

Supporting Information

Managing Film Crystallization via Low-toxic Antisolvents: Stabilizing Ag₃BiI₆ Perovskite like Solar cells under Ambient Conditions

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1. Experimental Section

1.1 Materials

N, N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%), chlorobenzene (99.8%), Xylene (IPA, 99.7%), Petroleum Ether (IPA, 99.7%), Silver iodide (AgI, Powder, 99.999%), Bismuth Iodide (BiI₃, powder, 99.999%), Lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI, 98%), 2,2',7,7'-tetrakis (N,Np-dimethoxy-phenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD, 99.8%) were bought from Sigma-Aldrich. Zinc bis(trifluoromethanesulfonyl)imide (Zn-(TFSI)₂, 98%) were purchased from TCI. Absolute Ethanol (Eth, 99.9%) was got from Changshu Hongsheng Fine Chemical Co., Ltd.

1.2 Solution- Preparation

The Ag₃BiI₆ precursor solutions were prepared by dissolving silver(I) iodide, bismuth (III) iodide at the desired ratios in a mixed solvent system (DMSO:DMF, 3:1 v/v), stirred at room temperature overnight. For the preparation of spiro-OMeTAD solution, 73.4 mg spiro-OMeTAD, 17.6 µL Li-TFSI solution (520 mg Li-TFSI in 1 mL ACN), and 28.8 µL ethanol were mixed in 1 mL chlorobenzene and stirred overnight. In its pristine form, spiro-OMeTAD suffers from low hole mobility and conductivity, which limits its effectiveness as a hole transport material (HTM).

The inclusion of a dopant, such as LiTFSI, not only increases the number of charge carriers but also helps tune the electronic properties, including energy level alignment at the interfaces. To optimize the conductivity of spiro-MeOTAD, we systematically varied the dopant concentrations.

At lower dopant concentrations ($< 17.0 \mu\text{L}$), it affected the device performance due to insufficiency of dopant to induce good hole mobility. However, at higher dopant concentrations beyond $18.0 \mu\text{L}$, we encountered solubility challenges, particularly with the dissolution of LiTFSI in the spiro-MeOTAD matrix. This led to issues with uniformity of films. Based on these observations, the optimal dopant concentration was found to be $17.6 \mu\text{L}$ of LiTFSI dissolved in $28.8 \mu\text{L}$ of ethanol, which provided the best balance between solubility, conductivity, and overall device performance.

Also in perovskite solar cells, tert-butylpyridine (TBP) is commonly used in combination with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) to improve solubility and prevent phase segregation between LiTFSI and spiro-MeOTAD, ensuring a smoother hole transport layer (HTL) and better interfacial contact. However, in this perovskite case, TBP showed a tendency to wash off the Ag_3BiI_6 material, because of which we replaced it with ethanol in our study. Hence, we have arrived at a combination of $17.6 \mu\text{L}$ and ethanol as the best dopant concentration and solvent type respectively. This formulation ensured efficient doping without compromising the material's integrity or performance, as confirmed by subsequent device testing.

The water-based TiO_2 colloid precursor was prepared according to previous work.[42] Briefly, the TiO_2 -CL nanoparticles were synthesized following modified nonhydrolytic sol-gel method and the nanocrystals sediment were dispersed in ultrapure water to make a suspension.

1.3 Ag_3BiI_6 Solar Cells Fabrication

FTO-coated glass slides were cleaned following a optimized procedure and used as substrates for solar cells. Cleaning of the FTO included ultrasonication in a 1% Helmanex surfactant solution, water and ethanol (15 min in each medium), drying under N_2 flow, and plasma treatment at 1000 mTorr for 15 min (Harrick Plasma cleaner). A compact TiO_2 blocking layer (c- TiO_2 ; thickness $\approx 10 \text{ nm}$) was deposited onto the FTO at 5000 rpm for 30s and then annealed at 180°C for 10 min then 500°C in air. Upon cooling to ambient temperature, A mesoporous titania layer (m- TiO_2 ; thickness $\approx 150 \text{ nm}$) was deposited by spin coating at 5000 rpm, 30s followed by drying at 80°C

and sintering at 450 °C in air. The precursor solution was spin-coated at 4000 rpm for 30s, respectively. And 140 μ L CB was dropped at 15th second, while the [1:5] 350 μ L Xylene and 500 μ L Mixed solvent was dropped at 20th second. Then, the films were annealed on a hot stage at 70 °C for 10 min and 130°C for 15 mins. For the hole-transport layer, it was obtained by spin coating the Spiro-MeOTAD solution on the top of perovskite film at 3000 rpm for 30 s. At last, on top of the Spiro-OMeTAD layer, 80 nm Ag electrode was thermally evaporated.

1.4 Solar Cell Characterization

An Keithley 2420 Series precision source/measure unit was used to perform current density–voltage (J–V) characterization. During the test, the cells were illuminated under AM 1.5G irradiation (100 mW cm⁻²) by a Xeon lamp solar simulator (94023A Oriel Sol3A, class AAA). A Newport calibrated KG5-filtered Si reference cell was used to calibrate the light intensity. The scanning rate of the J–V curves was 50 mV s⁻¹ (voltage step of 10 mV and delay time of 200 ms), and the scanning scope and direction was from –0.01 to 1.15 V (forward).

Quantum efficiency measurements were carried out using an Oriel Xenon lamp (450 W) and a monochromator with a bandwidth of 5 nm.

1.5 Ag₃BiI₆ Film Characterization

UV-visible absorption spectra were collected using Shimadzu UV-1800 spectrometer. The top-view SEM images of the perovskite films and the cross-sectional SEM images of the PSC devices were recorded by a scanning electron microscope (Quanta FEG 450) under 5 kV electron beam accelerate voltage. XRD patterns of Lead -free inspired films were collected from a Rigaku Ultima IV X-Ray diffractometer operated with an X-ray generator voltage and current of 50 kV and 60 mA respectively and using a Cu K α source (λ = 1.54187 Å). Data analysis was performed with the Rigaku PDXL data processing software. XPS spectra were collected using a Thermo Fisher Scientific K-Alpha. Samples were prepared by drop-casting a concentrated NP dispersion in toluene on clean glass substrates and dried. Each spectrum was referenced to the peak energy position observed for adventitious carbon (C 1s 284.8 eV).

2. Ag₃BiI₆ Films treated with different antisolvents

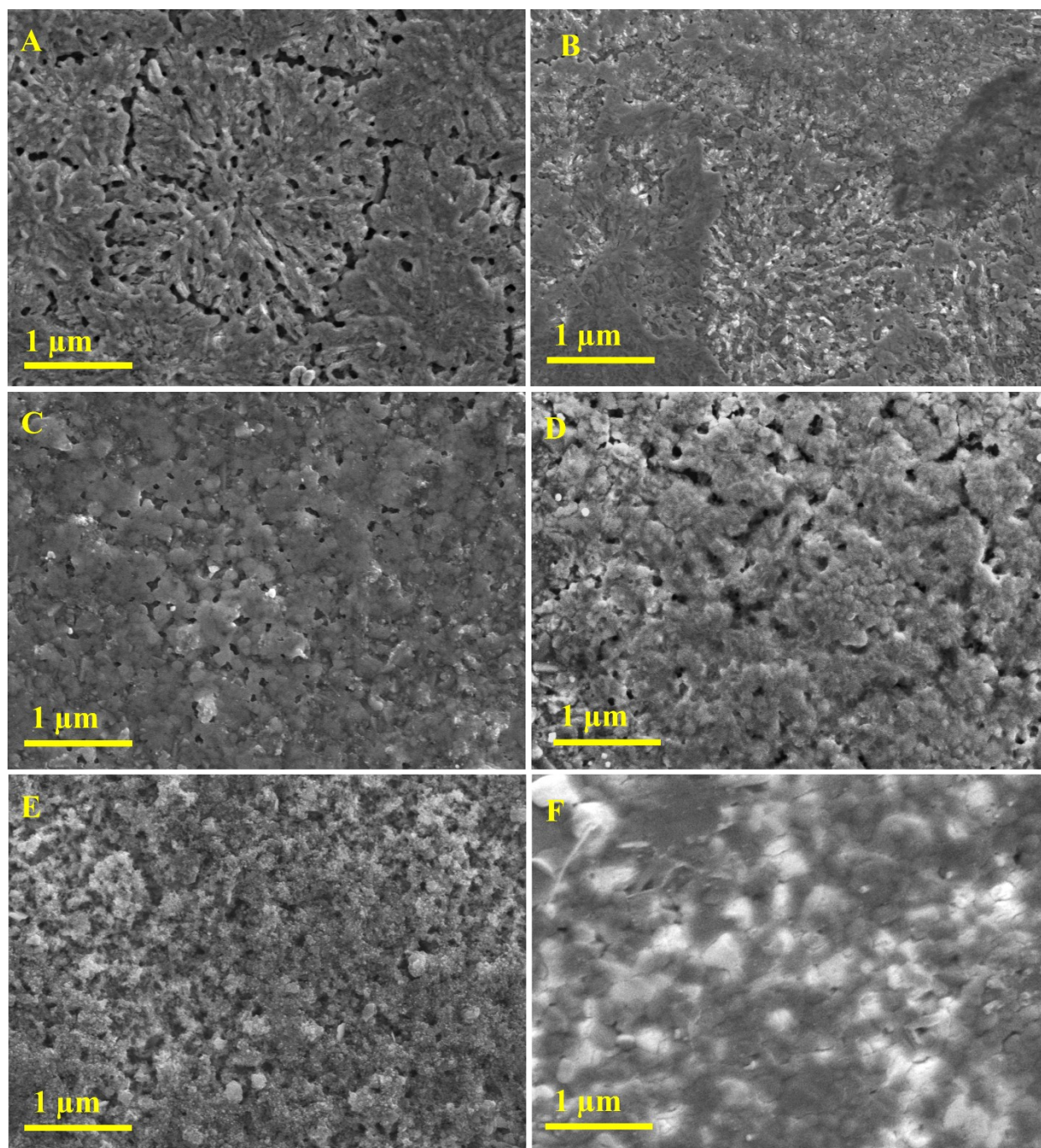


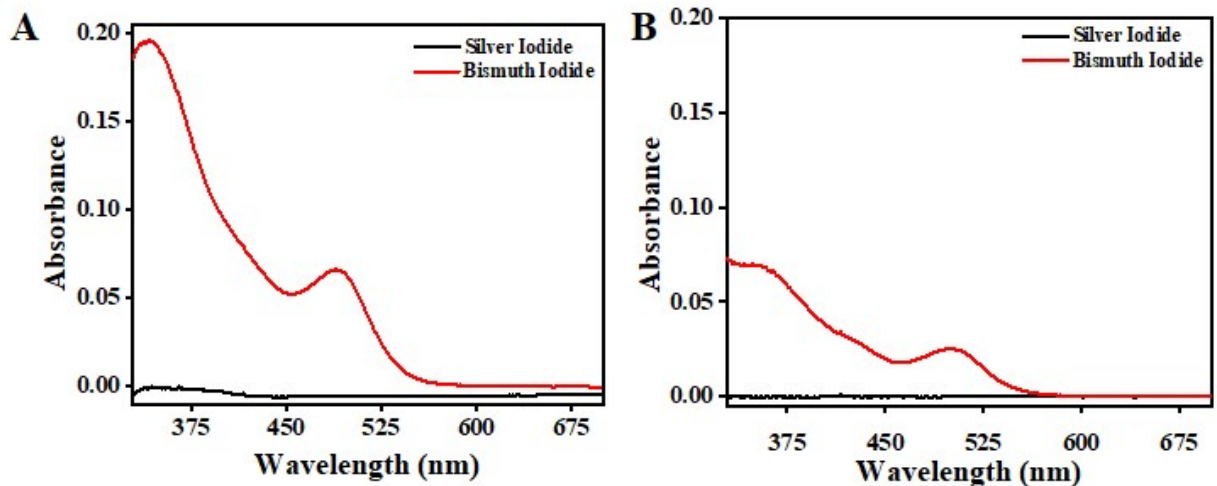
Figure 1. FESEM images of Ag_3BiI_6 films treated with different antisolvents (A) hexane, (B) diethyl ether, (C) chloroform, (D) ethyl acetate, (E) toluene, (F) chlorobenzene, the scale bar is $1\mu\text{m}$.

Thin films obtained using hexane, toluene, chloroform, ethyl acetate, diethyl ether, chlorobenzene are shown in **Figure 1**. A frosted, or needle like crystals were observed for films treated with hexane, diethyl ether and chloroform as anti-solvents due to a very quick and rapid evaporation

that occurs as a consequence of their low boiling points (BP) (hexane BP: 69 °C, diethyl ether BP:34.6 °C, chloroform BP: 62 °C). The morphology of Ag₃BiI₆ films obtained on treating with the polar solvent ethyl acetate is also uneven and poor as the solvent partially dissolves Ag₃BiI₆. Toluene treatment displays a low-quality surface due to its comparatively lower BP of 110 °C compared to CB (BP:131.7 °C) and Xy (BP:139.1°C), resulting in an inhomogeneous nucleation. Both CB and Xy exhibited comparable BPs and evaporation rates. Therefore, the new antisolvent formulation containing Xy was evaluated against chlorobenzene, which was considered as the reference.

Table S1: Properties of common solvents and antisolvents used in Ag₃BiI₆ film fabrication.

Solvent	Density [g ml⁻¹]	Boiling point [°C]	Dipole moment [D]	δ_D [MPa^{1/2}]	δ_P	δ_H
CB	1.11	131	1.69	19.0	4.3	2.0
Xy	0.86	139	0.33-0.37	17.4	1.0	3.1
DMF	0.95	153	3.86	17.4	13.7	11.3
DMSO	1.1	189	3.96	18.4	16.4	10.2



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figure S2. UV-Visible absorption of the corresponding supernatant of the Ag_3BiI_6 precursors (AgI , BiI_3) in (A) CB, (B) Xy.

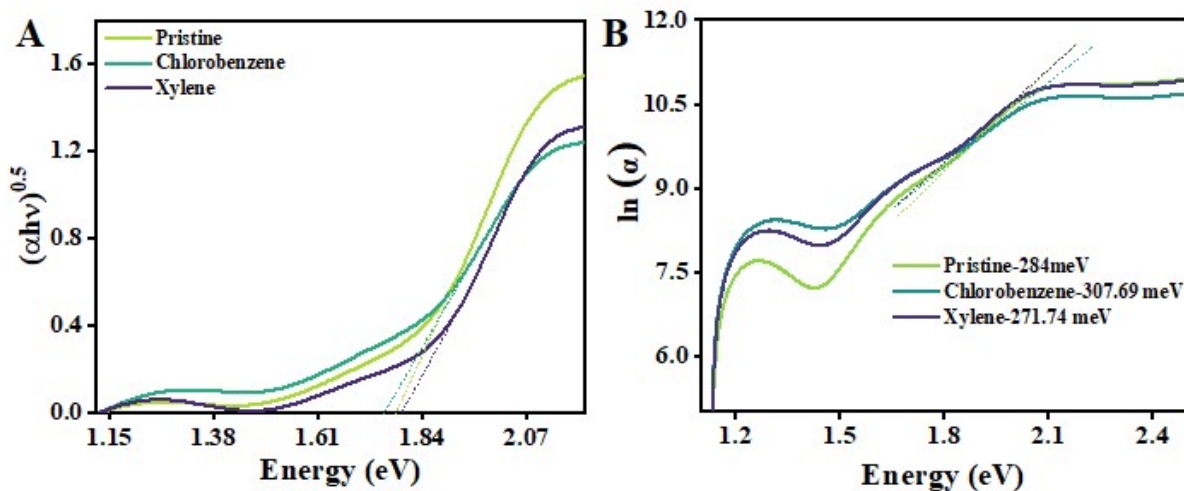


Figure S3. (A) Tau plot of Ag_3BiI_6 films treated without and with different antisolvents (B) Plots of $(\ln \alpha)$ as a function of energy ($h\nu$) extracted from absorption spectra to determine the Urbach energy for Ag_3BiI_6 films treated with different antisolvents.

Table S2: Photovoltaic parameters, E_g , V_{OC} (deficit), and E_U of Ag_3BiI_6 solar cells treated with different antisolvents.

Sample Info	V _{OC} (V)	E _g (eV)	Eu (meV)	V _{OC} (Deficit) (V)
Pristine	0.51	1.77	284	1.26
CB	0.53	1.78	307.69	1.25
Xy	0.54	1.78	271.74	1.24
MS	0.57	1.76	234.71	1.19

Table S3: Summary of XRD quantitative analysis performed on Ag₃BiI₆ without and with different antisolvent.

Sample Code	FWHM	12° Intensity	AgI Intensity	Ratio (1:2)
Pristine	0.210	1391	599	2.322
CB	0.218	1360	812	1.674
Xy	0.160	3873	899	4.308

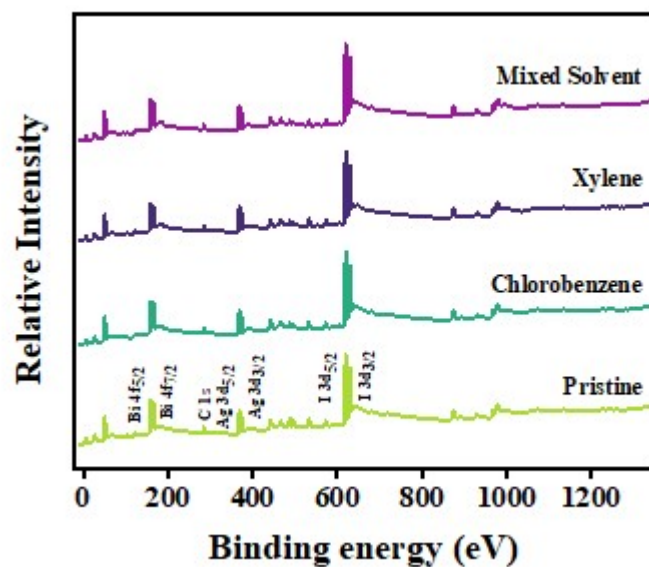


Figure S4. Survey spectra of Ag_3BiI_6 films and films treated with different antisolvent.

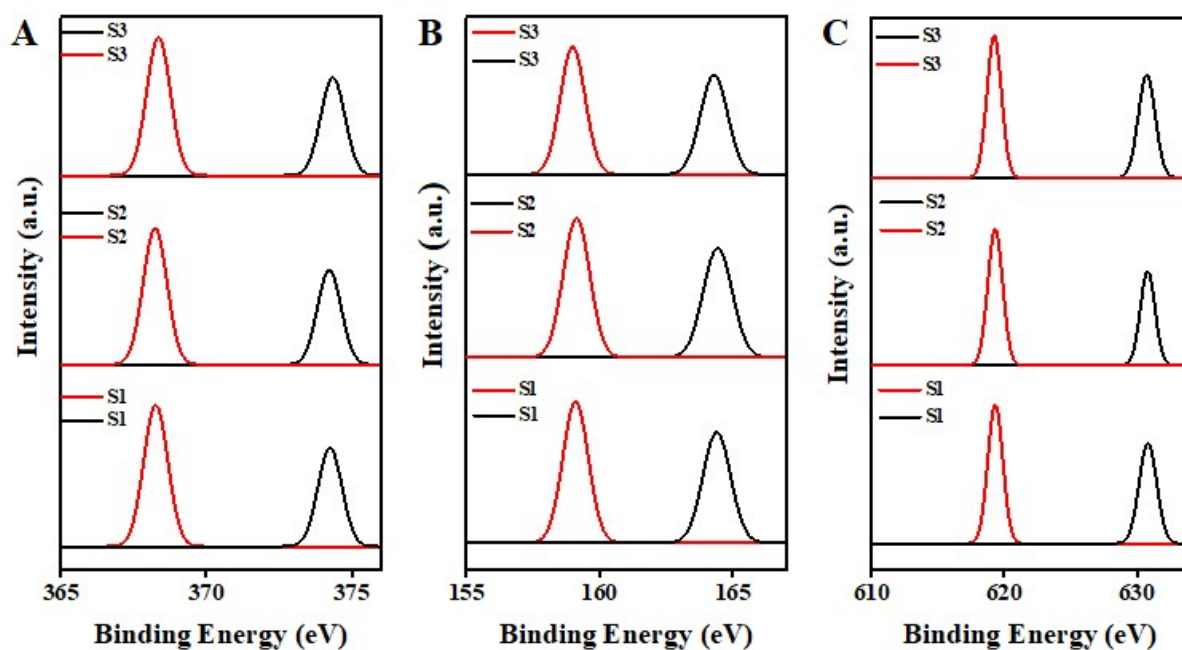


Figure S5. X-ray photoelectron spectroscopy (XPS) Gaussian spectra of (A) Ag 3d peaks (B) Bi 4f peaks (C) I 3d peaks, for Pristine [S1] and samples treated with CB[S2], Xy[S3].

Table S4: Summary of XPS quantitative analysis performed on Ag₃BiI₆ for Pristine ,CB , Xy.

Sample Info	Atomic Sensitivity of Silver	Relative Intensity of silver	Atomic sensitivity of Bismuth	Relative intensity of Bismuth	Atomic Sensitivity of iodine	Relative intensity of Iodine
Pristine	11.62	0.83684	9.6	1	24.58	2.23378
CB	11.74	0.49742	9.04	1	24.96	1.83231
Xy	13.78	0.72012	7.88	1	26.05	1.35301

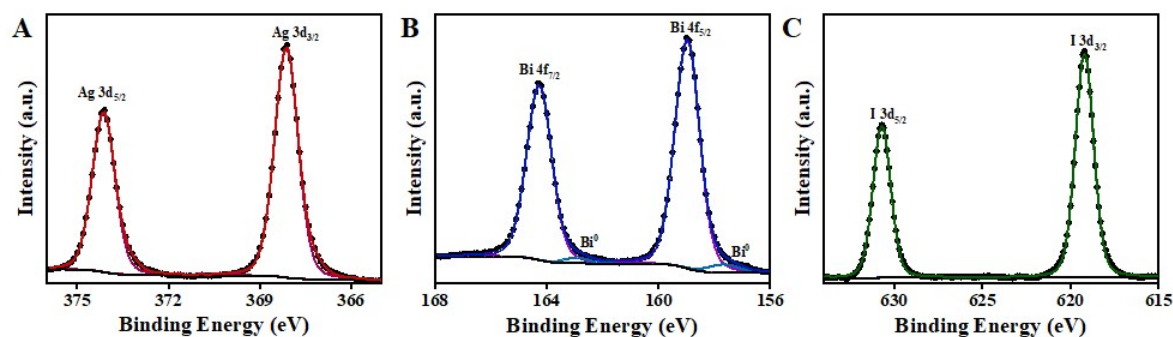


Figure S6. X-ray photoelectron spectroscopy (XPS) spectra of (A) Ag 3d peaks (B) Bi 4f peaks (C) I 3d peaks Ag₃BiI₆ samples treated with Mixed Antisolvent.

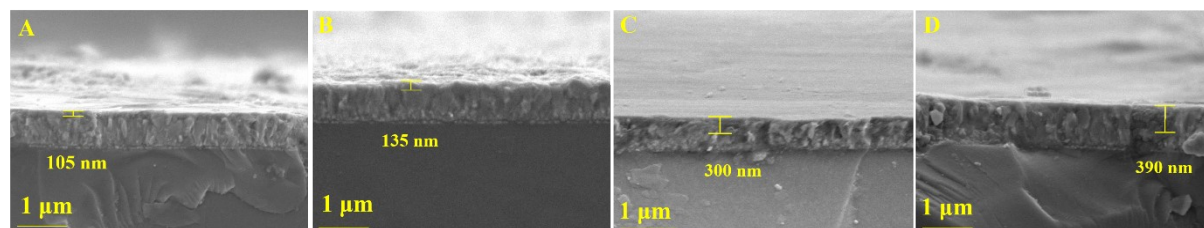


Figure S7. The cross-sectional FESEM images for (CL+ML) TiO₂ films spin-coated with similar rpm parameters as indicated in **Table S4**. The layers from top to the bottom are mesoporous TiO₂, Compact TiO₂, FTO, and glass, respectively. The TiO₂ layer thickness are listed in the top and

bottom of each image, the scale bar is 1 μ m. The marked portion is combined thickness of ETL(CL+ML).

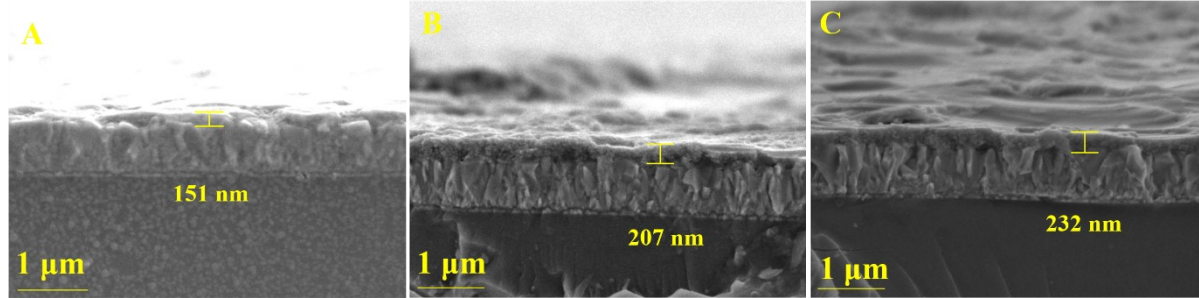


Figure S8. The cross-sectional FESEM images for (CL +ML) TiO₂ films spin-coated with different rpm parameters as indicated in **Table S5**. The layers from top to the bottom are mesoporous TiO₂, Compact TiO₂, FTO, and glass, respectively. The TiO₂ layer thickness are listed in the top and bottom of each image, the scale bar is 1 μ m. The marked portion is combined thickness of ETL (CL+ML)

Table S5: Summary of device performance metrics for Ag₃BiI₆ solar cells treated with xylene antisolvent measured under AM1.5G 100 mW cm⁻² illumination under forward direction voltage scans for equal thickness of CL and ML of TiO₂.

Sample	Spinning speed (CL+ML) deposition (rpm)	Thickness (nm)	V _{oc} (V)	J _{sc} (mAcm ⁻²)	FF (%)	PCE (%)	R _s (Ω cm ⁻²)	R _{sh} (Ω cm ⁻²)
1	9000+9000	105	0.43	14.97	29.05	1.90	239.81	591.09
			0.39 $\pm$ 0.03	8.58 $\pm$ 5.92	28.31 $\pm$ 3.75	1.28 $\pm$ 0.50	342.6 $\pm$ 201.14	677 $\pm$ 228.57
2	7000+7000	135	0.48	2.25	45.73	0.47	547.89	5905.60
			0.41 $\pm$ 0.08	3.23 $\pm$ 0.91	35.92 $\pm$ 7.65	0.48 $\pm$ 0.20	731.85 $\pm$ 319.66	3302.19 $\pm$ 1800.78
3	5000+5000	300	0.54	2.76	51.16	0.76	643.80	11730.06
			0.42 $\pm$ 0.06	3.58 $\pm$ 1.39	33.70 $\pm$ 9.56	0.51 $\pm$ 0.21	851 $\pm$ 521.81	9986.32 $\pm$ 10027.79
4	4000+4000	390	0.43	4.99	30.47	0.65	539.32	1020.27
			0.27 $\pm$ 0.08	4.13 $\pm$ 0.39	27.69 $\pm$ 1.50	0.32 $\pm$ 0.15	489.18 $\pm$ 83.08	5579 $\pm$ 4312.45

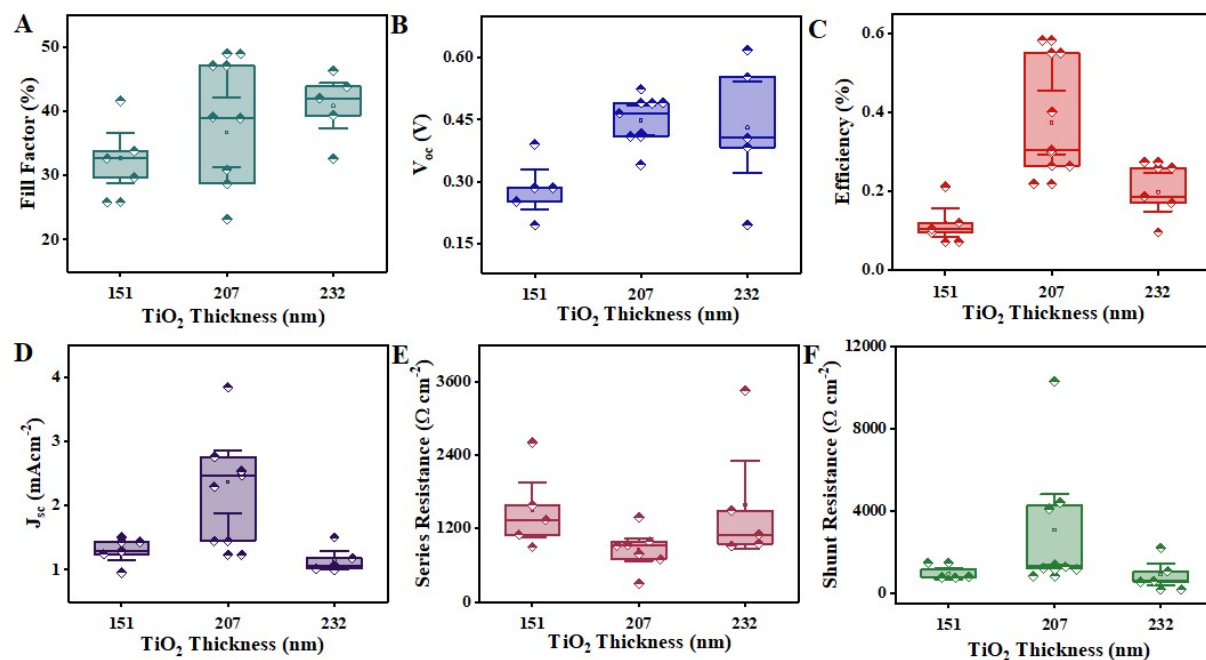


Figure S9. Statistical distribution of photovoltaic performance parameters in forward scan under 1 sun (AM 1.5 illumination) (A) FF, (B) J_{sc}, (C) V_{oc}, (D) PCE, (E) R_s, (F) R_{sh} against the CL and ML spin-coated with different rpm parameters.

3. Tuning Electron Transport Layer

Keeping the optimum coating speed of ML as achieved previously at 5000 rpm, we tried to vary the speed of CL and found any further decrease brings down the performance. A higher series resistance of 2601.66 Ωcm⁻² and 953.57 Ωcm⁻² and low shunt resistance of 1473.453 Ωcm⁻² and 2195.01 Ωcm⁻² was observed for 151 nm and 232 nm. The bad series and shunt resistance in these devices with thin CL can be ascribed to the occurrence of voids, which is further hampered by to higher density of TiO₂. So the devices with equal (CL + ML) coating speeds performed better as one supports the other and, among them 300 nm thickness achieved with equal coating speeds of 5000 rpm of CL and ML gave the best results as explained in the main text (Section 3.3.1).

Table S6: Summary of device performance metrics for Ag₃BiI₆ treated with xylene antisolvent

Sample	Spinning speed (CL+ML) deposition (rpm)	Thickness (nm)	V _{oc} (V)	J _{sc} (mAcm ⁻²)	FF (%)	PCE (%)	R _s (Ωcm ⁻²)	R _{sh} (Ωcm ⁻²)
1	5000+5000	300	0.54	2.79	51.16	0.76	643.8	10308.74
			0.39±0.03	3.58±1.39	33.70±7.13	0.5±0.21	851±521.81	9986.32±10027.79
2	7000+5000	232	0.61	1.5	46.38	0.17	953.57	2195.01
			0.41±0.08	1.15±0.21	40.86±5.25	0.19±0.07	1584±1073.754	909.78±784.81
3	6000+5000	207	0.55	3.84	42.03	0.27	1495.18	11730.06
			0.44±0.06	3.58±1.39	36.72±9.56	0.37±0.14	858.46±327.66	3086.38±3238.72
4	9000+5000	151	0.39	1.50	41.66	0.10	2601.66	1473.45
			0.28±0.07	1.28±0.21	32.74±5.86	0.12±0.053	1506.39±664.27	946.9785±351.28

measured with AM1.5G 100 mW cm⁻² illumination under forward direction voltage scans for different thickness of CL and ML of TiO₂.

4. Understanding distribution of Ag₃BiI₆ on varying thickness of TiO₂

Energy Dispersive X-ray (EDX) mapping was performed at various points located at the center of mesoporous TiO₂ (with different thickness) to examine the best structure that facilitates the maximum and uniform penetration of Ag₃BiI₆ and the images are illustrated in the **Figure S10**. The analysis reveals that, for TiO₂ layers with lower thicknesses (CL + ML), the penetration and distribution of Ag₃BiI₆ is insufficient, and non-uniform, as shown in the corresponding **Figure S10**. With an increase in TiO₂ thickness, the penetration of Ag₃BiI₆ improves, resulting in a more uniform distribution and a comparatively flat surface morphology. However, with further increase in thickness, both penetration and uniformity in Ag₃BiI₆ distribution decreases. This hinders the interaction between the ETL and Ag₃BiI₆ giving a lower device performance as observed in PCE of these cells. These observations are summarized in Table S5. Thus, the analysis indicates 300 nm thickness of ETL to possess the best electron transport layer structure. Consequently, the further analysis of the antisolvent effect was conducted for this optimum thickness of ETL (300 nm).

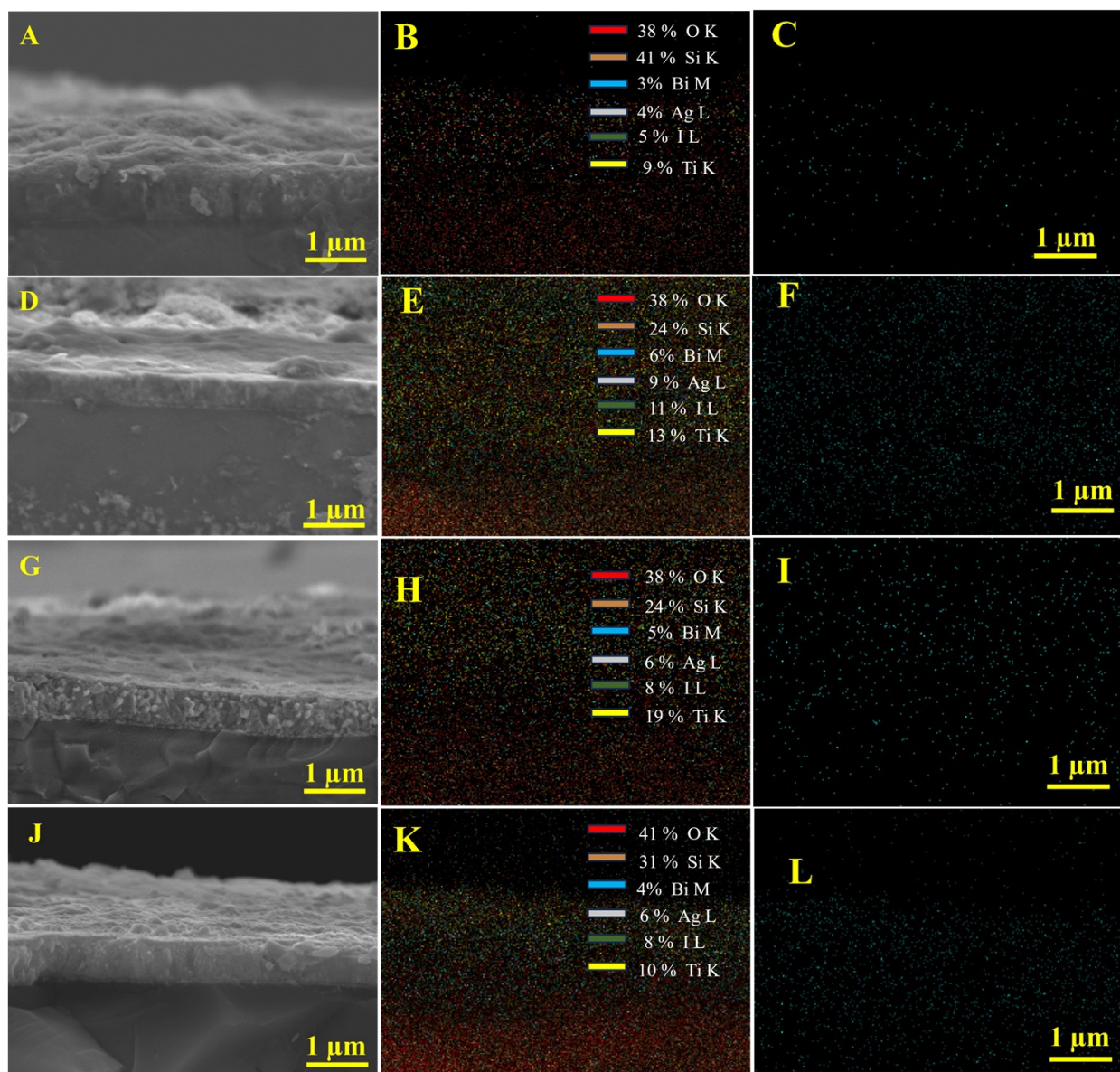


Figure S10: The EDX mapping and cross-sectional FESEM images for Ag_3BiI_6 spin coated on top of varying thickness of (CL+ML) TiO_2 films (A-C) 105 nm, (D-F) 135 nm, (G-I) 300 nm, (J-L) 390 nm. The layers from top to the bottom are Ag_3BiI_6 , mesoporous TiO_2 , Compact TiO_2 , FTO, and glass, respectively.

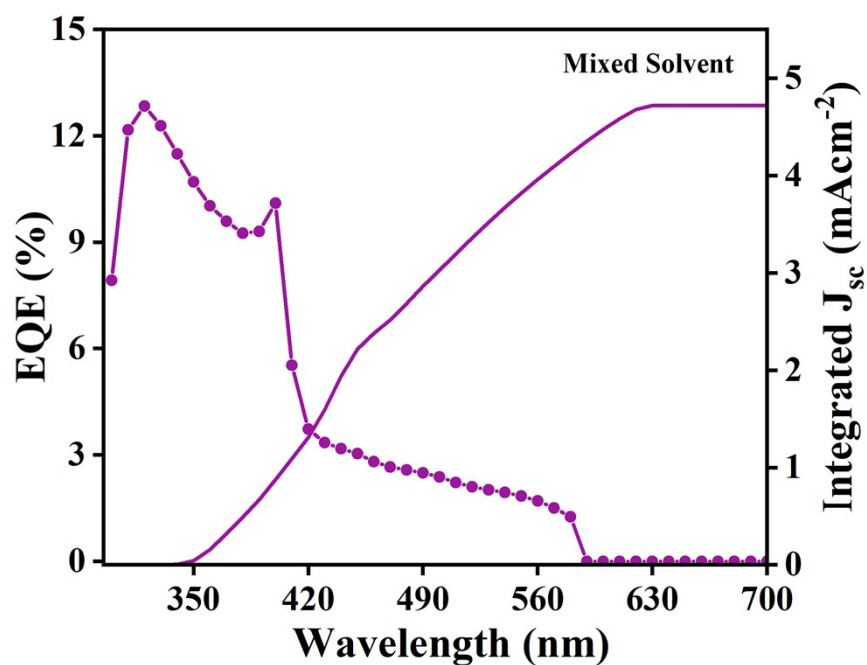


Figure S11. Representative EQE and J_{int} value of Mixed solvent treated Ag_3BiI_6 device

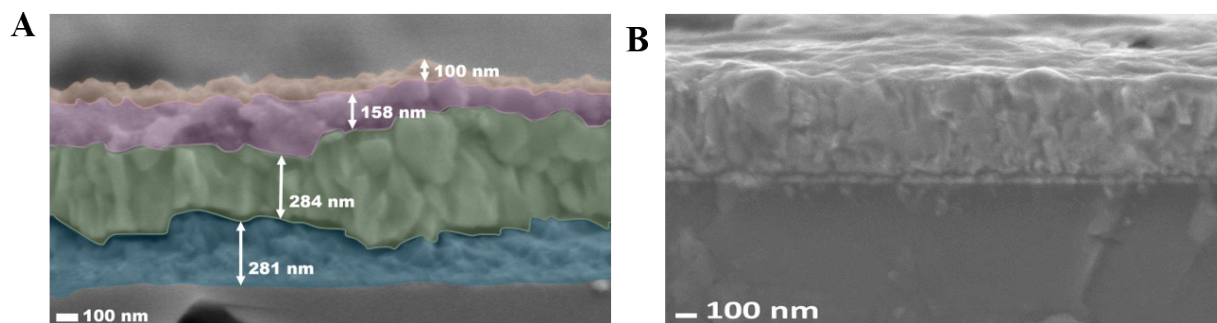


Figure S12. (A-B) FESEM cross-sectional image of Ag_3BiI_6 devices after prolonged irradiation (300 min) employing (A) Li (TFSI) (B) Zn (TFSI)₂ as a dopant for spiro-MeOTAD. The image in A is colored to show the obvious separation that occurs between layers.

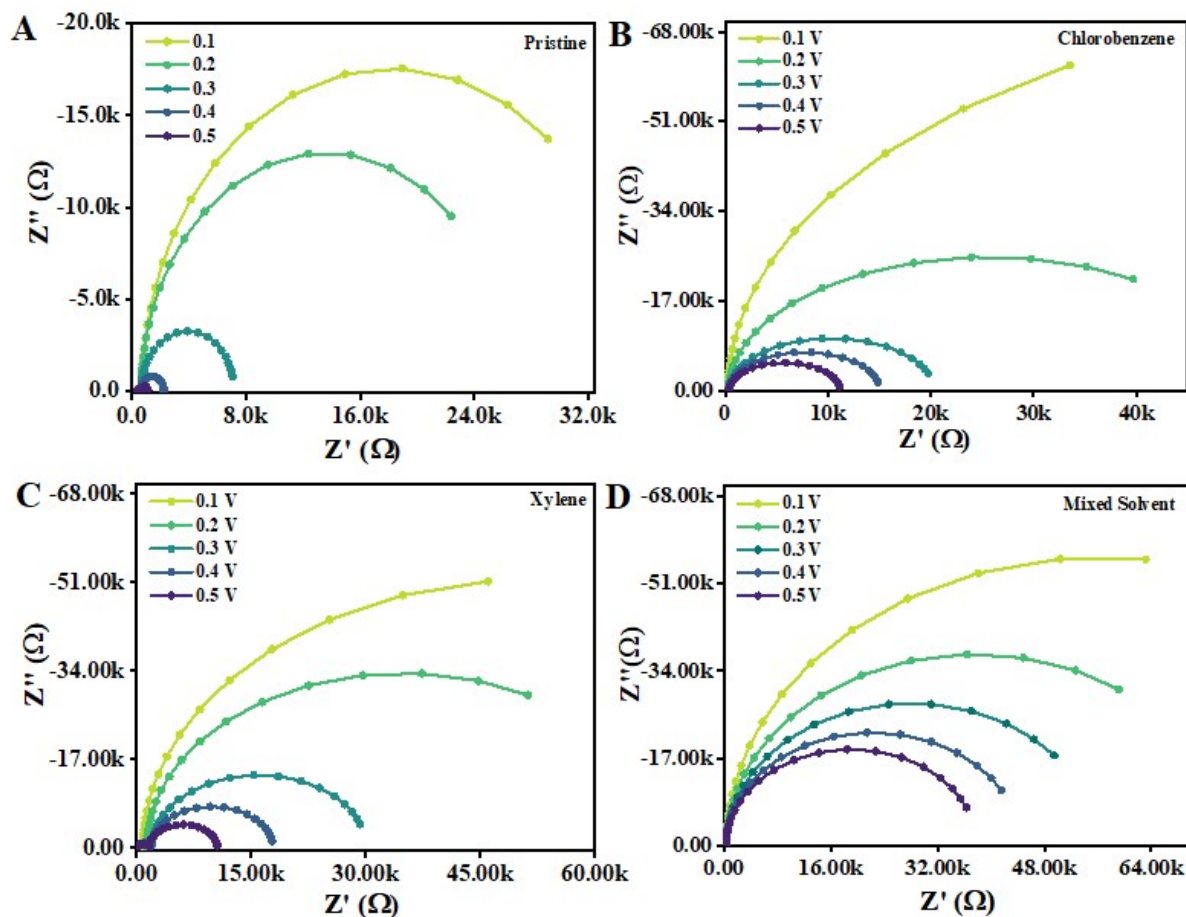


Figure S13. (A-D) Nyquist plots under dark in the frequency range of 1Hz to 1MHz by applying forward bias at different externally applied bias voltages of 0.1 to 0.5 V.