Supporting Information

Charge transfer enhancement at CZTS Photocathodes interface by ITO for Efficient Solar Water Reduction

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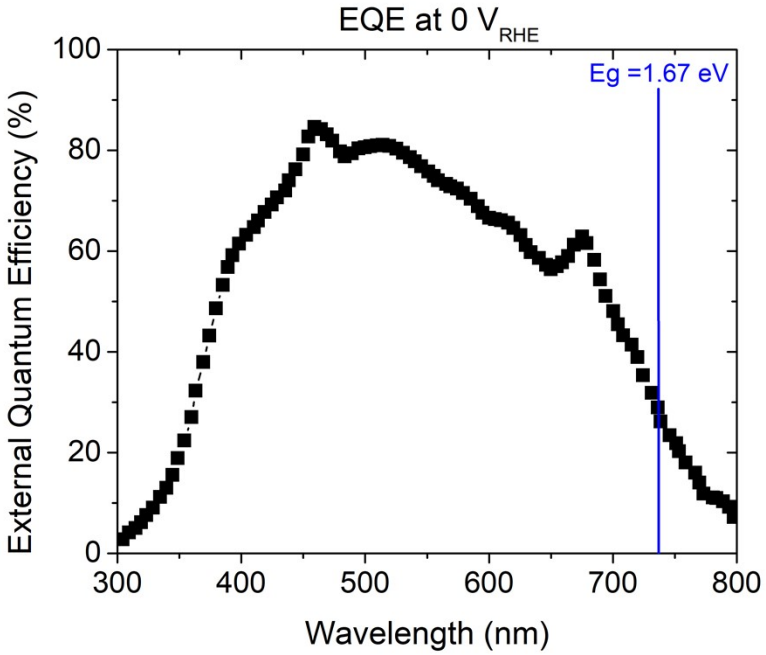


Figure S1 External Quantum Efficiency (EQE) of CZTS/CdS/ITO/Pt photocathode stacks in 1 M K_2HPO_4/KH_2PO_4 (pH 7) solution under applied potential of 0 V_{RHE}. d(EQE)/dE is used for band gap extraction.

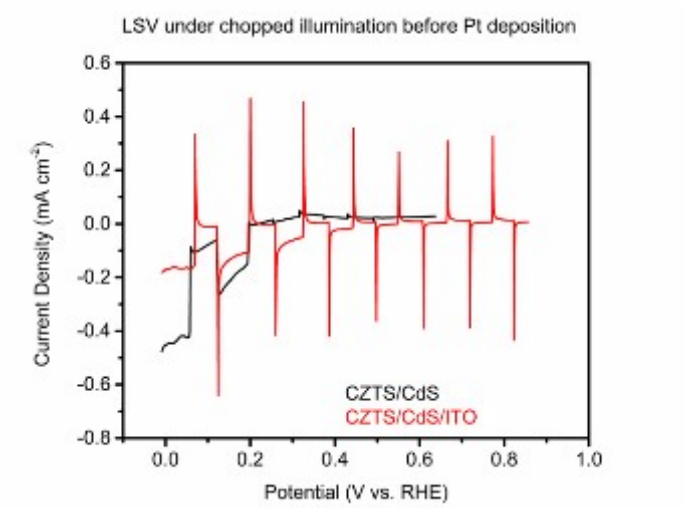


Figure S2 Current density-potential curves of CZTS/CdS and CZTS/CdS/ITO in 0.1 M Na_2SO_4 electrolyte (pH 9.5) under chopped solar-simulated AM 1.5G light irradiation.

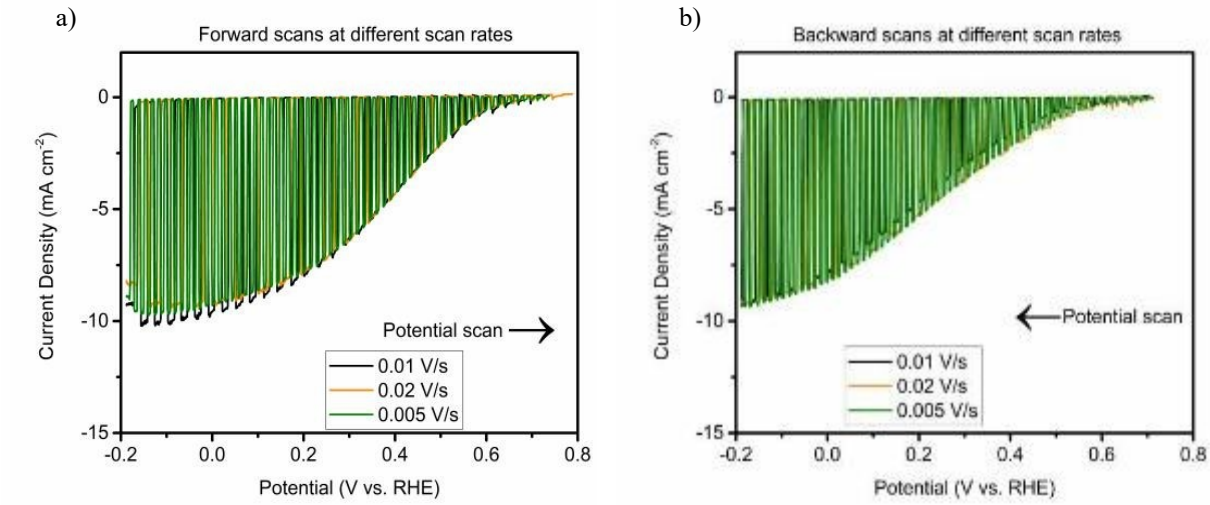


Figure S3 Current-density potential curves of CZTS/CdS/Pt at different scan rates of 0.01 V/s, 0.02 V/s and 0.005 V/s in 1 M K_2HPO_4/KH_2PO_4 (pH 7) solution under chopped AM 1.5G light irradiation for (a) Anodic and (b) Cathodic directions.

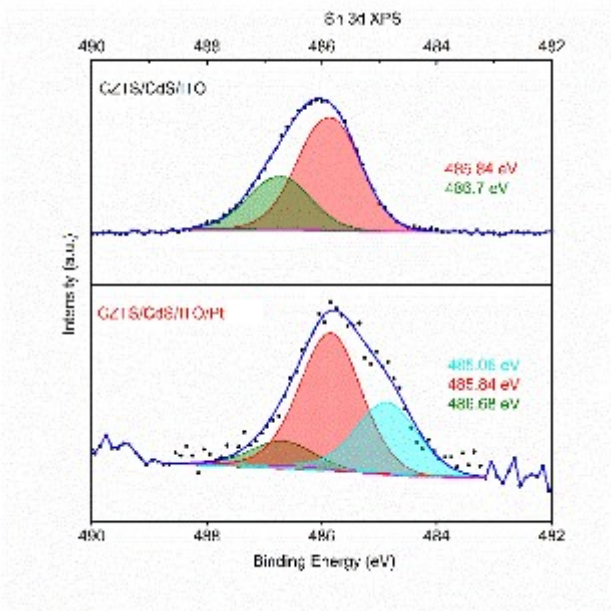


Figure S4 Sn 3d XPS spectra of CZTS/CdS/ITO (top panel) vs CZTS/CdS/ITO/Pt (bottom panel). The peaks are assigned to Sn^{4+} (green) and Sn^{2+} (red) in tin oxide and metallic tin (blue).[1]

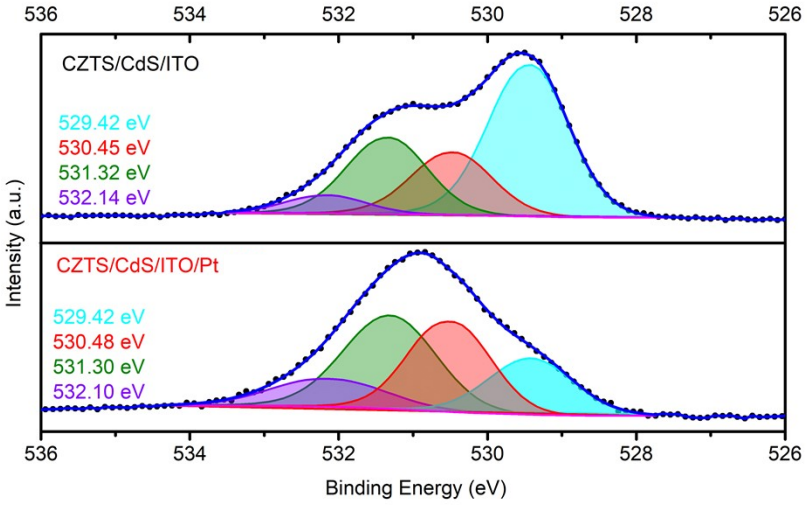


Figure S5 O 1s XPS spectra of CZTS/CdS/ITO and CZTS/CdS/ITO/Pt. The peaks are assigned to lattice oxygen (blue) and oxygen adjacent to oxygen-deficient positions (red) in indium oxide (In_2O_3), surface hydroxide or oxyhydroxide (green), and unidentified surface contaminants (purple).

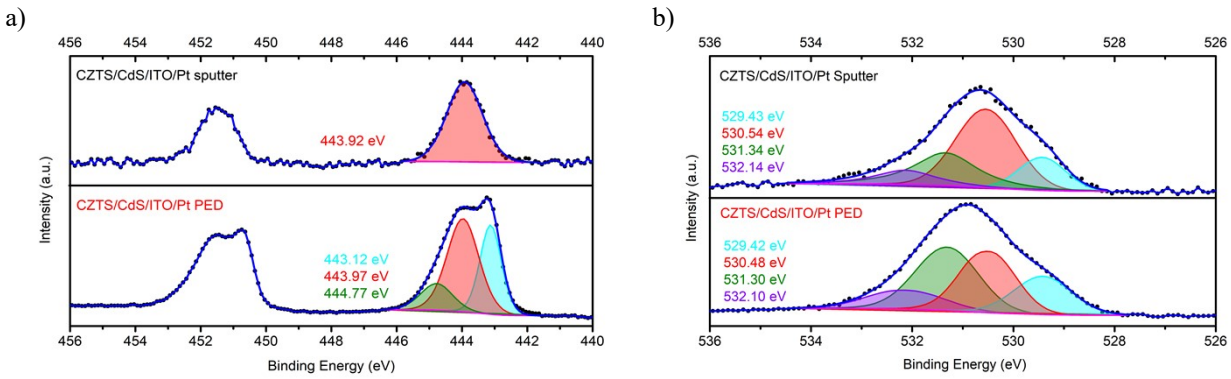


Figure S6 (a) In 3d XPS spectra of CZTS/CdS/ITO with Pt sputter vs CZTS/CdS/ITO with Pt photoelectrodeposited (PED). (b) Corresponding O 1s XPS Spectra. The peaks are assigned to indium oxide (In_2O_3) (red), indium hydroxide ($In(OH)_3$) (green), metallic indium (In) (blue), and unidentified surface contaminants (purple).

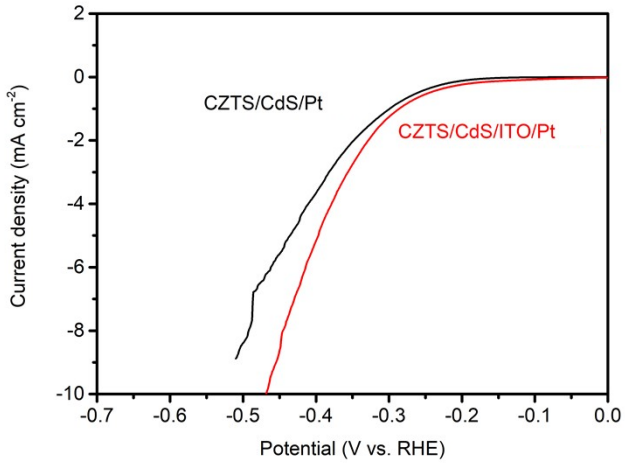


Figure S7 Dark current density - voltage measurement at a scan rate of 1 mV/s in 1 M K_2HPO_4/KH_2PO_4 solution (pH 7).

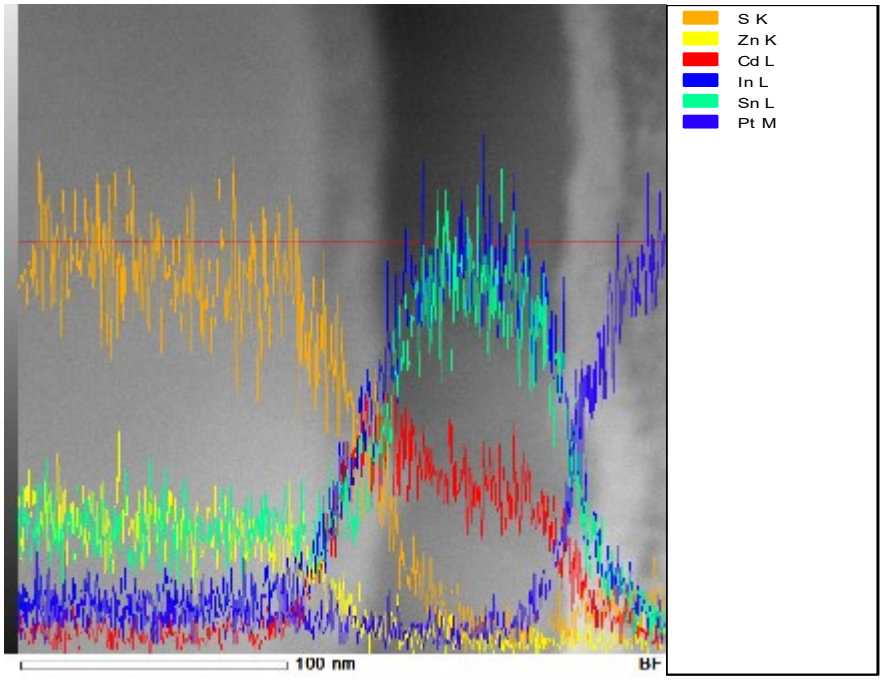


Figure S8 TEM EDX Line scan of CZTS/CdS/ITO interface.

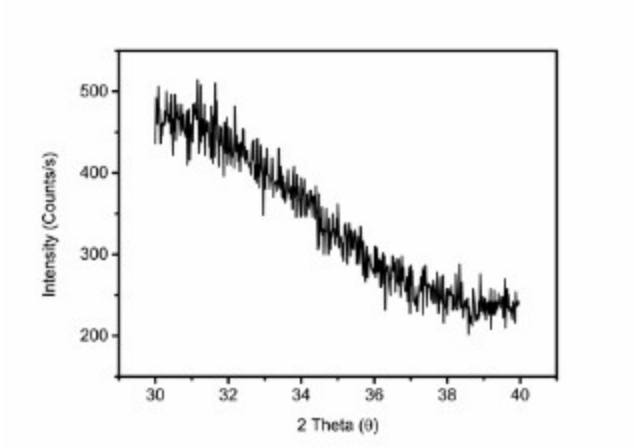


Figure S9 X-ray diffractogram of ITO sputtered on glass at room temperature under DC power of 75 W for 7 min.

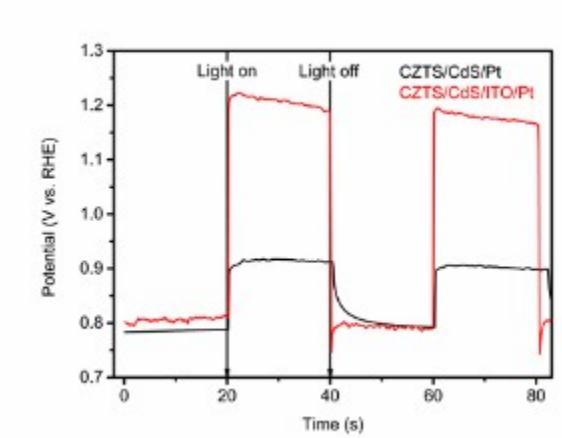


Figure S10 Open circuit potential measurements for CZTS/CdS/Pt (black) and CZTS/CdS/ITO/Pt (red) in 1 M K_2HPO_4/KH_2PO_4 solution (pH7) under constant AM 1.5G light irradiation.

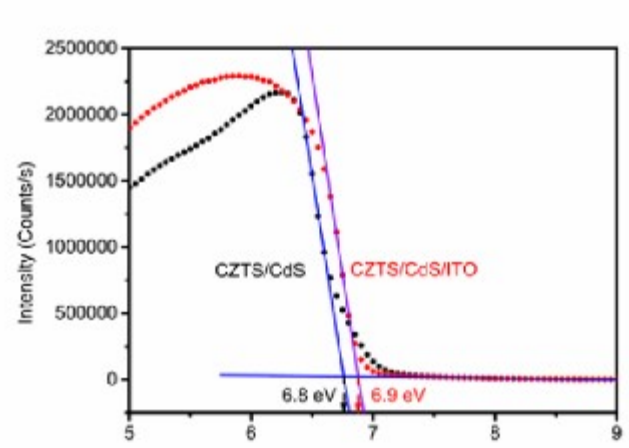


Figure S11 UPS He(I) spectra at an applied bias of -10V for CZTS/CdS (black) and CZTS/CdS/ITO (red).

	In	Sn	O
Before Pt deposition	38.27	4.19	57.55
After Pt deposition	20.76	1.64	77.60

Table S1 Atomic ratios of ITO films before and after Pt photoelectrodeposition determined by XPS.

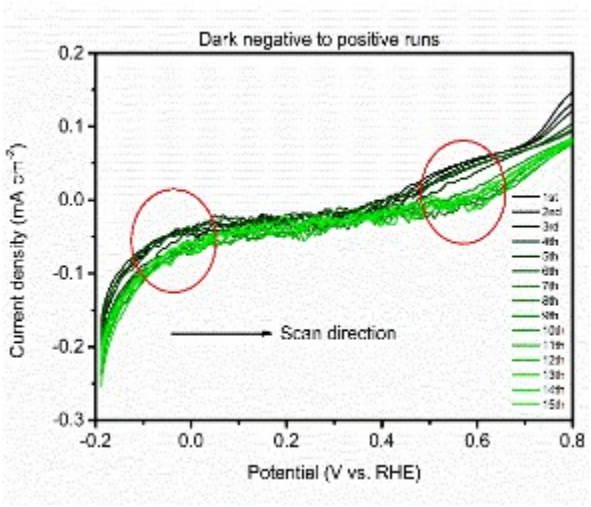


Figure S12 Linear sweep voltammetry scans done in the dark condition from -0.2 V_{RHE} to 0.8 V_{RHE}

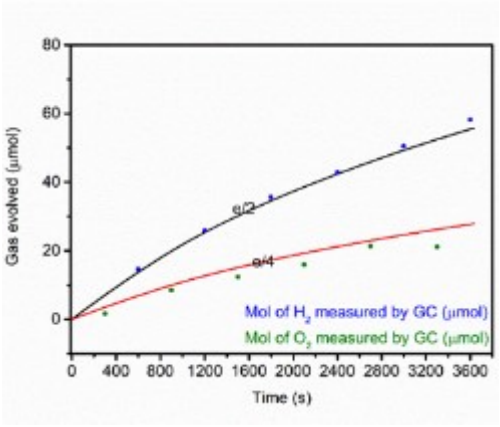
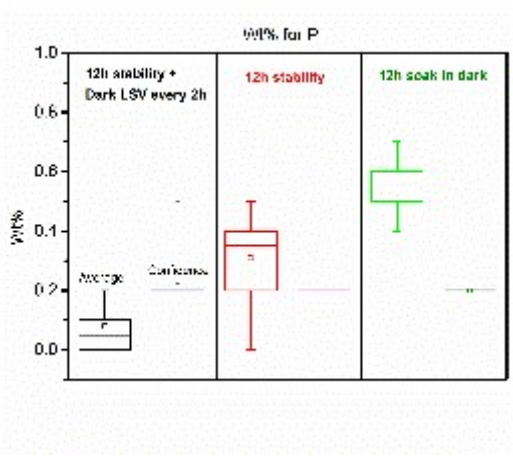


Figure S13 Time-course curves of H_2 and O_2 evolution of CZTS/CdS/ITO/Pt photocathode in the same electrolyte under the same measurement conditions. Solid lines represent the time-course curve for $e^-/2$ (black) and $e^-/4$ (red) determined from current measured and dots representing H_2 (blue) and O_2 (green) measured by Gas Chromatography (GC) at regular intervals of 10 min.

a)



b)

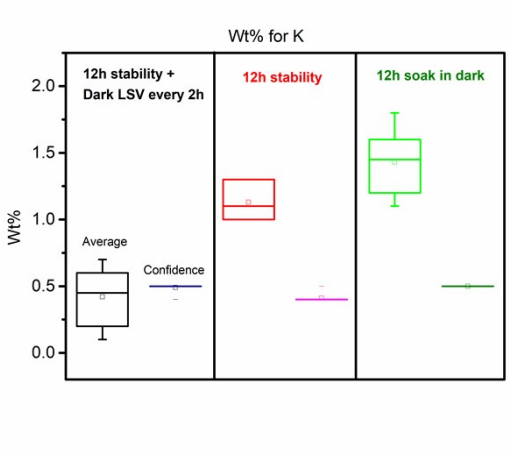
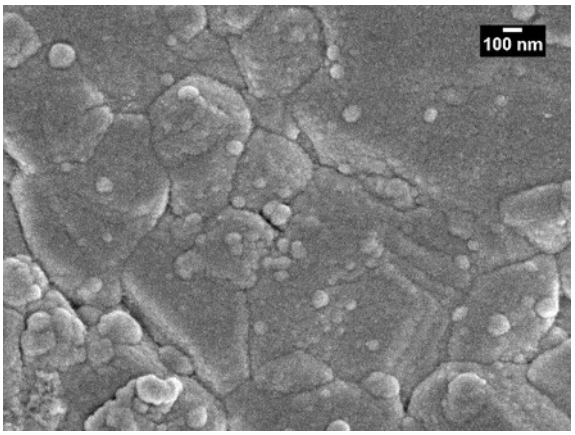


Figure S14 Box plots of SEM EDX measured Wt% of (a) P and (b) K. Each plot is divided into 3 sections representing 3 different experimental conditions: (1-black) 12h stability test of CZTS/CdS/ITO/Pt at 0 V_{RHE} in 1 M K_2HPO_4/KH_2PO_4 (pH 7) solution under constant AM 1.5G illumination with recovery dark LSV done at every 2h interval. (2-red) 12 stability test of CZTS/CdS/ITO/Pt under same applied bias in same electrolyte and illumination without any recovery dark LSV. (3-green) CZTS/CdS/ITO/Pt soaked in 1 M K_2HPO_4/KH_2PO_4 (pH 7) solution in the dark without any bias applied. Within each section, 2 box plots are presented. First is the box plot of 10 measured EDX points. Second is labelled confidence is the degree of overlap with other surrounding peaks.

a)



b)

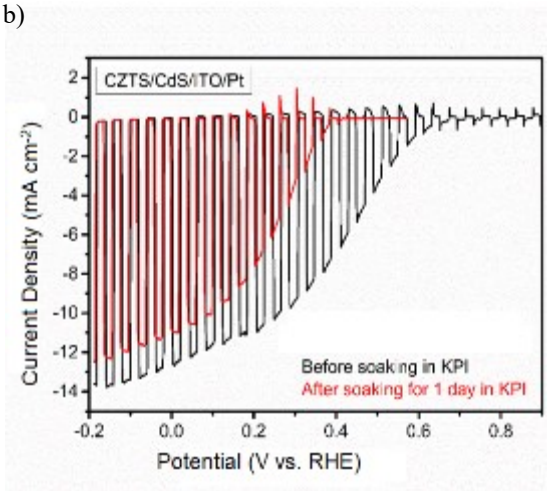


Figure S15 Scanning Electron Microscope (SEM) of CZTS/CdS/ITO/Pt after immersing in 1M K_2HPO_4/KH_2PO_4 (pH 7) overnight in the dark without any applied potential. (b) Current density-potential curve of CZTS/CdS/ITO/Pt under chopped solar-simulated AM 1.5G light irradiation before and after immersing in 1M K_2HPO_4/KH_2PO_4 (pH 7) for 1 day in the dark.

1. W. Xia, H. Wang, X. Zeng, J. Han, J. Zhu, M. Zhou and S. Wu, *CrystEngComm*, 2014, **16**, 6841-6847.