Supplementary Information

Combination of full-coverage Sb_2S_3 thin films and *spiro*-OMeTAD:P3HT hybrid hole transporting materials for efficient solar cells

Yang Yang, Chengwu Shi*, Kai Lv, Qi Wang, Xun Sun, Wangchao Chen

School of Chemistry and Chemical Engineering, Anhui Province Key Laboratory of Advanced Catalytic Materials and Reaction Engineering, Hefei University of Technology, Hefei 230009, P. R. China

1. The schematic diagram of the architecture of the full-coverage and crystalline Sb_2S_3 thin film solar cells

Figure S1 showed the architecture of the full-coverage and crystalline Sb_2S_3 thin film solar cells.

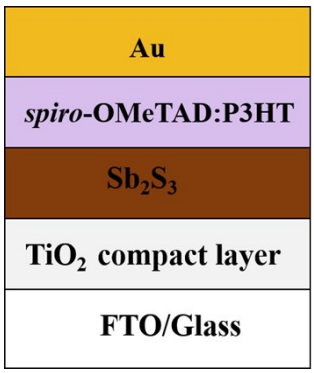

Fig. S1 The architecture of the full-coverage and crystalline Sb_2S_3 thin film solar cells

* Corresponding author. Tel.: +86 551 62901450; fax: +86 551 62901450.

E-mail address: shicw506@foxmail.com, shicw506@hfut.edu.cn

2. The EDS and UV-Vis spectra of the Sb_2S_3 thin films for 160℃ and 160℃+300℃

Figure S2 showed the EDS spectrum of the Sb_2S_3 thin films for 160℃. From Fig. S2, the corresponding atomic ratio of Sb and S was 1:1.89.

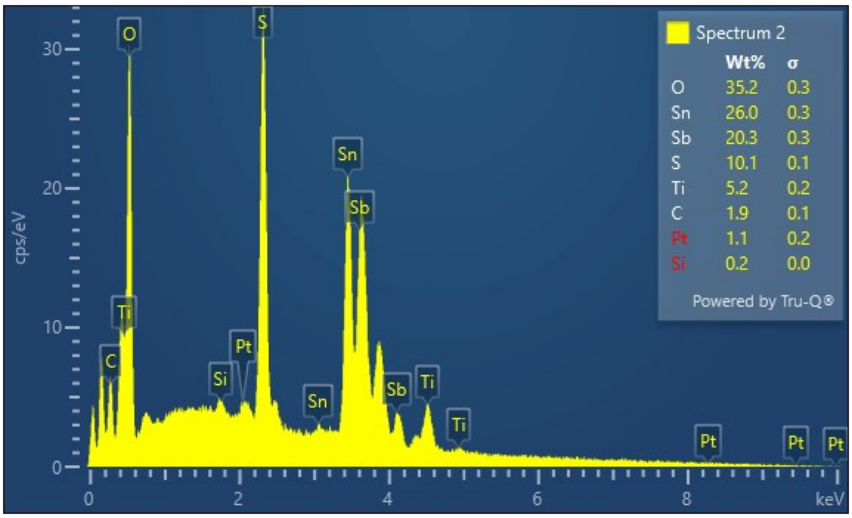

Fig. S2 EDS spectrum of the Sb_2S_3 thin films for 160℃

Figure S3 showed the EDS spectrum of the Sb_2S_3 thin films for 160℃+300℃. From Fig.S3, the corresponding atomic ratio of Sb and S was 1:1.82.

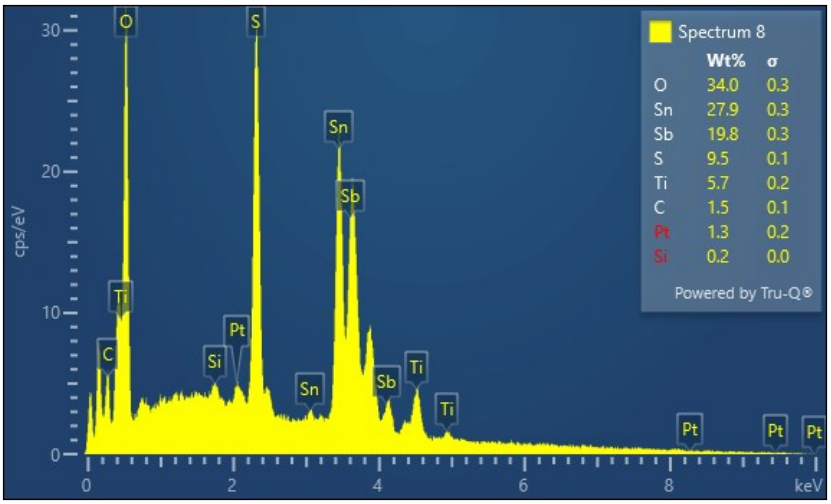

Fig. S3 EDS spectrum of the Sb_2S_3 thin films for 160℃+300℃

Figure S4 showed the UV-Vis spectra of the Sb_2S_3 thin films for 160℃ and

160℃+300℃. The absorption onsets of the Sb_2S_3 thin films was 590 nm for 160℃ and 780 nm for 160℃+300℃. The red-shift of the absorption onsets should be because the Sb_2S_3 thin films were amorphous for 160℃ and crystalline for 160℃+300 ℃.

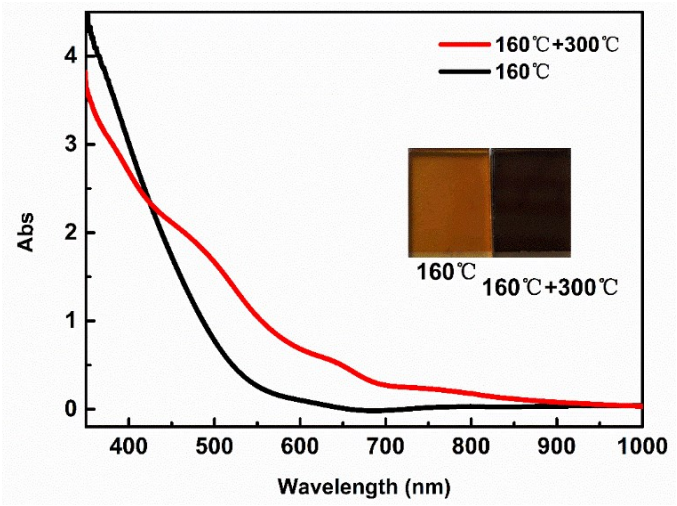

Fig. S4 UV-Vis of Sb_2S_3 thin films for 160℃ and 160℃+300℃

3. The optimization of the *spiro*-OMeTAD content for the full-coverage and crystalline Sb_2S_3 thin film solar cells

For the optimization of the *spiro*-OMeTAD content, the *spiro*-OMeTAD solution containing 73.2mg *spiro*-OMeTAD, 29μL 4-*tert*-butylpyridine, 21 μL Li-TFSI solution (520mg Li-TFSI in 1 mL acetonitrile), 1mL chlorobenzene was prepared to obtain the hole transporting material solution with 73.2mg *spiro*-OMeTAD in 1mL chlorobenzene. The solution with 73.2mg *spiro*-OMeTAD was diluted by chlorobenzene in volume ratios of 3:1, 3:3, 3:5, 3:9, respectively. The hole transporting material solutions with 54.9 mg, 36.6 mg, 27.5 mg, 18.3 mg *spiro*-OMeTAD were obtained. The photovoltaic performance parameters of the full-coverage and crystalline Sb_2S_3 thin film solar cells with various contents of *spiro*-

OMeTAD were listed in Table S1. It can be found that the optimal content of *spiro*-OMeTAD was 27.5 mg.

Table S1 Photovoltaic performance parameters of the full-coverage and crystalline Sb_2S_3 thin film solar cells with various content of *spiro*-OMeTAD

spiro-OMeTAD contents (mg)		V_{oc} (V)	J_{sc} (mA·cm^{-2})	FF (%)	PCE (%)
73.2	Best	0.61	11.64	52.04	3.67
	Average*	0.58±0.02	11.60±0.06	50.25±2.26	3.36±0.30
54.9	Best	0.60	12.66	60.06	4.54
	Average*	0.60±0.02	11.59±0.56	60.31±2.48	4.20±0.39
36.6	Best	0.61	14.14	56.48	4.86
	Average*	0.61±0.00	13.72±0.46	56.91±0.66	4.72±0.15
27.5	Best	0.60	15.38	56.21	5.19
	Average*	0.60±0.02	15.42±0.58	55.32±0.19	5.08±0.14
18.3	Best	0.58	14.99	56.79	4.97
	Average*	0.60±0.02	14.23±0.68	56.72±0.69	4.83±0.21

*Average: 4 solar cells.

4. The optimization of the P3HT content for the full-coverage and crystalline Sb_2S_3 thin film solar cells

Table S2 Photovoltaic parameters of the full-coverage and crystalline Sb_2S_3 thin film solar cells with various content of P3HT in the hybrid hole transporting materials

spiro-OMeTAD(mg)	P3HT (mg)		V_{oc} (V)	J_{sc} (mA·cm^{-2})	FF (%)	PCE (%)
27.5	7.5	Best	0.62	13.60	55.59	4.7
		Average*	0.61±0.01	13.29±0.28	55.91±0.52	4.56±0.12
	5	Best	0.62	13.93	58.16	5.02

	Average*	0.61±0.01	14.16±0.28	57.08±0.94	4.95±0.06
3	Best	0.6	15.24	55.16	5.12
	Average*	0.62±0.01	14.41±0.72	56.52±1.19	5.04±0.07
1.5	Best	0.61	15.73	57.12	5..48
	Average*	0.61±0.01	15.74±0.12	56.47±0.53	5.42±0.10
0	Best	0.59	15.39	57.81	5.28
	Average*	0.59±0.01	15.38±0.13	55.98±1.23	5.08±0.07

*Average: 4 solar cells.

For the optimization of the P3HT content, the *spiro*-OMeTAD solution containing 55 mg *spiro*-OMeTAD, 22 μL 4-*tert*-butylpyridine, 16 μL Li-TFSI solution (520mg Li-TFSI in 1 mL acetonitrile), 1mL chlorobenzene and the P3HT solution containing 15 mg P3HT, 1mL chlorobenzene were separately prepared to obtain the hole transporting material solution with 55 mg *spiro*-OMeTAD and 15 mg P3HT in 1mL chlorobenzene. The hybrid hole transporting material solutions with 27.5 mg *spiro*-OMeTAD and 7.5 mg, 5.0 mg, 3.0 mg, 1.5 mg, 0 mg P3HT were prepared by mixing the 55 mg *spiro*-OMeTAD solution, 15 mg P3HT solution, chlorobenzene in volume ratios of 1:1:0, 3:2:1, 5:2:3, 5:1:4, 1:0:1, respectively. The photovoltaic performance parameters of the full-coverage and crystalline Sb_2S_3 thin film solar cells with various content of P3HT were listed in Table S2. It can be found that the optimal content of the hybrid hole transporting materials was 27.5 mg of *spiro*-OMeTAD and 1.5 mg of P3HT.

5. Detailed photovoltaic performance parameters of the full-coverage and crystalline Sb_2S_3 thin film solar cells with 27.5mg *spiro*-OMeTAD

Table S3 Detailed photovoltaic performance parameters of the full-coverage and crystalline Sb_2S_3 thin film solar cells with 27.5mg *spiro*-OMeTAD

Solar cells	V_{oc}(V)	J_{sc}(mA·cm^{-2})	FF (%)	PCE (%)
1	0.59	15.39	57.81	5.28
2	0.61	15.47	55.60	5.22
3	0.58	15.57	56.45	5.11
4	0.60	15.13	56.15	5.07
5	0.59	15.52	55.21	5.06
6	0.59	15.61	55.18	5.06
7	0.60	15.23	55.54	5.05
8	0.60	15.36	54.62	5.05
9	0.59	15.40	55.23	5.04
10	0.59	15.04	56.06	5.01
11	0.59	15.58	54.72	5.00
12	0.59	15.35	55.03	5.00
13	0.59	15.04	55.78	4.98
14	0.59	15.00	55.95	4.97
15	0.59	15.63	53.97	4.96
16	0.58	15.45	55.04	4.94
17	0.59	15.18	55.32	4.91
18	0.59	15.39	54.12	4.90

Table S3 listed the detailed photovoltaic performance parameters of the full-coverage and crystalline Sb_2S_3 thin film solar cells of 160℃+300 ℃ with 27.5mg *spiro*-OMeTAD

6. Detailed photovoltaic performance parameters of the full-coverage and crystalline Sb_2S_3 thin film solar cells with 27.5mg *spiro*-OMeTAD:1.5mg P3HT

Table S4 listed the detailed photovoltaic performance parameters of the full-

coverage and crystalline Sb_2S_3 thin film solar cells of 160℃+300 ℃ with 27.5mg *spiro*-OMeTAD:1.5mg P3HT

Table S4 Detailed photovoltaic performance parameters of the full-coverage and crystalline Sb_2S_3 thin film solar cells with 27.5mg *spiro*-OMeTAD:1.5mg P3HT

Solar cells	V_{oc}(V)	J_{sc}(mA·cm^{-2})	FF (%)	PCE (%)
1	0.62	15.75	58.11	5.65
2	0.61	15.86	57.08	5.50
3	0.61	15.84	56.98	5.49
4	0.62	15.62	56.15	5.46
5	0.62	15.82	55.78	5.45
6	0.61	15.83	56.15	5.43
7	0.61	15.25	58.31	5.42
8	0.61	15.72	55.99	5.35
9	0.60	15.75	56.17	5.31
10	0.60	15.73	55.83	5.26
11	0.60	15.45	56.25	5.25
12	0.61	15.42	55.97	5.23
13	0.61	15.71	54.13	5.21
14	0.60	15.81	55.65	5.21
15	0.60	15.73	55.12	5.20
16	0.62	14.57	57.64	5.19
17	0.60	15.61	55.23	5.15
18	0.60	15.80	54.09	5.14

7. The statistic analysis of the photovoltaic performance parameters of the full-coverage and crystalline Sb_2S_3 thin film solar cells with 27.5mg *spiro*-OMeTAD and 27.5mg *spiro*-OMeTAD:1.5mg P3HT

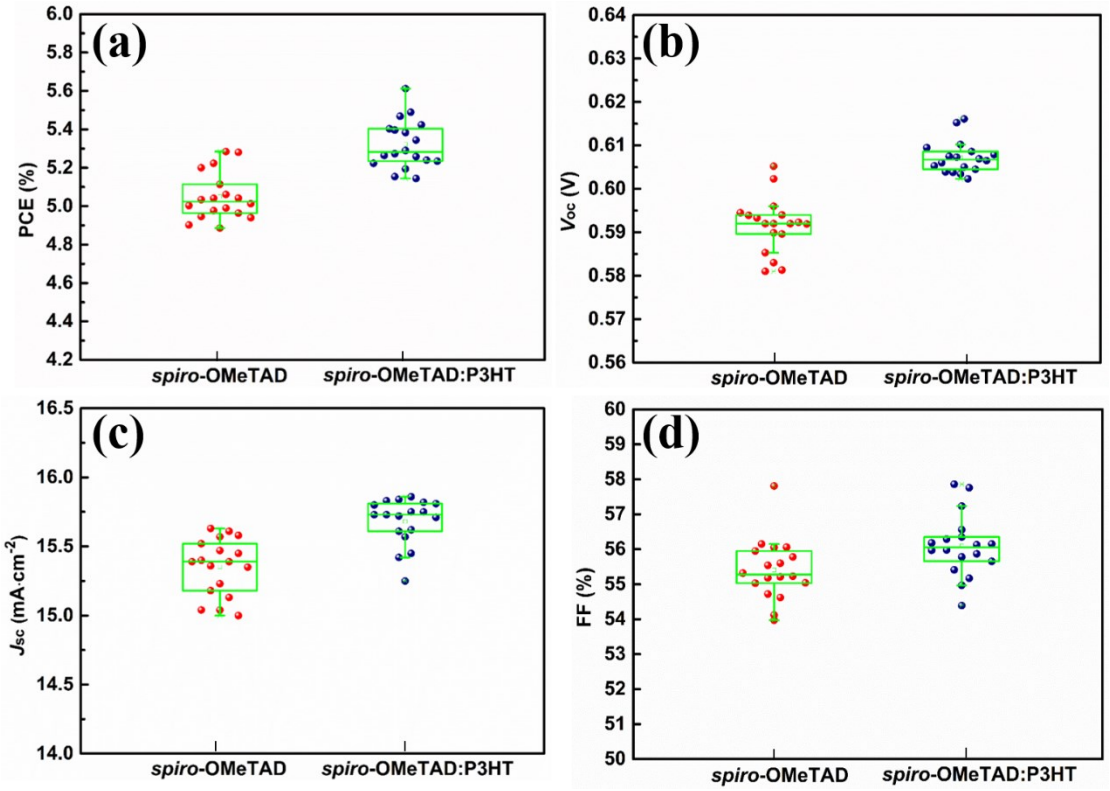

Fig. S5 The statistic analysis of the photovoltaic performance parameters of the full-coverage and crystalline Sb_2S_3 thin film solar cells with 27.5mg *spiro*-OMeTAD and 27.5mg *spiro*-OMeTAD:1.5mg P3HT

Figure S5 showed the statistic analysis of the PCE, V_{oc}, J_{sc} and FF of the full-coverage and crystalline Sb_2S_3 thin film solar cells with 27.5mg *spiro*-OMeTAD and 27.5mg *spiro*-OMeTAD:1.5mg P3HT.

8. The cross-sectional SEM images of the full-coverage and crystalline Sb_2S_3 thin film solar cells with 27.5mg *spiro*-OMeTAD and 27.5mg *spiro*-OMeTAD:1.5mg P3HT

Figure S6 showed the cross-sectional SEM images of the full-coverage and crystalline Sb_2S_3 thin film solar cells with 27.5mg *spiro*-OMeTAD and 27.5mg *spiro*-

OMeTAD:1.5mg P3HT. From Fig. S6，it can be seen that the thickness of *spiro*-OMeTAD and *spiro*-OMeTAD:P3HT were both 90 nm. The result should be due to the low content of P3HT in the *spiro*-OMeTAD:P3HT hybrid hole transporting materials.

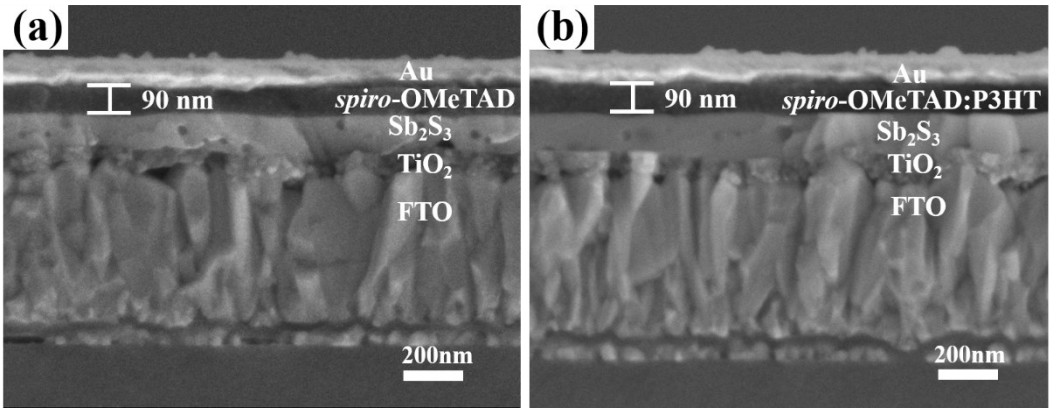

Figure S6 The cross-sectional SEM images of the full-coverage and crystalline Sb_2S_3 thin film solar cells with 27.5mg *spiro*-OMeTAD (a) and 27.5mg *spiro*-OMeTAD:1.5mg P3HT (b)

9. The storage stability of the full-coverage and crystalline Sb_2S_3 thin film solar cells with 27.5mg *spiro*-OMeTAD and 27.5mg *spiro*-OMeTAD:1.5mg P3HT

Figure S7 showed the storage stability of the full-coverage and crystalline Sb_2S_3 thin film solar cells with 27.5mg *spiro*-OMeTAD and 27.5mg *spiro*-OMeTAD:1.5mg P3HT. When the unencapsulated full-coverage and crystalline Sb_2S_3 thin film solar cell was stored in air with the relative humidity of < 30% for 30 days, the PCE of the corresponding solar cells with *spiro*-OMeTAD:P3HT still remained ~98% of the initial values, while the PCE with *spiro*-OMeTAD decreased to 85%. Therefore, the storage stability of the full-coverage and crystalline Sb_2S_3 thin film solar cells with

the *spiro*-OMeTAD:P3HT was superior to that with *spiro*-OMeTAD.

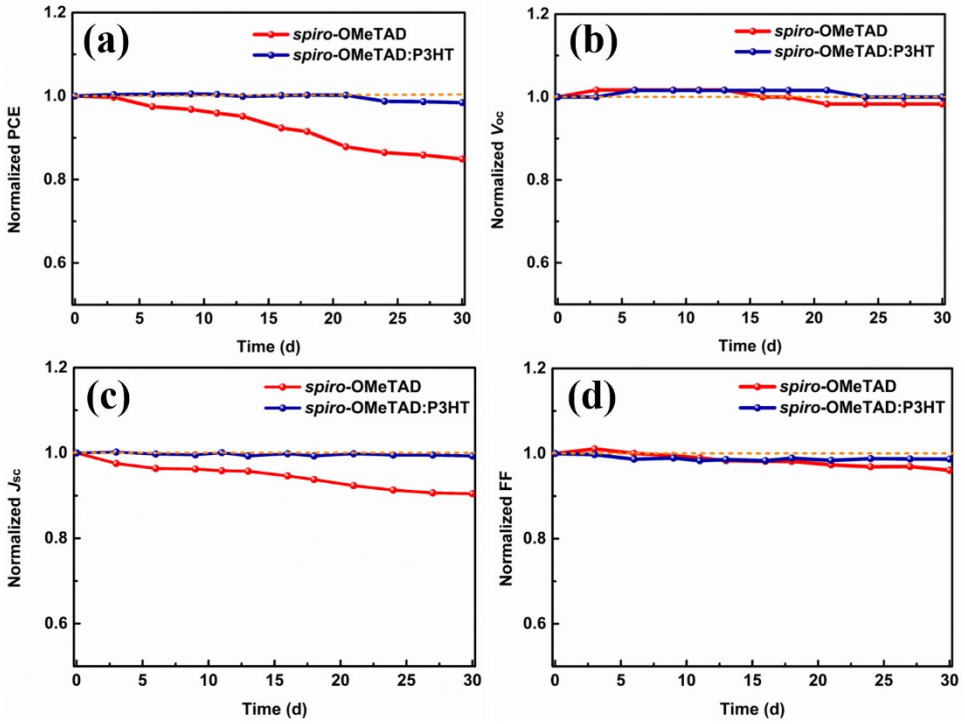

Fig. S7 The storage stability of the full-coverage and crystalline Sb_2S_3 thin film solar cells with 27.5mg *spiro*-OMeTAD and 27.5mg *spiro*-OMeTAD:1.5mg P3HT