhao Y et al. NiFePB-modified  $\text{ZnO}/\text{BiVO}_4$  photoanode for PEC water oxidation. *Dalton Trans.* 2023;52:5760-5770. [DOI: 10.1039/d3dt00013c]
8. Mao G, Li C, Li Z et al. Efficient charge migration in  $\text{TiO}_2@\text{PB}$  nanorod arrays with core–shell structure for photoelectrochemical water splitting. *CrystEngComm.* 2022;24:2567-2574. [DOI: 10.1039/d1ce01710a]
9. Khan AZ, Kandiel TarekA, Abdel-Azeim S, Jahangir TN, Alhooshani K. Phosphate ions interfacial drift layer to improve the performance of CoFe–Prussian blue hematite photoanode toward water splitting. *Appl Catal B Environ.* 2022;304:121014. [DOI: 10.1016/j.apcatb.2021.121014]
10. Li Y, Chen Y, Wu Q et al. Revealing long-lived electron–hole migration in core–shell  $\alpha/\gamma\text{-Fe}_2\text{O}_3/\text{FCP}$  for efficient photoelectrochemical water oxidation. *Catal Sci Technol.*

2022;12:250-258. [DOI: 10.1039/D1CY01628H]

11. Ulusoy Ghobadi TG, Ghobadi A, Buyuktemiz M et al. A Robust, Precious-Metal-Free Dye-Sensitized Photoanode for Water Oxidation: A Nanosecond-Long Excited-State Lifetime through a Prussian Blue Analogue. *Angew Chem Int Ed*. 2020;59:4082-4090. [DOI: 10.1002/anie.201914743]
12. Pal D, Maity D, Sarkar A et al. Multifunctional Ultrathin Amorphous CoFe-Prussian Blue Analogue Catalysts for Efficiently Boosting the Oxygen Evolution Activity of Antimony-Doped TiO<sub>2</sub> Nanorods Photoanode. *ACS Appl Energy Mater*. 2022;5:15000-15009. [DOI: 10.1021/acsaem.2c02608]