

## Supporting Information

### Chemical bath deposition of $\text{Sb}_2\text{S}_3$ thin films using the mixing solution of $\text{SbCl}_3$ and sodium citrate as a novel Sb source for assembling efficient solar cells

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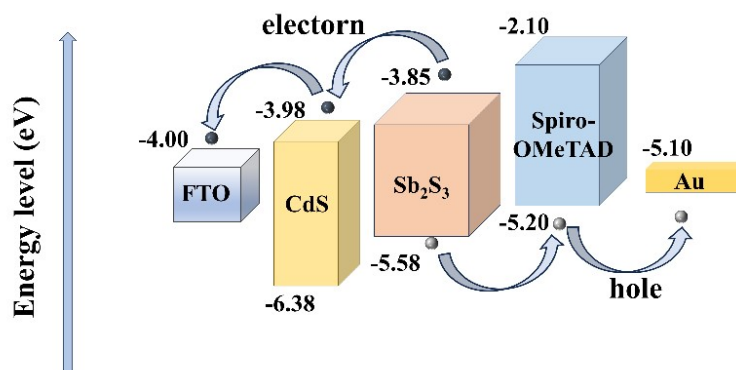
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#### 1. The band diagram of $\text{Sb}_2\text{S}_3$ solar cells.

The energy level alignment of  $\text{Sb}_2\text{S}_3$  solar cells based on device structure of FTO/CdS/ $\text{Sb}_2\text{S}_3$ /spiro-OMeTAD/Au was shown in **Figure S1**.



**Figure S1.** The band diagram of  $\text{Sb}_2\text{S}_3$  solar cells.

**2. The influence of SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and the growth time using the SbCl<sub>3</sub> concentration of 120 mM and the growth temperature of 60 °C on Sb<sub>2</sub>S<sub>3</sub> thin films and the photovoltaic performance of the corresponding solar cells**

When the SbCl<sub>3</sub> concentration and growth temperature were 120 mM and 60 °C, the molar ratios of SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and growth times were changed to be 1:2:1, 1:2:2, 1:2:4 and 5, 7, 9 h in CBD, Sb<sub>2</sub>S<sub>3</sub> thin films were prepared and subsequently annealed in N<sub>2</sub> at 300 °C for 10 min. The detailed photovoltaic performance parameters of the corresponding solar cells were listed in **Table S1**. When the molar ratios of SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> were 1:2:1, 1:2:2, 1:2:4, the optimal growth times were all 7 h. When the growth time was 7 h, the optimal molar ratio of SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was 1:2:2.

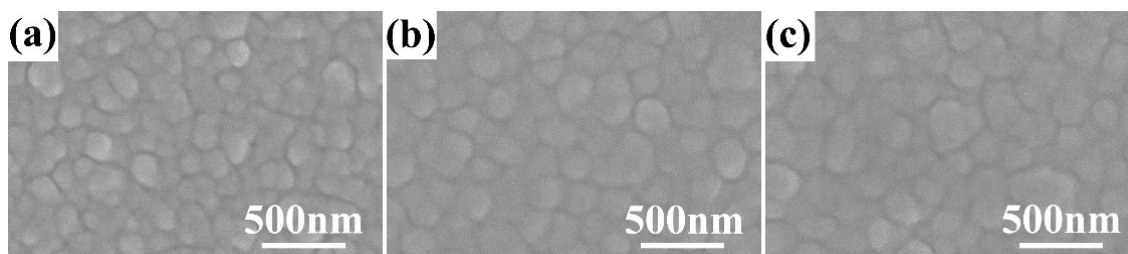
**Table S1.** The photovoltaic performance parameters of Sb<sub>2</sub>S<sub>3</sub> solar cells\*

SbCl <sub>3</sub> : sodium citrate: Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Growth time (h)	Value	$V_{oc}$ (V)	$J_{sc}$ (mA·cm <sup>-2</sup> )	FF	PCE (%)
1:2:1	5	Best	0.72	11.00	0.48	3.84
		Average	0.72±0.01	10.78±0.17	0.48±0.01	3.73±0.06
	7	Best	0.72	11.82	0.50	4.24
		Average	0.72±0.01	11.47±0.31	0.50±0.01	4.10±0.16
	9	Best	0.72	11.80	0.47	3.99
		Average	0.72±0.01	11.38±0.35	0.47±0.02	3.88±0.11
1:2:2	5	Best	0.72	11.52	0.52	4.30
		Average	0.72±0.01	11.13±0.35	0.51±0.02	4.10±0.18
	7	Best	0.72	11.90	0.54	4.64
		Average	0.72±0.01	11.81±0.18	0.53±0.01	4.55±0.06
	9	Best	0.71	11.85	0.52	4.37
		Average	0.72±0.01	11.55±0.20	0.51±0.01	4.26±0.08
1:2:4	5	Best	0.71	11.40	0.50	4.10

	Average	0.71±0.01	10.98±0.37	0.50±0.01	3.89±0.14
	Best	0.71	11.84	0.54	4.53
7	Average	0.72±0.01	11.73±0.16	0.53±0.02	4.43±0.08
	Best	0.71	11.68	48.26	4.01
9	Average	0.72±0.01	10.96±0.70	0.47±0.02	3.70±0.11

\*CdS thin film: the growth time of 22 min. Sb<sub>2</sub>S<sub>3</sub> thin film: the SbCl<sub>3</sub> concentration of 120 mM, the growth solution volume of 80 mL, the growth temperature of 60 °C, the annealing in N<sub>2</sub> at 300 °C for 10 min. Average: 6 solar cells

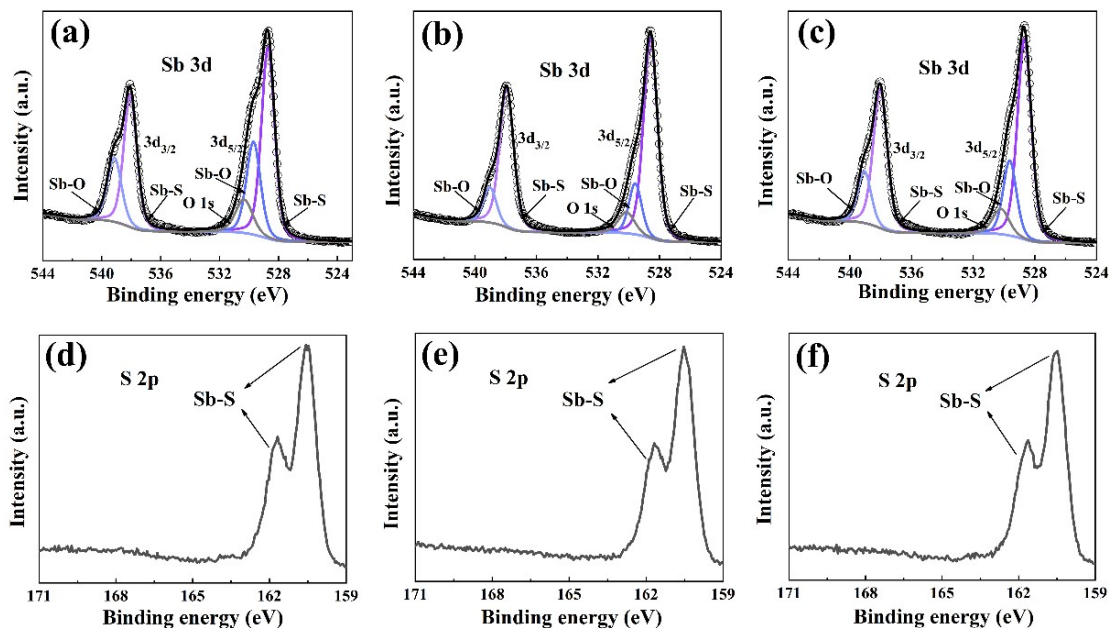
When the SbCl<sub>3</sub> concentration was 120 mM, the molar ratio of SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was 1:2:2, the growth temperature and growth times were 60 °C and 5, 7, 9 h, Sb<sub>2</sub>S<sub>3</sub> thin films were prepared and its surface SEM images were showed in **Figure S2**. It can be seen that the three Sb<sub>2</sub>S<sub>3</sub> thin films with the different growth time were all compact and full-coverage from **Figure S2**.



**Figure S2.** The surface SEM images of Sb<sub>2</sub>S<sub>3</sub> thin films without annealing

The growth time: (a) 5 h, (b) 7 h, (c) 9 h

Figure S3 showed the Sb 3d and S 2p XPS spectra of Sb<sub>2</sub>S<sub>3</sub> thin films without annealing with the growth time of 5 h, 7 h, 9 h. From **Figure S3** (a)(b)(c), the O 1s was located at 530.5 eV and the area of O 1s peak decreased with the increase of growth time from 5h to 7h, and then increased with the increase of growth time from 7h to 9h. The result was in accordance with the changes of the molar ratio of Sb-O:Sb-S/O in **Figure 2**(d)(e)(f). From **Figure S3** (d)(e)(f), the S 2p XPS spectra of Sb<sub>2</sub>S<sub>3</sub> thin films with the growth time of 5 h, 7 h, 9 h only presented the S<sup>2-</sup> peak of S-Sb bond at 161.9 eV and 160.5 eV, the SO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> peak were not be observed. The result further indicated the O in Sb<sub>2</sub>S<sub>3</sub> thin films was derived from Sb-O bonds.

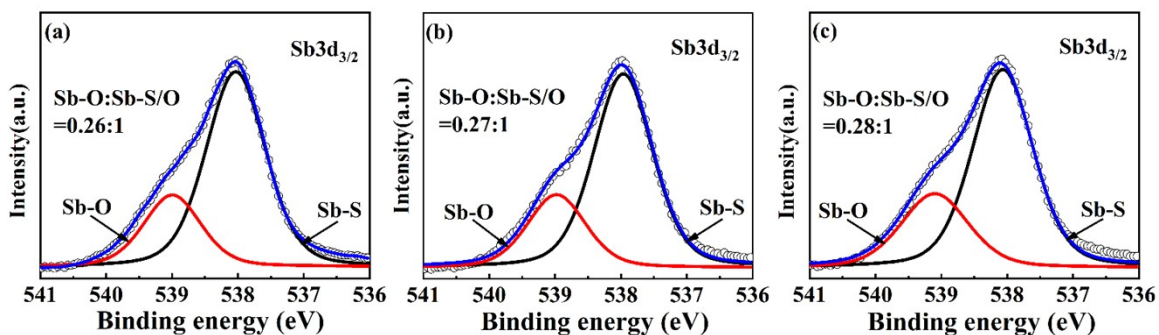


**Figure S3.** The Sb 3d and S 2p XPS spectra of Sb<sub>2</sub>S<sub>3</sub> thin films without annealing  
The growth time: (a)(d) 5 h, (b)(e) 7 h, (c)(f) 9 h

### 3. The influence of the SbCl<sub>3</sub> concentration using the SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> of 1:2:2, the growth temperature of 60 °C, the growth time of 7 h on Sb<sub>2</sub>S<sub>3</sub> thin films and the photovoltaic performance of the corresponding solar cells

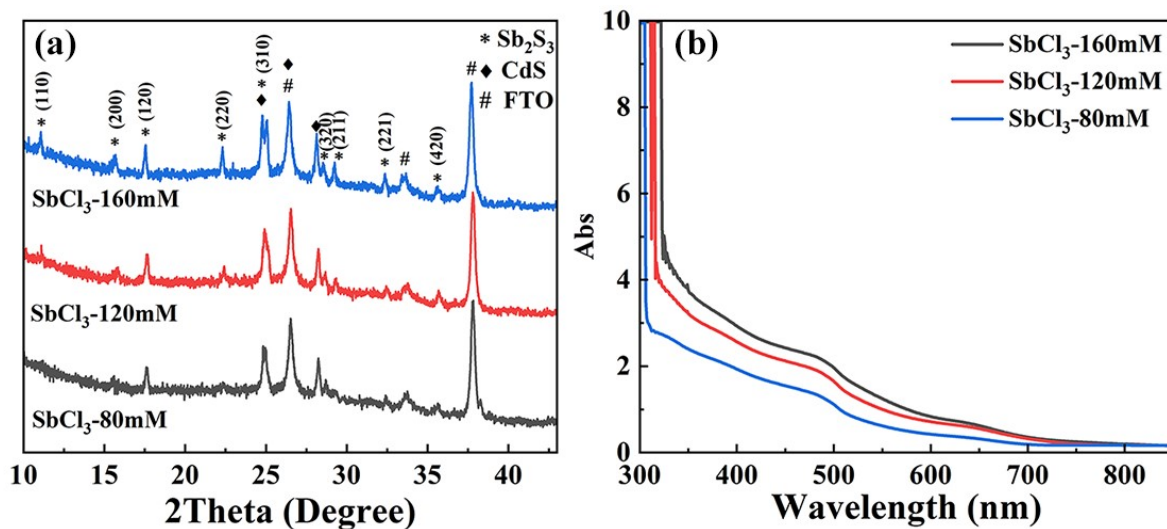
When the molar ratio of SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was 1:2:2, the growth temperature and growth time were 60 °C and 7 h, the SbCl<sub>3</sub> concentrations were changed to be 80, 120, 160 mM in CBD, Sb<sub>2</sub>S<sub>3</sub> thin films were prepared. **Figure S4** showed the Sb 3d<sub>3/2</sub> XPS spectra of Sb<sub>2</sub>S<sub>3</sub> thin films without annealing. The molar ratios of Sb-O:Sb-S/O in Sb<sub>2</sub>S<sub>3</sub> thin films without annealing were 0.26:1 of 80 mM, 0.27:1 of 120 mM, 0.28:1 of 160 mM, and slightly increased with the increase of the SbCl<sub>3</sub> concentration. **Figure S5** showed the XRD patterns and UV-Vis absorption spectra of Sb<sub>2</sub>S<sub>3</sub> thin films with annealing. From **Figure S5**, the diffraction peak intensity and the absorbance of Sb<sub>2</sub>S<sub>3</sub> thin films with

annealing increased with the increase of the  $\text{SbCl}_3$  concentration from 80 mM to 120 mM and 160 mM. The result should be related to the thickness increase of  $\text{Sb}_2\text{S}_3$  thin films. **Figure S6** showed the EDS spectrum of the  $\text{Sb}_2\text{S}_3$  thin film with annealing using the  $\text{SbCl}_3$  concentration of 120 mM. The atomic ratio of S:Sb was 1.21 and lower than the theoretical stoichiometric ratio of  $\text{Sb}_2\text{S}_3$ .

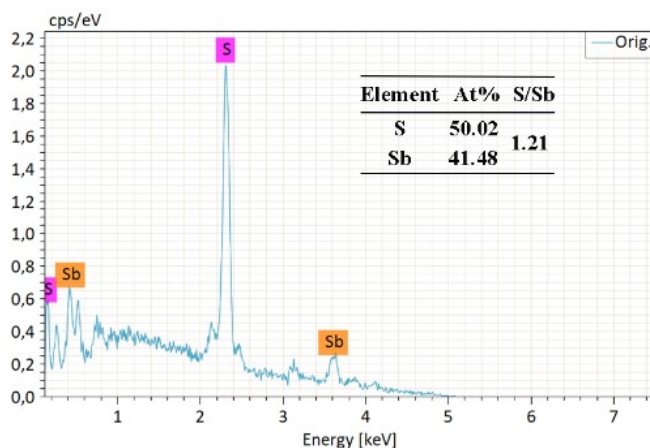


**Figure S4** Sb  $3d_{3/2}$  XPS spectra of  $\text{Sb}_2\text{S}_3$  thin films without annealing

The  $\text{SbCl}_3$  concentration: (a) 80 mM, (b) 120 mM, (c) 160 mM



**Figure S5** (a) XRD patterns (b) UV-Vis absorption spectra of  $\text{Sb}_2\text{S}_3$  thin films with annealing using different  $\text{SbCl}_3$  concentrations



**Figure S6.** The EDS spectrum of the  $\text{Sb}_2\text{S}_3$  thin film with annealing using the  $\text{SbCl}_3$  concentration of 120 mM

**Table S2** listed the photovoltaic performance parameters of  $\text{Sb}_2\text{S}_3$  solar cells. From the PCE, it can be seen that the optimal  $\text{SbCl}_3$  concentration was 120 mM.

**Table S2.** The photovoltaic performance parameters of  $\text{Sb}_2\text{S}_3$  solar cells\*

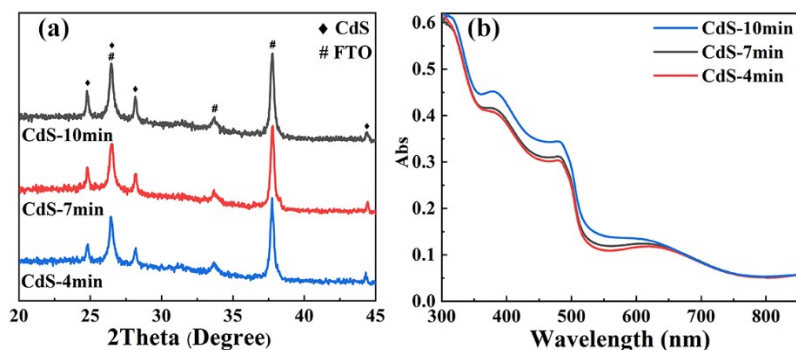
$\text{SbCl}_3$ concentration (mM)	Value	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA}\cdot\text{cm}^{-2}$ )	FF	PCE (%)
80	Best	0.72	10.92	0.52	4.08
	Average	$0.72\pm 0.01$	$10.78\pm 46.19$	$0.51\pm 0.01$	$3.95\pm 0.13$
120	Best	0.72	11.90	0.54	4.64
	Average	$0.72\pm 0.01$	$11.81\pm 0.18$	$0.53\pm 0.02$	$4.55\pm 0.06$
160	Best	0.71	11.15	0.54	4.23
	Average	$0.70\pm 0.01$	$10.82\pm 0.48$	$0.53\pm 0.01$	$4.05\pm 0.25$

\*CdS thin film: the growth time of 22 min.  $\text{Sb}_2\text{S}_3$  thin film: the  $\text{SbCl}_3$ : sodium citrate:  $\text{Na}_2\text{S}_2\text{O}_3$  of 1:2:2, the growth solution volume of 80 mL, the growth temperature of 60 °C, the growth time of 7 h, the annealing in  $\text{N}_2$  at 300 °C for 10 min. Average: 6 solar cells

#### 4. The influence of CdS thin films on the photovoltaic performance of $\text{Sb}_2\text{S}_3$ solar cells

**Figure S7** showed the XRD patterns and UV-Vis absorption spectra of CdS thin films

using the growth times of 10, 7, 4 min. The result was similar to our previous reports.<sup>1</sup>



**Figure S7** (a) XRD patterns (b) UV-Vis absorption spectra of CdS thin films with the growth times of 10 min, 7 min, 4 min

When the growth time of CdS thin films was 22 min, 18 min, 14 min, 10 min, 7 min, 4 min, the photovoltaic performance parameters of the corresponding  $\text{Sb}_2\text{S}_3$  solar cells were listed in **Table S3**. From the PCE, it can be seen that the optimal growth time of CdS thin films was 7 min.

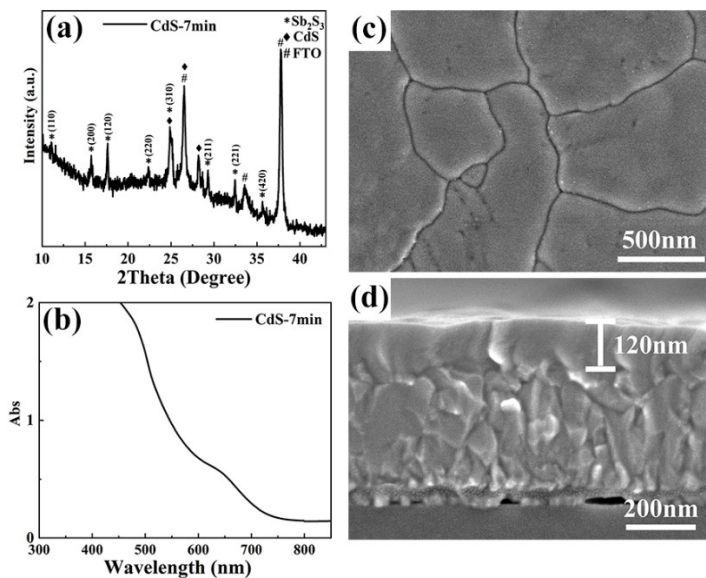
**Table S3.** The photovoltaic performance parameters of  $\text{Sb}_2\text{S}_3$  solar cells with CdS thin films using the different growth time\*

Growth time (min)	Value	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA}\cdot\text{cm}^{-2}$ )	FF	PCE (%)
22	Best	0.72	11.90	0.54	4.64
	Average	$0.72\pm 0.01$	$11.81\pm 0.18$	$0.53\pm 0.02$	$4.55\pm 0.06$
18	Best	0.72	11.98	0.54	4.68
	Average	$0.72\pm 0.01$	$12.10\pm 0.20$	$0.54\pm 0.01$	$4.66\pm 0.04$
14	Best	0.72	12.00	0.57	4.96
	Average	$0.72\pm 0.01$	$12.22\pm 0.43$	$0.54\pm 0.02$	$4.75\pm 0.17$
10	Best	0.73	12.16	0.58	5.19
	Average	$0.73\pm 0.01$	$12.25\pm 0.18$	$0.57\pm 0.02$	$5.10\pm 0.08$
7	Best	0.73	13.10	0.59	5.63
	Average	$0.73\pm 0.01$	$12.72\pm 0.29$	$0.58\pm 0.01$	$5.39\pm 0.16$

4	Best	0.71	12.36	0.58	5.10
	Average	0.71±0.01	12.43±0.31	0.57±0.01	5.02±0.08

\*Sb<sub>2</sub>S<sub>3</sub> thin film: the SbCl<sub>3</sub> concentration of 120 mM, the SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> of 1:2:2, the growth solution volume of 80 mL, the growth temperature of 60 °C, the growth time of 7 h, the annealing in N<sub>2</sub> at 300 °C for 10 min. Average: 6 solar cells

**Figure S8** showed the XRD pattern, UV-Vis absorption spectrum, surface and cross-sectional SEM images of Sb<sub>2</sub>S<sub>3</sub> thin films on the CdS thin films with the growth time of 7 min. The result was similar to that of Sb<sub>2</sub>S<sub>3</sub> thin films on the CdS thin film with the growth time of 22 min, shown in **Figure S5** and **Figure 3(b)(e)**.



**Figure S8** (a) XRD pattern, (b) UV-Vis absorption spectrum, (c) surface and (d) cross-sectional SEM images of the Sb<sub>2</sub>S<sub>3</sub> thin film on the CdS thin film with the growth time of 7 min

### 5. The photovoltaic performance optimization of Sb<sub>2</sub>S<sub>3</sub> solar cells

The photovoltaic performance of Sb<sub>2</sub>S<sub>3</sub> solar cells was optimized by adjusting the SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, raising the growth temperature, and introducing thioacetamide.



**Table S4** listed the photovoltaic performance parameters of the corresponding solar cells. When the growth temperature increased to 90 °C and the SbCl<sub>3</sub> concentration was 120 mM, SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was changed from 1:2:2 to 1:2.3:2 and 1:2.6:2. From **Table S4**, the optimal growth time was 3 h of 1:2:2, 5 h of 1:2.3:2, 7 h of 1:2.6:2. The PCE of the corresponding solar cells was 5.44% of 3 h and 1:2:2, 5.87% of 5 h and 1:2.3:2, 5.72% of 7 h and 1:2.6:2. Therefore, the optimal SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and growth time was 1:2.3:2 and 5 h. The PCE of the corresponding solar cells was 5.87%.

When the growth temperature was 90 °C and the SbCl<sub>3</sub> concentration was 120 mM, the SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>: thioacetamide was changed from 1:2.3:2:0 to 1:2.3:1.75:0.25, 1:2.3:1.5:0.5 and 1:2.3:1.25:0.75 by adding thioacetamide. From **Table S4**, the optimal growth time was all 6h for the SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>: thioacetamide of 1:2.3:1.75:0.25, 1:2.3:1.5:0.5, 1:2.3:1.25:0.75. The PCE of the corresponding solar cells was 6.13% of 1:2.3:1.75:0.25, 6.32% of 1:2.3:1.5:0.5, 5.87% of 1:2.3:1.25:0.75. Therefore, the optimal SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>: thioacetamide and growth time was 1:2.3:1.5:0.5 and 6 h. The PCE of the corresponding solar cells was 6.32%.

**Table S4.** The photovoltaic performance parameters of Sb<sub>2</sub>S<sub>3</sub> solar cells\*

SbCl <sub>3</sub> : Sodium citrate: Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> : thioacetamide	Growth time (h)	Value	$V_{oc}$ (V)	$J_{sc}$ (mA·cm <sup>-2</sup> )	FF	PCE (%)
1:2:2:0	2	Best	0.73	13.65	0.50	4.93
		Average	0.72±0.01	13.14±0.68	0.49±0.01	4.62±0.22
	3	Best	0.73	14.99	0.50	5.44
		Average	0.74±0.01	13.61±0.83	0.49±0.01	4.93±0.31
	4	Best	0.72	14.94	0.49	5.22
		Average	0.73±0.01	13.48±0.68	0.49±0.02	4.75±0.24
1:2.3:2:0	3	Best	0.72	11.81	0.54	4.56
		Average	0.72±0.02	11.55±0.24	0.53±0.02	4.34±0.18
	5	Best	0.74	14.11	0.56	5.87

		Average	0.73±0.01	13.71±0.62	0.55±0.01	5.54±0.24
		Best	0.74	13.01	0.54	5.24
	7	Average	0.73±0.01	12.83±0.38	0.53±0.02	5.01±0.16
		Best	0.71	9.95	0.53	3.77
	3	Average	0.70±0.01	9.70±0.30	0.53±0.01	3.60±0.17
		Best	0.72	13.07	0.54	5.06
1:2.6:2:0	5	Average	0.72±0.01	12.87±0.19	0.53±0.01	4.95±0.10
		Best	0.72	14.45	0.55	5.72
	7	Average	0.73±0.01	13.78±0.59	0.55±0.01	5.51±0.22
		Best	0.75	14.68	0.55	6.04
	5	Average	0.75±0.01	14.30±0.33	0.54±0.01	5.78±0.19
		Best	0.75	14.89	0.55	6.13
1:2.3:1.75:0.25	6	Average	0.75±0.01	14.47±0.29	0.55±0.01	5.97±0.13
		Best	0.75	14.31	0.54	5.78
	7	Average	0.74±0.01	13.86±0.38	0.53±0.02	5.49±0.19
		Best	0.75	14.64	0.55	6.10
	5	Average	0.75±0.01	14.57±0.25	0.55±0.01	5.98±0.09
		Best	0.75	15.10	0.56	6.32
1:2.3:1.5:0.5	6	Average	0.75±0.01	14.70±0.25	0.56±0.0.1	6.21±0.09
		Best	0.74	14.79	0.55	6.00
	7	Average	0.75±0.01	14.22±0.34	0.54±0.01	5.74±0.15
		Best	0.75	13.94	54.77	5.70
	5	Average	0.75±0.01	13.74±0.25	0.54±0.02	5.51±0.18
		Best	0.75	14.18	0.55	5.87
1:2.3:1.25:0.75	6	Average	0.75±0.01	13.95±0.31	0.54±0.0.1	5.63±0.16
		Best	0.75	14.09	0.54	5.72
	7	Average	0.75±0.01	13.64±0.35	0.53±0.01	5.47±0.13

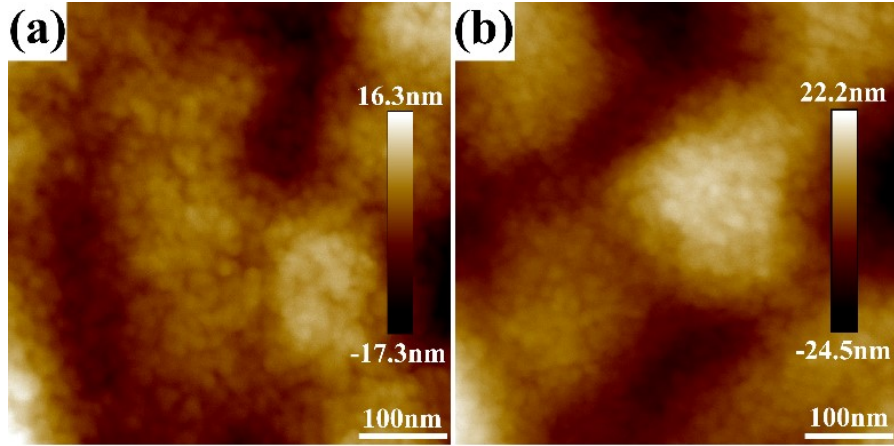
\*CdS thin film: the growth time of 7 min. Sb<sub>2</sub>S<sub>3</sub> thin film: the SbCl<sub>3</sub> concentration of 120 mM, the growth solution volume of 80 mL, the growth temperature of 90 °C, the annealing in N<sub>2</sub> at 300 °C for 10 min. Average: 6 solar cells

**Table S5.** The photovoltaic performance parameters of Sb<sub>2</sub>S<sub>3</sub> solar cells\*

Solution volume (mL)	Substrate position	Growth Time(h)	Value	$V_{oc}$ (V)	$J_{sc}$ (mA·cm <sup>-2</sup> )	FF	PCE (%)
80	Top	5	Best	0.69	13.71	0.46	4.29
			Average	0.69±0.01	12.83±0.57	0.45±0.02	3.99±0.23
	Top	6	Best	0.70	13.77	0.50	4.80
			Average	0.71±0.01	13.32±0.22	0.47±0.02	4.50±0.17
	Top	7	Best	0.69	13.21	0.47	4.27
			Average	0.69±0.01	11.96±0.89	0.44±0.02	3.68±0.45
80	Bottom	5	Best	0.75	14.64	0.55	6.10
			Average	0.75±0.01	14.57±0.25	0.55±0.01	5.98±0.09
	Bottom	6	Best	0.75	15.10	0.56	6.32
			Average	0.75±0.01	14.70±0.25	0.55±0.01	6.05±0.09
	Bottom	7	Best	0.74	14.79	0.55	6.00
			Average	0.75±0.01	14.22±0.34	0.54±0.01	5.74±0.15
40	Bottom	6	Best	0.79	15.02	0.55	6.57
			Average	0.76±0.02	15.19±0.23	0.55±0.01	6.30±0.15

\*CdS thin film: the growth time of 7 min. Sb<sub>2</sub>S<sub>3</sub> thin film: the SbCl<sub>3</sub> concentration of 120 mM, the SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>: thioacetamide of 1:2.3:1.5:0.5, the growth temperature of 90 °C, the growth time of 6 h, the annealing in N<sub>2</sub> at 300 °C for 10 min. Average: 6 solar cells

The photovoltaic performance of Sb<sub>2</sub>S<sub>3</sub> solar cells can be also optimized by decreasing the growth solution volume and changing the CdS/FTO substrate position in CBD. **Table S5** listed the photovoltaic performance parameters of Sb<sub>2</sub>S<sub>3</sub> solar cells with different growth solution volumes and substrate positions. When the growth solution volume was 80 mL, the optimal growth time was 6 h, and the PCE of Sb<sub>2</sub>S<sub>3</sub> solar cells was 6.32% with bottom and 4.80% with top. When the CdS/FTO substrate was located on bottom, the PCE of Sb<sub>2</sub>S<sub>3</sub> solar cells with 40 mL was 6.57% and higher than 6.32% with 80 mL.

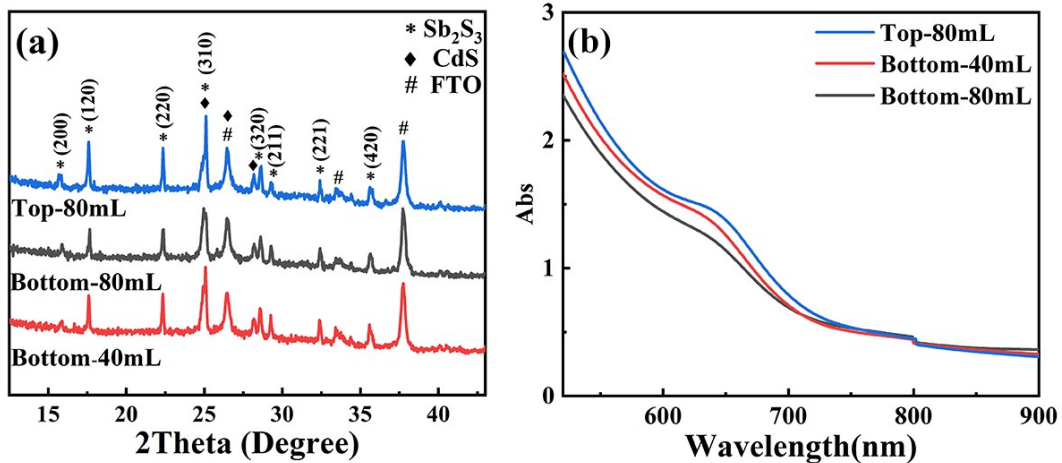


**Figure S9** AFM images of  $\text{Sb}_2\text{S}_3$  thin films with different growth position

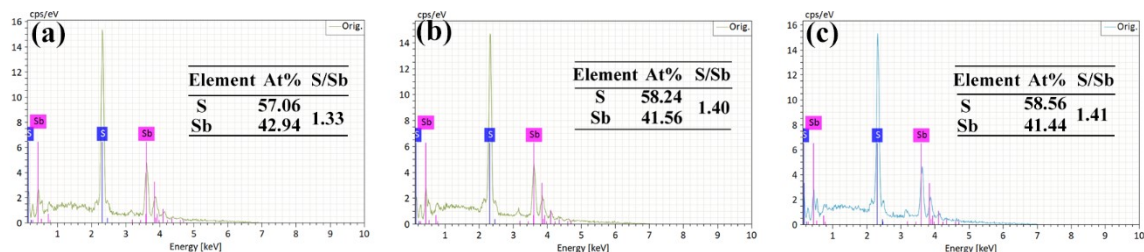
(a) Top, (b) Bottom

When the growth solution volume was 80 mL, the AFM images of  $\text{Sb}_2\text{S}_3$  thin films with different growth position were showed in **Figure S9**. The result was accordance with that of the SEM images in **Figure 5(a)(b)** and further demonstrated that the  $\text{Sb}_2\text{S}_3$  thin films without annealing were composed of the nanoparticles with the size of  $< 10$  nm.

When the growth solution volume was 80/40 mL and the CdS/FTO substrate position was located on top/bottom, the XRD patterns and UV-Vis absorption spectra of the  $\text{Sb}_2\text{S}_3$  thin films were showed in **Figure S10**. The diffraction peak intensity and absorbance for  $\text{Sb}_2\text{S}_3$  thin films was related to the thickness of  $\text{Sb}_2\text{S}_3$  thin films.



**Figure S10** (a) XRD patterns (b) UV-Vis absorption spectra of the  $\text{Sb}_2\text{S}_3$  thin films



**Figure S11** The EDS spectra of  $\text{Sb}_2\text{S}_3$  thin films with the different growth position and the growth solution volume

(a) Top-80 mL, (b) Bottom-80 mL, (c) Bottom-40 mL

When the growth solution volume was 80/40 mL and the CdS/FTO substrate position was located on top/bottom, the EDS spectra of the  $\text{Sb}_2\text{S}_3$  thin films were showed in **Figure S11**. The atomic ratio of S:Sb in  $\text{Sb}_2\text{S}_3$  thin films was 1.33 with Top and 80 mL, 1.40 with Bottom and 80 mL, 1.41 with Bottom and 40 mL. Compared with the S:Sb atomic ratio of 1.21 using the  $\text{SbCl}_3$ : sodium citrate:  $\text{Na}_2\text{S}_2\text{O}_3$  of 1:2:2 and the growth temperature of 60 °C in **Figure S6**, the S:Sb atomic ratio can be improved by adding thioacetamide and raising growth temperature (90 °C).

## 6. The further improvement of the photovoltaic performance by enhancing the annealing temperature, changing the growth solution volume and applying the hybrid hole transport layer for $\text{Sb}_2\text{S}_3$ solar cells

**Table S6.** The photovoltaic performance parameters of  $\text{Sb}_2\text{S}_3$  solar cells\*

Solution volume (mL)	Annealing temperature (°C)	Annealing time (min)	Value	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA}\cdot\text{cm}^{-2}$ )	FF	PCE (%)
40	350	10	Best	0.80	15.59	0.56	6.89
			Average	$0.79\pm 0.01$	$15.52\pm 0.14$	$0.55\pm 0.01$	$6.72\pm 0.10$
40	350	20	Best	0.78	16.29	0.55	6.95
			Average	$0.78\pm 0.01$	$15.81\pm 0.27$	$0.56\pm 0.01$	$6.83\pm 0.06$
48	350	20	Best	0.78	16.41	0.56	7.08
			Average	$0.77\pm 0.01$	$16.27\pm 0.36$	$0.56\pm 0.01$	$6.93\pm 0.12$

56	350	20	Best	0.76	15.88	0.55	6.71
			Average	0.77±0.01	15.76±0.17	0.55±0.01	6.64±0.07
64	350	20	Best	0.76	15.63	0.55	6.53
			Average	0.76±0.01	15.37±0.62	0.55±0.02	6.51±0.05

\*CdS thin film: the growth time of 7 min. Sb<sub>2</sub>S<sub>3</sub> thin film: the SbCl<sub>3</sub> concentration of 120 mM, the SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>: thioacetamide of 1:2.3:1.5:0.5, the growth temperature of 90 °C, the growth time of 6 h. Average: 6 solar cells

**Table S6** listed the photovoltaic performance parameters of the Sb<sub>2</sub>S<sub>3</sub> solar cells with different annealing temperature and time and growth solution volume. Because the 6.89% PCE with the annealing temperature and time of 350 °C and 10 min was higher than 6.57% PCE with the annealing temperature and time of 300 °C and 10 min, the optimal annealing temperature was 350 °C. When the growth solution volume and annealing temperature was 40 mL and 350 °C, the optimal annealing time was 20 min. When the annealing temperature and time was 350 °C and 20 min, the optimal growth solution volume was 48 mL.

**Table S7.** The photovoltaic performance parameters of Sb<sub>2</sub>S<sub>3</sub> solar cells\*

Hole transport layer	Sample	$V_{oc}$ (V)	$J_{sc}$ (mA·cm <sup>-2</sup> )	FF	PCE (%)
<i>spiro</i> -OMeTAD + TMT-TTF	1	0.78	16.89	0.58	7.63
	2	0.77	16.91	0.58	7.53
	3	0.80	16.21	0.58	7.49
	4	0.78	16.85	0.57	7.46
	5	0.76	16.81	0.58	7.44
	6	0.77	16.78	0.57	7.42
	7	0.78	16.49	0.57	7.42
	8	0.79	16.16	0.58	7.38
	9	0.77	16.58	0.57	7.29
	Average	0.78±0.01	16.63±0.29	0.58±0.01	7.45±0.10

\*CdS thin film: the growth time of 7 min. Sb<sub>2</sub>S<sub>3</sub> thin film: the SbCl<sub>3</sub> concentration of 120 mM, the

SbCl<sub>3</sub>: sodium citrate: Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>: thioacetamide of 1:2.3:1.5:0.5, the growth temperature of 90 °C, the growth time of 6 h, the annealing temperature of 350 °C, the annealing time of 20 min.

**Table S7** listed the photovoltaic performance parameters of the Sb<sub>2</sub>S<sub>3</sub> solar cells using the hybrid hole transport layer of *spiro*-OMeTAD:TMT-TTF (36.6 mg *spiro*-OMeTAD:1.0 mg TMT-TTF). From **Table S7**, the Sb<sub>2</sub>S<sub>3</sub> solar cells with the hybrid hole transport layer of *spiro*-OMeTAD:TMT-TTF achieved the PCE of 7.63%, along with the  $V_{oc}$  of 0.78 V,  $J_{sc}$  of 16.89 mA·cm<sup>-2</sup>, FF of 58.00%.

## 7. The PCE summary of the previously reported Sb<sub>2</sub>S<sub>3</sub> solar cells fabricated by various methods

**Table S8** listed the PCE summary of the previously reported Sb<sub>2</sub>S<sub>3</sub> solar cells fabricated by various methods. It can be seen that the highest PCE of Sb<sub>2</sub>S<sub>3</sub> solar cells was still 7.5% before 2022. Until recently, Sb<sub>2</sub>S<sub>3</sub> solar cells achieved the 8.00% PCE by CBD using potassium antimony tartrate as Sb source, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and thioacetamide as S source. This work achieved the PCE of 7.63%, which is second only to the highest PCE of 8.00%.

**Table S8.** The PCE summary of the previously reported Sb<sub>2</sub>S<sub>3</sub> solar cells fabricated by various methods

Method	Sb source	S source	Device structure	PCE (%)	Year
TE	Sb <sub>2</sub> S <sub>3</sub> powder		FTO/CdS/Sb <sub>2</sub> S <sub>3</sub> /Ag	1.27	2014 [2]
TE	Sb <sub>2</sub> S <sub>3</sub> powder		FTO/ZnO/Sb <sub>2</sub> S <sub>3</sub> /P3HT/Ag	2.40	2012 [3]
TE	Sb <sub>2</sub> S <sub>3</sub> powder		FTO/c-TiO <sub>2</sub> /Li-doped m-TiO <sub>2</sub> /Sb <sub>2</sub> S <sub>3</sub> / <i>spiro</i> -OMeTAD/Au	4.42	2018 [4]
TE	S powder and Sb <sub>2</sub> S <sub>3</sub> powder		FTO/bl-TiO <sub>2</sub> /TiO <sub>2</sub> array/Sb <sub>2</sub> S <sub>3</sub> / <i>spiro</i> -OMeTAD/Au	5.80	2019 [5]
RTE	Sb <sub>2</sub> S <sub>3</sub> powder		FTO/c-TiO <sub>2</sub> /Cu-doped Sb <sub>2</sub> S <sub>3</sub> /Au	4.61	2019 [6]
RTE	Sb <sub>2</sub> S <sub>3</sub> powder		FTO/c-TiO <sub>2</sub> /Sb <sub>2</sub> S <sub>3</sub> (Se-treated)/Au	5.40	2019 [7]
ALD	trisdimethyl	H <sub>2</sub> S	FTO/c-TiO <sub>2</sub> /Sb <sub>2</sub> S <sub>3</sub> /	5.77	2014 [8]

	-amino antimony		P3HT/PEDOT:PSS/Au		
VTD	Sb <sub>2</sub> S <sub>3</sub> powder		ITO/CdS/Sb <sub>2</sub> S <sub>3</sub> /Au	4.50	2020 [9]
VTD	Sb <sub>2</sub> S <sub>3</sub> powder		ITO/CdS/Sb <sub>2</sub> S <sub>3</sub> /Au	4.73	2020 [10]
TD	SbCl <sub>3</sub>	Thiourea	FTO/TiO <sub>2</sub> /Sb <sub>2</sub> S <sub>3</sub> / <i>spiro</i> -OMeTAD/Au	5.12	2019 [11]
TD	Sb <sub>2</sub> O <sub>3</sub>	butyldithiocarbamic acid	FTO/TiO <sub>2</sub> /Sb <sub>2</sub> S <sub>3</sub> / <i>spiro</i> -OMeTAD:P3HT/Au	5.65	2021 [12]
TD	Sb <sub>2</sub> O <sub>3</sub>	butyldithiocarbamic acid	FTO/c-TiO <sub>2</sub> /Sb <sub>2</sub> S <sub>3</sub> / <i>spiro</i> -OMeTAD/Au	6.56	2019 [13]
HT	Potassium antimony tartrate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	FTO/CdS/Sb <sub>2</sub> S <sub>3</sub> /PbS/Carbon	6.16	2022 [14]
HT	Potassium antimony tartrate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	FTO/CdS/Sb <sub>2</sub> S <sub>3</sub> /P3HT/Au	6.21	2022 [15]
HT	Potassium antimony tartrate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	FTO/CdS/Sb <sub>2</sub> S <sub>3</sub> / <i>spiro</i> -OMeTAD/Au	6.31	2022 [16]
HT	Potassium antimony tartrate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	FTO/CdS/Sb <sub>2</sub> S <sub>3</sub> / <i>spiro</i> -OMeTAD/Au	6.40	2020 [17]
HT	Sb <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	FTO/CdS/Sb <sub>2</sub> S <sub>3</sub> / <i>spiro</i> -OMeTAD/Au	6.51	2023 [18]
HT	Potassium antimony tartrate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	FTO/SnO <sub>2</sub> /CdS/Sb <sub>2</sub> S <sub>3</sub> / <i>spiro</i> -OMeTAD/Au	6.84	2022 [19]
HT	Potassium antimony tartrate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	FTO/TiO <sub>2</sub> /CdS/Sb <sub>2</sub> S <sub>3</sub> /Carbon	7.23	2023 [20]
HT	Potassium antimony tartrate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	ITO/CdS:In/Sb <sub>2</sub> S <sub>3</sub> / <i>spiro</i> -OMeTAD/Au	7.31	2022 [21]
CBD	SbCl <sub>3</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	FTO/TiO <sub>2</sub> /Sb <sub>2</sub> S <sub>3</sub> / <i>spiro</i> -OMeTAD/Au	4.61	2018 [22]
CBD	SbCl <sub>3</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	FTO/c-TiO <sub>2</sub> /m-TiO <sub>2</sub> /Sb <sub>2</sub> S <sub>3</sub> /P3HT/Au	5.06	2010 [23]
CBD	SbCl <sub>3</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	FTO/c-TiO <sub>2</sub> /m-TiO <sub>2</sub> /Sb <sub>2</sub> S <sub>3</sub> / <i>spiro</i> -OMeTAD/Ag	6.00	2017[24]
CBD	SbCl <sub>3</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	FTO/c-TiO <sub>2</sub> /m-TiO <sub>2</sub> /Sb <sub>2</sub> S <sub>3</sub> /PCPDTBT(PCBM)/Au	<b>7.50</b>	<b>2014 [25]</b>
CBD	Potassium antimony tartrate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> and thioacetamide	FTO/CdS/Sb <sub>2</sub> S <sub>3</sub> / <i>spiro</i> -OMeTAD/Au	<b>8.00</b>	<b>2022 [26]</b>
CBD	SbCl <sub>3</sub> -sodium citrate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> and thioacetamide	FTO/CdS/Sb <sub>2</sub> S <sub>3</sub> / <i>spiro</i> -OMeTAD:TMT-TTF/Au	<b>7.63</b>	<b>This work</b>

TE: Thermal evaporation, RTE: Rapid thermal evaporation, ALD: Atomic layer deposition, VTD: Vapor transport deposition, TD: Thermal decomposition, HT: Hydrothermal, CBD: Chemical bath deposition



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