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11 Figure S1. a) & c) show the surface and cross-section morphologies of precursor layers; b) & d) show

12 the surface and cross-section morphologies of pre-heat layers. After pre-heat process, the thickness of

13 precursor film was decreased from 1.3µm to 820nm, which indicates the remove of organic solvents

14 that used in preparation of CTS precursor solution.

15 Table S1. Hall measurements of CTS thin films annealed under different amount of SnS powder. All

16 CTS thin films annealed with SnS show relatively low hole concentration. Slightly increase was

17 present while the amount of SnS over 0.2g. Overall, the whole hole concentration are in a low state.

Sample	SPECIFIC RESISTENCE	SQUARE RESISTENCE	HALL COEFFICIENT	HALL MOBILITY	CARRIER CONCENTRATI ON
SnS-0.01	g 6.490e+00 Ω•cm	1.298e+05 Ω•□ ⁻¹	1.105e+02 cm ³ ·C ⁻¹	1.703e+01cm ² ·V ⁻¹ ·S ⁻¹	5.649e+16 cm ⁻³
SnS-0.1g	3.743e+00 Ω•cm	7.486e+04 Ω•□ ⁻¹	6.436e+01 cm ³ ·C ⁻¹	1.719e+01cm ² ·V ⁻¹ ·S ⁻¹	9.698e+16 cm ⁻³
SnS-0.2g	g 4.623e+00 Ω•cm	9.246e+04 Ω•□ ⁻¹	7.781e+01 cm ³ ·C ⁻¹	1.683e+01cm ² ·V ⁻¹ ·S ⁻¹	8.021e+16 cm ⁻³
SnS-0.3g	g 4.680e+00 Ω•cm	9.360e+04 Ω•□ ⁻¹	5.854e+01 cm ³ ·C ⁻¹	1.251e+01cm ² ·V ⁻¹ ·S ⁻¹	1.066e+17 cm ⁻³
SnS-0.4g	2.290e+00 Ω•cm	4.580e+04 Ω•□ ⁻¹	2.985e+01 cm ³ ·C ⁻¹	1.304e+01cm ² ·V ⁻¹ ·S ⁻¹	2.091e+17 cm ⁻³
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Figure S2. XRD and Raman spectra of CTS annealed under different amount of SnS powder mixed with S atmosphere. With increasing the amount of SnS powder, the crystallinity was improved and no other obvious secondary phases were found, except Cu₂Sn₃S₇. At this moment, high pressure of annealing atmosphere may have been an unavoidable reason for the better crystallinity. However, as mentioned above, the hole concentration was increased to an level of 10¹⁷cm⁻³ while the amount of SnS powder over 0.2g. In addition, the hole mobility was slightly decreased from 17 to 13 cm²·V⁻¹·S⁻¹ with increase the amount of SnS powder.



Figure S3. XRD spectra of the residue after annealing process. Same Sn-compounds, that is SnS₂, were
formed. Sn₃S₄ was coexisted with SnS₂ while the excessive SnS was added.

Table S2. The properties of final CTS based solar cells.

Measurement-cm ²	Voc V	Jsc mA·cm ⁻²	Fill Factor	Efficiency
S-0.62cm ²	0.102	9.37	26.55	0.255
S+Sn-0.61cm ²	0.146	12.40	28.30	0.516
S+SnS-0.48cm ²	0.153	15.68	28.41	0.682