Supporting Information

Aluminium-doped cadmium sulfide homojunction photoelectrode with optimal film quality and water-splitting performance

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Equations related in this work

1.Theoretical maximum photocurrent density (J_{abs})

Theoretical maximum photocurrent density (J_{abs}) is the photocurrent density assuming that all absorbed photons can be converted into current (i.e., APCE = IPCE/LHE = 100%), it is a constant with the AM 1.5G spectrum and the light harvesting efficiency of the fixed photoelectrode. In the case of J_{abs}, it can be calculated according to the following equation:

$$J_{abs} = \int_{\lambda_1}^{\lambda_2} \frac{\lambda \times \mathrm{LHE}(\lambda) \times P(\lambda)}{1240} d(\lambda)$$

Eq. S1

where λ and P(λ) are the light wavelength (nm) and the corresponding power density ($mW\ cm^{-2}\ nm^{-1}$) for the standard solar spectrum AM 1.5G (ASTMG-173-03), respectively. $LHE(\lambda)$ is light absorption efficiency. The integrated power ($W{\bullet}m^{-2}$) was then divided by 1.23 V vs. RHE to convert it (**Figure S6**).[1]

2. The charge separation efficiency (η_{sep}) and charge injection efficiency (η_{inj})

Photocurrent density arising from PEC water oxidation can be described by the following equation:

$$J_{H_2O} = J_{abs} \times \eta_{sep} \times \eta_{inj}$$

Eq. S2

η_{sep} is the ratio of photogenerated holes which have migrated to the semiconductor/electrolyte interfaces, and η_{inj} is the ratio of photogenerated holes paticipated in water oxidation reaction. In this work, the widely used Na_2S/Na_2SO_3 was chosen as the hole scavenger.[2] η_{sep} and η_{inj} were calculated according to the Eq.S3 and Eq. S4, respectively：

$$\eta_{sep} = \frac{J_{Na_2S/Na_2SO_3}}{J_{abs}}$$

Eq. S3

$$\eta_{inj} = \frac{J_{H_2O}}{J_{Na_2S/Na_2SO_3}}$$

Eq. S4

J_{Na_2S/Na_2SO_3} and J_{H_2O} are the photocurrent densities measured with aqueous (0.25 M Na_2S/0.35 M Na_2SO_3, pH=12.9) and with aqueous (KOH/0.35 M Na_2SO_3, pH=12.9), respectively (**Figure S7**).

Supplemental Figures

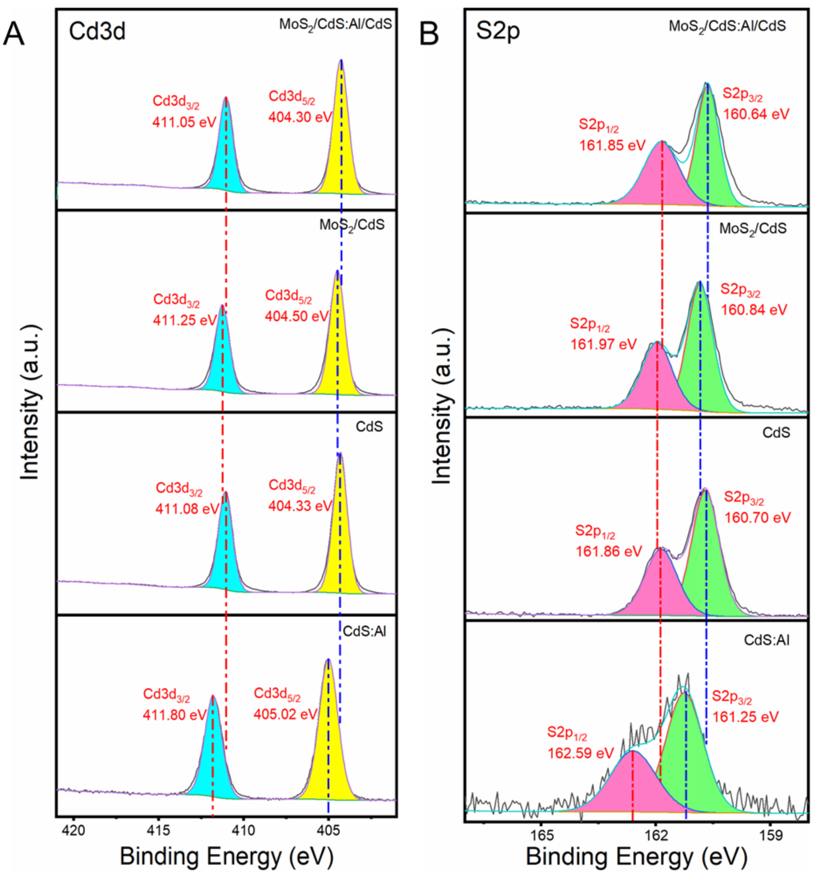

Figure S1. XPS Binding energy of Cd and S in different composition. (A) Cd3d (B) S2p

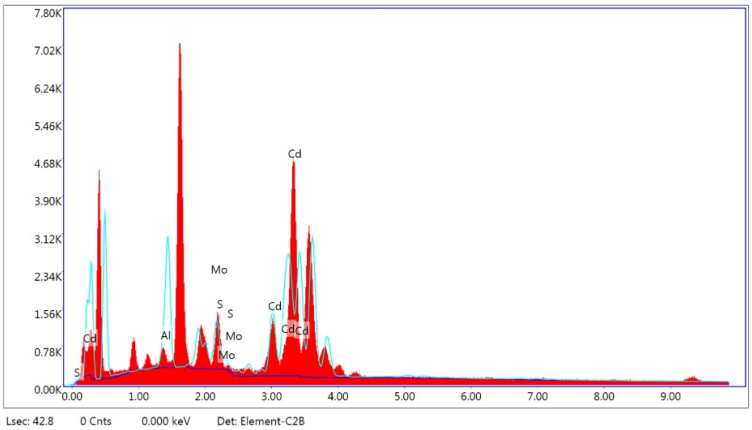

Figure S2. The elemental composition of MoS_2/CdS:Al/CdS electrode analyzed by EDS.

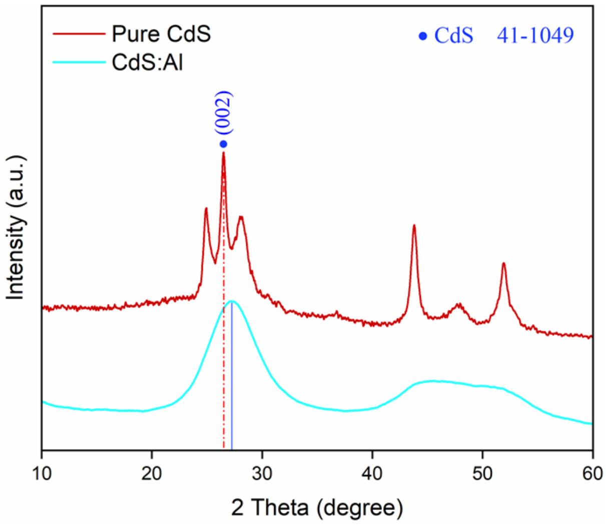

Figure S3. The PXRD patterns of the as-prepared of CdS:Al film.

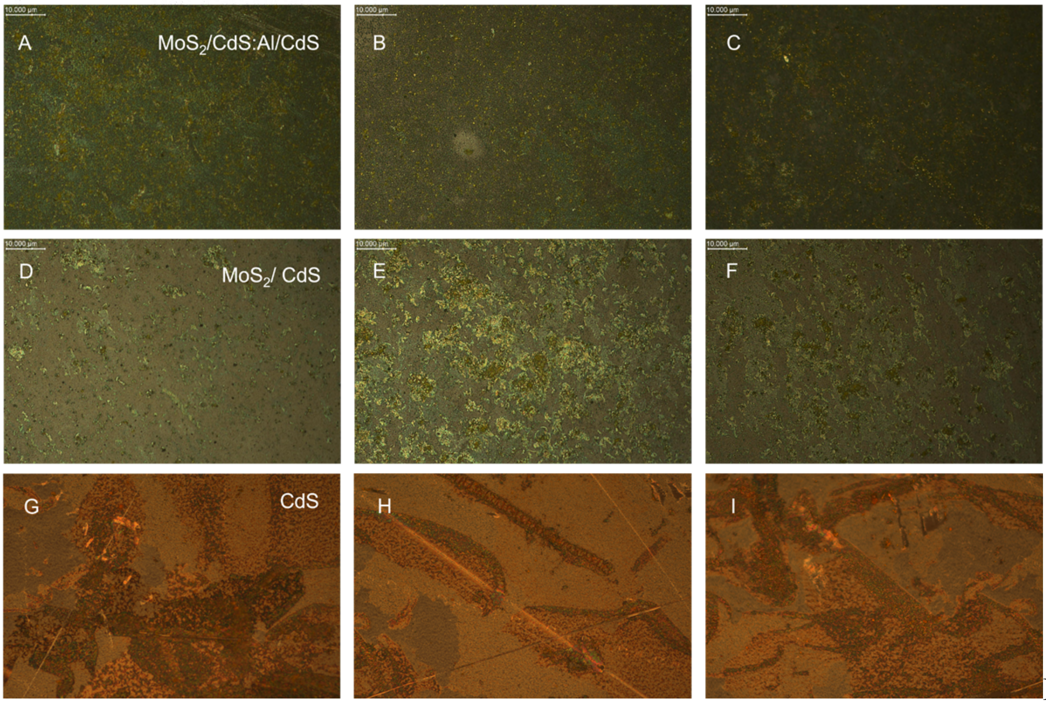

Figure S4. Optical microscope images of (A-C) MoS_2/CdS:Al/CdS films, (D-F) MoS_2/CdS films, (G-I) CdS films at 50 times magnification.

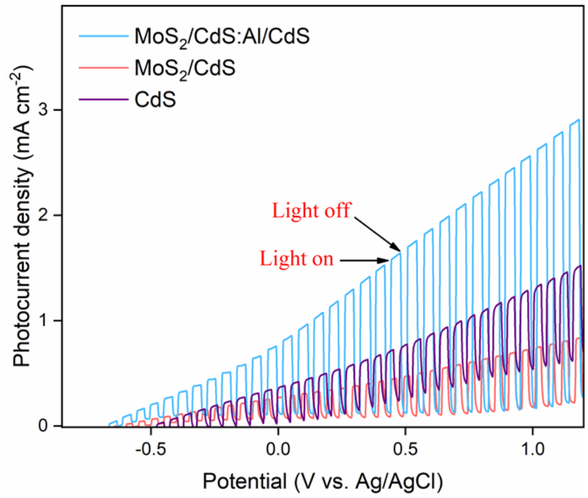

Figure S5. The LSV curves measured of CdS, MoS_2/CdS and MoS_2/CdS:Al/CdS with aqueous (KOH/Na_2SO_3) under chopped illumination.

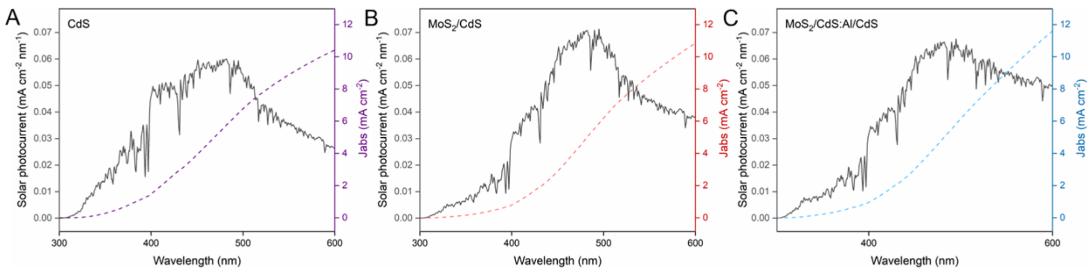

Figure S6. J_{abs} of (A) CdS; (B) MoS_2/CdS; (C) MoS_2/CdS:Al/CdS photoanodes (assuming 100% absorbed photo-to-current conversion efficiency for photons).

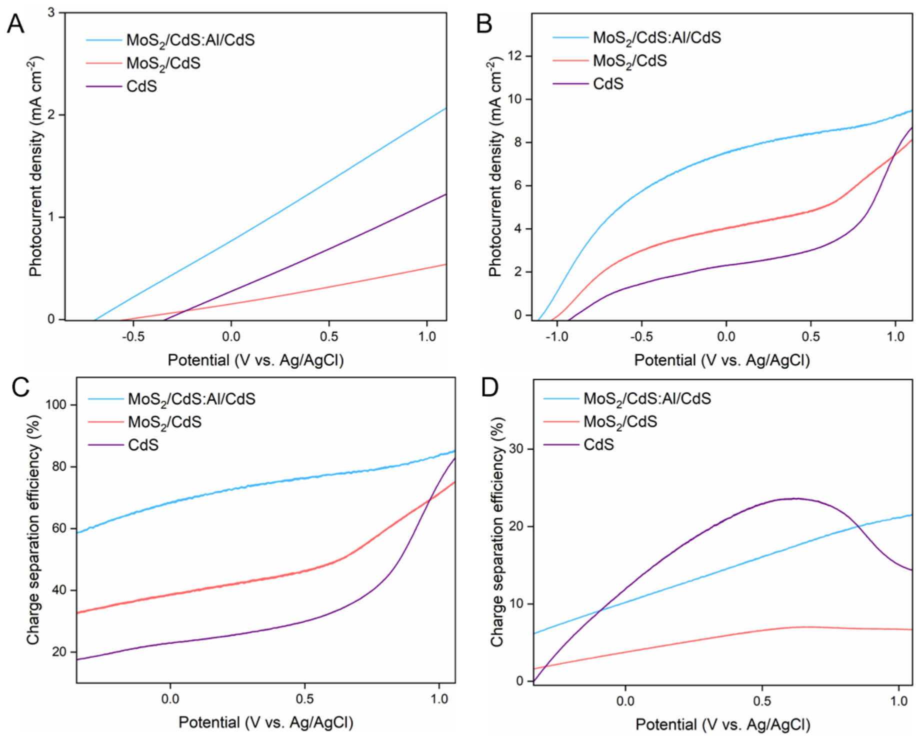

Figure S7. (A) LSV plots measured with aqueous (KOH/Na_2SO_3) and (B) LSV plots measured with aqueous (Na_2S/Na_2SO_3); (C) bulk charge separation efficiency (η_{sep}) and (D) Surface charge injection efficiency (η_{inj}) of the fabricated photoanodes.

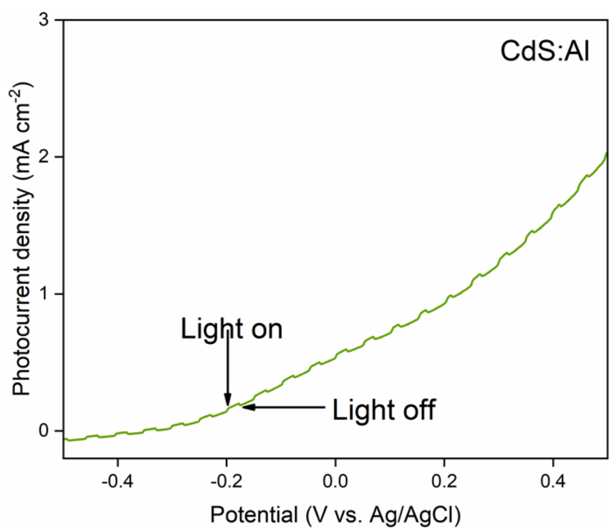

Figure S8. LSV test on CdS:Al film under chopped illumination.

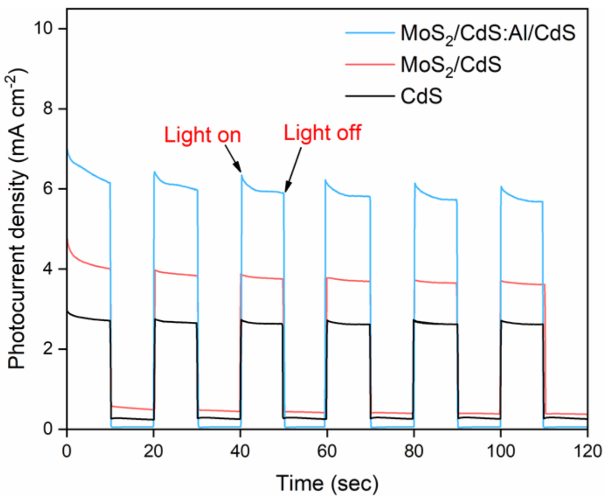

Figure S9. The I-T curves at a constant bias voltage (0.58 V vs. $V_{Ag/AgCl}$) of CdS, MoS_2/CdS and MoS_2/CdS:Al/CdS.

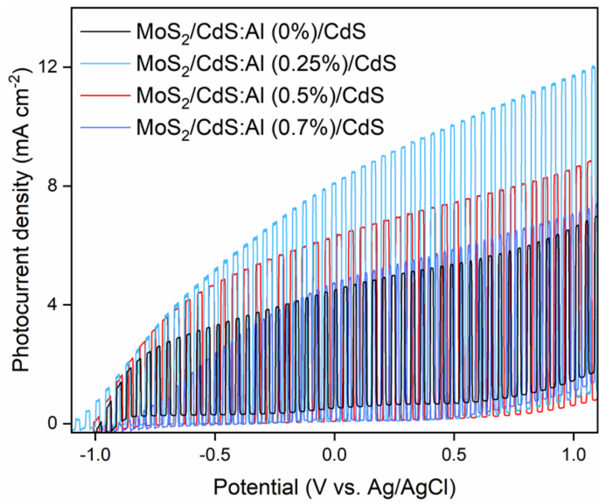

Figure S10. LSV under chopped illumination of the different atomic ratio of Al element in MoS_2/CdS:Al/CdS, all the samples were prepared using 20 SILAR cycles, the default SILAR cycles of the CdS layer and the atomic ratio of Al in CdS:Al layer of MoS_2/CdS:Al/CdS was set as 20 times and 0.25 at%, respectively.

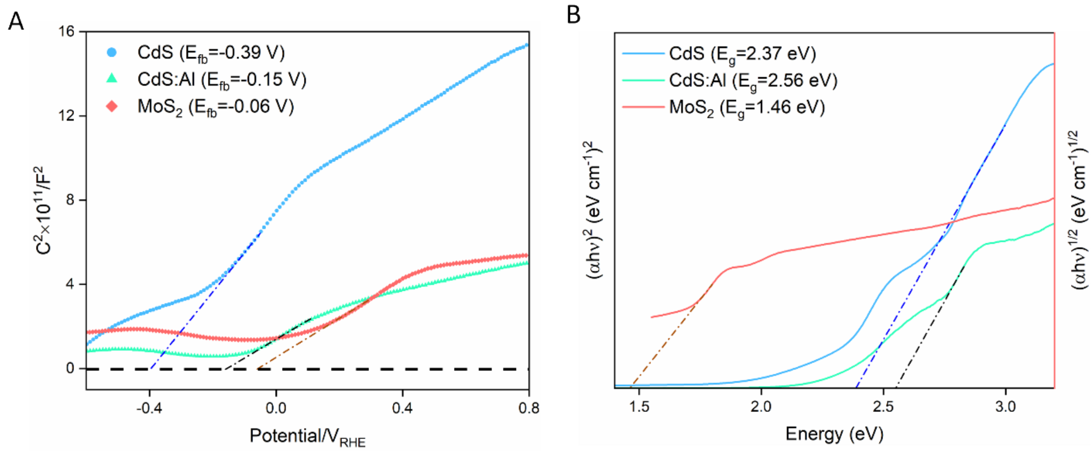

Figure S11. (A) Mott-Schottky plot of CdS, CdS:Al and MoS_2 in darkness; (B) The tauc-plot of CdS, CdS:Al and MoS_2.

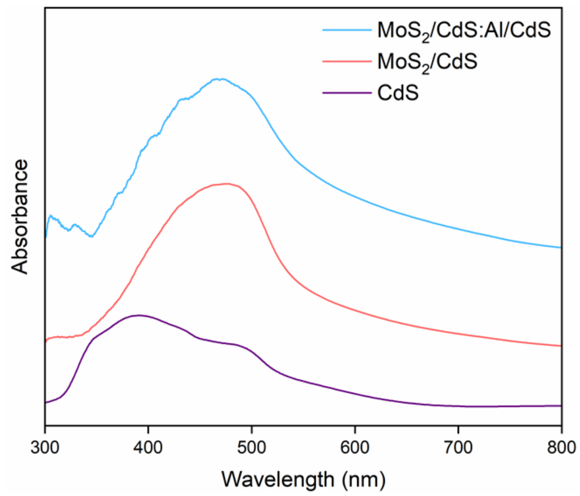

Figure S12. The absorbance spectra of MoS_2/CdS:Al/CdS film, MoS_2/CdS film and CdS film.

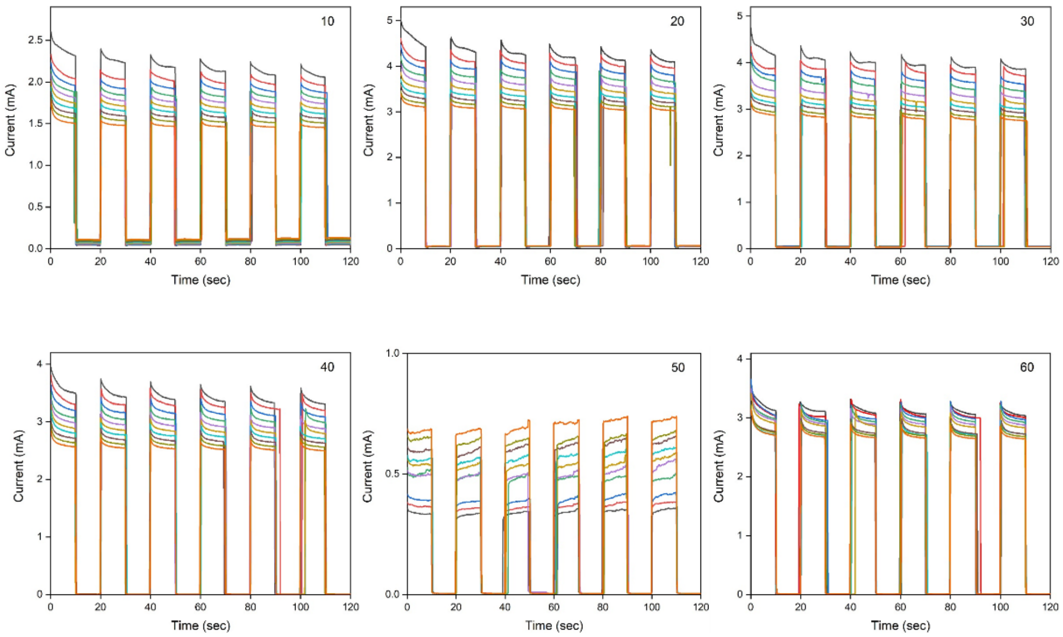

Figure S13. The chronoamperometry tests for 10-60 SILAR cycles over the MoS_2/CdS:Al/CdS samples.

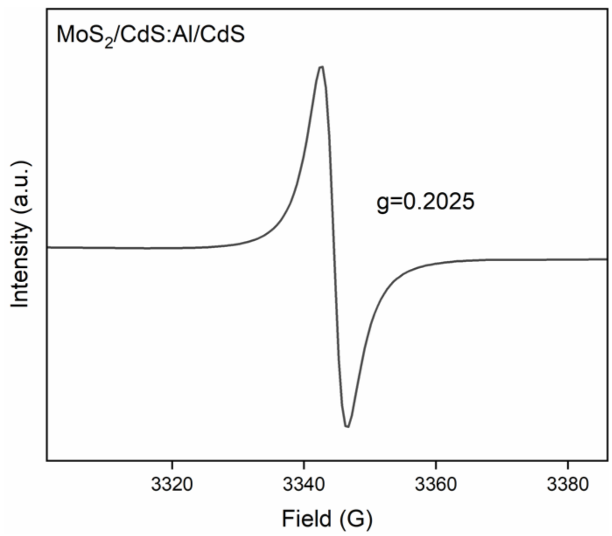

Figure S14. EPR spectra of MoS_2/CdS:Al/CdS after 5 min illumination.

Video S1. Hydrogen production video of MoS_2/CdS:Al/CdS films.

References

1. L. Li, H. Zhang, C. Liu, P. Liang, N. Mitsuzaki and Z. Chen, *Journal of Materials Science*, 2018, **54**, 659-670.
2. A. Kudo and Y. Miseki, *Chemical Society Reviews*, 2009, **38**, 253-278.