Electronic Supplementary Material (ESI) for EES Catalysis.

Effect of Charge Selective Contacts on the Quasi Fermi Level Splitting of $CuGa_3Se_5$ Thin Film Photocathodes for Hydrogen Evolution and Methylviologen Reduction

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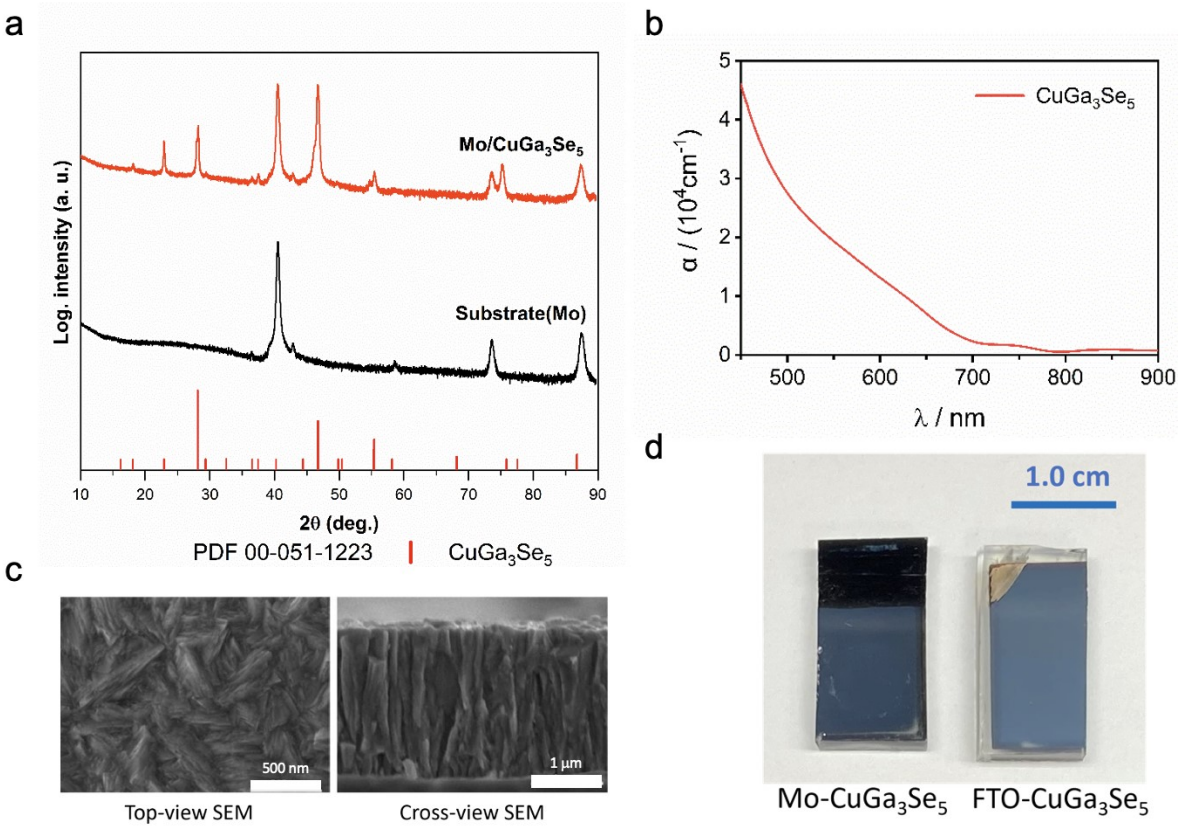

Figure S1. a) XRD pattern of CGSe film on Mo substrate. b) Optical absorption spectrum. c) SEM images of the Mo-CGSe electrode. d) Photograph of the two films on Mo and FTO.

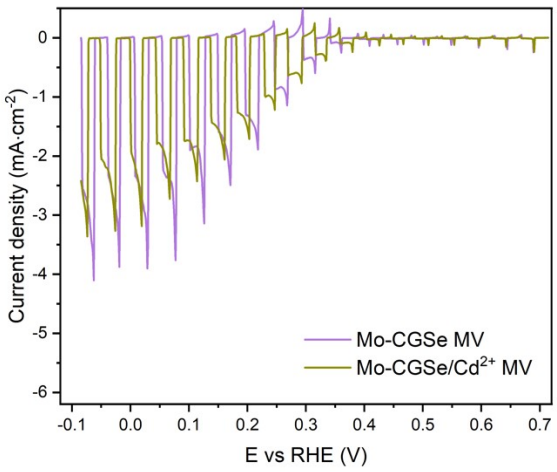

Figure S2. Linear sweep voltammetry (LSV) scans under chopped illumination (400 nm, 81 $mW \cdot cm^{-2}$) for Mo-CGSe MV junction before and after $Cd(OAc)_2$ treatment.

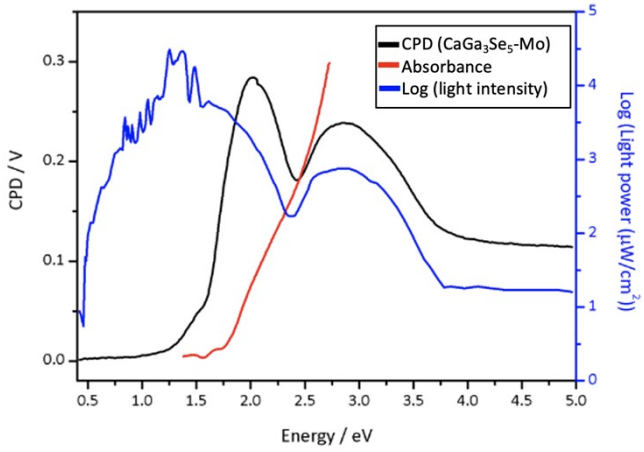

Figure S3. Overlay of the logarithmic irradiance with the optical absorbance and surface photovoltage spectrum of a CGSe film on Mo.

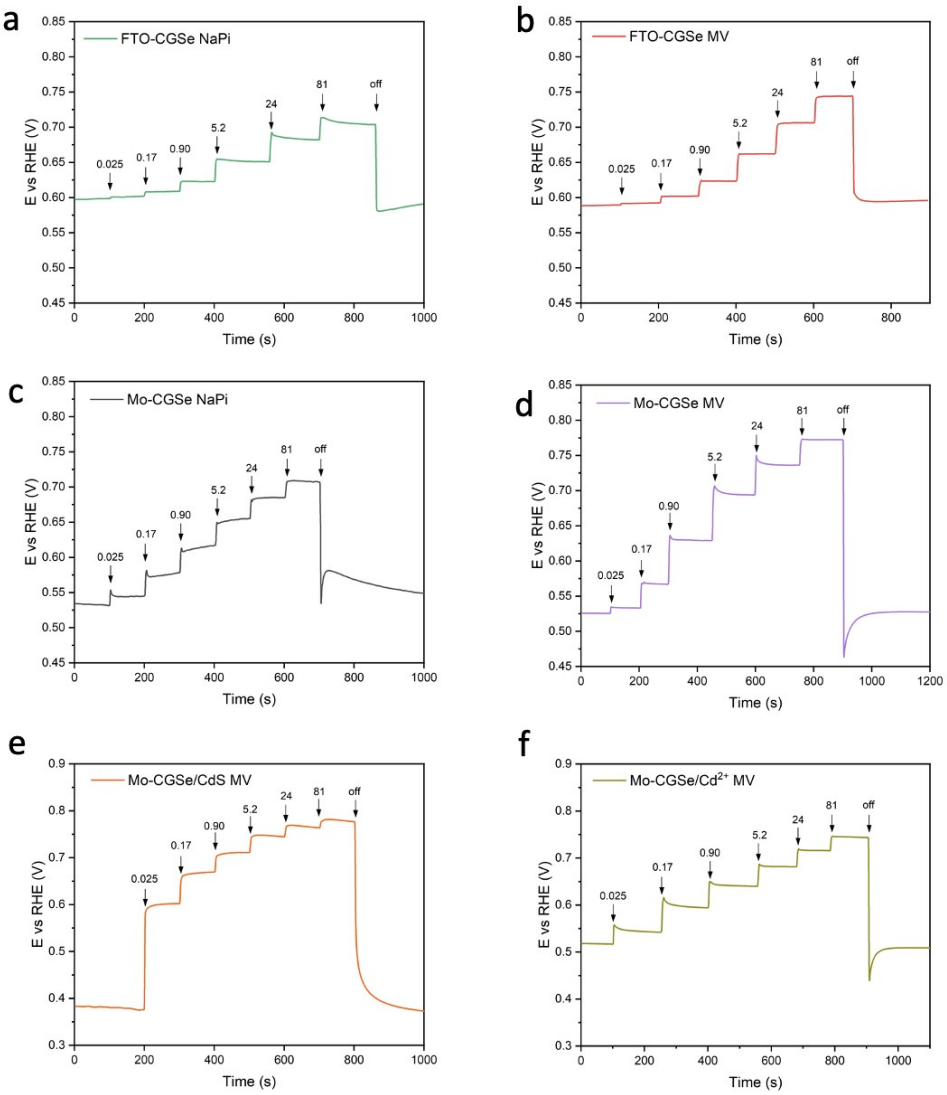

Figure S4. Open circuit potential (OCP) data in the dark and under 400 nm monochromatic illumination of variable intensity (irradiances given in $mW \cdot cm^{-2}$). (a) FTO-CGSe/NaPi. (b) FTO-CGSe/MV c) Mo-CGSe/NaPi. d) Mo-CGSe/MV. e) Mo-CGSe/CdS/MV. f) Mo-CGSe/Cd^{2+}/MV. Electrolytes were de-aerated by continuous N_2 bubbling.

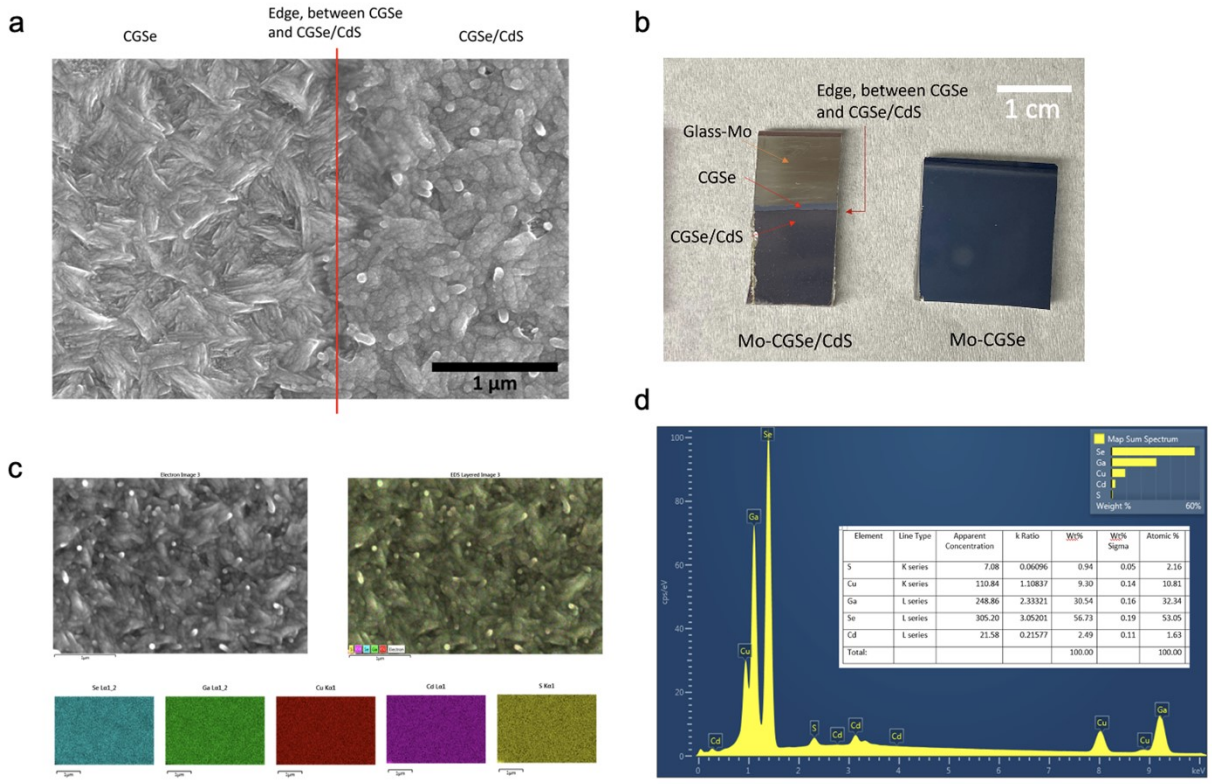

Figure S5. (a) Top-view SEM image of the Mo-CGSe/CdS electrode, showing the region where the left part is the CGSe surface and the right part is the CGSe/CdS surface. This corresponds to the border marked in the photograph, and is the result from masking half of the sample with scotch tape. (b) Photograph of the Mo-CGSe/CdS and the Mo-CGSe electrodes. (c)(d) EDS mapping, elemental spectrum and quantification results of the Mo-CGSe/CdS surface.

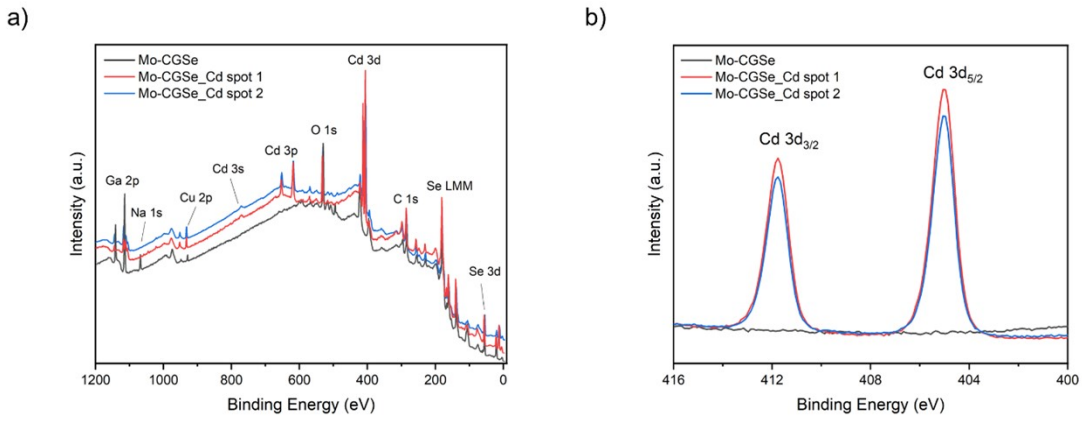

Figure S6. XPS data of Mo-CGSe and Mo-CGSe/Cd^{2+}. (a) Survey spectrum. (b) Cd 3d region.