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Supplementary Information

Dual-layer synergetic optimization of high-efficiency planar perovskite solar cells using nitrogen-rich nitrogen carbide as additive

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Experimental section

Materials: All reagents and materials were obtained from commercial channels and used without further treatment. Perovskite precursor reagents and 2,2,7,7-tetrakis (N, N-di-p-methoxyphenyl-amine) 9,9-spirobifluorene (Spiro-OMeTAD) were supplied by Xi'an Polymer Light Technology Corp. 4-tert-butyl pyridine (TBP) was purchased from Tokyo Chemical Industry Co., Ltd. Bis(trifluoromethyl-sulfonyl)-imide lithium salt (Li-TFSI), Chlorobenzene (CB, 99.9%) and dimethylformamide (DMF, 99%) were obtained from Sigma-Aldrich. Dimethyl sulfoxide (DMSO, 99%) and SnO₂ colloidal dispersion (15 wt% in H₂O) were bought from Alfa Aesar. The indium tin oxide (ITO, 15 Ω sq⁻¹) was supplied by Wuhu Jinghui Electronic Technology Co., Ltd. 3-amino-1,2,4-triazole (C₂H₄N₄, 96%) was purchased from Aladdin Reagent Co., Ltd. Deionized water (18.2 MΩ) acquired from the ultrapure purification system.

Preparation of g-C₃N₅ dispersion solution: The pristine brown-red g-C₃N₅ powder was obtained by a one-step thermal polymerization method.^[26] In a typical process, about 2 g of 3-amino-1,2,4-triazole powder was dispersed in an Al₂O₃ ceramic crucible and kept half-covered. Subsequently, the crucible was heated to 500°C in a muffle furnace at a heating rate of 5°C/min and held at 500°C for 3 h. After cooling to room temperature, the brown-red powder was subjected to several wash-centrifugation cycles and further ground for use after overnight drying. Next, the synthesized g-C₃N₅ powder was dispersed in H₂O at different concentrations (0.05, 0.1, 0.15, and 0.2 mg mL⁻¹). The above dispersion solution was further mixed with SnO₂ colloidal solution in a ratio of 1:1 and stirred overnight to obtain SnO₂:g-C₃N₅ precursor solution. Meanwhile, g C_3N_5 powder was dispersed in a mixture of DMF and DMSO (volume ratio: 4 to 1), and PbI₂ (580.9 mg) and MAI (190.8 mg) were further added to obtain perovskite@g- C_3N_5 precursor solution. The mass fraction of g-C₃N₅ was 0.1-0.4 wt% relative to the total solute weight of the perovskite precursor solution.

In addition, a CsFAMA precursor solution was obtained in the same way for comparison, in which FAI (172 mg), MABr (22.4 mg), PbBr₂ (73.4 mg) and PbI₂ (507.1 mg) using magnetic stirring were added to a mixture of DMF: DMSO (volume ratio: 4 to 1), then 40 μ L of CsI (1.5 mol L⁻¹ in DMSO) was poured to obtain the final CsFAMA precursor solution.

Perovskite solar cell fabrication: The pre-patterned indium tin oxide (ITO) glass substrates were washed extensively with detergent, deionized water, acetone, isopropanol, and ethanol in an ultrasonic bath for 15 min, followed by 10 min of O_3 /ultraviolet treatments. Subsequently, the processed substrates were covered with a SnO₂ or SnO₂:g-C₃N₅ layer at 3,600 r.p.m. for 40 s, and then placed on a hot plate at a constant temperature of 180°C for 30 min. Then, 30 µL above perovskite or perovskite@g-C₃N₅ precursor was dispersed on the ITO/SnO₂ substrates through a twostep spin coating strategy (1500 rpm for 10 s and 5500 rpm for 30 s) with a chlorobenzene (CB) solution as an anti-solvent. The coated perovskite film was transferred to a hot plate and annealed at 120°C for 50 min. After cooling to room temperature naturally, the Spiro-OMeTAD solution (72 mg mL⁻¹ in chlorobenzene) doped with 18 µL Li-TFSI (520 mg mL⁻¹ in acetonitrile) and 29 µL tBP, was uniformly deposited on the as-formed perovskite film with a speed of 4,000 r.p.m. for 40 s. All these processes were executed in a nitrogen-filled glovebox with H₂O/O₂ content < 1ppm at a display temperature of 20-25°C. In the final step, the unfinished devices were deposited sequentially with a 10 nm MoO₃ layer and a 100 nm Ag layer by thermal evaporation under high vacuum (less than 2.8×10^{-4} Pa). The defined active area of the devices was maintained at 0.15 cm².

Characterization: The powder X-ray diffraction (PXRD) curves were measured on a Bruker Discovery D8 diffractometer using Cu-K α radiation (λ =1.54 Å). Fourier transform infrared (FTIR) spectra were recorded on a Thermo Scientific Nicolet iS50 instrument. The morphological characteristics of the perovskite thin films and material were recorded via field emission scanning electron microscopy (SEM, Hitachi S4700) and transmission electron microscopy (TEM, JEOL-2100F). The water contact angle analysis was further recorded via the static advancing contact. The atomic force microscope (AFM) measurement was performed on the Multimode 8 AFM from Bruker. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were recorded on the Thermo Scientific Escalab 250Xi instrument equipped with Mg-K α source to expose chemical bonds and energy level status. The UV-Vis DRS spectra and light transmission spectrum were executed on an ocean optics spectrum testing system with DH-2000-BAL UV-VIS-NIR light source. Photoluminescence (PL) and transient fluorescence decay spectra of the films were characterized by performing a Laser405-1HS illuminant and a FLS920 from Edinburgh Instruments Ltd./UK. The current density-voltage (J-V) curves and space charge limited current (SCLC) curves were monitored via Keithley 2400 source meter equipped with a simulated AM 1.5 G solar system (irradiance of 100 mW ⋅ cm⁻²). The external quantum efficiency (EQE) was obtained on an SRF50 system with a with wavelength range of 300-900 nm. The electrochemical impedance spectroscopy (EIS) was characterized via using a Zennium-IM6 electrochemical workstation under dark.

Theoretical calculation details: All calculations are implemented by performing a first-principles VASP package based on density functional theory (DFT). The exchange-correlation effect is described using the Perdue-Burke-Ernzerhof (PBE) method with a plane wave cut-off energy of 450 eV. The unit cell is subjected to structural relaxation for optimization calculations. During the optimization process, all atoms are in a relaxed state until the relaxation converges to an accuracy of 1×10^{-5} eV/unit, and the interaction force between atoms is less than 0.03 eV/Å. The Brillouin zone is divided by the number of K-point grids centered on the Γ point. While $2 \times 2 \times 1$ grid of K-points is used for electronic states analysis. Under periodic conditions, a vacuum region of 15 Å along the z-axis is used to eliminate interactions between adjacent cells of the slab model. The DFT-D2 method of Grimme is enabled to describe van der Waals (vdW) interactions, taking into account the dipole correction in the (001) direction when calculating the electronic properties.



Figure S1. Synthetic process and proposed production mechanism of $g-C_3N_5$.



Figure S2. The survey spectra of pure $g-C_3N_5$ powder.



Figure S3. Total density of states of g-C₃N₅.



Figure S4. The AFM images of **a**) the pristine SnO_2 film and **b**) the SnO_2 :g-C₃N₅ film.



Figure S5. The Tauc plots of $(\alpha h\nu)^{1/2}$ vs. the photo energy of the SnO_2 and SnO_2:g- C_3N_5 films.



Figure S6. The photocurrent densities of the SnO_2 :g- C_3N_5 film.



Figure S7. The full-width half-maximum values of the (110) plane for the perovskite and perovskite@g-C $_3N_5$ films.



Figure S8. The Tauc plots of $(\alpha h\nu)^{1/2}$ vs. the photo energy of the perovskite and perovskite@g-C₃N₅ films.



Figure S9. The UPS spectra of the perovskite and perovskite@g-C₃N₅ films.



Figure S10. High-resolution XPS I 3d spectra.



Figure S11. The SCLC measurement curves of electron-only devices of the resultant films.



Figure S12. Absorption coefficient based on the UV-vis absorption spectra *versus* energy for the resultant films to obtain Urbach energies.



Figure S13. The theoretical model of a) MAI-terminated and b) PbI₂-terminated.



Figure S14. The theoretical model of **a**) g-C₃N₅-modulated MAPbI₃ with an iodide vacancy **b**) g-C₃N₅-modulated MAPbI₃ with a Pb-I antisite.



Figure S15. The cross-sectional SEM image of the device.



Figure S16. The box plots of the a) V_{OC} , b) J_{SC} , c) FF, d) PCEs distribution for control, S1 and S2 devices with different content of g-C₃N₅ dispersion (0 to 0.2 mg mL⁻¹). 20 devices for each point.



Figure S17. The box plots of the **a**) V_{OC} , **b**) J_{SC} , **c**) FF, **d**) PCEs distribution for control, S1 and S2 devices with different content of g-C₃N₅ dispersion (0 to 0.4 wt%). 20 devices for each point.



Figure S18. a) *J-V* curves of the champion CsFAMA-based devices for the control, A1 and A2; **b**) The PCE distribution of the resultant devices; **c**) Stabilized power conversion efficiency measured at each maximum power point for the CsFAMA-based A2 cells.



Figure S19. XRD patterns before and after aging under high humidity environment (air condition, >50% humidity) for **a**) the control films and **b**) the g-C₃N₅@perovskite

films.



Figure S20. Maximum power point tracking measured for the A2 cells (1 Sun illumination without ultraviolet filter; xenon lamp, 450 W, 100 mW cm⁻², room temperature and N_2 atmosphere).

PSCs	PCE (%)	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF	Ref.
ITO/SnO ₂ +g-C ₃ N ₅ /CsFAMA+g-C ₃ N ₅ /spiro- MeOTAD/Ag	22.34	23.97	1.18	0.79	This work
ITO/SnO ₂ +g-C ₃ N ₅ /MAPbI ₃ +g-C ₃ N ₅ /spiro- MeOTAD/Ag	20.68	23.04	1.14	0.79	This work
FTO/TiO ₂ /MAPbI ₃ +g-C ₃ N ₄ /spiro-MeOTAD/Ag	19.49	24.31	1.07	0.74	1
FTO/TiO ₂ /MAPbI ₃ +U-C ₃ N ₄ /spiro-MeOTAD/Ag	18.72	23.41	1.06	0.75	2
FTO/SnO ₂ /MAPbI ₃ +g-C ₃ N ₃ /spiro-MeOTAD/Au	19.91-	22.43	1.12	0.78	3
FTO/SnO ₂ +Sulfur-doped g-C ₃ N ₄ /CsFAMA/spiro- MeOTAD/Ag	20.38	23.43	1.13	0.76	4
FTO/SnO ₂ /CsFAMA+SWCNTs/spiro-MeOTAD/Au	16.10	20.70	1.13	0.69	5
ITO/SnO ₂ /CsFAMA+PTI/spiro-MeOTAD/Au	19.07	21.84	1.13	0.77	6
ITO/TiO ₂ /MAPbI ₃ + Ti ₃ C ₂ T _x /spiro-MeOTAD/Au	17.41	22.26	1.03	0.76	7
FTO/SnO _{2:} Eu ³⁺ /MAPbI ₃ : Eu ³⁺ /spiro-MeOTAD/Ag	20.14	22.57	1.13	0.79	8
ITO/TiO ₂ +Gd ³⁺ /CsFAMA+ DRCN5T /spiro- MeOTAD/Ag	20.53	23.61	1.12	0.78	9

Table S1 Comparison the performance of the state-of-the-art PSCs of the same typereported in the literature (PCEs denote champion values).

Samples	Trap density (cm ⁻³)
SnO ₂ (Dark)	$2.04 imes 10^{16}$
SnO ₂ (After illumination)	1.74×10^{16}
SnO ₂ :g-C ₃ N ₅ (Dark)	$6.82 imes 10^{15}$
SnO ₂ :g-C ₃ N ₅ (After illumination)	3.62×10^{15}

Table S2 Summary of the trap states density and mobility in SnO2 and SnO2: SnO2:g-
 C_3N_5 under dark and AM 1.5G illumination.

	bandgap	SECO	WF	VBM	CBM	
SnO ₂	4.02	16.37	4.85	8.08	4.06	
SnO _{2:} g-C ₃ N ₅	4.05	16.76	4.46	8.02	3.97	
perovskite	1.60	17.06	4.16	5.52	3.92	
perovskite@g-C ₃ N ₅	1.60	17.08	4.14	5.47	3.87	

Table S3 Bandgaps, secondary-electron cut-off (SECO), work function (WF),VBM and CBM for SnO_2 and $SnO_{2:g}$ - C_3N_5 , as well as perovskite andperovskite@g- C_3N_5 .

Sample	A_1	$ au_l$ (ns)	A_2	$ au_2$ (ns)	$ au_{ave}$ (ns)
perovskite	1077.2	27.24	8261	8.24	13.96
perovskite@g-C ₃ N ₅	1688.7	39.37	8651	15.59	23.44
ITO/SnO ₂ /perovskite	1813.1	38.03	8774	14.59	22.80
ITO/ SnO _{2:} g-C ₃ N ₅ /perovskite	586.5	40.87	9915	14.56	18.30
ITO/SnO _{2:} g-C ₃ N ₅ /perovskite@g-C ₃ N ₅	586.6	28.49	8650	9.23	12.56

Table S4 Summary of fitting parameters of time-resolved PL (TRPL) spectra.

The average carrier lifetime (τ_{ave}) is obtained by the following formula: $\tau_{ave} = (A_1\tau_l + A_2\tau_2)/(A_1 + A_2)$, where A_1 and A_2 are the fitting amplitudes.

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