Supporting Information

A New Insight of Li-Doped $Cu_2ZnSn(S,Se)_4$ Thin Films: Li-Induced Na Diffusion from Soda Lime Glass by a Cation-Exchange Reaction

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Characterizations:

The thickness of the thin film was measured by a step profiler (AMBIOS, XP-100). The X-ray diffraction (XRD) patterns were taken with a Bruker D8 X-ray diffractometer. The scanning electron microscope (SEM) images were collected using a Hitachi S-4800. The energy dispersive X-ray spectrometry (EDS) was characterized by Bruker AXS XFlash detector 4010 built on the Hitachi S-4800 (20 keV of incident electron beam energy and ~1.0 μm of the sampled depth). Chemical compositions were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) (ICP-PLASMA 1000). X-ray photoelectron spectra (XPS) were measured with VGESCALAB (VG Co., U.K.) by using Al Kα X-ray source (hν=1486 eV), and the binding energy was calibrated by the C1s (284.6 eV). Photocurrent density-voltage curves were recorded under the standard AM1.5 illumination (100 $mW \cdot cm^{-2}$) with a Keithley 2400 source meter. *C-V* curves were measured with Agilent E4890A under dark condition. Note that the frequency of 1000 Hz and ac amplitude of 50 mV were applied for *C-V* measurement. The external quantum efficiency (EQE) spectra were measured by a Zolix SCS100 QE system.

Table S1. The chemical compositions of the selenized CZTSSe thin films by ICP-MS measurement. [a]Li/Cu ratio is a target ratio in the precursor solution.

Li/Cu[a]	Zn/Sn	S/(S+Se)	Cu/(Zn+Sn)
0	1.27	0.080	0.684
0.05	1.24	0.086	0.713
0.10	1.24	0.085	0.701
0.12	1.29	0.075	0.67
0.24	1.24	0.080	0.687
0.36	1.25	0.081	0.67
0.48	1.25	0.083	0.678

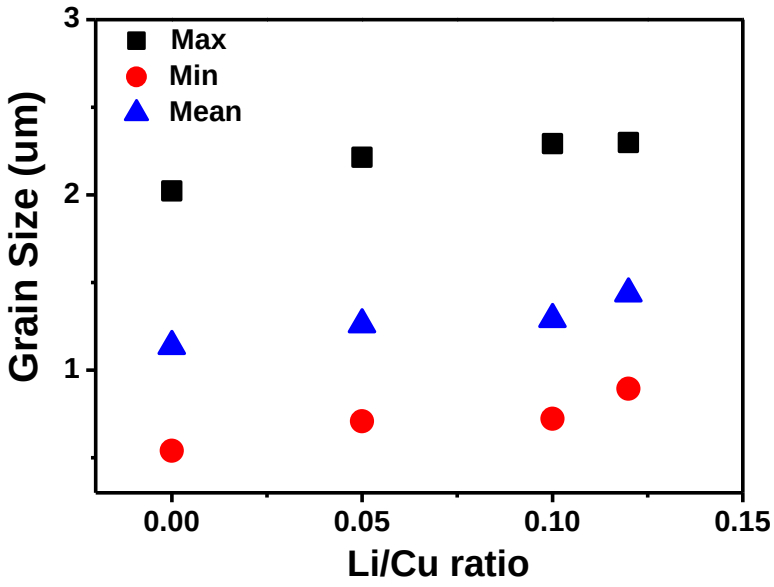

Figure S1. The grain sizes of Li-doped CZTSSe thin films with the different Li/Cu ratios in the precursor solutions.

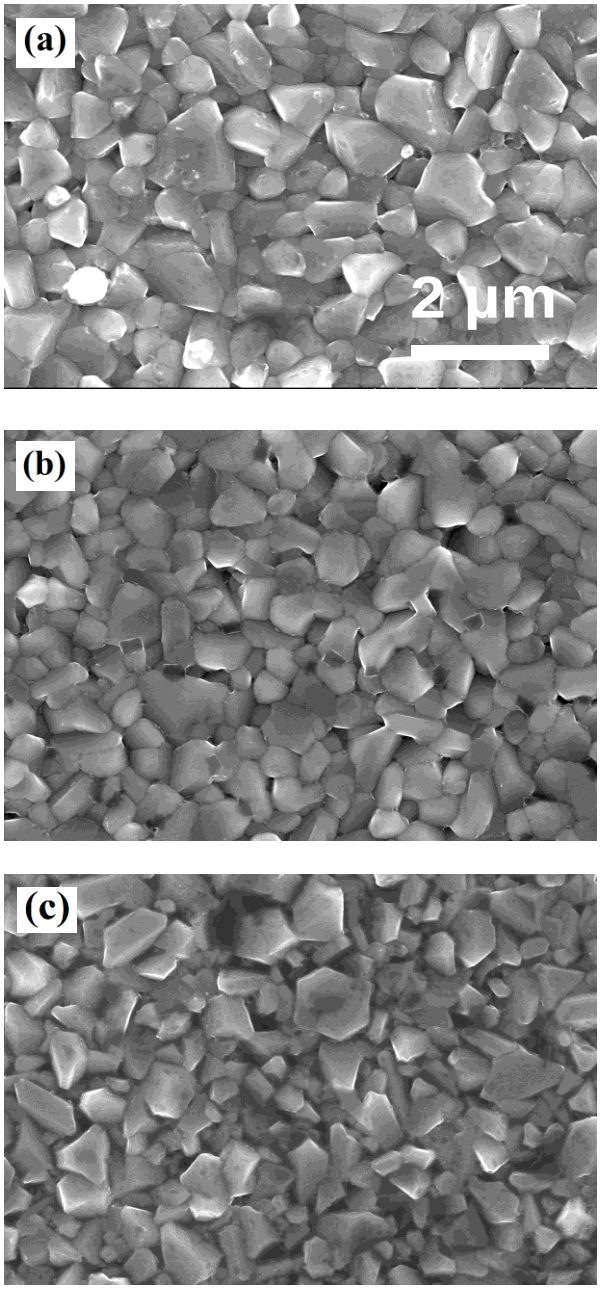

Figure S2. Top-view SEM images of Li-doped CZTSSe thin films deposited on the SLG substrate with different molar ratios of Li/Cu in the precursor solutions. (a) 0.24; (b) 0.36; (c) 0.48.

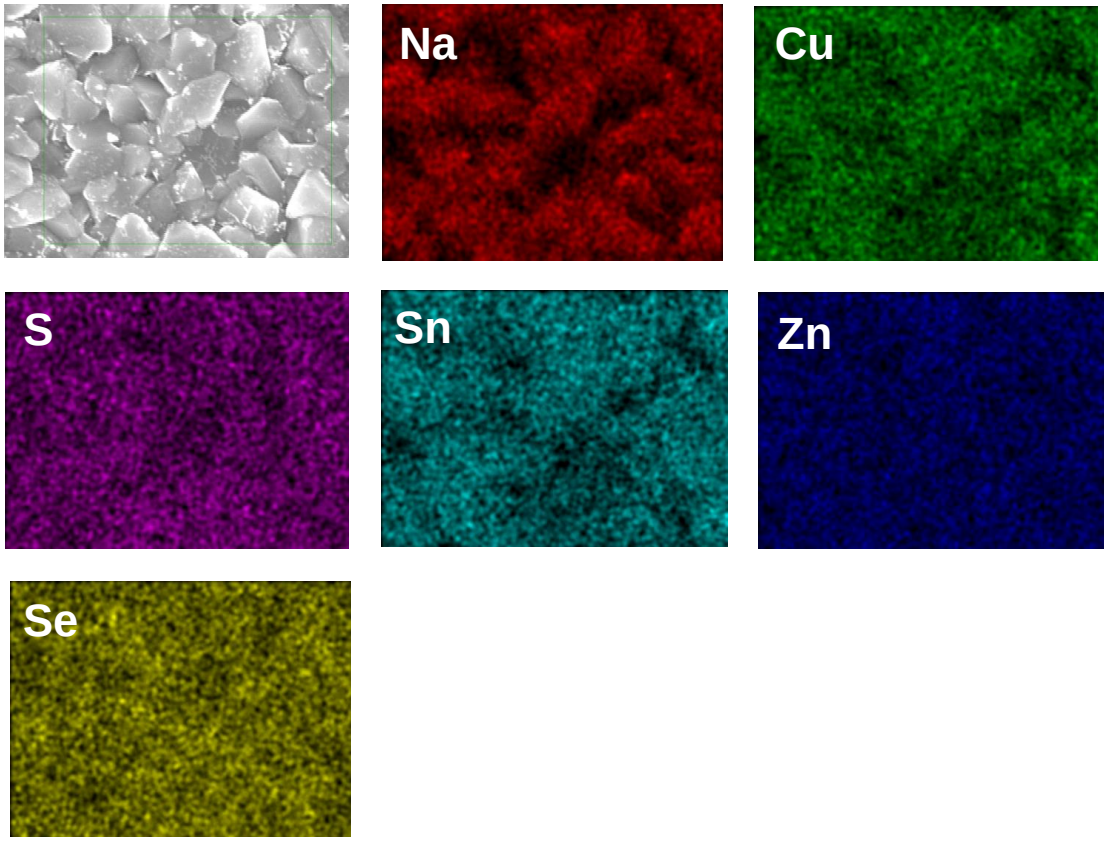

Figure S3. EDS elemental mapping images of the selenized CZTSSe thin film with a Li/Cu ratio of 0.24 in the precursor solution.

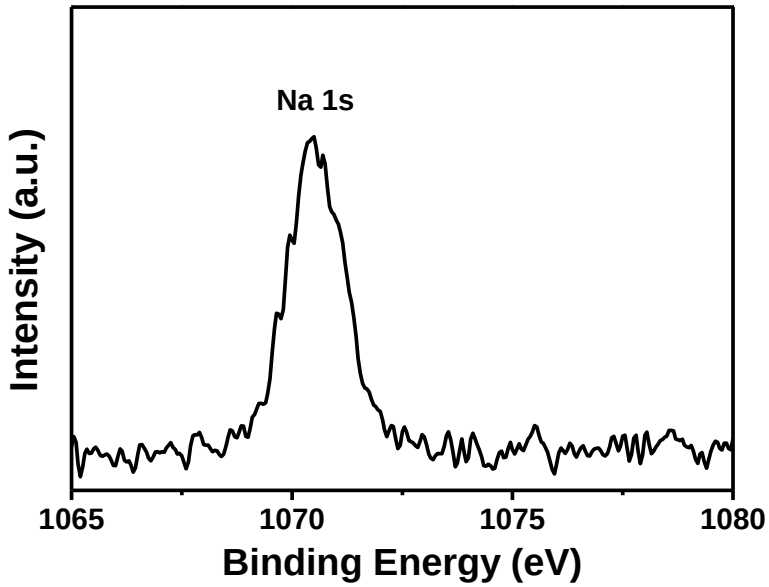

Figure S4. XPS spectrum of Na on the surface of the Li-doped CZTSSe thin film.

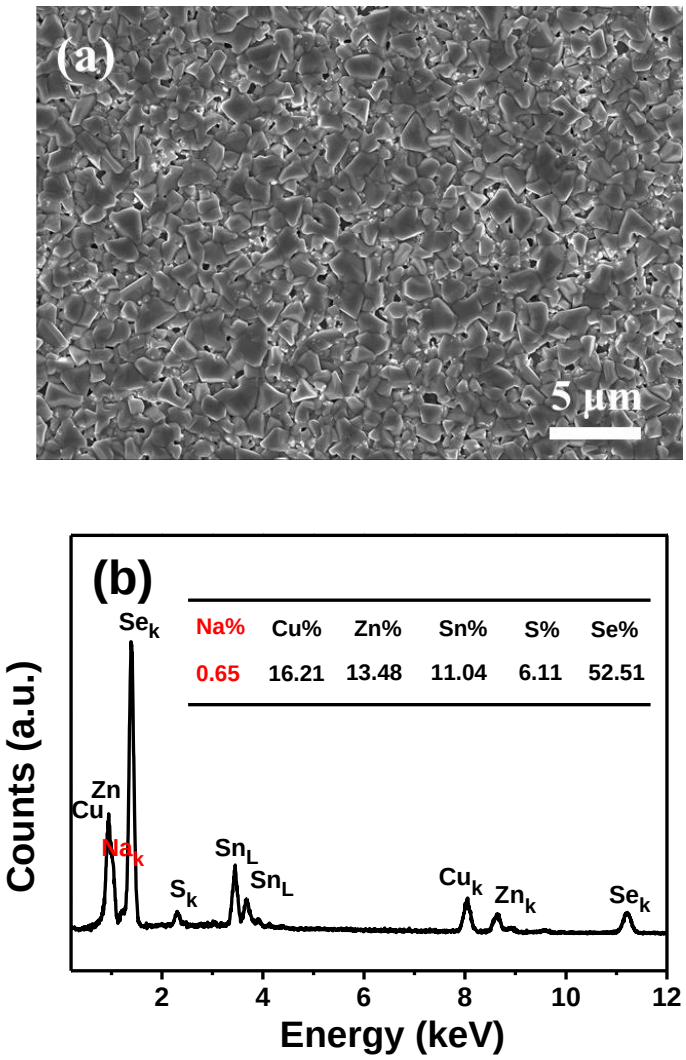

Figure S5. The top-view SEM image (a) and EDS spectrum (b) of the selenized Li-doped CZTSSe thin film after washing.

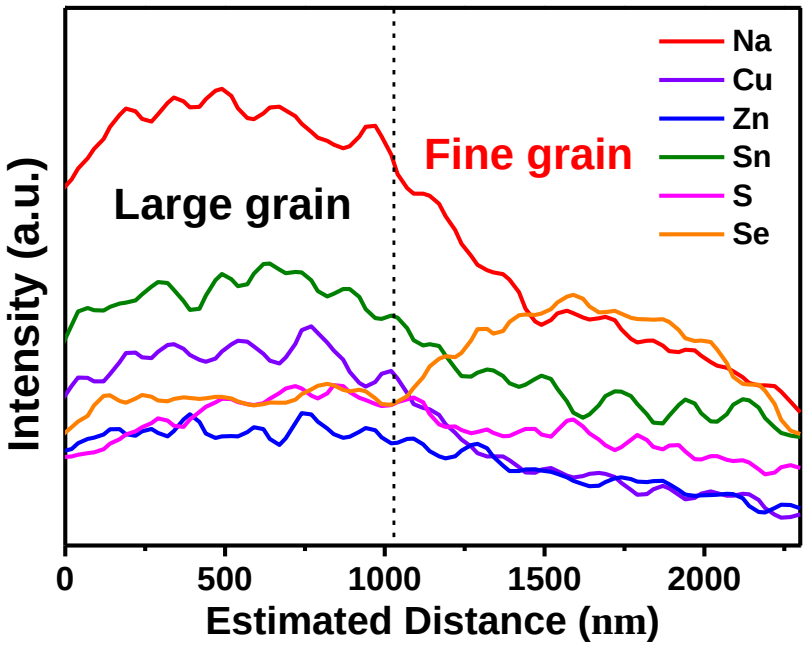

Figure S6. EDS scan lines of the selenized CZTSSe thin film with a Li/Cu ratio of 0.24 in the precursor solution.

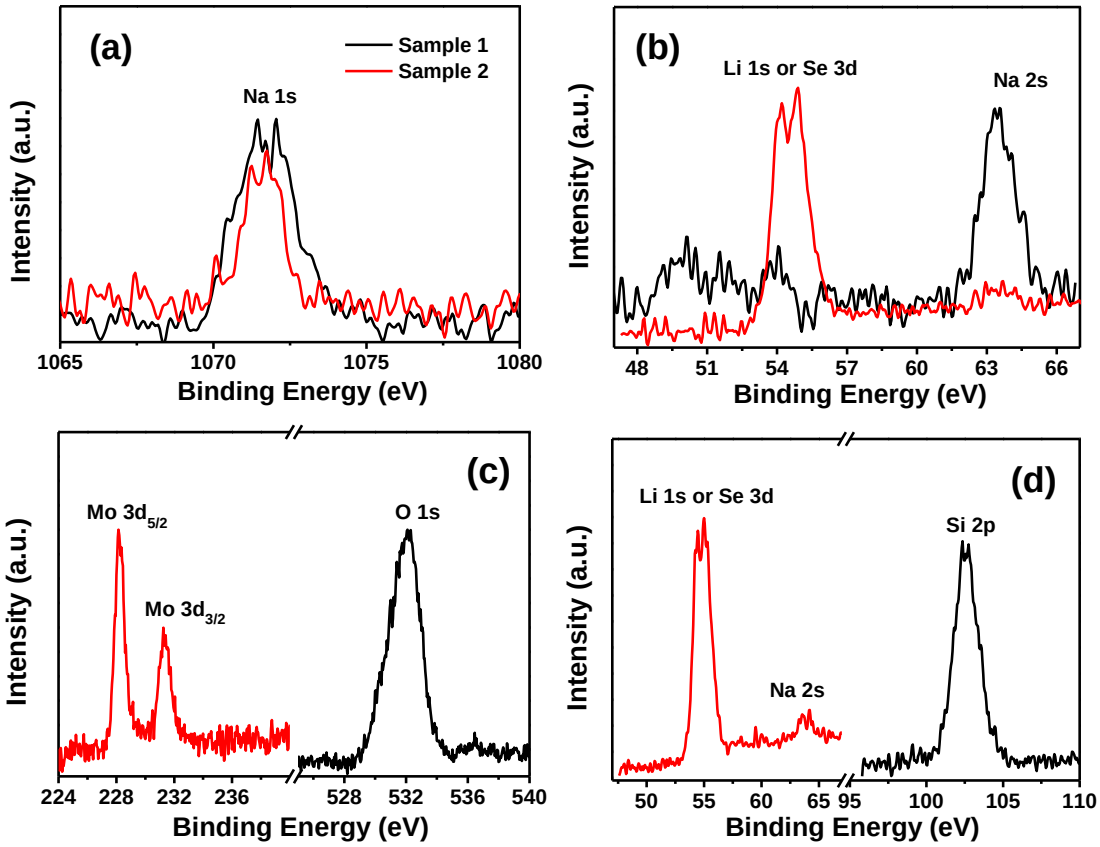

Figure S7. XPS spectra of SLG (sample 1) and Mo/SLG (sample 2) layers after peeling off Mo electrode and Li-doped CZTSSe thin film. (a) Na 1s; (b) Li 1s and Se 3d; (c) Mo 3d and O1s; (d) Li 1s, Se 3d and Si 2p.

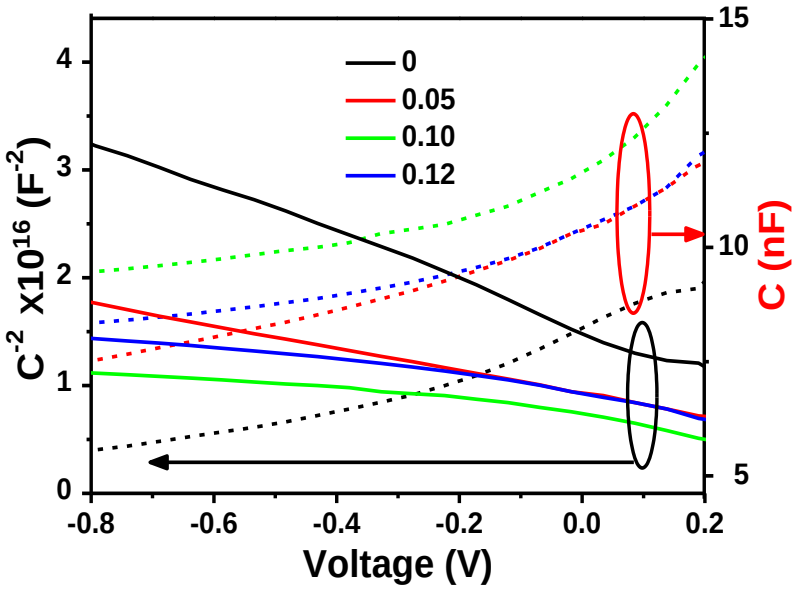

Figure S8. *C-V* and C^{-2}-*V* curves of the selenized CZTSSe solar cells with the different Li/Cu ratios in the precursor solutions.