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Supporting Information

Stannite Quaternary $Cu_2M(M = Ni, Co)SnS_4$ as Low Cost Inorganic Hole Transport Materials in Perovskite Solar Cells

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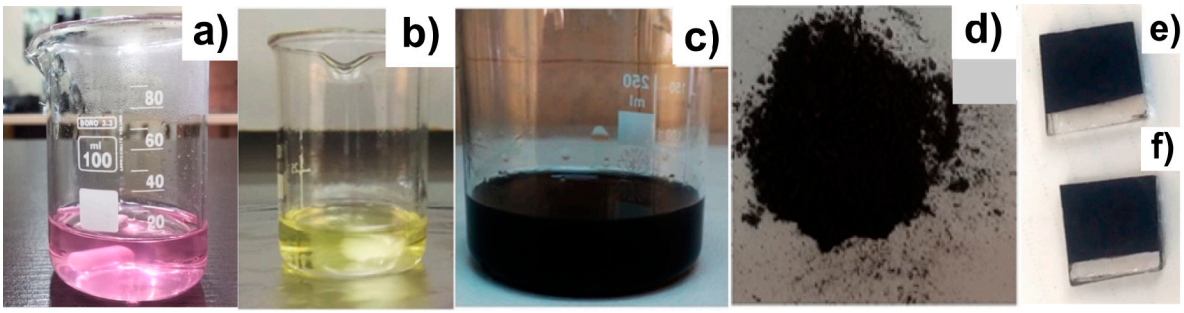

Figure S1. Suspension of (**a**) CCoTS, (**b**) CNiTS precursors, (**c**) CMTS autoclaved suspension, (**d**) purified CMTS powder, deposited films of (**e**) CCoTS and (**f**) CNiTS on the perovskite layer.

Figure S2a, shows XRD patterns of the synthesized CMTS. As can be seen, three diffraction peaks are located at around 2θ~28, 33, 47, and 56, which correspond to the polycrystalline tetragonal stannite (space group I$\bar{4}$2m) for CNiTS (JCPDS card No. 26-0513), and tetragonal stannite (space group I$\bar{4}$2m) for CCoTS (JCPDS card No. 26-0513). These observations are in good agreement with the previous reports on CNiTS and CCoTS [1–4]. The presence of secondary phases such as NiS in CNiTS and CoS in CCoTS are the challenges of the multi-phase nature of these materials. In addition, Raman spectra is an appropriate analysis to explore the additional phases of the material. Figure S1b shows the Raman spectrum of the samples. As can be seen, the main peaks placed at 330 (CNiTS) and 320 (CCoTS) cm^{-1} are related to the A_1 symmetry mode of pure sulfur anion vibrations, and the blue shift of Raman peak arises from force constants $f_{M\text{-}S}$ (M = Ni and Co) [1–5]. As can be seen in Figure S2b, no secondary phases are depicted in the Raman spectra, which is a good evidence of the high purity of CMTS samples.

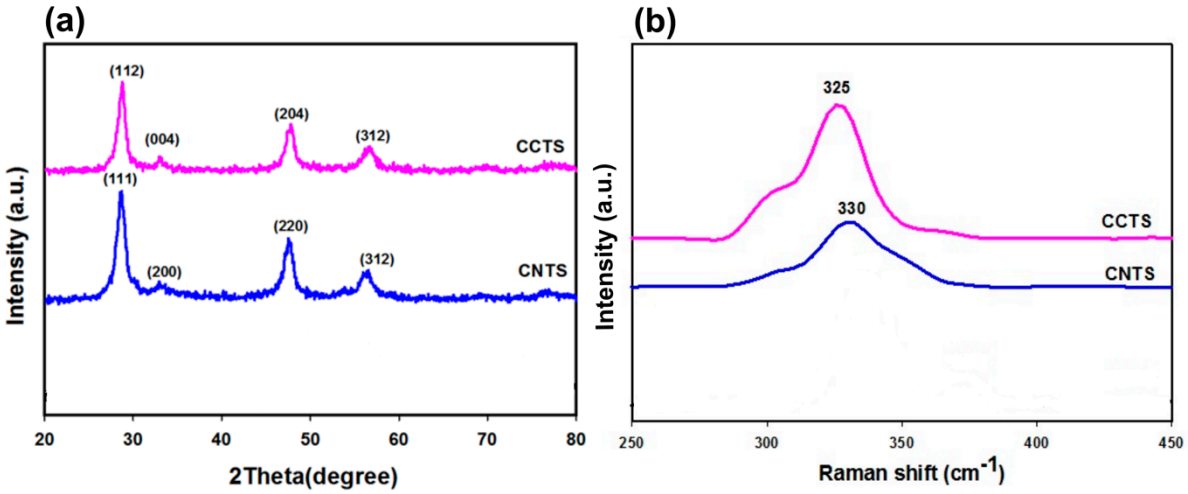

Figure S2. (**a**) X-ray diffraction pattern, and (**b**) Raman spectrum of CNiTS and CCoTS films.

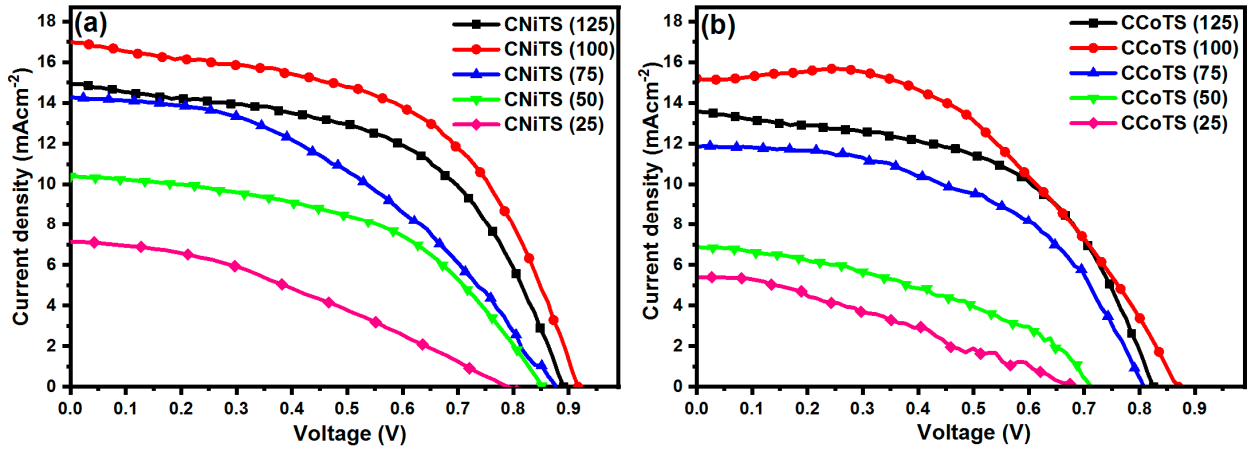

Figure S3. (**a**), (**b**) J-V curves of the CM(M = Ni, Co)TS-based PSCs with 25, 50, 75, 100 and 125 mg mL^{-1} concentrations, measured under illumination of an AM 1.5 G solar simulator (100 mW cm^{-2}).

Table S1. Photovoltaic parameters of CM(M = Ni, Co)TS-based devices with different concentrations of CMTS as hole transport material (HTM), by Au back contact.

HTM Concentration (mg mL^{-1})	HTM	V_{oc}(V)	J_{sc}(mAcm^{-2})	FF(%)	PCE(%)
25	CNTS	0.78	7.13	55	3.08
	CCTS	0.67	5.4	33	1.18
50	CNTS	0.85	10.40	50	4.46
	CCTS	0.7	6.88	42	2.04
75	CNTS	0.8	11.85	52	4.94
	CCTS	0.8	11.85	52	4.94
100	CNTS	0.92	17.75	54	8.85
	CCTS	0.87	16.87	50	7.31
125	CNTS	0.89	14.95	54	7.25
	CCTS	0.82	13.59	54	6.10

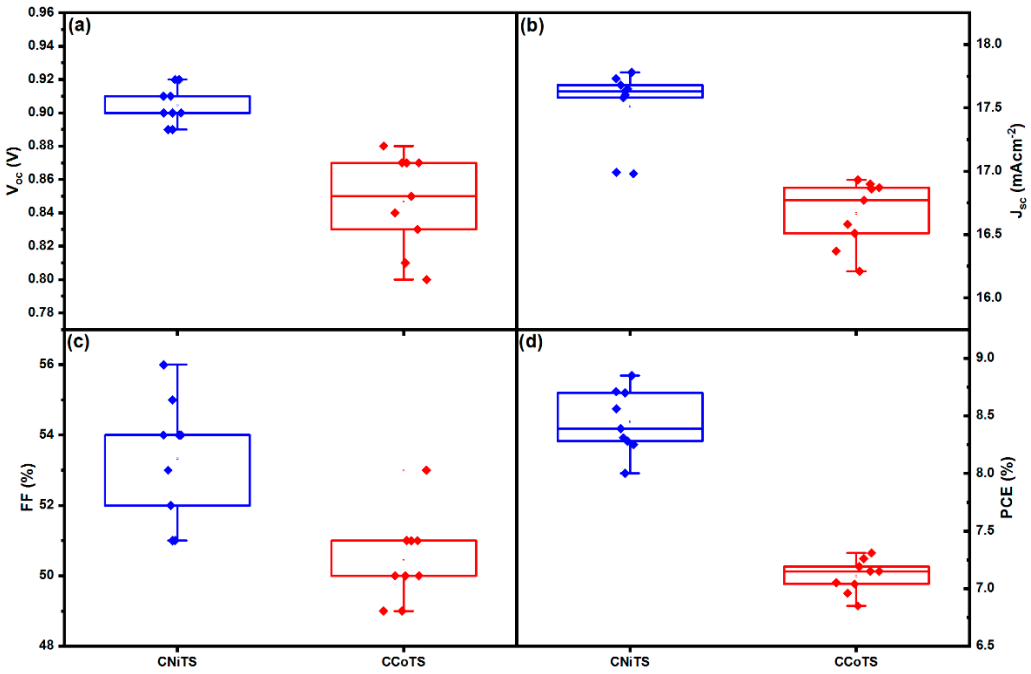

Figure S4. Statistical photovoltaic parameters including: (**a**) V_{oc}, (**b**) J_{sc}, (**c**) FF, and (**d**) power conversion efficiency (PCE), for CM(M = Ni, Co)TS (100 mg ml^{-1}) based devices.

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