

Supplementary Information

In-situ formed ternary-based hybrid ink to fabricate Cu₂ZnSn(S,Se)₄ solar cell absorbers

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Additional results

FT-IR spectra of pure PM, metal chloride-PM solution, and sulfur-PM solution

FT-IR analysis of pure PM, Cu-PM, Zn-PM, Cu/Sn-PM, and S-PM samples formed by dissolving copper (II), zinc (II), copper (II)/ tin (II), and powder sulfur in PM solvent are carried out (Fig. S1). The band at 733 cm⁻¹ in pure PM solution is assigned to C-S stretching vibration. Noted that comparing with the pure PM solution, an obviously wavenumber red shift of the C-S band is observed in all samples. These red shifts indicate that PM strongly interacts with metal ions and powder sulfur through sulfur atom site.

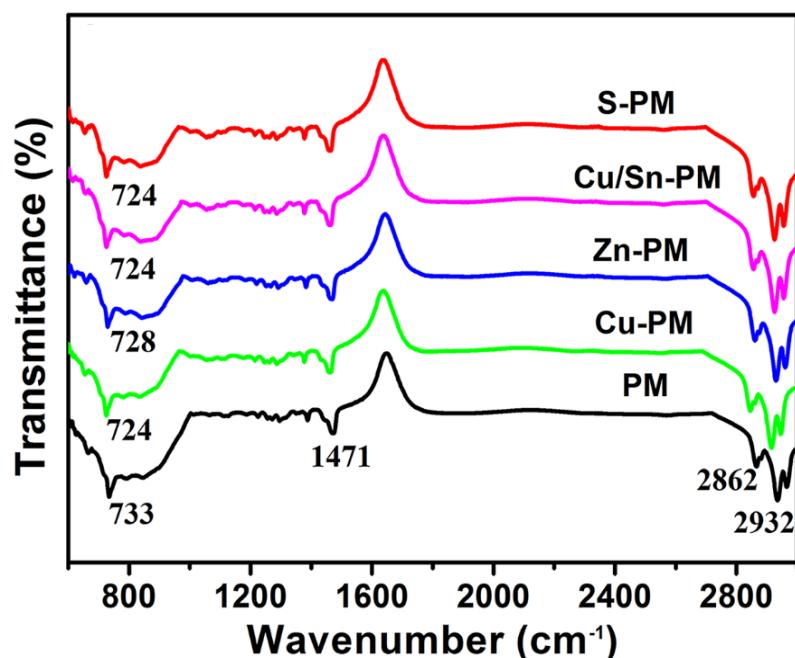


Fig. S1 FT-IR spectra of pure PM, Cu-PM, Zn-PM, Cu/Sn-PM, and S-PM solution.

The schematic diagram of the detailed experiment.

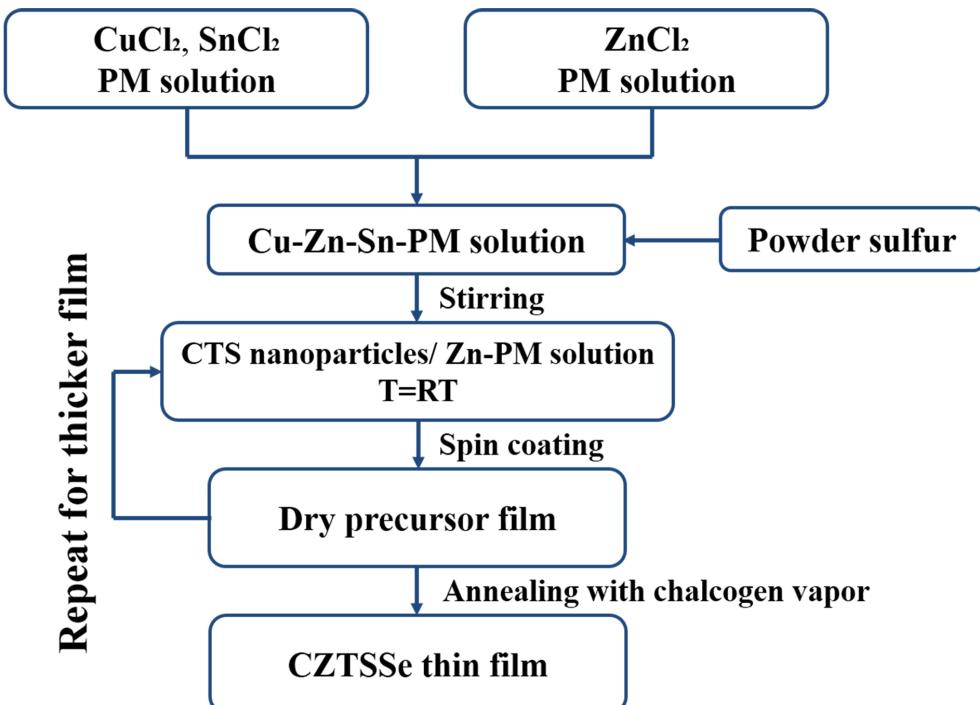


Fig. S2 Schematic diagram of the hybrid-ink spin-coating process for CZTSSe thin films.

XRD pattern of Cu₂ZnSn(S,Se)₄ precursor films before annealing treatment

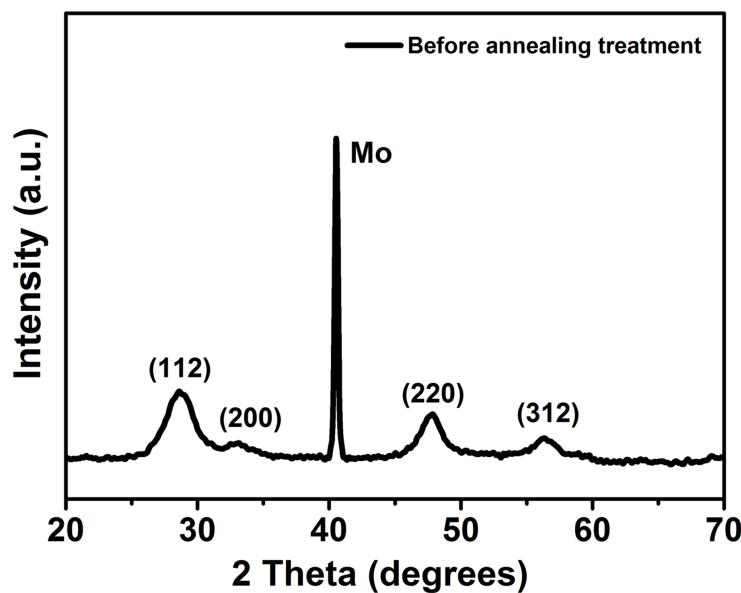


Fig. S3 XRD pattern of Cu₂ZnSn(S,Se)₄ precursor films before annealing treatment corresponds well with the standard patterns of Cu₂SnS₃ (JCPDS no. 89-4714).

XPS spectra

XPS was used to investigate the chemical state of the CZTSSe thin films. Fig. S4 shows XPS spectra of the CZTSSe thin film. In the high-resolution spectrum of Cu 2p (Fig. S4 (a)), two peaks at 932.1 and 951.8 eV appear, indicative of Cu (I) with a splitting of 19.7 eV, which is consistent with the standard separation of 19.9 eV.^{1,2} No satellite peaks are found at the higher binding energy direction. Therefore, it can be concluded that only monovalent copper exists in the sample, indicating that Cu (II) in the starting material has been reduced during the process. The Zn 2p (Fig. S4 (b)) peaks located at 1022.1 and 1045.2 eV show a peak separation of 23.1 eV, consistent with the standard splitting of 23.0 eV, suggesting the presence of Zn (II).^{1,2} The presence of Sn (IV) (Fig. S4 (c)) is confirmed by the peak splitting of 8.5 eV of the two peaks located at 486.7 and 495.2 eV, respectively.^{1,2} The binding energies of S 2p can be assigned to 161.6 eV. The Se 3d peak at 54.5 eV and the Se 3p core located at 166.8 eV, which are in good accordance with values reported previously, were assigned to Se 3p_{1/2} (Fig. S4 (d), (e)).^{3,4}

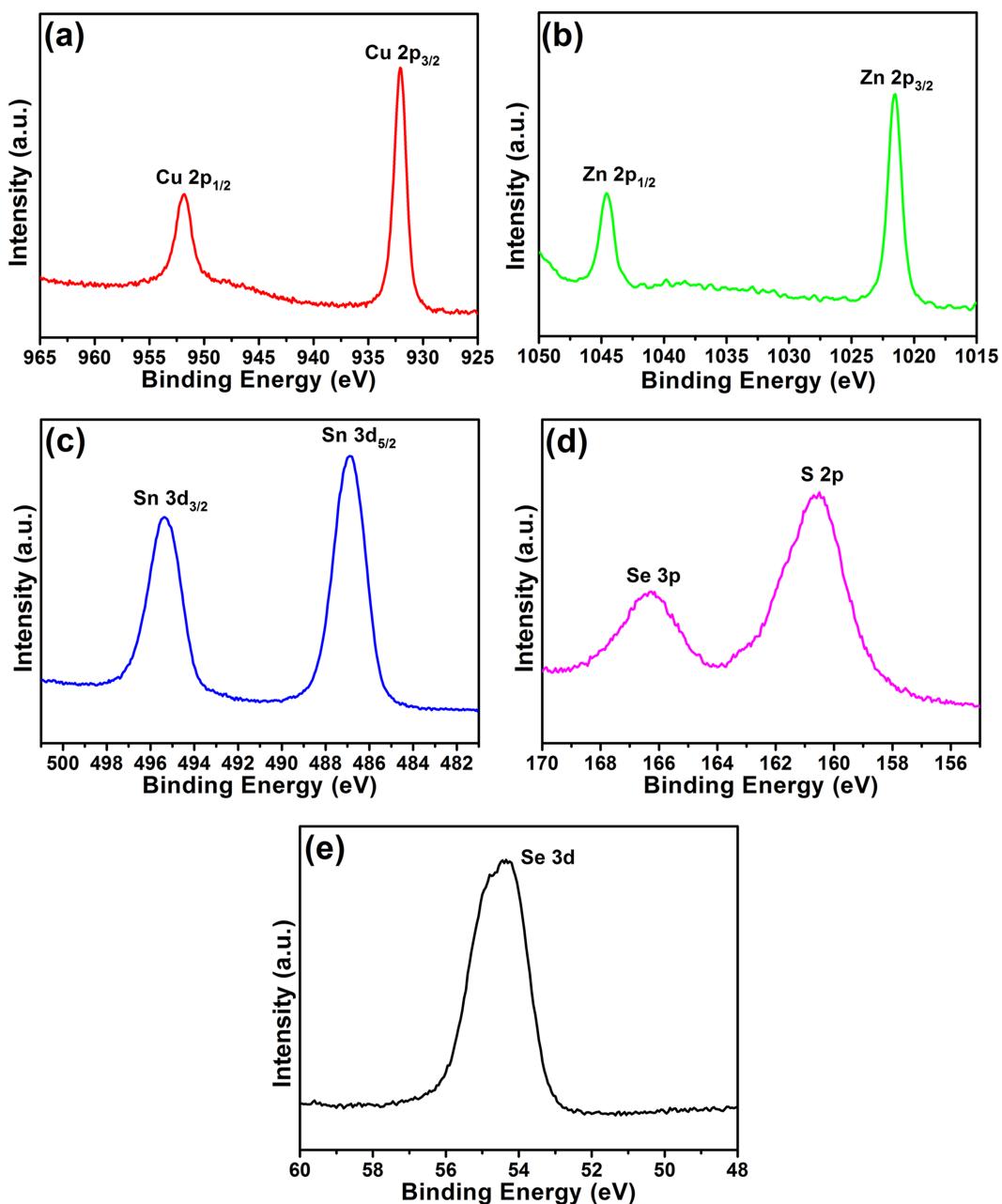


Fig. S4 XPS spectra of CZTSSe thin film.

References

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