Supporting information

Experiment Section

Materials

Indium nitrate ($In(NO_3)_3$) was purchased from Macklin. Cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$) were supplied from Sinopharm Chemical Reagent Co., Ltd. (China).

Characterizations

X-ray powder diffraction (XRD) patterns were characterized using Bruker D8 Advanced X-ray diffractometer. The surface morphology and structure of the samples were recorded on transmission electron microscopy (Tecnai G2 F20 S-TWIN, FEI). UV-vis diffuse reflectance spectra (DRS) were obtained by UV-3600 spectrophotometer (Tokyo, Japan). The morphology and local atomic structure were determined using transmission electron microscopy (TEM, JEOL-2100F) and aberration-corrected high-angular annular dark field scanning transmission electron microscopy operated at 80 kV (HAADF-STEM, JEM-ARM200F). Ultrafast transient absorption (TA) spectra are collected over a femtosecond laser amplifier system (Pharos PH2 SP, Light Conversion). The curves show multi-exponential fitting that includes consideration of the instrument response function (~190 fs). X-ray photoelectron spectroscopy (XPS) was measured on PHIQUANTERA II. The TS-SPV signal was recorded by using a 500 MHz digital phosphor oscilloscope (TDS 5054, Tektronix). The effective surface areas of the as-prepared samples were measured by nitrogen adsorption-desorption isotherms on the Micrometrics ASAP 2020 system, employing a fitting analysis based on the Brunauer-Emmett-Teller (BET) equation.

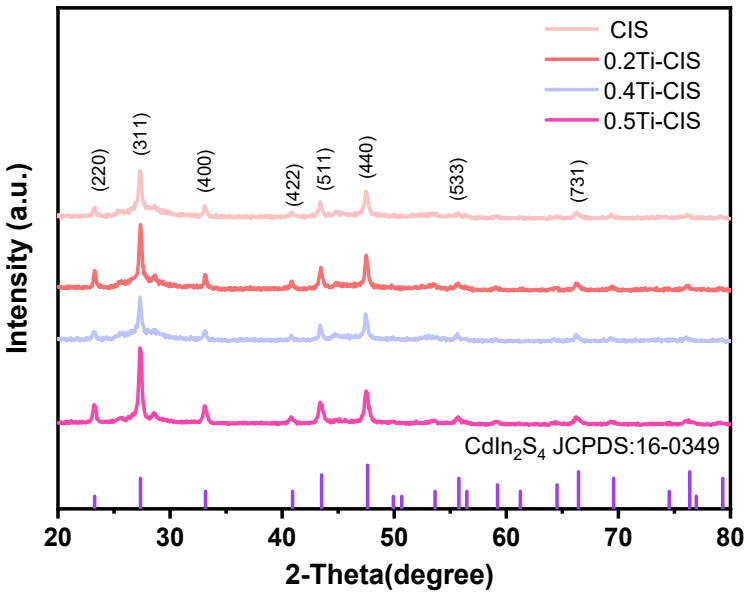

Figure S1. XRD of CIS and Ti-CIS.

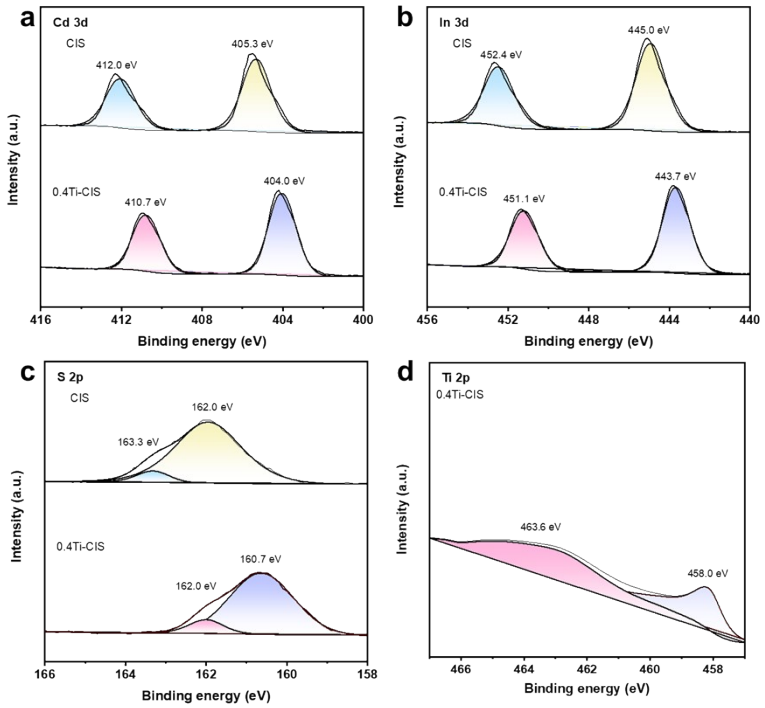

Figure S2. X-ray photoelectron spectra: (a) Cd 3d, (b) In 3d, (c) S 2p, (d) Ti 2p of CIS and 0.4Ti-CIS.

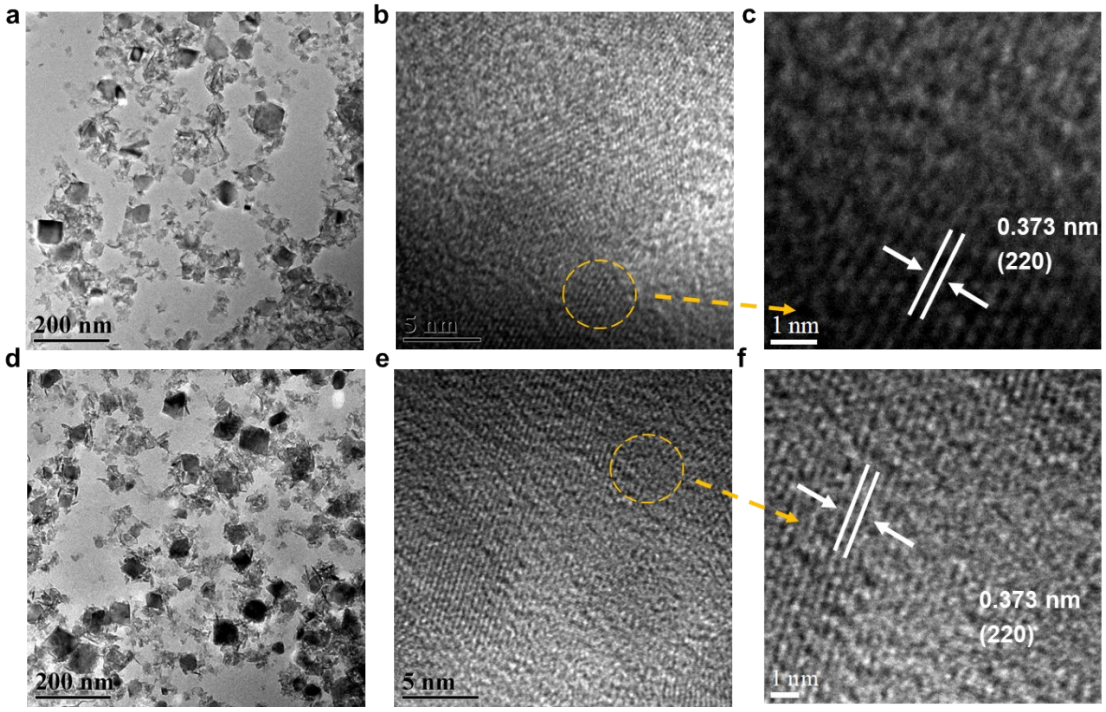

Figure S3. (a) TEM of CIS (b-c) HRTEM of CIS, (d) TEM of 0.4Ti-CIS (e-f) HRTEM of 0.4Ti-CIS.

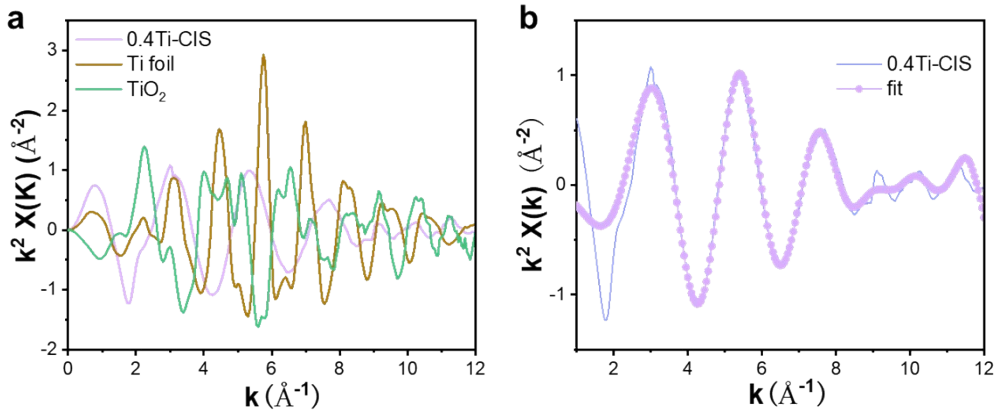

Figure S4. (a) EXAFS spectra in K space for 0.4Ti-CIS, Ti foil and TiO_2, (b) K-space fitting curve K-space fitting curve.

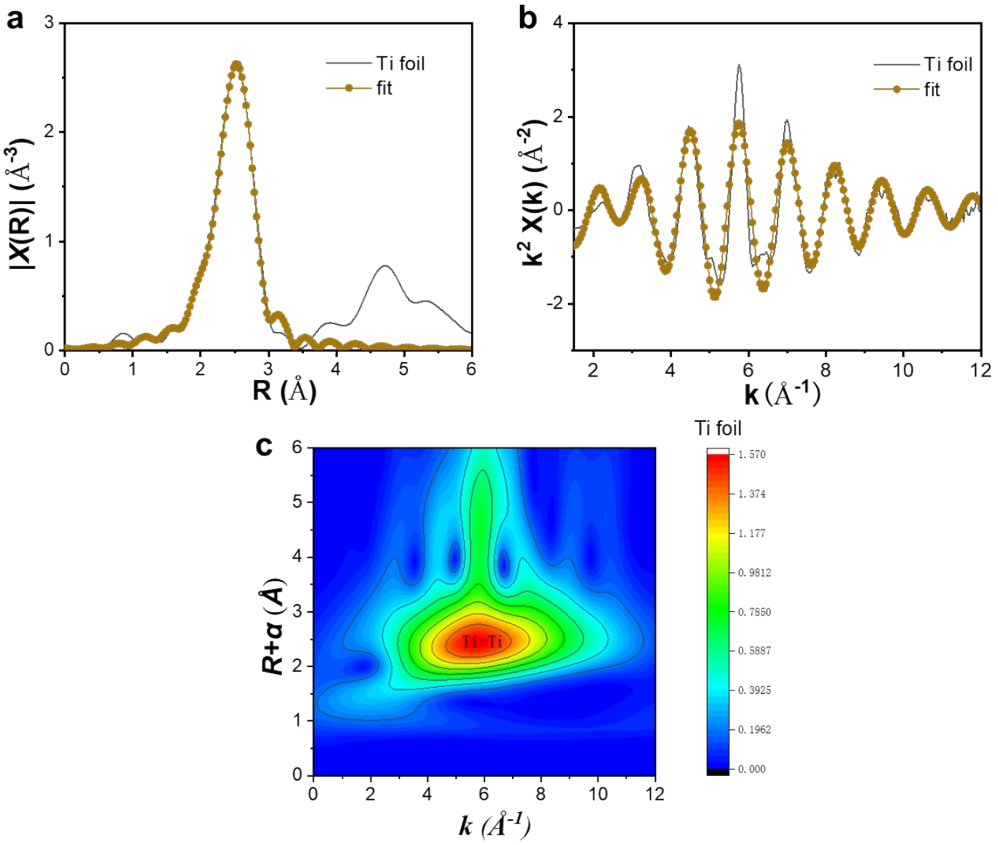

Figure S5. (a) The R-space fitting curve, (b) K-space fitting curve and (c) wavelet transform of Ti foil.

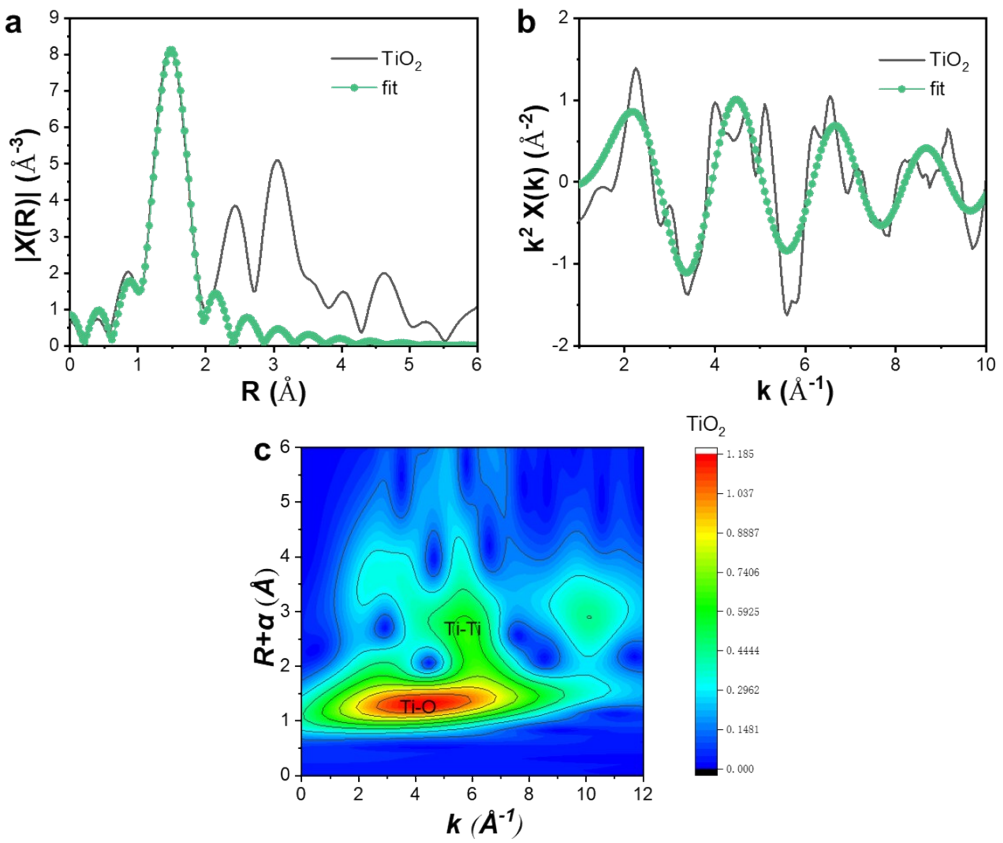

Figure S6. (a) The R-space fitting curve, (b) K-space fitting curve and (c) wavelet transform of TiO_2.

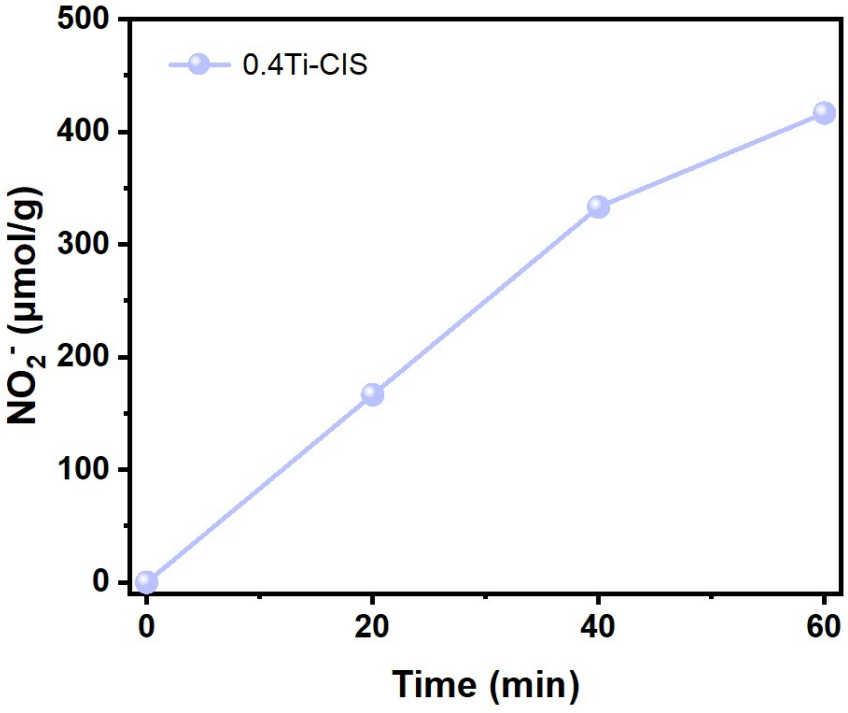

Figure S7. The NO_2^- formation during the NO_3^- photoreduction process over 0.4Ti-

CIS.

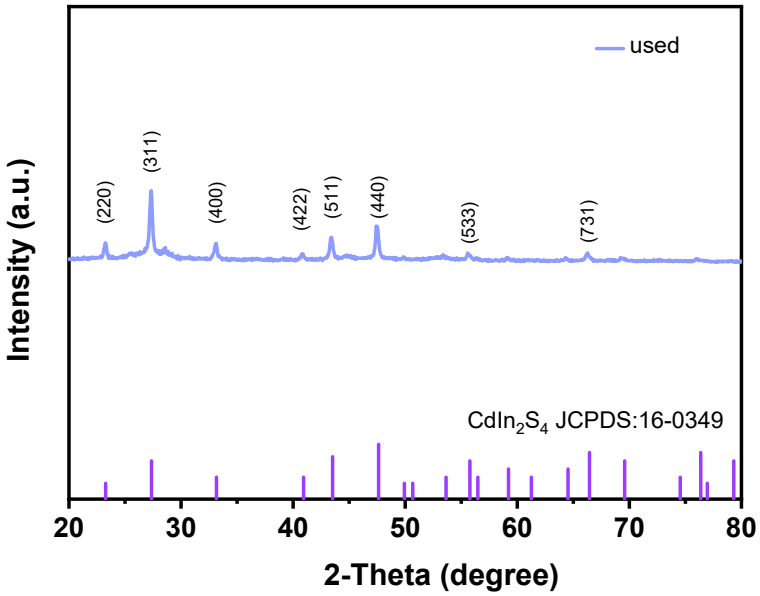

Figure S8. XRD result of 0.4Ti-CIS after cycles.

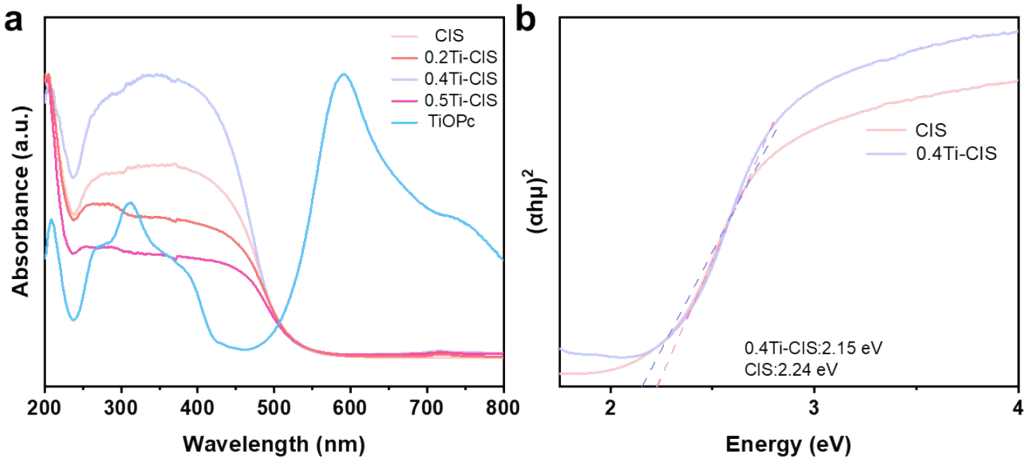

Figure S9. (a) UV-vis DRS of all catalysts and TiOPc. (b) Tauc-Plot of CIS and 0.4Ti-CIS.

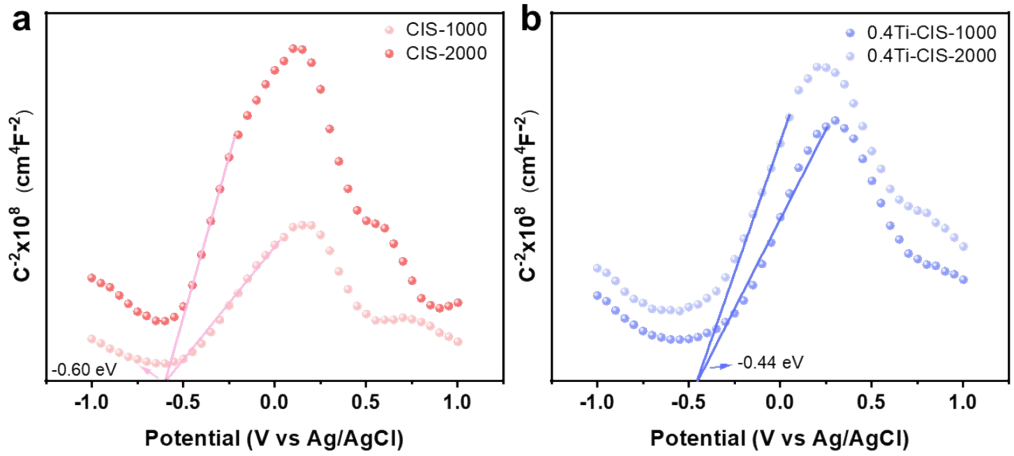

Figure S10. Mott-Schottky curves of (a) CIS and (b) 0.4Ti-CIS.

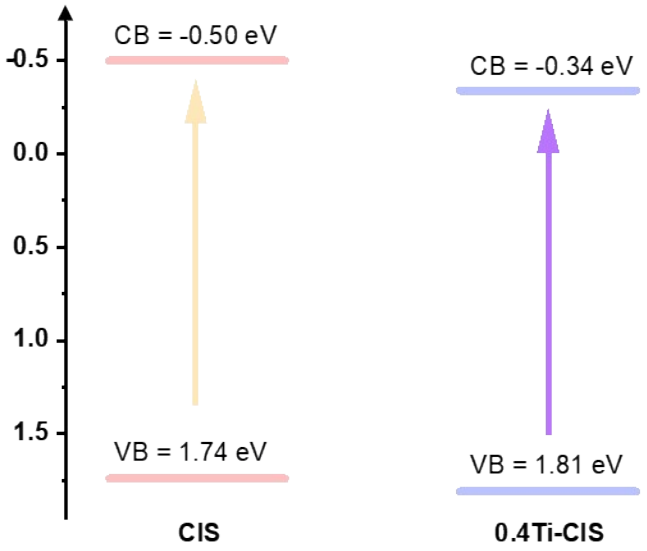

Figure S11. Band structure of CIS and 0.4Ti-CIS.

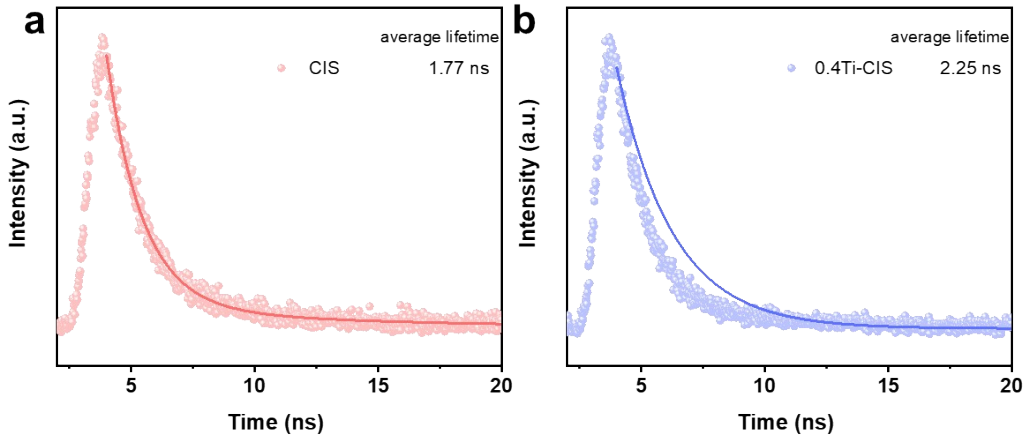

Figure S12. TRPL spectra of (a) CIS and (b) 0.4Ti-CIS.

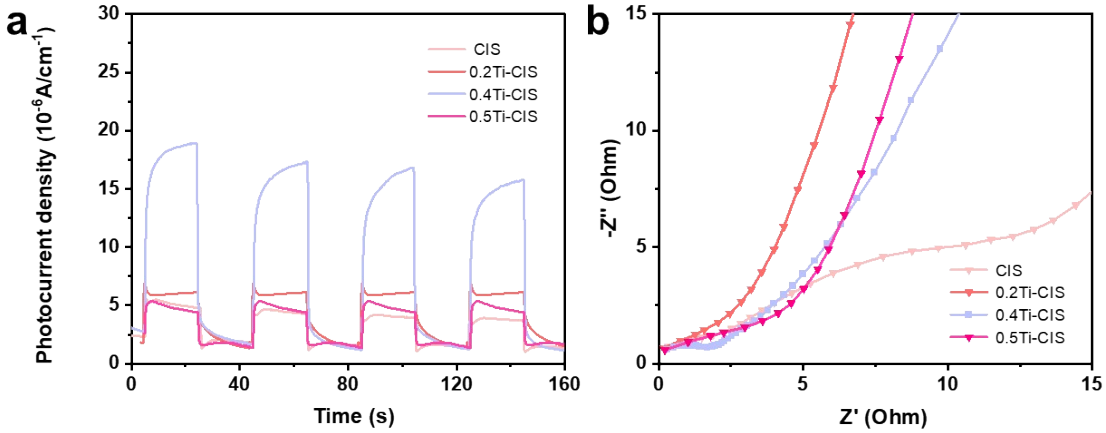

Figure S13. (a) Transient photocurrent density curves, and (b) Nyquist plots of CIS and 0.4Ti-CIS.

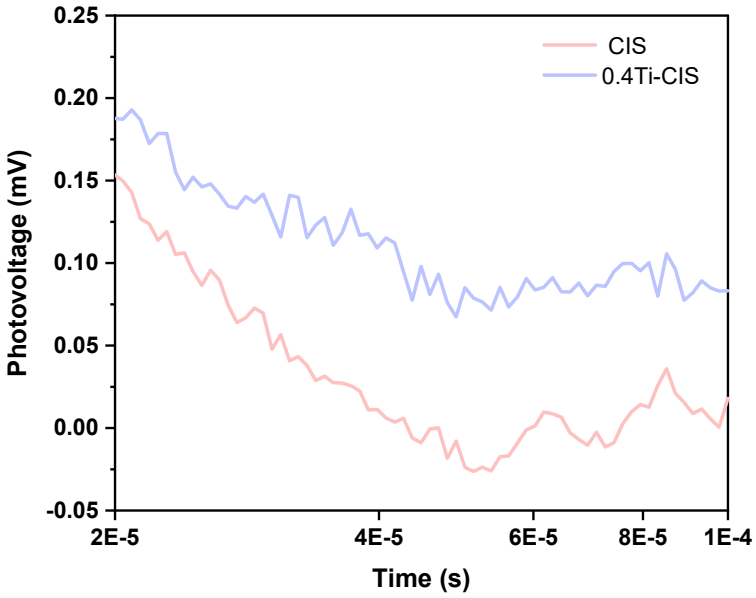

Figure S14. Surface photovoltage of CIS and 0.4Ti-CIS.

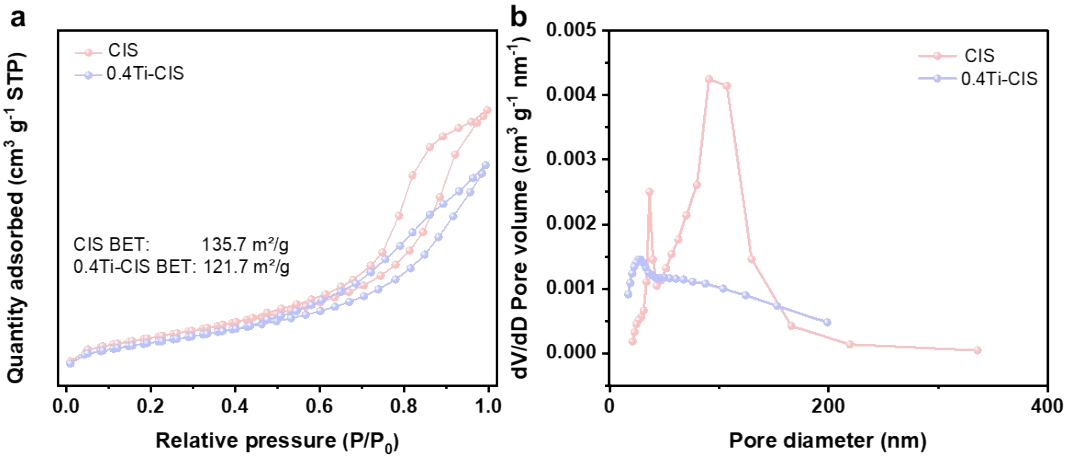

Figure S15. (a) Nitrogen adsorption-desorption isotherms of CIS and 0.4Ti-CIS (b) pore size distribution of CIS and 0.4Ti-CIS.

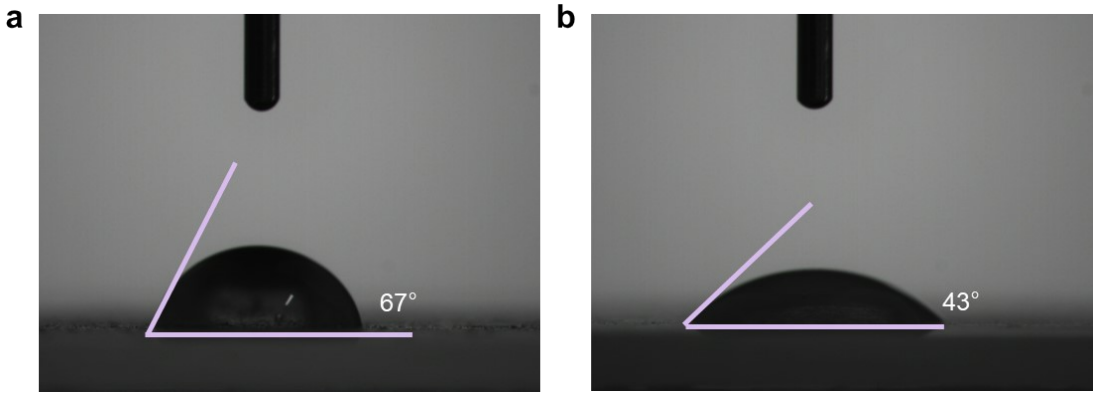

Figure S16. Water contact Angle of (a) CIS and (b) 0.4Ti-CIS.

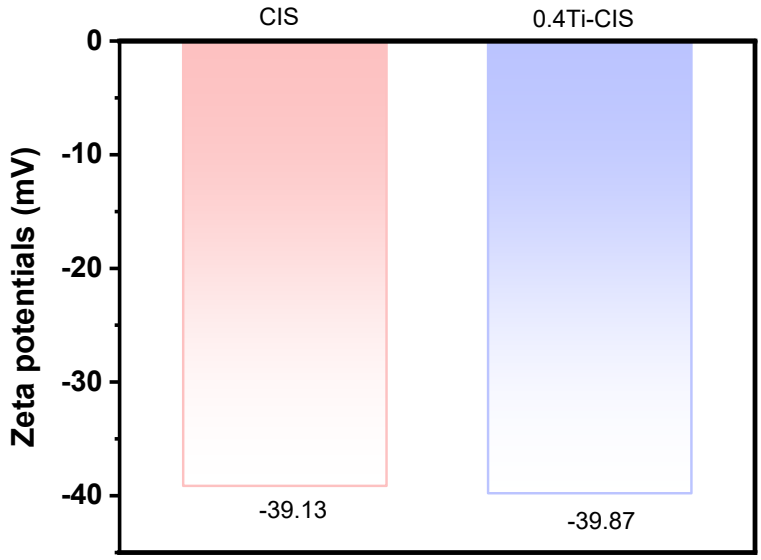

Figure S17. Zeta potential of CIS and 0.4Ti -CIS.

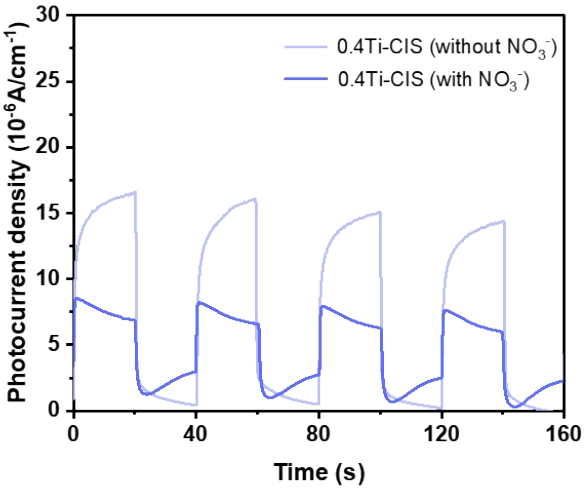

Figure S18. Transient photocurrent density curves with or without NO_3^- for 0.4Ti-CIS.

Table S1. EXAFS fitting parameters at the Ti K-edge for various samples(S_0^2=0.80).

Sample	Shell	*CN*[a]	*R*(Å)[b]	σ^2(Å^2)[c]	ΔE_0(eV)[d]	*R* factor
Ti K-edge						
Ti foil	Ti-Ti1	2*	2.73±0.01	0.0048	9.3	0.002
	Ti-Ti2	12*	2.92±0.01	0.0059	6.2	
TiO_2	Ti-O	6.0±0.1	1.96±0.01	0.0098	5.4	0.005

0.4Ti-CIS	Ti-N	2.2±0.1	2.02±0.01	0.0066	3.1	0.008
	Ti-O	1.1±0.1	1.95±0.01	0.0034	4.2	
	Ti-S	1.2±0.1	2.25±0.01	0.0061	5.4	

[a]*CN*, coordination number; [b]*R*, distance between absorber and backscatter atoms; [c]σ^2, Debye-Waller factor to account for both thermal and structural disorders; [d]ΔE_0, inner potential correction; *R* factor indicates the goodness of the fit. $S0^2$ was fixed to 0.80, according to the experimental EXAFS fit of Ti foil by fixing CN as the known crystallographic value. * This value was fixed during EXAFS fitting, based on the known structure of Ti-foil. Fitting range: $3.0 \leq k$ (/Å) ≤ 12.0 and $1.0 \leq R$ (Å) ≤ 3.0 (Ti foil); $3.0 \leq k$ (Å^{-1}) ≤ 11 and $1.0 \leq R$ (Å) $\leq$ ~3.0 (0.4Ti-CIS, TiO_2). A reasonable range of EXAFS fitting parameters: $0.700 < S_0^2 < 1.000$; $CN > 0$; $\sigma^2 > 0$ Å^2; $\Delta E_0 < 10$ eV; *R* factor < 0.02.

Table S2. Comparison of the photocatalytic ammonia synthesis performance with other *reported metal sulfides*.

Catalyst	**Optimal ammonia synthesis rate**	**Conditions**	**Reference**
0.4Ti-CIS	2572.8 μmol g^{-1} h^{-1}	300 W Xenon lamp, 10 mg catalyst and 100 mL of 10 mg L^{-1} NO_3^--N and 10 mL glycol	This work
$Mn_xIn_2S_y$	515.8 μmol g^{-1} h^{-1}	300 W Xe lamp, 10 mg catalyst and 100 mL solution containing 10 mg L^{-1} of NO_3^- and 10 mL ethylene glycol	ACS Nano, 2024, 18, 21585-21592.
PML-Cu-$CdIn_2S_4$	1979 μmol g^{-1} h^{-1}	300 W Xenon lamp, 10 mg catalyst and 100 mL of nitrate (0.16 M) and 10 mL ethylene glycol	Adv. Funct. Mater. 2025, 35, 2421669
V_{Cu-S} rich $CuIn_2S_4$	975.9 μmol g^{-1} h^{-1}	300 W Xe lamp, 10 mg catalyst and 100 mL 10 mg L^{-1} NO_3^-, 10 mL ethylene glycol	Appl. Catal. B, 2025, 362, 124776
Defect-rich $CaIn_2S_4$	406 μmol g^{-1} h^{-1}	300 W Xenon lamp, 10 mg catalyst was dispersed in 100 mL of reaction solution containing 10 mg L^{-1} of NO_3^- and 10 mL ethylene glycol	Small, 2024, 20, 2402808.
$Mo_{0.1}Ni_{0.1}Cd_{0.8}S$	3.2 mg L^{-1} h^{-1} g_{cat}^{-1}	0.2 g of photocatalyst was added to a 500 mL solution of 0.789 g L^{-1} ethanol as a hole scavenger	RSC Adv., 2016, 6, 49862-49867

MoS_2/In-Bi_2MoO_6	90 μmol g^{-1} h^{-1}	100 mg photocatalyst was sonicated in 100 mL of deionized water for 10 min and then dispersed with a constant temperature of 25 °C under a 300 W Xe lamp	ACS Catal. 2024, 14, 6292-6304
Cu/Ta_3N_5/$CdIn_2S_4$	256 μmol g^{-1} h^{-1}	250 W Xe lamp, 50 mg catalyst and 10 ml formic acid were dispersed into 75 mL nitrate solution (0.4 mmol L^{-1})	Appl. Catal. B, 2023, 327, 122416.
MXene QDs-$ZnIn_2S_4$	360.5 μmol g^{-1} h^{-1}	300 W Xe lamp, photocatalyst (0.1 g) was added to 200 mL of deionized water	InfoMat, 2024, 6, e12535
In_2S_{3-X}@ZnS	58.988 mg L^{-1} h^{-1} g_{cat}^{-1}	300 W Xe lamp, 30 mg of obtained samples were dissolved in 50 mL of 1 mmol L^{-1} CH_3OH aqueous solution, continuous N_2	Appl. Surf. Sci. 2024, 656, 159658
$FeMoS_x$	99.79 μmol g^{-1} h^{-1}	100 W Hg lamp, 1 mg mL^{-1} catalyst was added into an aqueous solution containing pyridinium chloride (50 mM) and sodium ascorbate (5 mM)	ACS Omega 2024, 9, 20629-20635