Performance Enhancement of AgBi₂I₇ Solar Cells by Modulating the Solvent-Mediated Adduct and Tuning Remnant BiI₃ on One-step Crystallization.

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SUPPLIMENTARY INFORMATION

EXPERIMENTAL SECTION

Materials: Titanium diisopropoxide bis(acetylacetonate) (Ti (acac)₂) 75 wt.% in isopropanol, Mesoporous TiO₂ (mp-TiO₂) paste (DYESOL 18NR-T), bismuth iodide (BiI₃), dimethyl sulfoxide (DMSO), n-butylamine, chlorobenzene (CB) were obtained from Sigma Aldrich. Titanium tetrachloride (TiCl₄), silver iodide (AgI), ethanol (EtOH) was purchased from Wako Chemicals. Poly(3-hexylthiophene-2,5-diyl) (P3HT) regioregular was purchased from Tokyo Chemical Industry (TCl).

AgBi₂**I**₇ **film fabrication:** Different wt.% (20, 40 and 60 wt.%) of AgI and BiI₃ were dissolved in 1:2 molar ratio in n-butylamine and DMSO and stirred at room temperature and at 70 °C for 30 min, respectively. UV-ozone treatment was performed before the spin-coating step in order to clean the substrate and make it hydrophilic. The AgBi₂I₇-butylamine solution was spin coated at 6000 rpm while the AgBi₂I₇-DMSO solution was spin coated at 1500 rpm for 30 seconds with CB dripping at 10 seconds before the end of spin-coating step for each case. The resulting films were annealed at 150 °C for the n-butylamine case and 90 °C for DMSO case for 30 min. For the Ag₂BiI₅ film, 20 wt. % AgI and BiI₃ were dissolved in 2:1 molar ratio followed by same procedure mentioned above.

Device fabrication: FTO conductive glass substrates (8 Ω sq⁻¹, Nippon Sheet Glass, 1.1 mm in thickness) were cleaned by ultrasonic treatment sequentially with 2% Hellmanex soap solution (in water), deionized water, and ethanol for 15 minutes each followed by UV-ozone treatment for 20 min. The TiO₂ compact layer was spray-coated using a solution of Ti (acac)₂ on to cleaned FTO substrates at 480 °C and kept at the same temperature for 30 min. The mesoporous TiO₂ solution was prepared by dissolving commercially available TiO₂ paste (18NR-T, Dyesol) in ethanol (weight ratio of 1:4) followed by spin coating at 4000 rpm/30 sec and sintering at 500 °C for 1 hour in a muffle furnace. The mesoporous coated substrates were given TiCl₄ treatment (100 mM) at 70 °C for 30 min followed by rinsing in water and ethanol and sintering at 500 °C for 30 min. The resulting mesoporous coated substrates were given UV-ozone treatment for 10 minutes before depositing the active layer following the same procedure mentioned above. 10 mg/mL P3HT solution in chlorobenzene (without any dopants) was spin-coated on AgBi₂I₇ coated substrates at 3000 rpm/30 sec and annealed at 120 °C for 30 min, which was followed by thermal deposition of Au metal electrode to complete the cell. To note, all the chemicals were used as received without further purification and all the processes were carried out in ambient conditions.

Device performance measurements and characterizations:

Peccell Technologies PEC-L01 solar simulator with a Keithley 2400 source meter (AM 1.5G, 100 mW/cm²) was used to measure a current-voltage characteristic plot of all devices. The IPCE spectrum was measured using Peccell technologies, PEC-S20 action spectrum measurement setup. The optical, structural and morphological analysis was carried out using UV-vis spectrometer (UV-1800, Shimadzu), X-ray diffractometer (D8 Discover, Brucker) and scanning electron microscope (SU8000, HITACHI). Long-term stability test of the devices was carried out on best performing cells (without encapsulation) by exposing them to an atmosphere with 50-60% relative humidity and at maximum power point tracking under 1 Sun illumination using the solar simulator.



Fig. S1: Dissolution of AgBi₂I₇ in n-butylamine and DMSO.



Fig. S2: Tauc plot of AgBi₂I₇ thin film from the UV-Vis spectroscopy to determine the optical gap by assuming the material as indirect bandgap semiconductor.



Fig. S3: XRD pattern of 20 wt.% AgBi₂I₇ (obtained from DMSO) and its corresponding JSPDS card.



Fig. S4: XRD pattern of (a) Ag_2Bil_5 thin film obtained from n-butylamine and DMSO, (b) comparison of zoomed XRD pattern of $AgBi_2l_7$ (20 and 40 wt.%) and Ag_2Bil_5 (20 wt.%), (c) XRD pattern of different concentration of $AgBi_2l_7$, and (f) XRD pattern of Ag_2Bil_5 and $AgBi_2l_7$ on glass substrates. # represents FTO peaks.



Fig. S5: Top surface SEM image of $AgBi_2I_7$ thin film obtained from n-butylamine.



Fig. S6: Top surface SEM image of 40 wt. % $AgBi_2I_7$ obtained from DMSO



Fig. S7: (a) Schematic illustration of device stacking layers and their corresponding energy band diagram, (b) best performing device J-V characteristic curve showing negligible hysteresis and (c) PCE histogram plot of AgBi₂I₇ devices obtained from n-butylamine and DMSO route.



Fig. S8: Device parameters of $AgBi_2I_7$ measured under simulated AM 1.5 sunlight of 100 mW/cm² irradiance. The data are represented as standard box plot with (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE.

Device architecture and solvent used	J _{sc} (mA/cm²)	V _{oc} (V)	FF	PCE (%)	References
$TiO_2/AgBi_2I_7$ (n-bultylamine)/P3HT	3.3	0.54	0.674	1.22	1
TiO ₂ /AgBi ₂ I ₇ (n-butylamine)/P3HT	1.6	0.46	0.56	0.4	2
TiO ₂ /AgBi ₂ I ₇ (DMF + HI)/spiro-OMeTAD	2.45	0.63	0.33	0.52	3
TiO ₂ /AgBi ₂ I ₇ (DMF +HI)/spiro-OMeTAD	2.76	0.69	0.436	0.83	4
TiO ₂ /AgBi ₂ I ₇ (DMSO)/P3HT	4.84	0.62	0.70	2.12	Present work

Table S1: Comparison of device parameters of previous reports and the present study



Fig. S9: (a) J-V characteristic curves of best performing AgBi₂I₇ devices with different wt. %, their corresponding histogram plot of (b) J_{sc} and (c) PCE.

Table S2: Device parameters of best performing AgBi₂I₇ (obtained from DMSO) with different wt. %

AgBi ₂ I ₇ wt. %	J _{sc} (mA/cm²)	V _{oc} (V)	FF	PCE (%)
20	5.07	0.55	0.71	2.0
40	3.95	0.49	0.52	1.03
60	1.74	0.46	0.35	0.29

Discussion S1

Dependence of current density and voltage of $AgBi_2I_7$ devices on light intensity was investigated by varying the intensity from 100 mW/cm² to 1 mW/cm². Fig. S9a shows the power law dependence of J_{sc} with light intensity ($J \propto I^{\alpha}$) in which logarithm of J_{sc} is plotted against light intensity. A sublinear relationship of generated current, gradually saturating at higher intensities, indicates lesser charge collection at higher light intensity attributed to space-charge-limited photocurrent due to non-optimal thickness or unsuitable electron/hole transporting layer or imbalanced charge carrier mobilities. According to previous reports, the conduction band of photoactive $AgBi_2I_7$ and TiO₂ electron transport layer are slightly mismatching^{1, 3} and also there is a large gap between the valence band level of $AgBi_2I_7$ and P3HT (HTM)^{1, 2} which can be the reasons for such behaviour. Fig. S9b depicts a semilogarithmic plot of V_{oc} against light intensity and the slope of the line here corresponds to 2.303*nkTq*⁻¹, where T is equal to room temperature (~300 K) in our case. A slope of 1.8, as calculated in our case, indicates presence of non-radiative trap-assisted recombination near V_{oc} .



Figure S10: (a) J_{sc} Vs light intensity and (b) V_{oc} Vs light intensity of AgBi₂I₇ solar cells.



Fig. S11: Exposure of AgBi₂I₇ thin film to 100 ^oC heat stress showing no visible degradation.

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