

Supplemental Information

Visible-light responsive S-vacancy ZnIn₂S₄/N-doped TiO₂ Nanoarrays Heterojunction for high-performance photoelectrochemical water splitting

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Figure S1 The XRD patterns of N-TZ-0.1.

Figure S2 SEM images of (a-b)TiO₂, (c-d)N-TiO₂ and (e-f) Sv-ZIS

Figure S3 SEM images of (a-b) N-TZ-0.01, (c-d)N-TZ-0.05 and (e-f)N-TZ-0.1

Figure S4 Photoelectrochemical water splitting video of heterostructure photocatalyst

Figure S5 Photocatalytic H₂/O₂ evolution performance of N-TZ-0.025

Figure S6 LSV curves of all samples under light (a) and dark (b) conditions, (c) photocurrent response, (d) electrochemical impedance spectroscopy (EIS) of all samples

Figure S7 UV-vis absorption spectra of Sv-ZIS

Figure S8 Measured IPCE in the visible-light range

Table S1 The representative research results of TiO₂-based heterojunction and homojunction

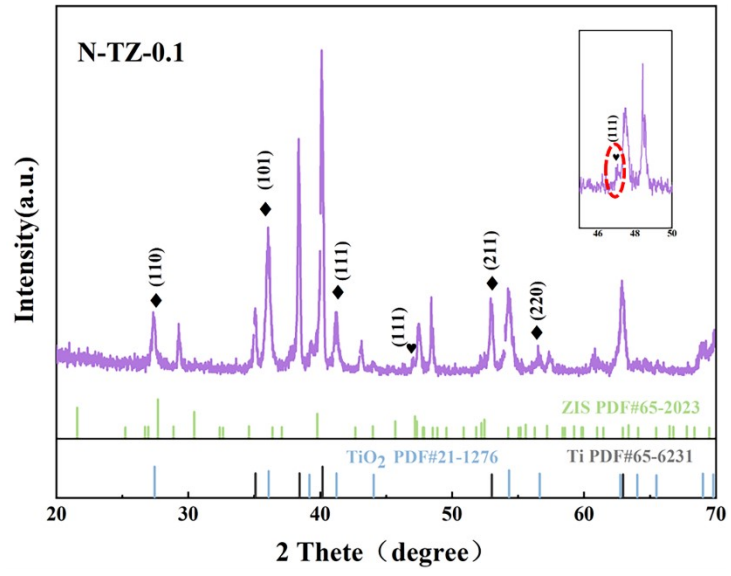


Figure S1. The XRD pattern of N-TZ-0.1.

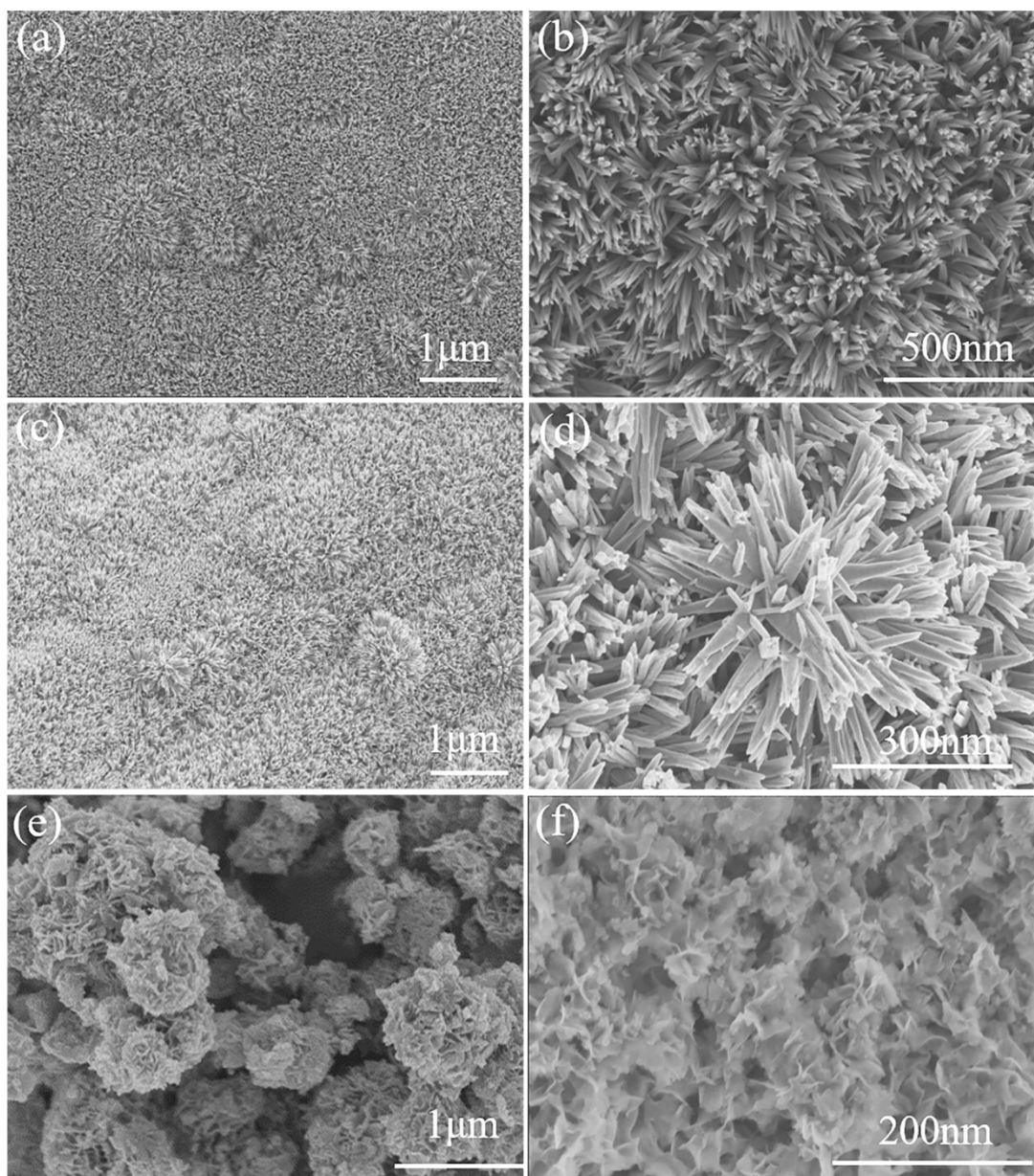


Figure S2 SEM images of (a-b) TiO_2 , (c-d)N- TiO_2 and (e-f) $\text{S}_v\text{-ZIS}$

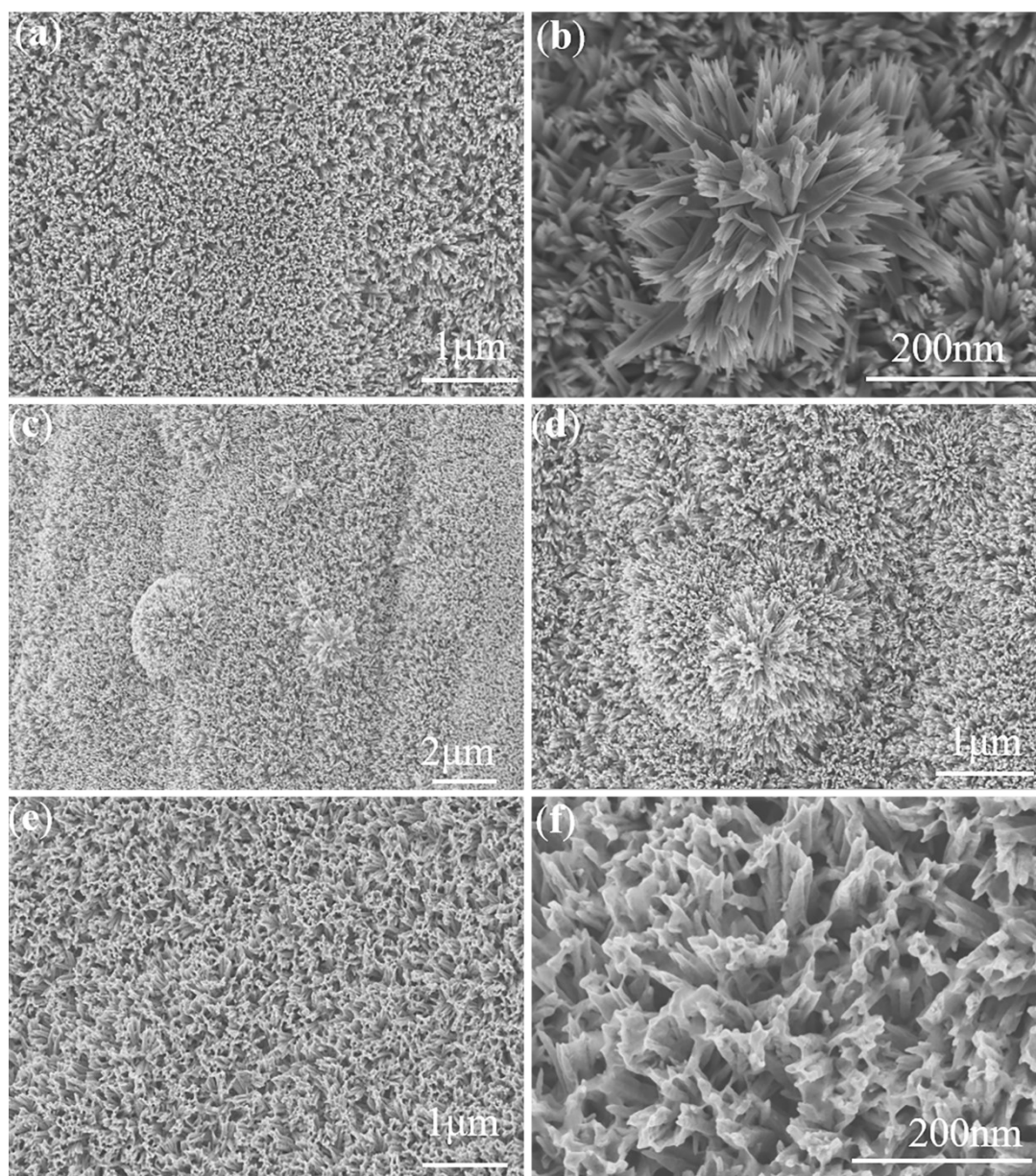


Figure S3 SEM images of (a-b) N-TZ-0.01, (c-d)N-TZ-0.05 and (e-f)N-TZ-0.1



Figure S4 Photoelectrochemical water splitting video of heterostructure photocatalyst

In this video, you can see that a large number of bubbles produced by both the photocathode and the photoirradiated photoanode, especially the number of hydrogen bubbles produced by the photocathode is higher than oxygen bubbles produced by the photoanode.

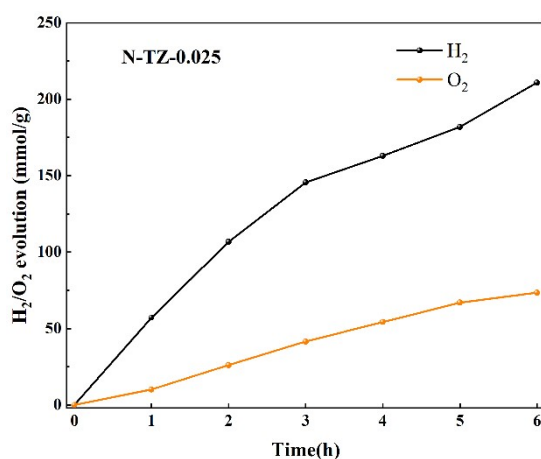


Figure S5. Photocatalytic H₂/O₂ evolution performance of N-TZ-0.025

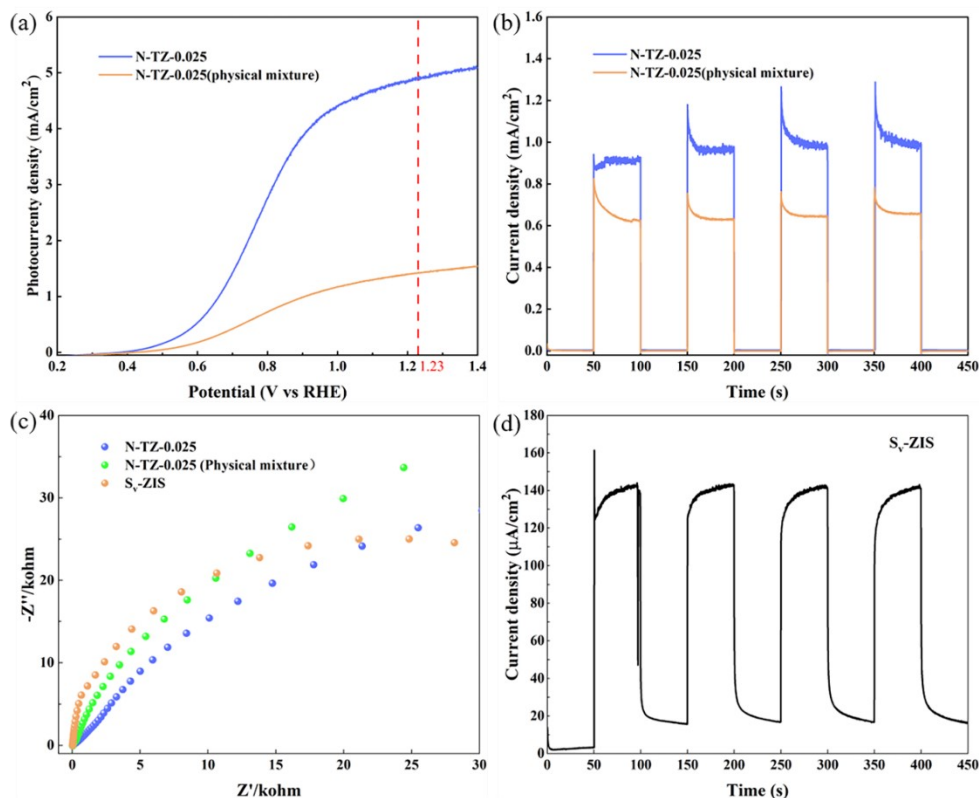


Figure S6. LSV curves (a) and photocurrent responses (b) of physically mixed N-TZ-0.025 and N-TZ-0.025 (a); (d) electrochemical impedance spectroscopy (EIS) of prepared samples; (d) photocurrent responses of pure Sv-ZIS.

As shown in Figure S6a and S6b, the photocurrent density of physically mixed N-TZ-0.025 reached 1.2 mA/cm^2 at the potential of 1.23 V vs. RHE , which is much smaller than N-TZ-0.025. In Figure S6b, it is obvious to find that the physically mixed N-TZ-0.025 sample has a weaker photocurrent response than the N-TZ-0.025. In Figure S6c, the N-TZ-0.025 has a smaller arc radius, which indicates that the separation efficiency of electron-hole pairs is higher in the N-TZ-0.025 sample as the interface charge transfer is faster. Figure S6c implies the electrochemical measurements of pure Sv-ZIS, it can be seen the separation efficiency of electron-hole pairs is low and the interface charge transfer resistance is high. When coupled with the TiO_2 nanocone, the i-t activity and electrochemical properties of Sv-ZIS have noticeable improvements. Figure S6d shows the i-t activity of pure Sv-ZIS and the photocurrent density was $\sim 140 \text{ } \mu\text{A/cm}^2$ under the same conditions as its counterpart samples, indicating the carrier recombination is severe.

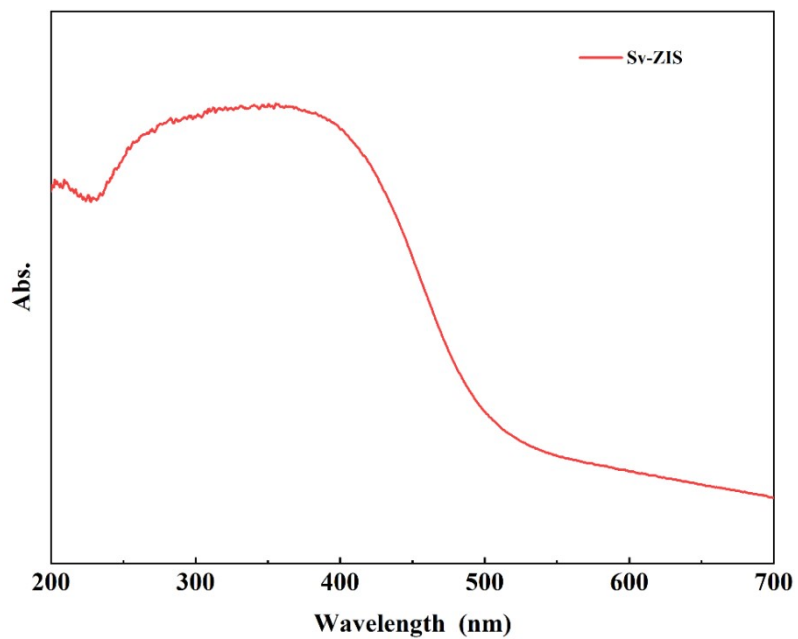


Figure S7 UV-vis absorption spectra of Sv-ZIS

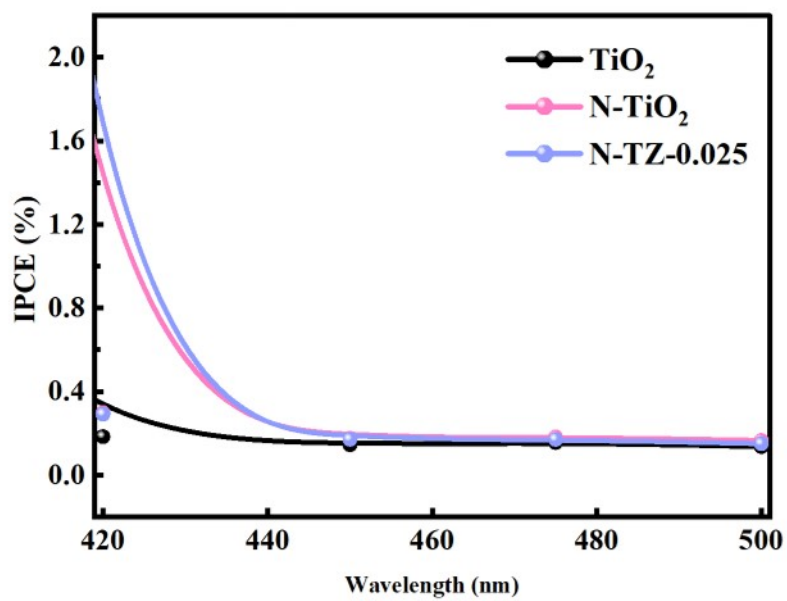


Figure S8 Measured IPCE in the visible-light range

Photoanode	electrolyte	Photocurrent density (at 1.23 V vs. RHE)	IPCE	Ref.
ZnIn ₂ S ₄ /TiO ₂	0.35M Na ₂ SO ₃ and 0.24M Na ₂ S	1.2 mA/cm ⁻²	21% at 380 nm	[1]
TiO ₂ /N-CDs	1.0 M NaOH	3.09 mA/cm ⁻²	65% at 390 nm	[2]
TiO ₂ -V _{Ti} /Fe ₂ O ₃	1.0 M KOH	1.45 mA/cm ⁻²	29.8% at 340 nm	[3]
TiO ₂ @Au ₂₅ /TiO ₂	0.5M Na ₂ SO ₄	1.35 mA/cm ⁻²	45.2% at 318 nm	[4]
Au/N-TiO ₂	1.0 M KOH	2.8 mA/cm ⁻²	60.7% at 300 nm	[5]
Y ₂ O ₃ /TiO ₂	1.0 M KOH	0.609 mA/cm ⁻²	22% at 350 nm	[6]
PCN/Cu-TiO ₂	0.2M Na ₂ SO ₄	1.89 mA/cm ⁻²	31.2% at 415 nm	[7]
TiO ₂ /BiVO ₄	0.2M Na ₂ SO ₄	2.36mA/cm ⁻²	38% at 350 nm	[8]
SrTiO ₃ /TiO ₂ /Au	1.0 M NaOH	2.11 mA/cm ⁻²	59% at 340 nm	[9]
CuInS ₂ /TiO ₂	0.5M Na ₂ SO ₄	1.11 mA/cm ⁻²	57.7% at 400 nm	[10]
Sv-ZnIn ₂ S ₄ /N-TiO ₂	0.5M Na ₂ SO ₄	4.9 mA/cm ⁻²	57.9% at 350 nm	This work

Table S1 The representative IPCE results of TiO₂-based photocatalysts.

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