Supplementary Information

10.21% Efficiency $Sb_2(S,Se)_3$ Thin Film Solar Cells with a Mixed Hole-Transport Materials

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Device Fabrication. In the solar cell fabrication, CdS was used as the electron transport layer, which was deposited by CBD method. The specific deposition process is as follows: Typically, 165 mL DI water, 23 mL of $CdSO_4$ (15 mmol L^{-1}) solution, 30 mL of aqueous ammonia solution, and 13 mL of thiourea (1.5 mol L^{-1}) solution were stirred for 3 minutes in a beaker. Then, FTO substrates were placed in the beaker and heated at 66 °C in a water-bath. After 16 min, the CdS film were taken out and rinsed with DI water. Finally, 15 mg mL^{-1} of $CdCl_2$ solution was spin-coated onto the CdS film and annealed at 400 °C in air for 10 min.

For $Sb_2(S,Se)_3$ films, they were prepared via hydrothermal deposition method, with sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$), sodium selenosulfate (Na_2SeSO_3), potassium antimonyl tartrate ($KSbC_4H_4O_7 \cdot 3H_2O$) as S, Se, and Sb sources. The Na_2SeSO_3 solution was prepared by a hydrothermal method, which involved reacting 0.16 g of selenium powder with 1.01 g of sodium sulfite (Na_2SO_3) in 40 mL of deionized water at 110°C for 360 minutes. The mixture of selenium powder and sodium sulfite must be thoroughly stirred prior to the reaction to prevent incomplete conversion. For the $Sb_2(S,Se)_3$ precursor solution, 1.63 g of $KSbC_4H_4O_7 \cdot 3H_2O$ was dissolved in 120 mL of deionized water at 25°C under stirring for 3 minutes. Subsequently, 4.76 g of $Na_2S_2O_3 \cdot 5H_2O$ was added and stirred for 1 minute until complete dissolution. Then, 16.5 mL of the Na_2SeSO_3 solution was introduced and stirred for 30 seconds, yielding a light-yellow turbid precursor solution. Hydrothermal synthesis was conducted at 135°C, with an optimal deposition window of 110 to 130 minutes. Finally, the $Sb_2(S,Se)_3$ film was taken out, dried, and annealed on hotplate at 350°C in a N_2-filled glove box.

The hole-transport layers were prepared by spin coating the precursor solutions of Spiro-OMeTAD and HPB-OMeDPA. For Spiro-OMeTAD solution, it was prepared by adding 36.6 mg of Spiro-OMeTAD (99.8%, Yingkou Youxuan Trading Co., Ltd.), 14.5 μL of tBP (96%, J&K), and 9.5 μL of a lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI, 98%, J&K) acetonitrile solution (520 mg mL^{-1}) to 1 mL chlorobenzene. The Spiro-OMeTAD solution was then spin-coated onto the $Sb_2(S,Se)_3$ surface at 3000 rpm for 30 seconds. Subsequently, the unfinished device was placed on a hotplate and annealed at 100 °C for 10 minutes. For the preparation of the HPB-OMeDPA solution, 29.76 mg of HPB-OMeDPA (prepared according to the reported method)[17] was used in place of 36.6 mg of Spiro-OMeTAD. The mixed hole-transport material was fabricated by combining Spiro-OMeTAD and HPB-OMeDPA at a molar ratio of 1:1. In both cases, all other reagents and procedural steps were maintained consistent with the standard Spiro-OMeTAD preparation process. Final, the Au (70 nm) film was used as a metal electrode for thermal evaporation with an aperture area of 0.105 cm^2.

Measurement and Characterization. The scanning electron microscopy (SEM) images of HTMs were visualized by cold-field emission scanning electron microscopy (SU8200). The X-ray photoelectron spectroscopy (XPS) of HTMs was in progress on Thermo Scientific K-Alpha+. The energy band positions of Spiro-OMeTAD and HPB-OMeDPA thin film were tested via ultraviolet photoelectron spectroscopy (UPS) (Thermo Fisher, ESCALAB 250Xi) with a bias of -5 V. The ultraviolet-visible absorption spectra of Spiro-OMeTAD and HPB-OMeDPA films were collected using a UV-Visible spectrophotometer (UV-Vis DRS, SOLID 3700) in the 300-900 nm range. The surface morphologies of $Sb_2(S,Se)_3$/Spiro-OMeTAD and $Sb_2(S,Se)_3$/HPB-OMeDPA films were collected by atomic force microscopy (AFM, Bruker). The ultrafast transient absorption (TA) of the Spiro-OMeTAD and HPB-OMeDPA films was carried on a pump-probe system (Helios, Ultrafast System LLC). A Keithley 2400 apparatus was used to measure the *J*-*V* characteristics under solar-simulated AM 1.5 sunlight (100 mW cm^{-2}) with a standard xenon-lamp-based solar simulator (Oriel Sol 3 A, Japan).

Supplementary Figures

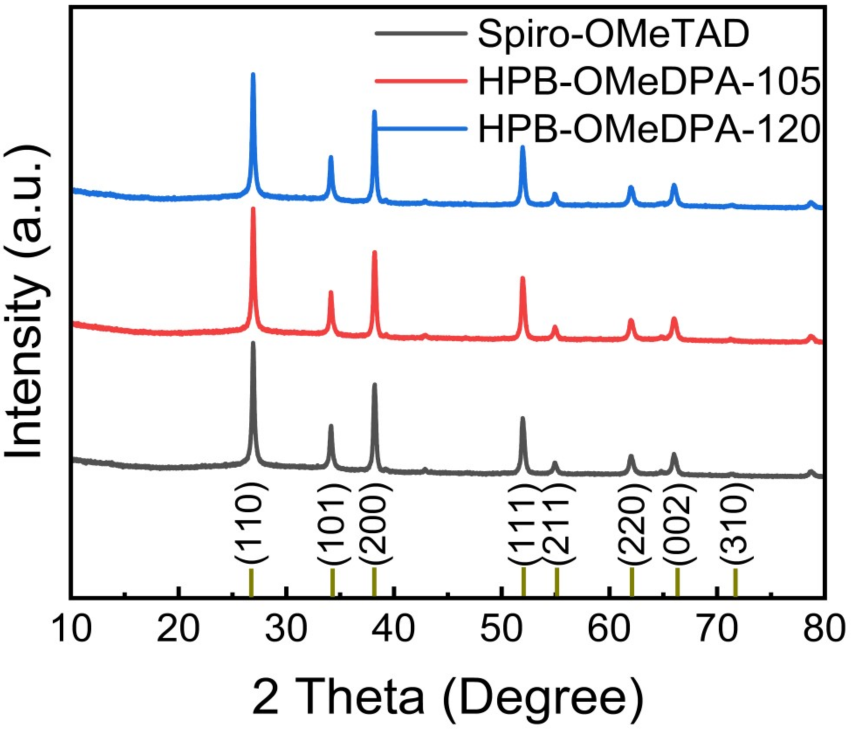

Figure S1. XRD test of the thin film annealed for the FTO/Spiro-OMeTAD device at 105 ℃; XRD test of the thin film annealed for the FTO/HPB-OMeDPA device at 105 ℃and 120 ℃. *All of the XRD patterns show diffraction peaks from FTO substrates, indicating there is no new crystalline phase from the HTMs*.

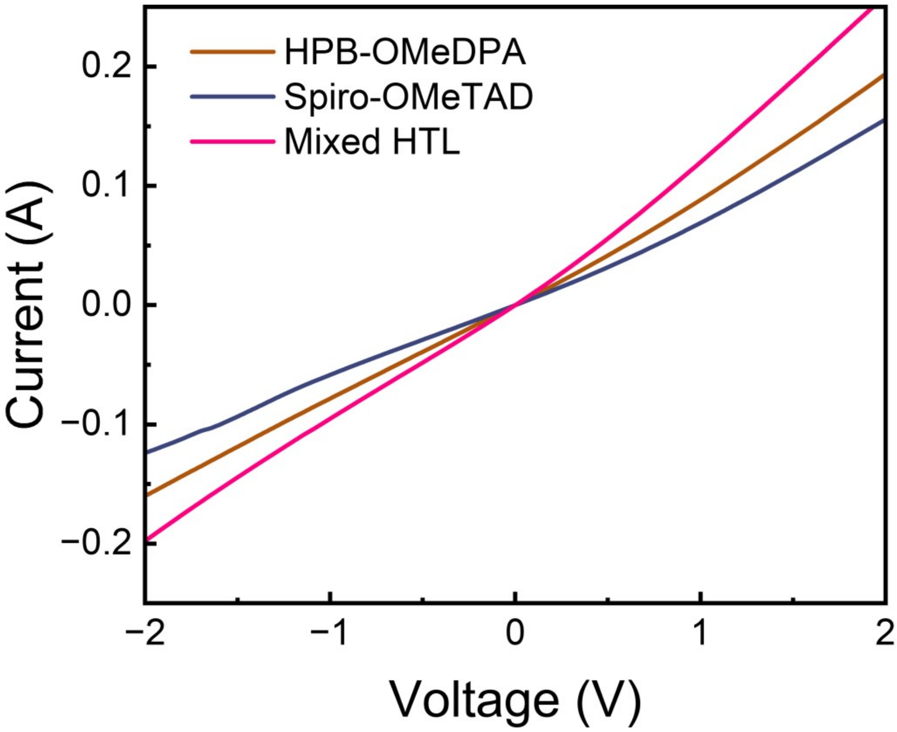

Figure S2. the conductivity of hole-transport materials based on the FTO/CdS/$Sb_2(S,Se)_3$ /HTL/Au device model through J-V testing.

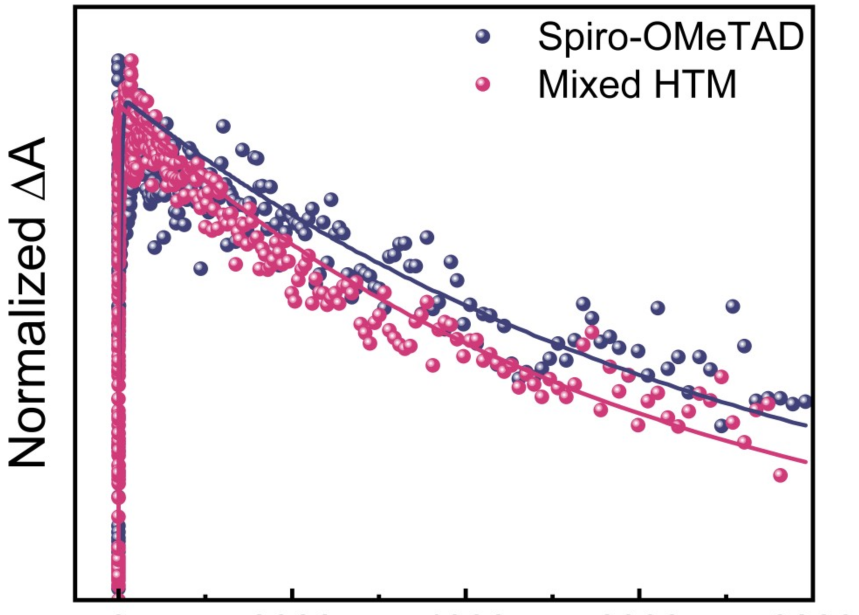

Figure S3. TAS decay kinetics at 629 nm of Spiro-OMeTAD and HPB-OMeDPA film.

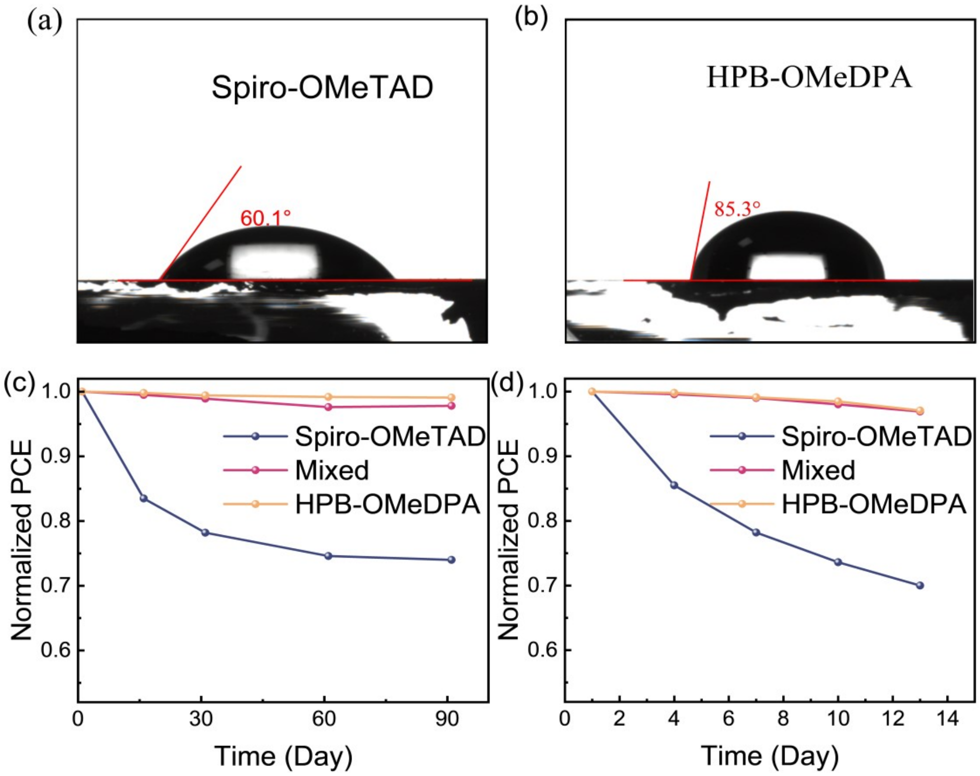

Figure S4. Contact angle measurements by dropping water on top of (a) Spiro-OMeTAD, (b) HPB-OMeDPA films. Stability of unencapsulated $Sb_2(S,Se)_3$ solar cells with different HTMs (Spiro-OMeTAD, HPB-OMeDPA, and mixed HTM). (c) Long-term stability under ambient conditions (room temperature, 15–50% RH) for 90 days. (d) Thermal stability at 50 °C for 14 days.