Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

TiO_2 spatially confined growth of $Sb_2(S,Se)_3$@TiO_2 NTs heterojunction photoanodes and their photoelectrochemical properties

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1. Supplemental Figures

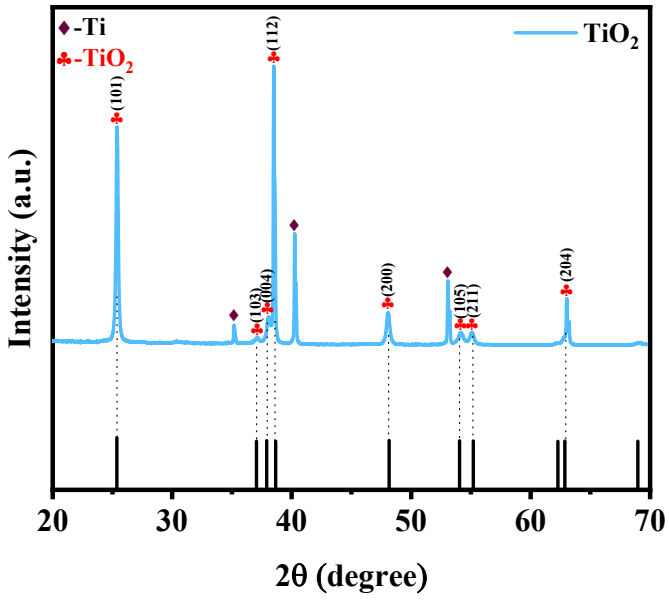


Fig. S1. The XRD diagram of monomeTiO_2.

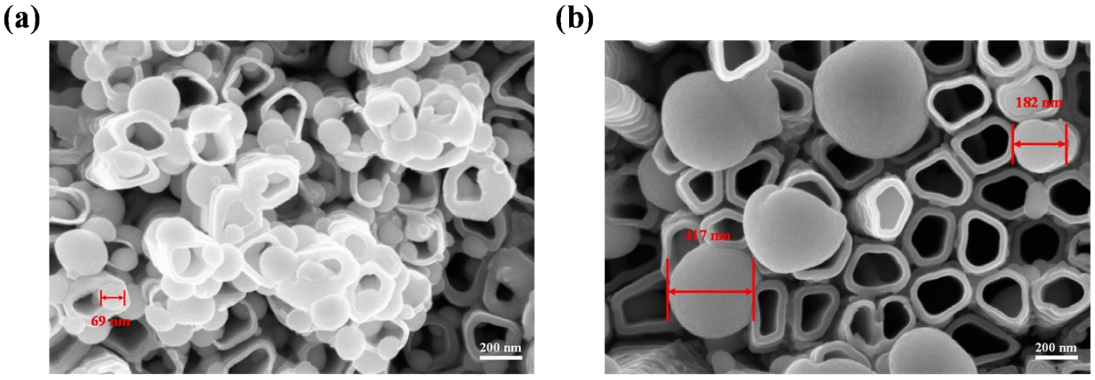
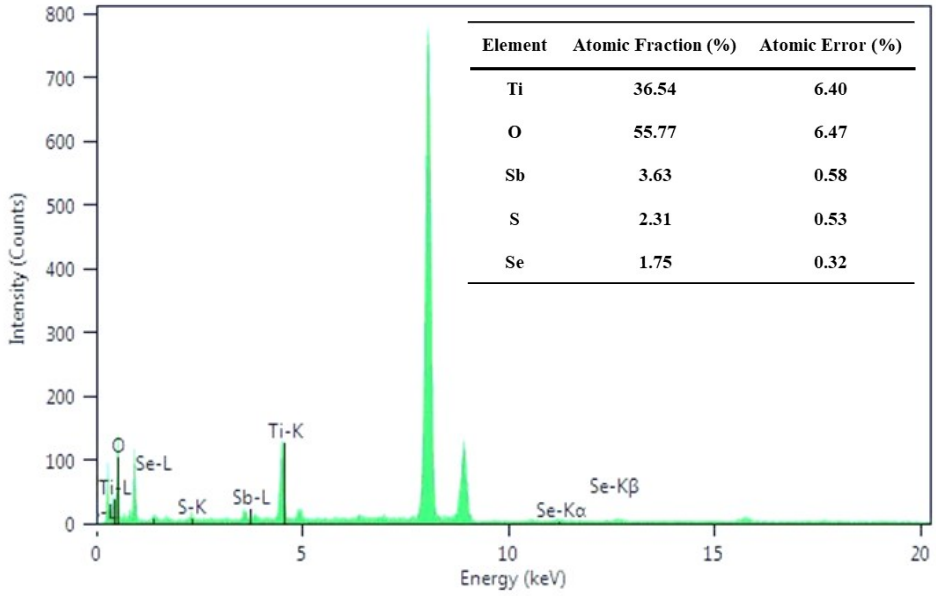


Fig. S2. (a) SEM image of $Sb_2(S,Se)_3@TiO_2$ at low concentrations of Se, (b) SEM image of $Sb_2(S,Se)_3@TiO_2$ at high concentrations of Se.



Element	Atomic Fraction (%)	Atomic Error (%)
Ti	36.54	6.40
O	55.77	6.47
Sb	3.63	0.58
S	2.31	0.53
Se	1.75	0.32

Fig. S3. EDS spectrum of $Sb_2(S,Se)_3@TiO_2$.

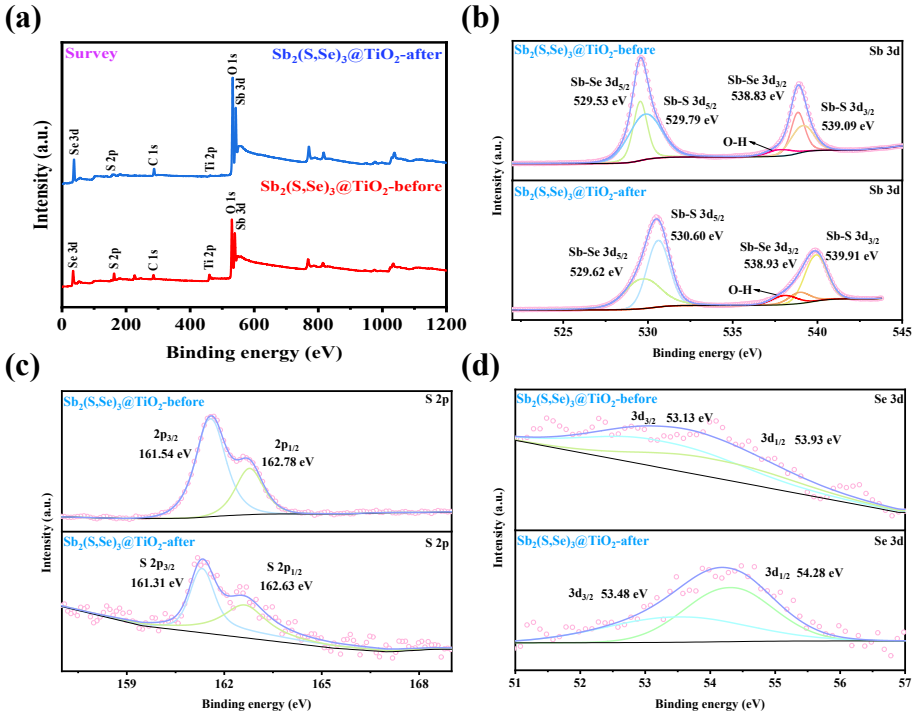


Fig. S4. (a) XPS survey spectrum, (b) Sb 3d, (c) S 2p and (d) Se 3d high-resolution XPS spectra for $Sb_2(S,Se)_3$@TiO_2 photoanodes before and after test.

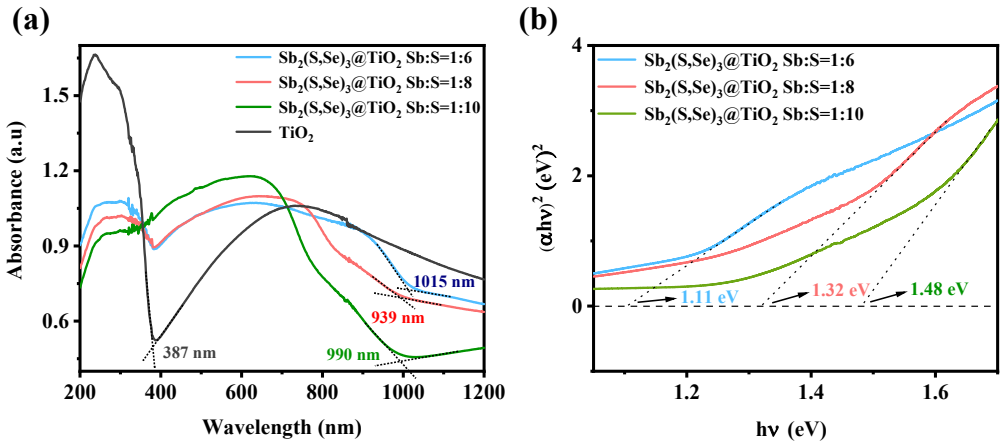


Fig. S5. (a) UV-vis-NIR spectra of $Sb_2(S,Se)_3$@TiO_2 at different S concentrations, (b) Semiconductor band gap of $Sb_2(S,Se)_3$@TiO_2 at different S concentrations.

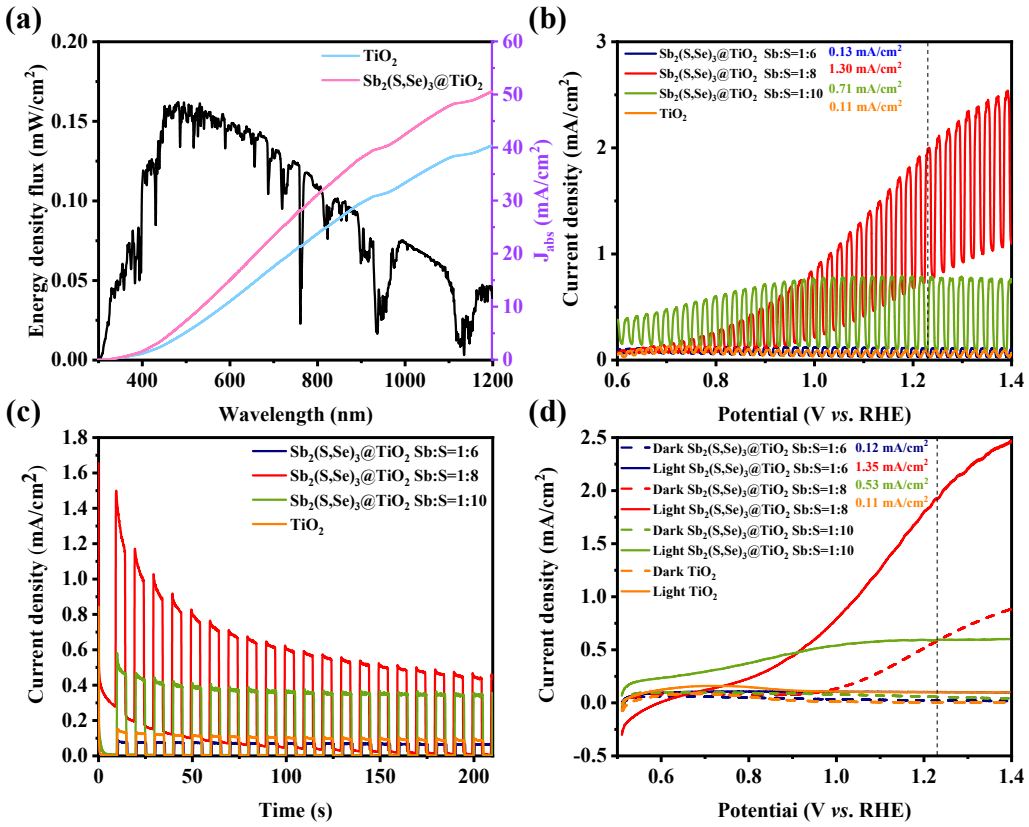


Fig. S6. (a) The current density fluxes and integrated current densities (J_{abs}) of monomers TiO_2 and $Sb_2(S,Se)_3$@TiO_2 heterojunctions were calculated, (b) J-V curves of TiO_2 NTs of the different samples, (c) J-t curves of TiO_2 NTs of the different samples, (d) LSV curves under full on or full off light.

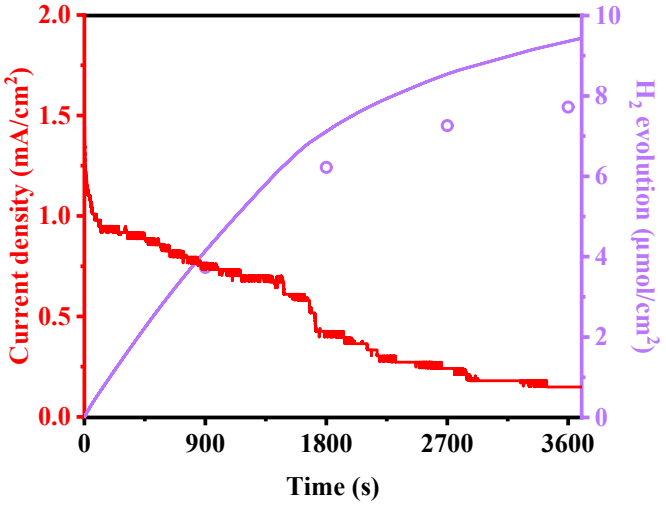


Fig. S7. H_2 evolution curve and the concurrent J-t curve of $Sb_2(S,Se)_3$@TiO_2 at 1.23 V *vs.* RHE in 0.5 M Na_2SO_4 under AM 1.5G illumination.

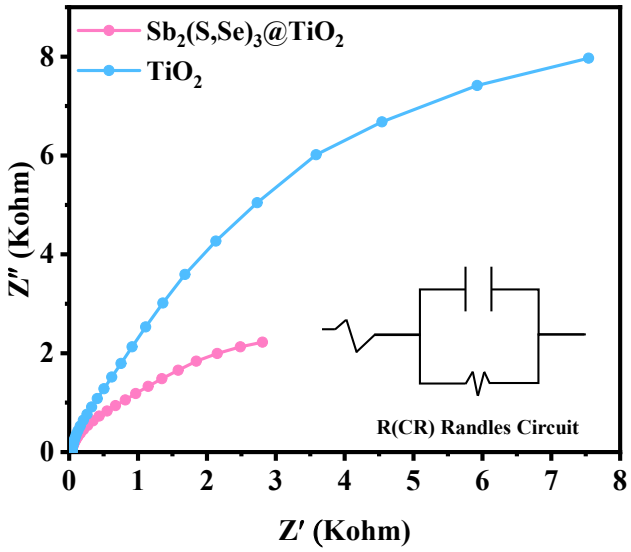


Fig. S8. Nyquist plots (EIS) under AM 1.5G illumination, the equivalent circuit model is shown in the illustration for data fitting.

2. The formula used in this work

The theoretical photocurrent density (J_{abs}) of the photocathode can be obtained by using the following equations:

$$\eta_{abs} = \left(1 - 10^{-A}\right) \times 100\% \#(S1)$$

$$I_{abs} = \frac{q}{hc}\int \lambda \phi_{\lambda} \eta_{abs} d\lambda \#(S2)$$

Here, J_{abs} is expressed as the theoretical photocurrent density, q is the charge of the electron, h is Planck's constant, c is the speed of light, ϕ_{λ} is the photon flux in the AM 1.5 G solar spectrum, and η_{abs} is the light absorption efficiency, A is photo absorbance.

Absorbed Photocurrent Efficiency

The IPCE values of TiO_2 and $Sb_2(S,Se)_3$@TiO_2 were calculated according to the following Eq. (S3):

$$IPCE = \frac{1240 J_{\lambda}}{P\lambda} \times 100\% \#(S3)$$

In the formula, J_{λ} was the photocurrent density (mA/cm^2) under monochromatic illumination at a certain wavelength, λ was the wavelength of the incident light (nm), and P was the optical power of monochromatic light with a certain wavelength (mW/cm^2), which could be measured by an optical power meter.

The APCE values of TiO_2 and $Sb_2(S,Se)_3$@TiO_2 were calculated according to the following Eq. (S4):

$$APCE = \frac{IPCE(\lambda)}{1 - 10^{-A(\lambda)}} \#(S4)$$

where A(λ) was the absorbance of material at different wavelengths.

Applied Bias Photocurrent Efficiency

The ABPE values of TiO_2 and $Sb_2(S,Se)_3$@TiO_2 were calculated according to the following Eq. (S5):

$$ABPE = \frac{J \times \left(1.23 - E_{app}\right)}{I_0} \#(S5)$$

where η was the conversion efficiency, J was the photocurrent density (mA/cm^2) obtained by using linear sweep voltammetry plots, E_{app} was the applied bias voltage (V), and I_0 was the incident

light irradiance (mW/cm^2).

Fill factor

The FF values of TiO_2 and $Sb_2(S,Se)_3$@TiO_2 were calculated according to the following E_q. (S6).

$$FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} \#(S6)$$

Faradaic efficiency

All hydrogen production experiments were performed in the solution of neutral 0.5 M Na_2SO_4 electrolyte under AM 1.5G illumination and collected by gas chromatograph. The area of the working electrode was 4 cm^{-2}. The faradaic efficiency of $Sb_2(S,Se)_3$@TiO_2 heterojunction could be calculated by the following formula:

$$\eta = \frac{zFn}{Q} \#(S7)$$

Here, z was the number of electrons transferred per mole of gas (4 for O_2 and 2 for H_2); F was the Faraday constant (F=96485 C/mol); n was Moles of H_2 produced (mol); Q was the total number of photogenerated charges passing through (C).