## **Supporting Information**

## Revealing Electronic Structure, Heterojunction Band Offset and Alignment of Cu<sub>2</sub>ZnGeSe<sub>4</sub>: A Combined Experimental and Computational Study toward Photovoltaic Applications

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**Figure S1:** The EDS spectra and the elemental mapping suggest even distribution of chemical constituents in CZGSe thin film.



**Figure S2:** (a, b) SEM images of CZGSe thin film. 2-D (c) and 3-D AFM (d) images CZGSe thin film.



**Table S1:** Calculated effective masses of holes  $\binom{m_h^*}{n}$  and electrons  $\binom{m_e^*}{n}$  along the high-symmetry directions of the Brillouin zone of CZGSe.

Direction	$m_{h}^{*}(m_{e})$	$m_{e}^{*}(m_{e})$
Ζ-Γ	0.0036	0.0057
Г–Х	0.0109	0.0099
Х-М	0.0525	0.0083
М-Г	0.0432	0.00342