Supporting Information

The Effects of SnS_2 Secondary Phases on Cu_2ZnSnS_4 Thin Film Solar Cells：A Promising Mechanical Exfoliation Method for Its Removal

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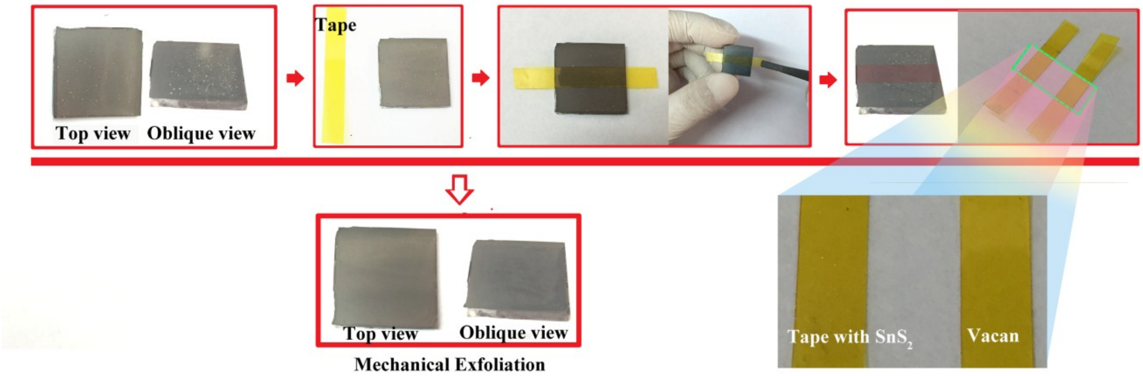
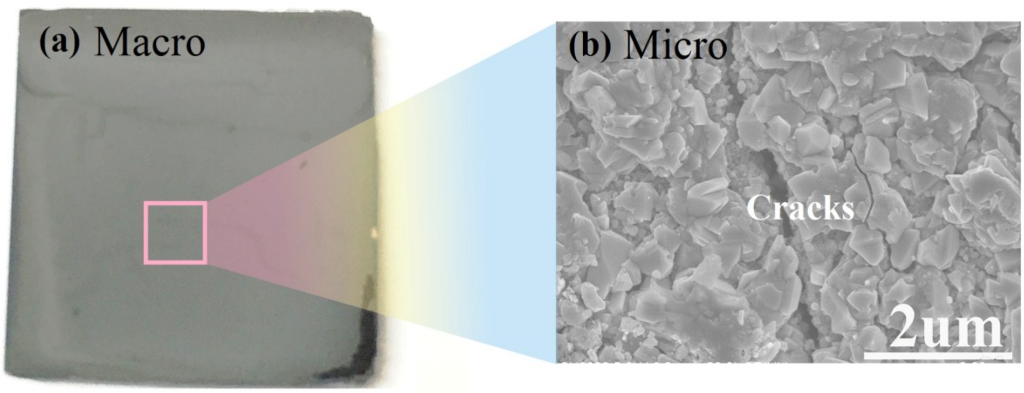


S1

Figure S1. shows the operating flow chart of mechanical exfoliation. A sticky tape was applied as an tool for the removal of SnS_2, it was slightly pasted on the front of absorber layer, then tear off the tape from one end. It was found that the glistening objects exist on the surface of the films were removed to the surface of the tape. Finally, the SnS_2 can be practically removed by repeating those steps mention above for several times.



S2

Figure S2. The (a) Photographic images and (b) SEM morphology of CZTS film that obtained by rapid cooling. The sample was annealed at 580 °C for 30 minutes and the heating rate is 48 °C /min. When the annealing process was finished, the temperature was dropping from 580 °C to room temperature by transferring the sample to the air (the sample was sealed up with a quartz tube during the whole annealing process). From analysis we can easily find that there are several apparently cracks on the surface. Besides, small cracks even exist in regions that seemed in good condition..

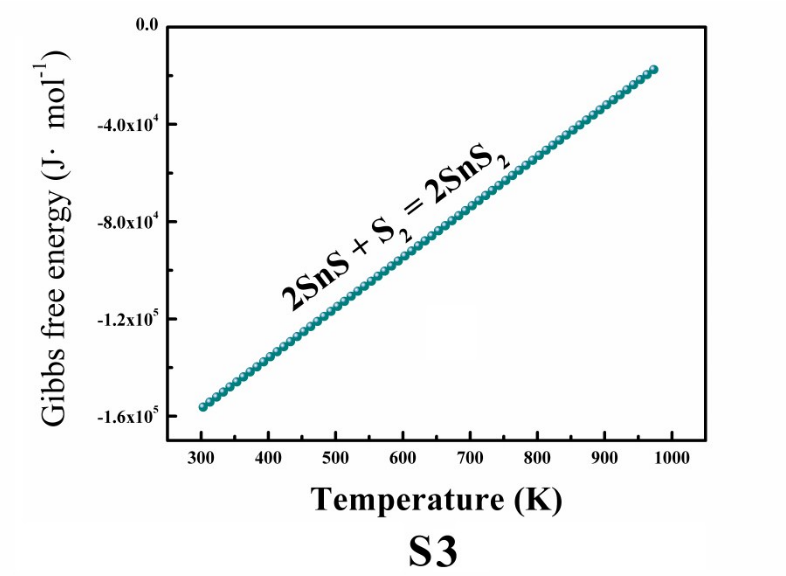
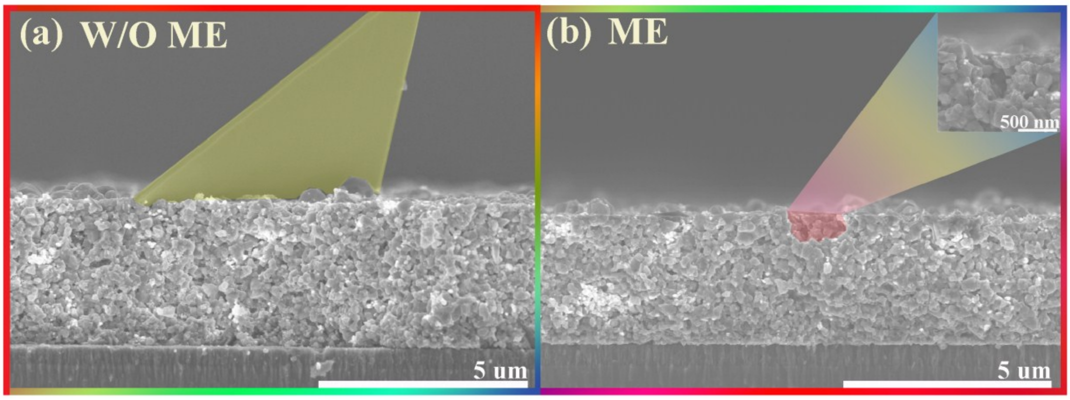
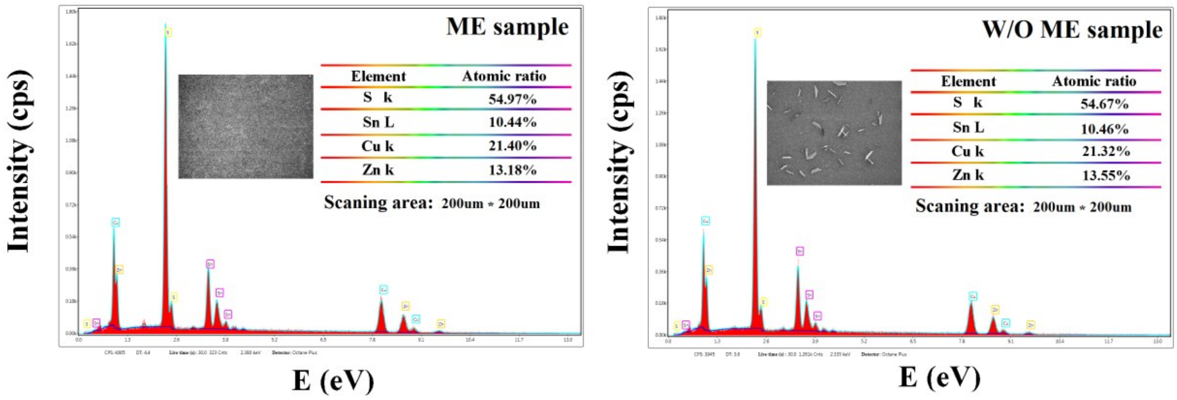


Figure S3. The gibbs free energy of the formation of SnS_2 that is dedrived from both SnS and S_2 has linear increase relation with the temperature [1]. Instreastingly, the gibbs free energy value of the reaction is remain negative in the range of 300 K to 900 K, which suggest that the formation of SnS_2 is spontaneous.



S4

Figure S4. The cross sectional images of (a) W/O ME sample and (b) ME sample. The size of the sheet-like SnS_2 is beyond 5um, which is larger than the thickness of the CZTS film. The bottom of the sheet was inserted into the surface of CZTS film slightly. When SnS_2 was removed away from the CZTS film, a shallow trenches was left on the CZTS films, which indicated that mechanical exfoliation can remove SnS_2 effectively.



S5

Figure S5. The Energy Dispersive X-Ray Spectroscopy of ME sample and W/O ME sample were detected by introducing EDX measurement, which is used for analyzing the composition ratio of ME sample and W/O ME sample. The scanning area is square region with side length value of 200 μm, the excitation voltage is 20 KeV.

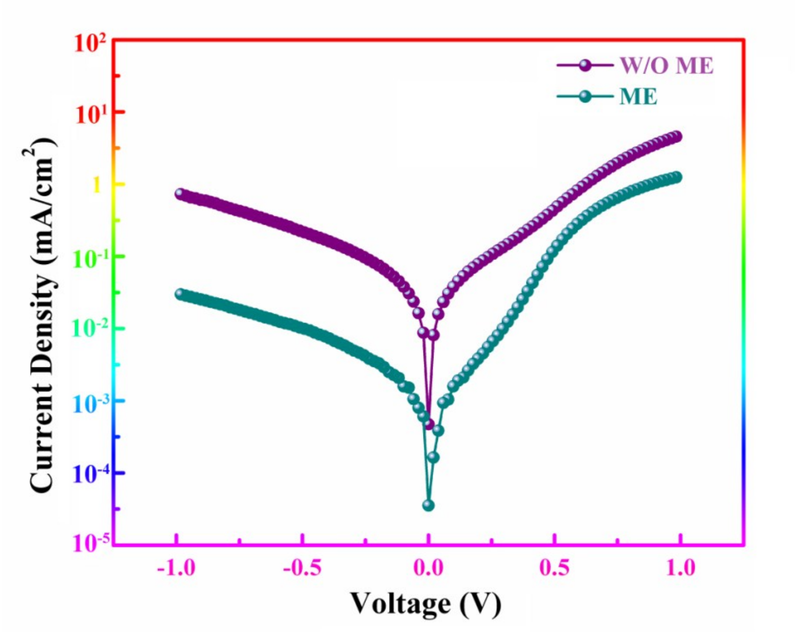
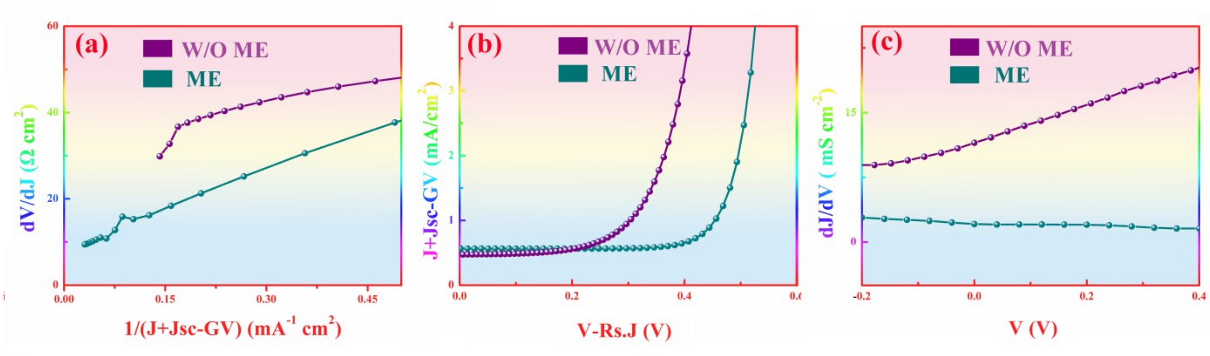


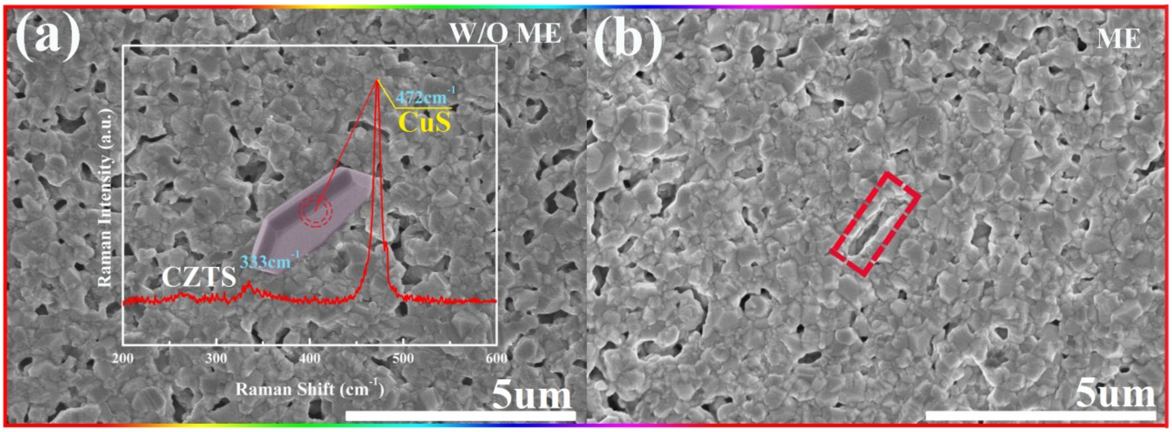
Fig. 6

Figure S6. Current density-voltage curves of the devices before and after the treatment of mechanical exfoliation under darkness, which is calculated from J-V characteristics under a dark dondition by Shockley diode equation: $J = J_0[\exp\left(\frac{qV}{AkT}\right) - 1]$.



S7

Figure S7. (a) dV/dJ against 1/(J+J_{sc}-G_{sh}V) plots, where R_s and n were extracted from the y-intercep and the slop respectively, (b) (J+Jsc-G_{sh}V) versus (V-R_sJ) plots for determination of n and J_0, (c) dJ/dV versus V curves, where G_{sh} was evaluated from the intercept value.



S8

Figure S8. (a) SEM images and Raman spectra of W/O ME Cu-rich CZTS films; (b) SEM images of Cu-rich CZTS films. The composition of such CZTS films is Cu/(Zn+Sn) = 1.1, Zn/Sn = 1.1.

References

[1] X. Yin, C. Tang, L. Sun, Z. Shen, H. Gong, Study on Phase Formation Mechanism of Non- and Near-Stoichiometric $Cu_2ZnSn(S,Se)_4$ Film Prepared by Selenization of Cu−Sn−Zn−S Precursors, Chem. Mater. 26 (2014) 2005-2014