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Electronic Supplementary Information for

An efficient organic solvent-free solution-processing strategy for high- mobility metal chalcogenide film growth

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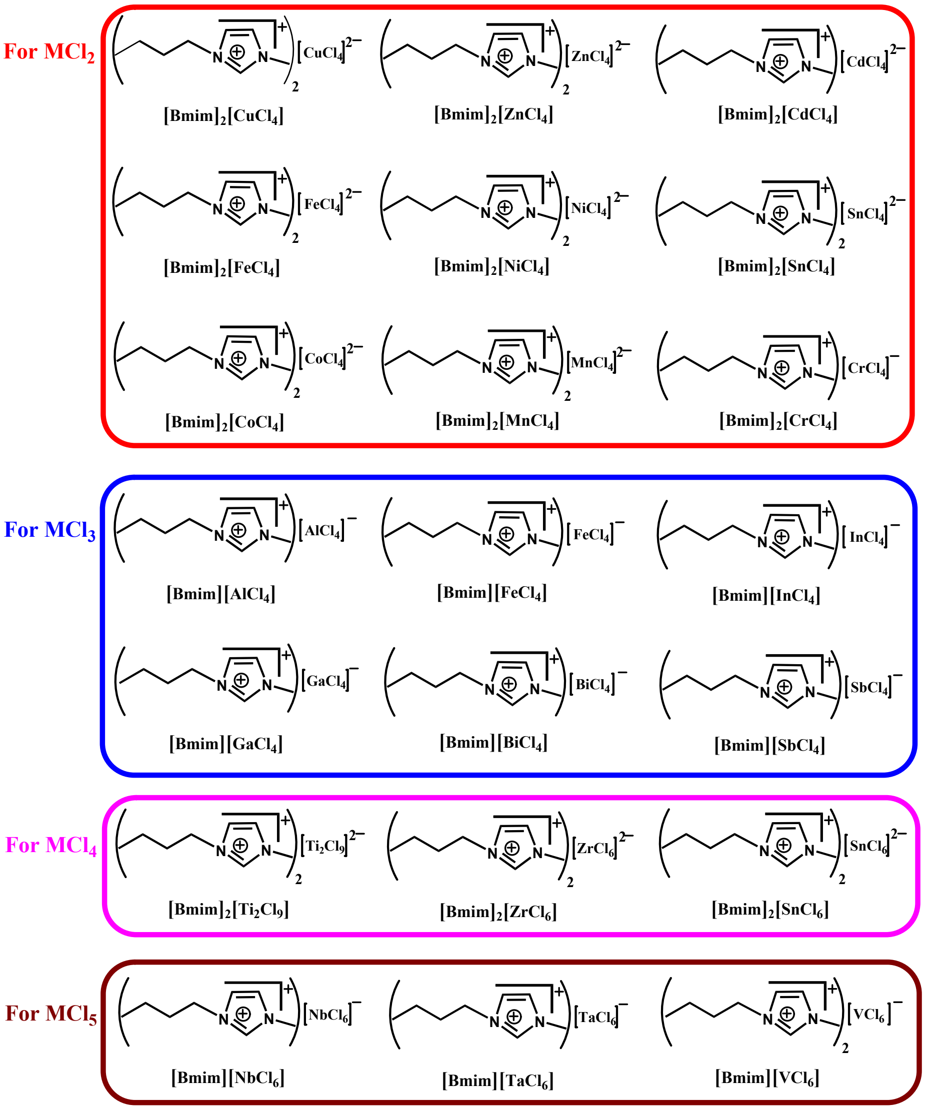


Fig. S1 Chemical structures of compounds produced by different valence metal chlorides with [Bmim][Cl].

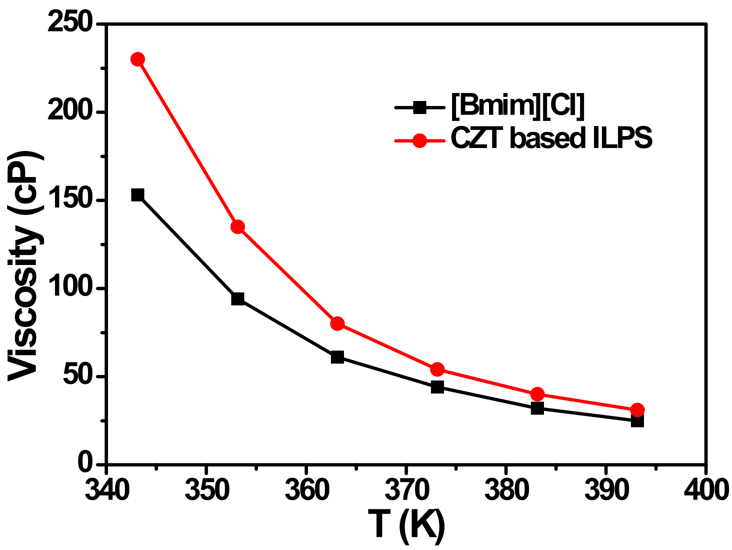


Fig. S2 The effect of temperature on the viscosity of [Bmim][Cl] and CZT based ILPS.

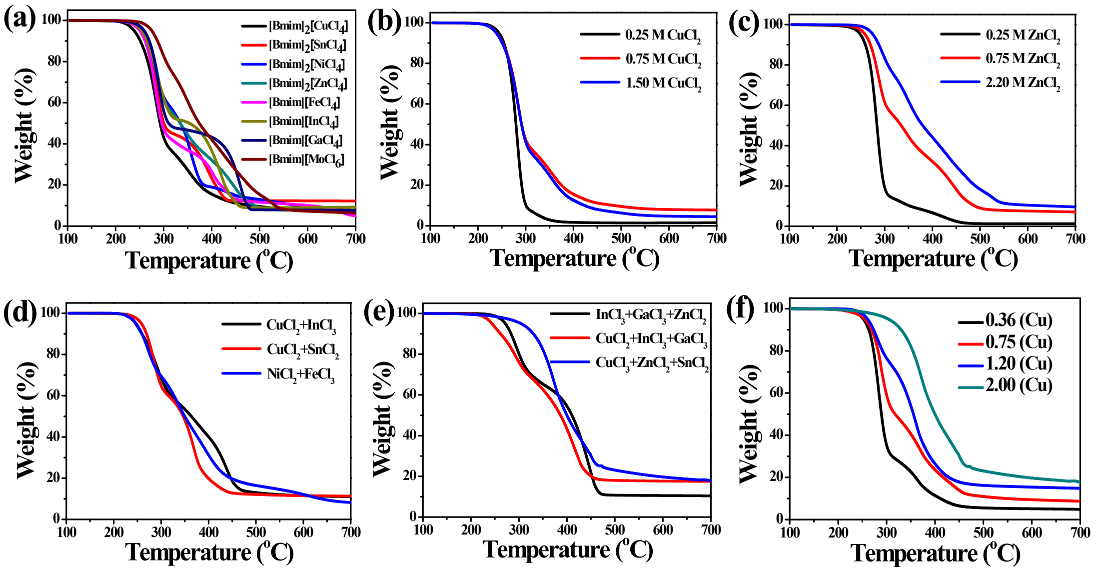
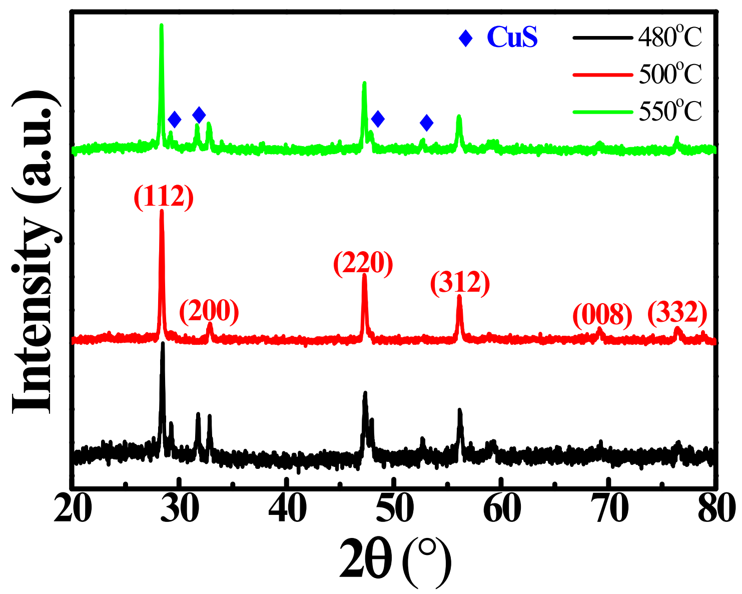


Fig. S3 TGA curves of various ILPSs for single (a-c), binary (d) and ternary (e-f) metal chlorides, respectively.

Thermal gravimetric analysis (TGA) data are plotted in Fig. S3 for various ILPS containing a variety of metal salts with different concentrations. As shown in Fig. S3a, most of single metal based ILPS exhibit substantial weight loss below temperatures of 260 °C, which corresponds to the thermal decomposition of [Bmim][Cl].[S1] Another weight loss feature is observed at temperatures just above 300 °C, which we attribute to $[Bmim]_{y-nx}[M_xCl_y]$. As shown in Fig. S3b-S3e, different valence states of metal ions and interacting modes with [Bmim][Cl] lead to ILPSs which exhibit a wide range of degradation temperatures from 260 to 470 °C. For instance, Zn, In and Ga based ILPSs show relatively higher decomposition temperatures than the other metal based ILPSs. Fig. S3b-S3c presents the relationship between the ion (Cu^{2+} and Zn^{2+}) concentration of the ILPSs and their thermal decomposition. The data does not show obvious change at the onset decomposing temperature. However, for Zn based ILPSs, the ILPSs with a higher metal ion concentration have a higher decomposition temperature. These results highlight the potential for the rational design of the degradation temperature of such ILPSs for target metal chalcogenide films. Binary and ternary metal ion based ILPSs (Fig. S3d-S3f) have similar thermal degradation temperatures ranging from 250 to 470 °C. For example, Fig. S3f shows the TGA profiles for Cu ion concentrations from 0.36 to 2 M in Cu-Zn-Sn based ILPSs. One easily sees how the Cu ion concentration significantly influences the pyrolysis of ternary Cu-Zn-Sn based ILPS.



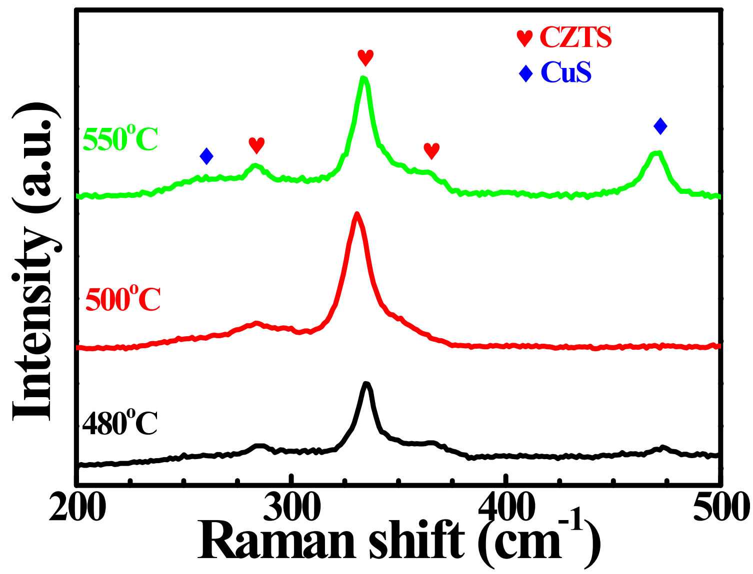


Fig. S4 XRD patterns and Raman spectra for the optimum synthesis of metal chalcogenide films (e.g. CZTS) under different annealing temperature. Distinct structure peaks indicate that annealing temperature at 500 oC is more suitable for the high-quality preparation of metal chalcogenide films

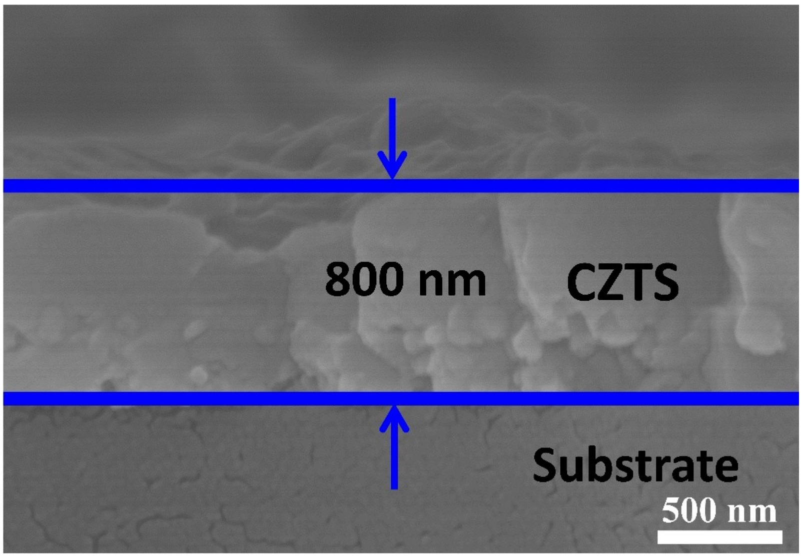


Fig. S5 SEM cross-sectional image of CZTS film prepared after three spin-coatings.

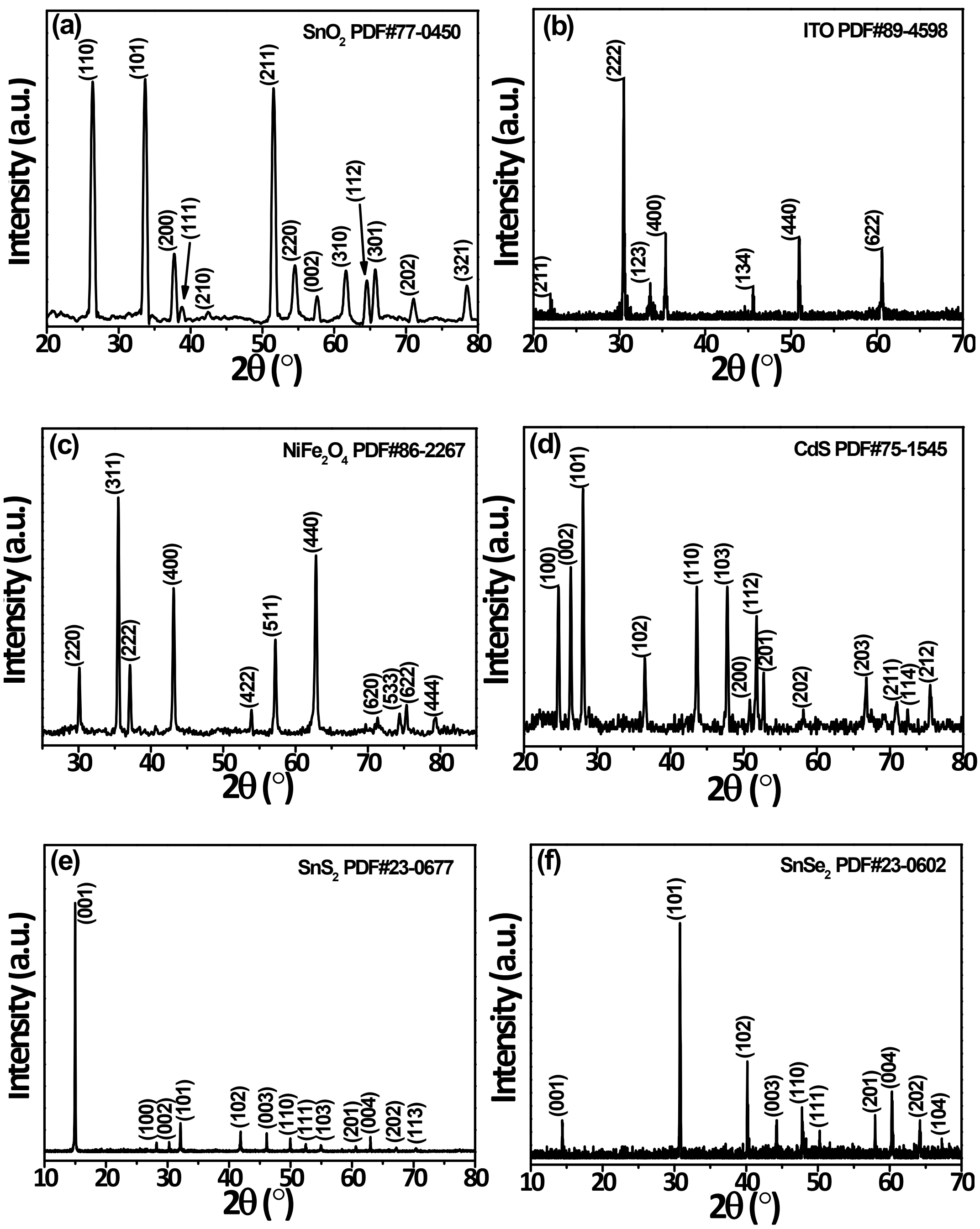


Fig. S6 XRD patterns of selected metal chalcogenide films including SnO_2, Sn-doped In_2O_3 (ITO), $NiFe_2O_4$, CdS, SnS_2 and $SnSe_2$.

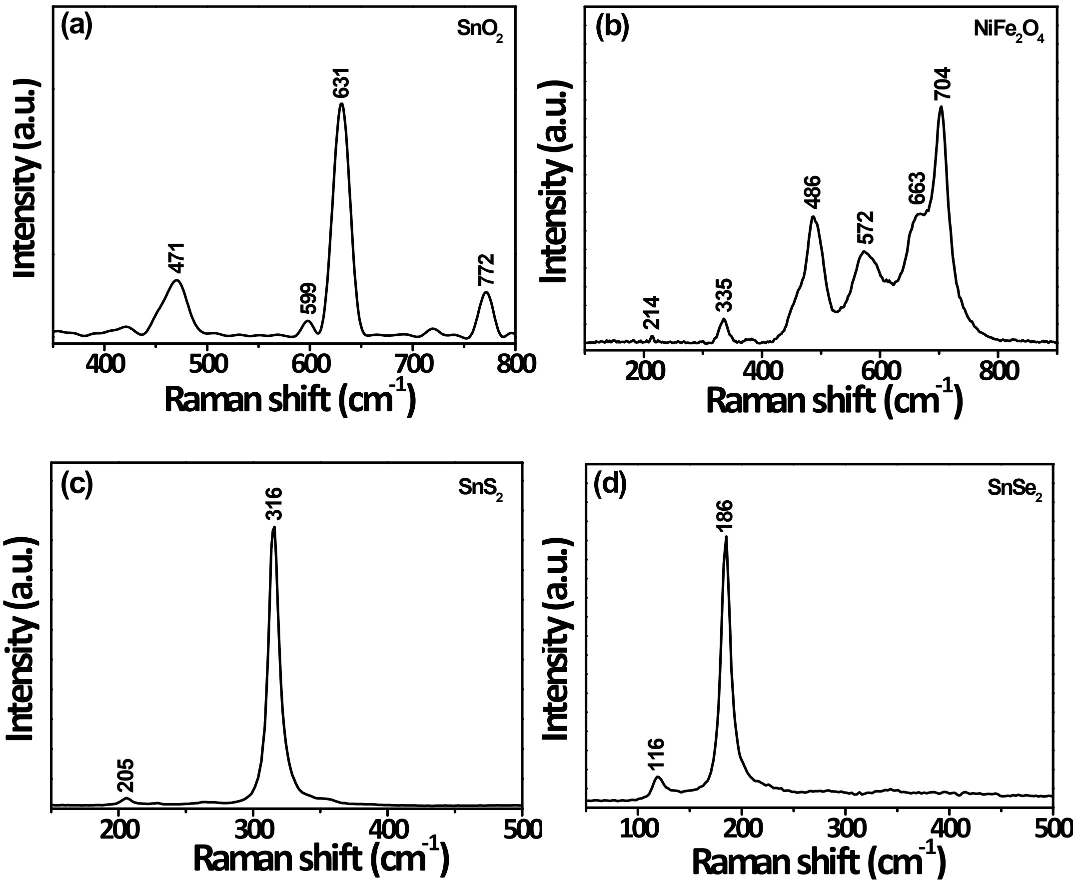


Fig. S7 Raman spectra of selected metal chalcogenide films (SnO_2, $NiFe_2O_4$, SnS_2 and $SnSe_2$).

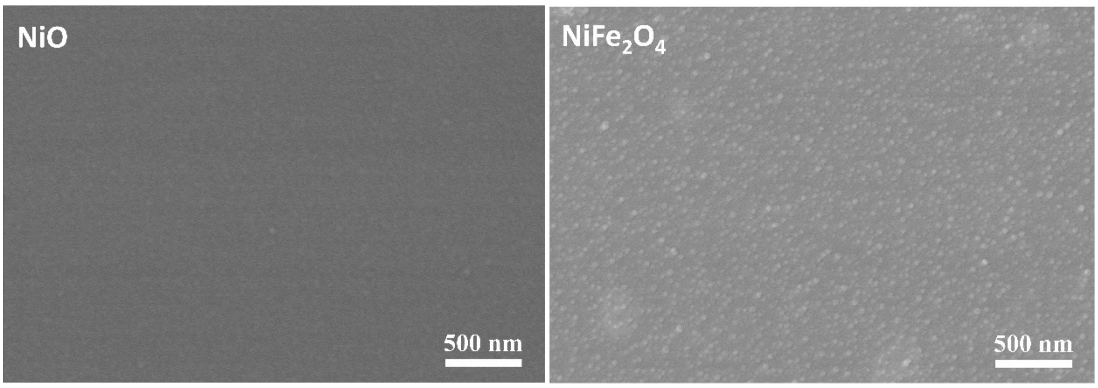


Fig. S8 SEM top view images of NiO and $NiFeO_4$ films.

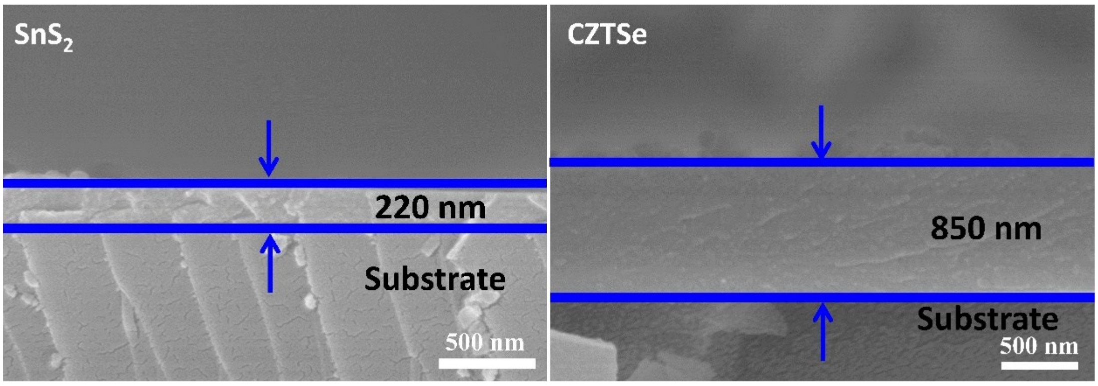


Fig. S9 SEM cross-sectional images of representative SnS_2 and CZTSe films.

References

(S1) N. Meine, F. Benedito and Rinaldi, R. Thermal stability of ionic liquids assessed by potentiometric titration. *Green Chem*. 2010, **12**, 1711-1714.