Supplementary Information For

Selective Removal of $Cu_{2-x}(S,Se)$ Phases from $Cu_2ZnSn(S,Se)_4$ Thin Films

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Raman Scattering Characterization

The Raman scattering map for CZTS (338 cm^{-1}) in Figure 4(b) of the text shows a uniform distribution of CZTS. In this figure, some regions appear darker than others because of surface roughness. The dark spots in this image correspond to depressions and protrusions on the surface below and above the confocal plan as well as cracks and voids. The CZTS Raman scattering map morphology matches well the morphology revealed by the FE-SEM image shown in Fig. 2(a) of the main text. The Raman scattering map for CZTS (338 cm^{-1}) shown in Fig. 4(d) does not change significantly after etching but the Raman scattering from CuS at 475 cm^{-1} shown in Fig .4(c)) disappears after etching, suggesting removal of the $Cu_{2-x}S$ phases by the 2-mercaptoethanol and ethylenediamine solution. Careful examination of the individual spectra show that randomly scattered orange spots in Fig. 4(c) are within the noise and do not necessarily correspond to presence of $Cu_{2-x}S$. To illustrate this, Fig. S1(a) shows Raman spectra collected from both the dark and bright regions of Fig.4(c). Similarly, careful examination of the individual spectra used to form Figure 6(c) show that randomly scattered orange spots in Fig. 6(c) are within the noise and do not necessarily correspond to presence of $Cu_{2-x}Se$. Fig. S1(b) shows Raman spectra collected from both the dark and bright regions of Fig.6(c) to illustrate that even the bright appearing regions do not show $Cu_{2-x}Se$ peaks and the scattering is within the noise.

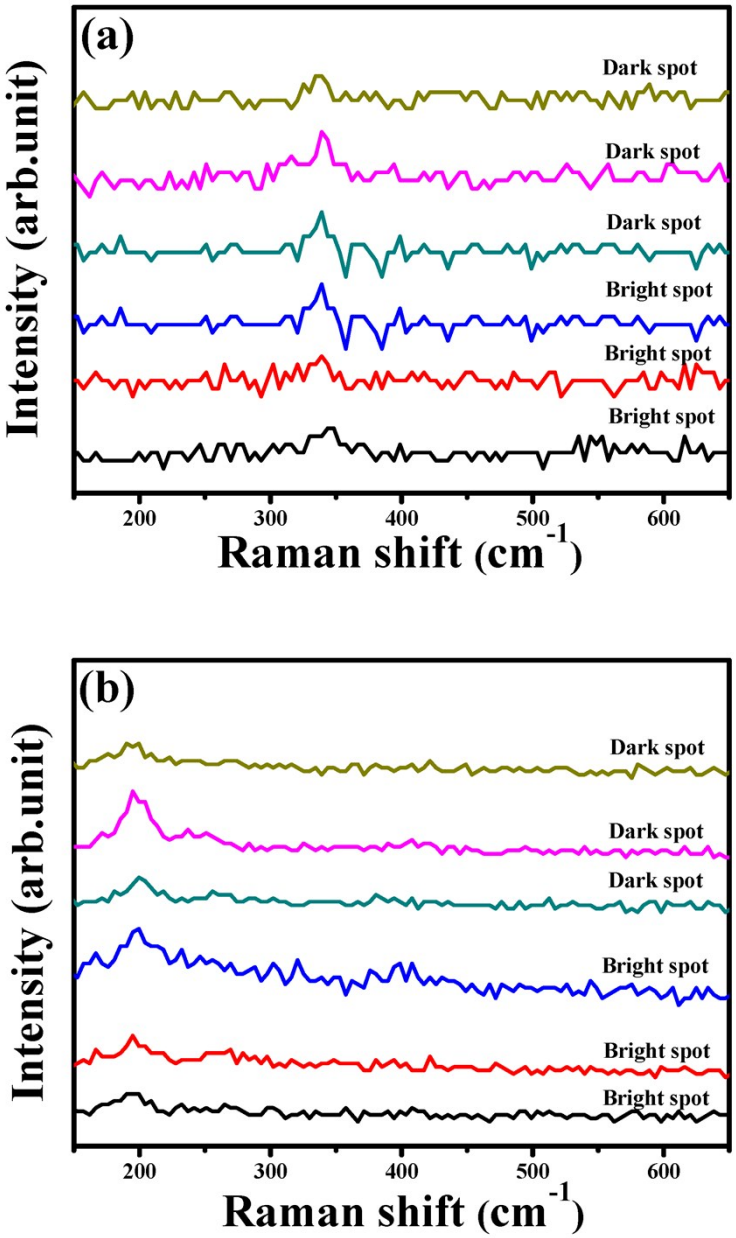

Fig. S1. Raman spectra in (a) are the collected from the dark and bright regions of Fig.4(c) which shows the Raman scattering image from CZTS films after etching. Raman spectra in (b) are the collected from the dark and bright regions of Fig. 6(c), which shows the Raman scattering from CZTSe films after etching. No Raman scattering from $Cu_{2-x}S$ and $Cu_{2-x}Se$ are observed after etching the CZTS and CZTSe films, which contained $Cu_{2-x}S$ and $Cu_{2-x}Se$ impurity phases, respectively.

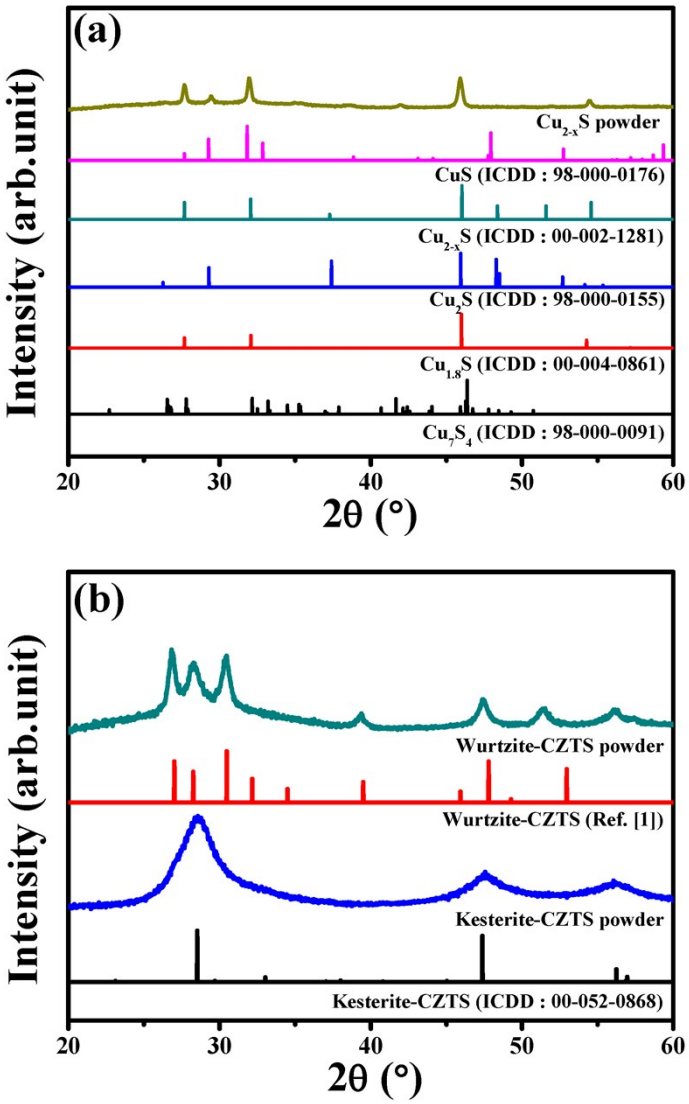

Fig. S2. X-ray diffraction patterns for $Cu_{2-x}S$ (a), kesterite-CZTS and wurtzite-CZTS NCs (b) prepared by microwave assisted solvothermal process. X-ray diffraction patterns were collected from nanocrystals drop cast and dried on a glass substrate from aqueous dispersions at room temperature. The diffraction pattern for Fig. S1 (a) matches the $Cu_{2-x}S$ compounds (CuS; ICDD-Ref.: 98-000-0091, $Cu_{2-x}S$; ICDD-Ref.: 00-002-1281, Cu_2S; ICDD-Ref.: 98-000-0155, $Cu_{1.8}S$; ICDD-Ref.:00-004-0861, and Cu_7S_4; ICDD-Ref.: 98-000-0091). However, the diffraction patterns for Fig. S2 (b) are consistent with the kesterite-(JCPDS No.: 26-0575) and wurtzite-CZTS phases.[1]

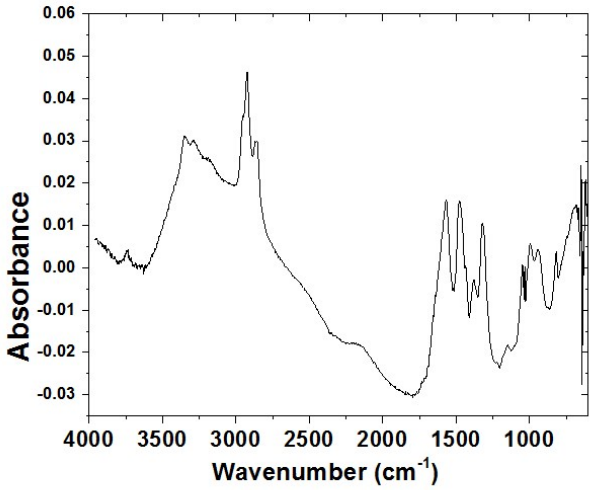

Fig. S3. Attenuated total reflection Fourier transform infrared spectrum of a film after etching in the etchant solution but before rinsing in deionized water. The absorption bands correspond to those of mercaptoethanol and ethylenediamine.

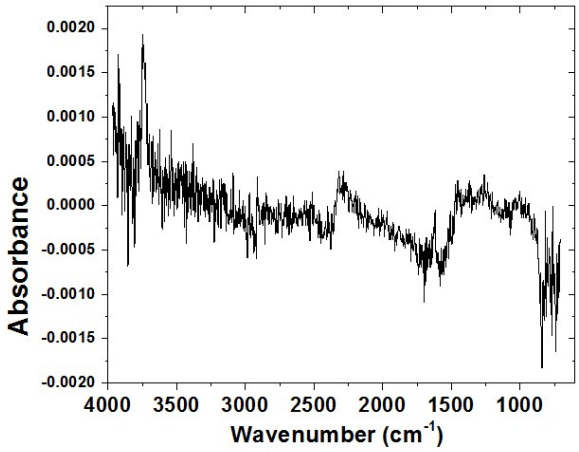

Fig. S4. Attenuated total reflection Fourier transform infrared spectrum of a film after etching in the etchant solution and after rinsing in deionized water. All infrared absorptions due to mercaptoethanol and ethylenediamine are eliminated after rinsing: the infrared absorption is at the noise level of our instrument. Same number of spectra (100) were averaged in spectra shown in Figures S3 and S4 and all other acquisition parameters were the same.

References

[1] Z. Li, A. L. K. Lui, K. H. Lam, L. Xi and Y. M. Lam, *Inorg. Chem.*, 2014, **53**, 10874-10880.