Electronic Supplementary Information

Band-aligned $C_3N_{4-x}S_{3x/2}$ stabilizes CdS/$CuInGaS_2$ photocathodes for efficient water reduction

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Experimental Section

Preparation of CIGS Films: In a typical experiment,[1] copper (II) nitrate trihydrate (0.5843 g), indium (III) nitrate hydrate (0.6461 g), and gallium (III) nitrate hydrate (0.1856 g) were dissolved in 4 ml methanol, and then 3.5 mL methanol with 0.375 g polyvinyl acetate was added into the above solution and stirred for 30 minutes. The precursor solution was spin-coated on fluorine-doped tin oxide (FTO) glass substrates at 2500 rpm for 30 s, then dried at 150 °C for 3 minutes followed by annealing at 250 °C for 8 minutes in air. The coating step was repeated six times to obtain an optimum thickness. After annealing at 350 °C in Muffle furnace for 1 h, the electrodes were then sulfurized in the presence of 40 mg of pristine sulfur powder in a tube furnace at 500 °C for 30 min.

Surface Modification with n-Type CdS Thin Layer: As previously reported, surface modification of the as-prepared CIGS film with CdS layer was achieved via facile chemical bath deposition method.[2] Specifically, the CIGS film on FTO was immersed in an aqueous solution containing 12.5 mM $CdSO_4$, 0.22 M $SC(NH_2)_2$, and 11 M NH_4OH(28–30%) at 60°C for 7 min to yield CdS-covered CIGS (CdS/CIGS) sample.

Preparation of the C_3N_4 powders: C_3N_4 powders were fabricated by directly heating low-cost melamine, as previously reported.[3] In details, 5 g melamine powder in an alumina crucible with a cover, then thermal decomposition was performed at 500 °C in a muffle furnace for 4 h with a heating rate of 20 °C/min and cooled down to room temperature automatically.

Electrophoretic Deposition (EPD) of $C_3N_{4-x}S_{3x/2}$: Before conducting EPD experiment, 20 mg as-prepared C_3N_4 powders were added to a 25 ml solvent of acetone with 40 mg iodine and 20 mg pristine sulfur powder as additives, sonicating for 30 min and served as the precursor solution. The electrophoresis deposition occurred in a two-electrode system with a Ti sheet as the anode and the CdS-covered CIGS film as the cathode. The potential was set to 20 V and the time of the deposition was set to 5 min using KEITHLEY 2400 (SN 006416). After the deposition of $C_3N_{4-x}S_{3x/2}$ by EPD, the films were annealed at 500 °C for 2 h under argon atmosphere. The solution

processed superstrate type CIGS solar cell with $C_3N_{4-x}S_{3x/2}$/CdS/CIGS configuration is obtained.

Structural Characterizations: The morphology and structure of the samples were observed by SEM (Hitachi S4800) and TEM (JEOL JEM-2010F, F20, 200 kV). The crystal structures of the samples were measured with an X-ray diffractometer (Bruker D8 Advanced Diffractometer, Cu Kα radiation, 40 kV). The optical absorption spectras of the samples were recorded in a UV/Vis spectrophotometer (CARY 500). Hematite MSCs were also analyzed using X-ray photoelectron spectroscopy (Thermo ESCALAB 250, Al Kα exciting radiation). All binding energies were referenced to the C 1s peak (284.6 eV).

PEC and EC measurements: All linear sweep voltammograms were measured by a CHI 660e electrochemical workstation in a three-electrode configuration using a Pt foil (2 cm^2) as counter electrode and an Ag/AgCl as reference electrode with an aqueous solution of K_2HPO_4/KH_2PO_4 (1 M) as the electrolyte. The linear sweep voltammetry was scanned from

-1 to -0.2 V vs. Ag/AgCl at a speed of 10 mV s^{-1}. The measurements were performed under one sun condition using a solar light simulator (Oriel, 91160, AM 1.5 globe). The power of the simulated light was adjusted to 100 mW cm^{-2}.

The electrochemical impedance spectra (EIS) and Mott-Schottky plots were measured under a Xe lamp illumination by using an electrochemical workstation (Parstat 2273, Princeton). The frequency range of EIS experiments was from 100 kHz to 100 mHz. Electrolyte: 1 M K_2HPO_4/KH_2PO_4 solution (pH=7). Potential: $0V_{RHE}$. The Mott-Scottky calculations were derived from impedance measurements in the dark sweeping from -1 to -0.2 V vs. Ag/AgCl at a speed of 10 mV s^{-1}. The alternating current (AC) potential frequency was 200 Hz with the amplitude of 10 mV.

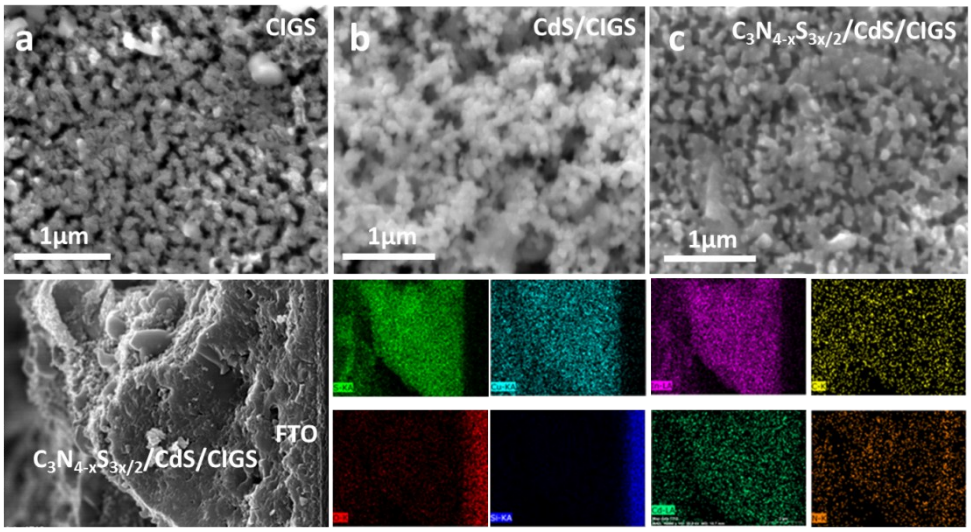

Figure S1. a-c) SEM images of (a) CIGS, (b) CdS/CIGS, and (c) $C_3N_{4-x}S_{3x/2}$/CdS/CIGS. d) EDS measurements of $C_3N_{4-x}S_{3x/2}$/CdS/CIGS.

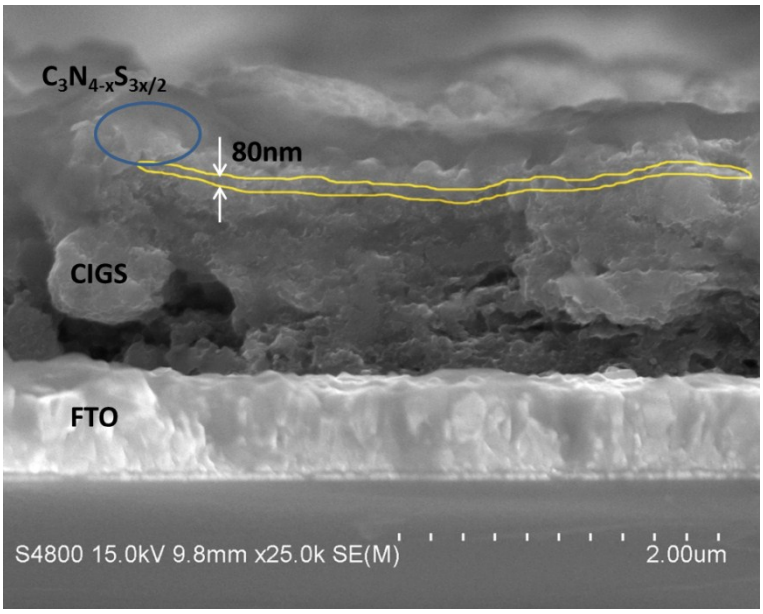

Figure S2. Cross-section SEM image of $C_3N_{4-x}S_{3x/2}$/CdS/CIGS electrode.

The corresponding cross-section SEM image showed the thickness of around 80 nm for CdS. And about 15nm for $C_3N_{4-x}S_{3x/2}$ layer, which seems too thick for the electron tunneling process. Therefore, we confirm that the $C_3N_{4-x}S_{3x/2}$ is introduced to form a CdS/CIGS junction.

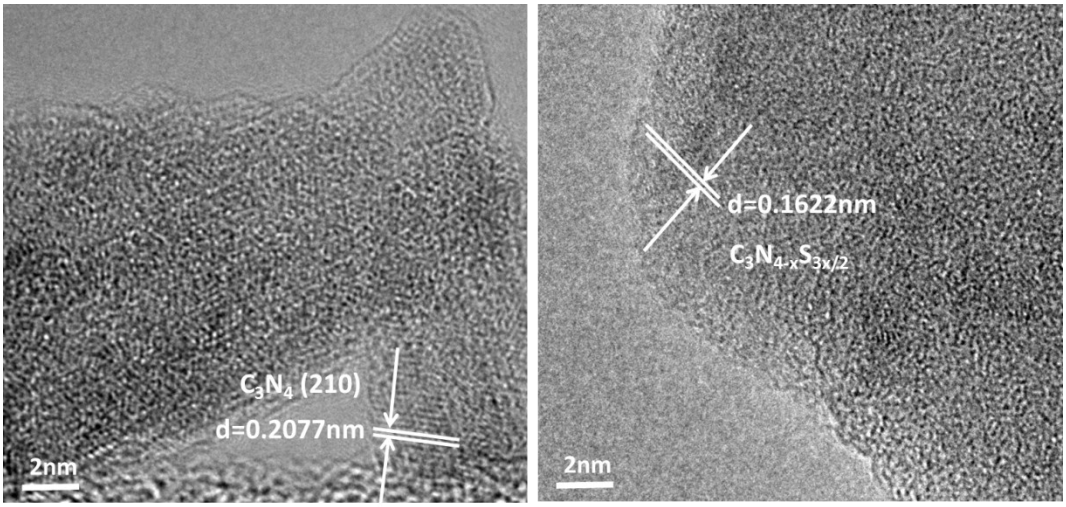

Figure S3. Typical TEM images of C_3N_4 (a) and $C_3N_{4-x}S_{3x/2}$ (b) particles.

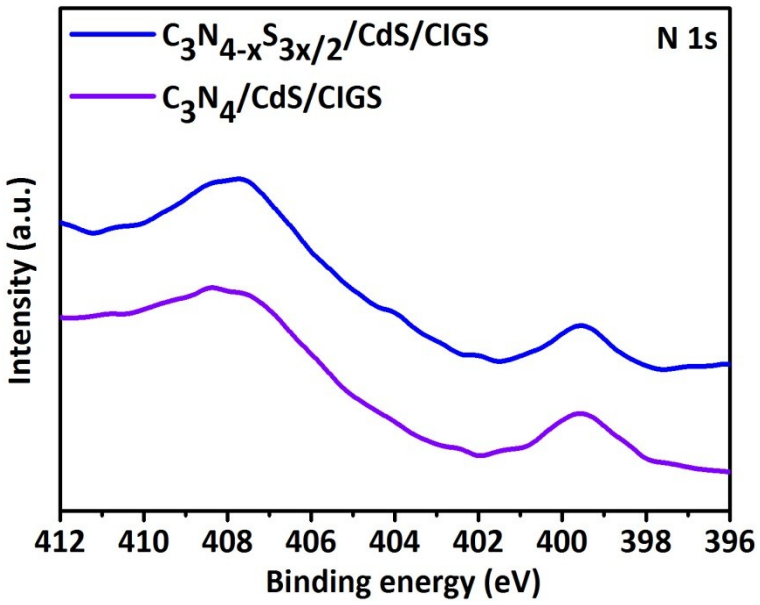

Figure S4. High resolution XPS spectra of N 1s in C_3N_4/CdS/CIGS and $C_3N_{4-x}S_{3x/2}$/CdS/CIGS samples.

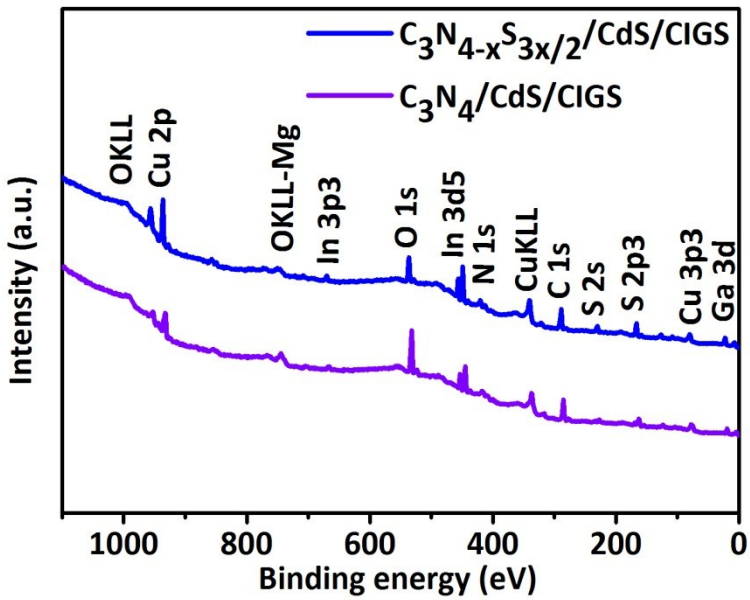

Figure S5. High resolution XPS spectrum of C_3N_4/CdS/CIGS and $C_3N_{4-x}S_{3x/2}$/CdS/CIGS photocathodes.

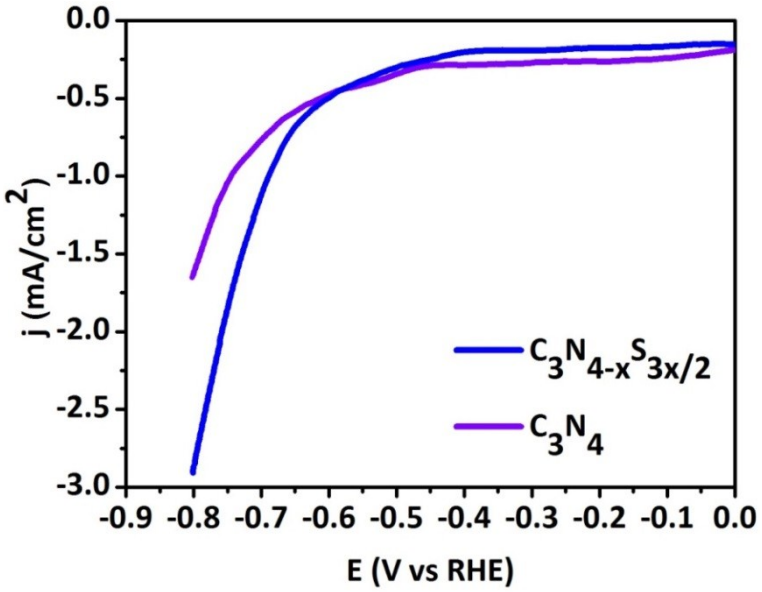

Figure S6. The Steady-state current density as a function of applied voltage during HER at 1 M K_2HPO_4/KH_2PO_4 solution (pH=7) over $C_3N_{4-x}S_{3x/2}$ and C_3N_4.

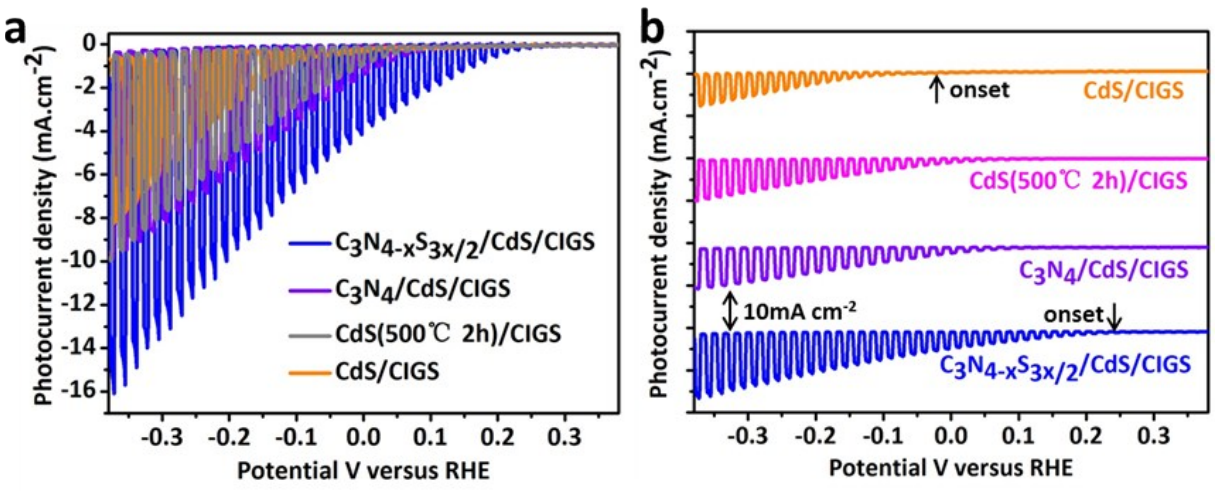

Figure S7. The Current–potential plots for CdS/CIGS, C_3N_4/CdS/CIGS and $C_3N_{4-x}S_{3x/2}$/CdS/CIGS photocathodes all the CdS/CIGS substrate using a chemical vapor deposition (CVD) route in a 1 M K_2HPO_4/KH_2PO_4 solution (pH=7) irradiated with chopped AM 1.5G illumination.

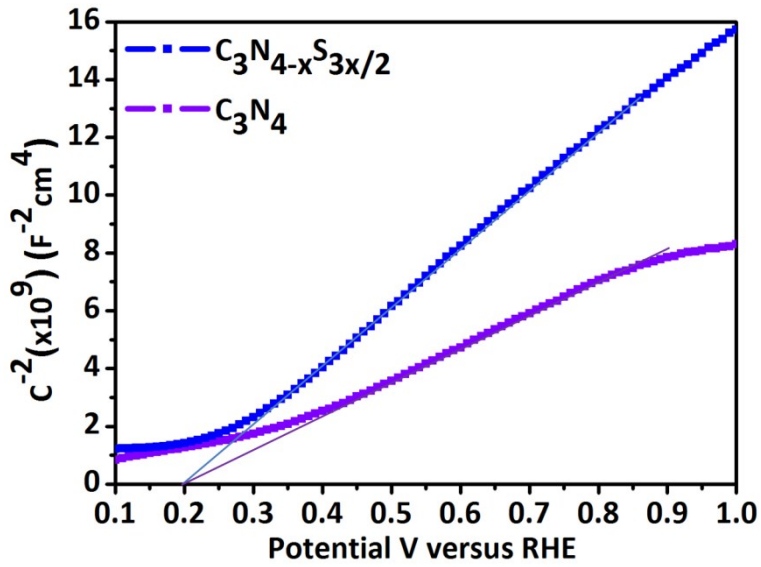

Figure S8. Mott–Schottky plots of C_3N_4 and $C_3N_{4-x}S_{3x/2}$ photocathodes. The ac amplitude is 10 mV and the frequency is 200 Hz.

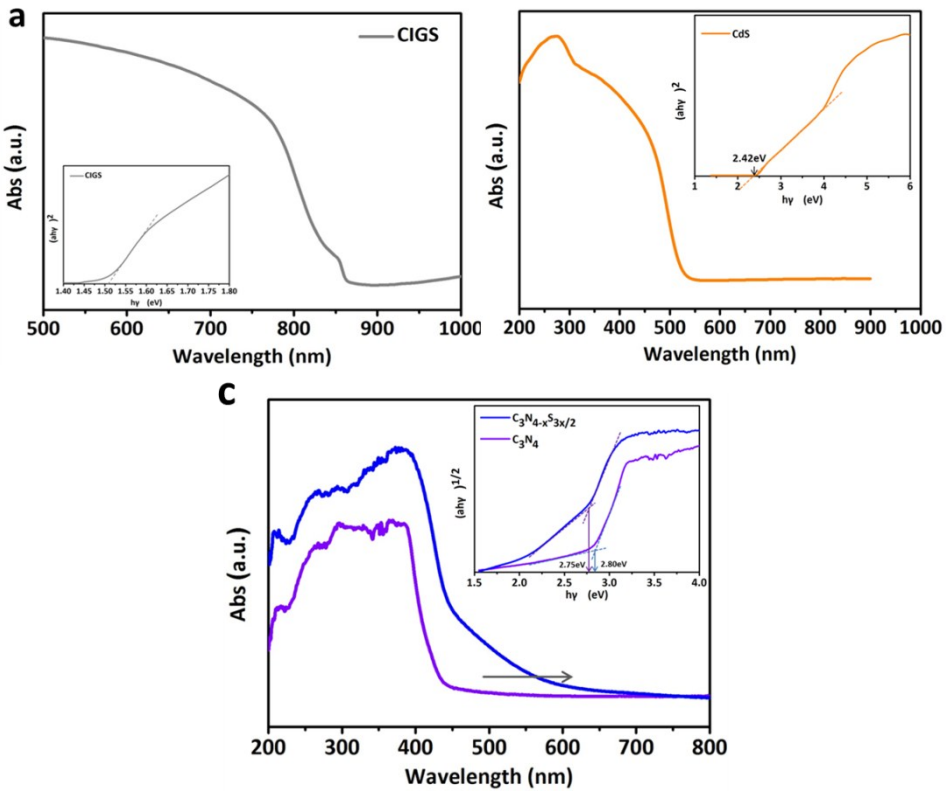

Figure S9. The UV-Vis plots of CIGS, CdS, $C_3N_{4-x}S_{3x/2}$ and g-C_3N_4.

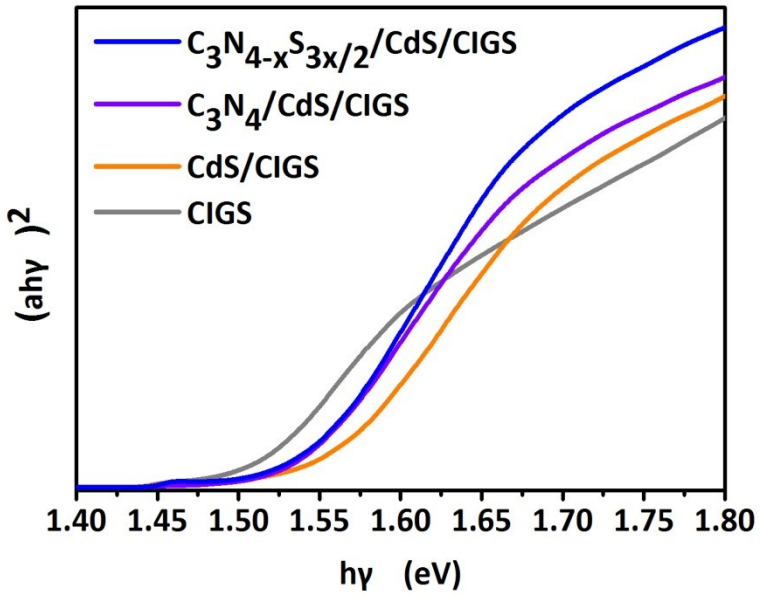

Figure S10. Absorbance spectra in the band edge region for samples CIGS, CdS/CIGS, C_3N_4/CdS/CIGS and $C_3N_{4-x}S_{3x/2}$/CdS/CIGS with an extrapolation of the spectra in order to determine the band gap values.

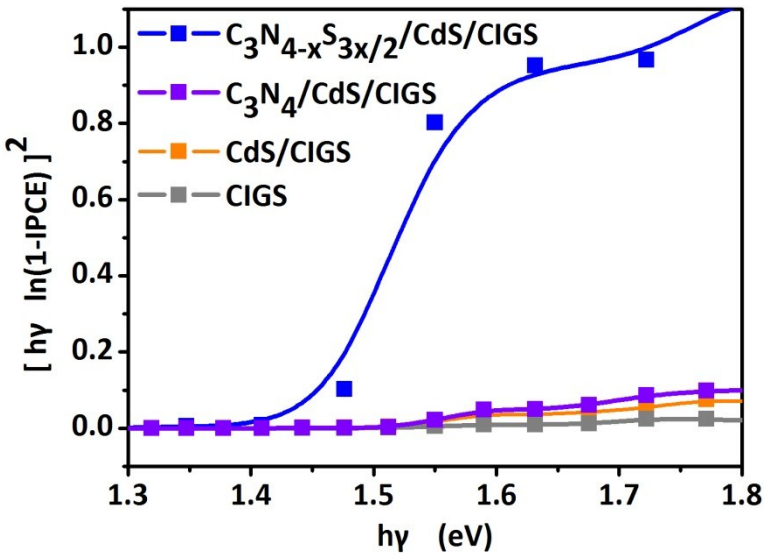

Figure S11. [hγ ln(1-IPCE)]^2 vs. band gap (eV) plots of CIGS, CdS/CIGS, C_3N_4/CdS/CIGS and $C_3N_{4-x}S_{3x/2}$/CdS/CIGS.

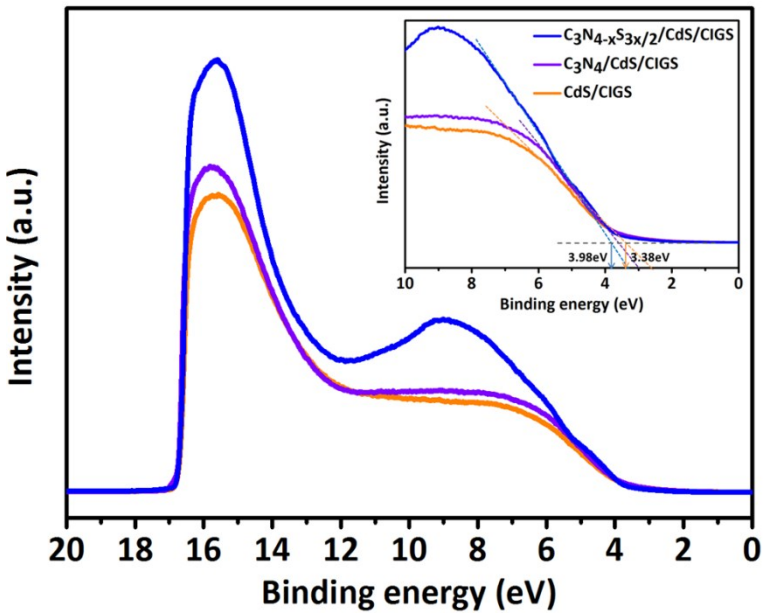

Figure S12. Ultraviolet Photoelectron Spectra of CdS/CIGS, C_3N_4/CdS/CIGS and $C_3N_{4-x}S_{3x/2}$/CdS/CIGS.

Method	Sample	Atomic ratio				
		Cu	In	Ga	S	In/Ga
ICP-AES	Electrolyte	1	0.847	0.153	--	5.54

Table S1. Atomic ratios of the $CuInGaS_2$ according to ICP-AES.

Method	Sample	Results (Mean Data)
		Cd
ICP-MS	CdS/CIGS	0.016mg.L^{-1}
	$C_3N_{4-x}S_{3x/2}$/CdS/CIGS	0.00001mg.L^{-1}

Table S2. Quantitative analysis of the Cd in 1 M K_2HPO_4/KH_2PO_4 solution after 20 h stability of CdS/CIGS and $C_3N_{4-x}S_{3x/2}$/CdS/CIGS photocathode according to ICP-MS.

References

1 Z. Guan, W. Luo, J. Feng, Q. Tao, Y. Xu, X. Wen, G. Fu, Z. Zou, *J. Mater. Chem. A,* 2015, **3**, 7840.

2 F. Jiang, Gunawan, T. Harada, Y. Kuang, T. Minegishi, K. Domen and S. Ikeda, *J. Am. Chem. Soc.*, 2015, **137**, 13691.

3 Y. Hou, F. Zuo, A. P. Dagg, J. Liu and P. Feng, *Adv. Mater.*, 2014, **26**, 5043.