

Supplementary Information

Bromide Substituted 2D Additive for Stable and Efficient Perovskite Photovoltaics

Muhammad Sohail Abbas^{a,b}, Sabir Hussain^{b,c}, Jianqi Zhang^b, Boxin Wang^b, Zhen Wang^{b,f},
Chen Yang^{c,d}, and Rashid Ahmad^{a*}.

^a *Department of Chemistry, University of Malakand, Chakdara, Dir-L, Pakistan.*

Corresponding Authors; M. S. A. gul.rao85@gmail.com and R. A. rashmad@gmail.com

^b *CAS Key Laboratory of Nanosystems and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, P. R. China.*

^c *University of Chinese Academy of Sciences, Beijing 100049, P. R. China.*^e *CAS Key Laboratory of Standardization and Measurement for Nanotechnology, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China.*

^d *MOE Key Laboratory of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China.*

Experimental Procedures

Preparation of perovskite precursor solution

Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) was purchased from Dyesol. Commercially available aqueous solution of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) from Clevis (PVP Al 4083), and all other reagents were procured from Sigma-Aldrich and used without any further purification. For all perovskite precursor solutions, DMF/DMSO mixture (4:1, v/v) was used as a solvent and solutions were prepared in 1 molar strength (based on PbI_2) and stirred overnight at 70 °C. For MAPbI_3 precursor solution, equimolar amounts of lead iodide (PbI_2) and MAI were mixed in the mixed solvent. For phase pure 2D/3D $[\text{An}_2\text{PbI}_2\text{Br}_2]_x[\text{MAPbI}_3]_{1-x}$ precursor solution, molar ratio between PbI_2 , $\text{CH}_3\text{NH}_3\text{I}$ (MAI) and $\text{C}_6\text{H}_5\text{NH}_3\text{Br}$ (AnBr) was respectively varied as 1:0.9:0.1, 1:0.8:0.2, 1:0.7:0.3. All perovskite solutions were filtered before perovskite film spin

Device fabrication

ITO coated glass substrates ($\approx 15 \Omega$ resistance) were washed by sonication in a water bath in a sequence for 15 minutes with detergent, deionized water, ethanol, acetone and isopropyl alcohol. The substrates were then dried with nitrogen flow and were treated with UV/ozone for 15 minutes. Later, PEDOT:PSS was spin coated on cleaned ITO coated substrate at 3500 rpm for 15 seconds then we annealed substrates on a hot plate at 150 °C, in the air for 15 minutes. The devices were then transferred to a nitrogen glove box with humidity level less than 0.1%. Perovskite film was deposited by spin coating 40 μL of perovskite precursor solution in a single step, at a rotating speed of 4500 rpm for 45 seconds and after 7 seconds, 200 μL of chlorobenzene were poured at once and followed by annealing inside the glove box at 120 °C for 10 minutes. PCBM was then spin casted over perovskite film. 30 μL of PCBM-61 solution (20 mg/mL in chlorobenzene) were spin coated at 4000 rpm for 30 seconds and then 30 μL of

BCP solution (1mg/mL in extra dry ethanol) were rotated for 30 seconds at 5000 rpm. Lastly, a 100 nm thick layer of Ag electrode was deposited in a thermal evaporator high vacuum.

J-V Characterization

Photovoltaic performance of the devices was recorded on Keithley 2420 digital source meter. The photocurrent was measured under 1 Sun illumination using an Oriel Newport 150W solar simulator (AM 1.5G), calibrated by a Newport Si reference detector (Oriel PN 91150V). The equilibrium quantum efficiency (EQE) spectra of the devices were performed with an Oriel Newport System (Model 66902). All these characterizations were performed in ambient air conditions at room temperature.

UV-Visible absorbance and PL emission characterization

The UV-visible absorbance and photoluminescence spectra of perovskite films was measured in optimized conditions for device fabrication and perovskite films were spin coated on a cleaned quartz glass substrate. Quartz glass substrates were also cleaned by the procedure followed for ITO coated substrates. UV-visible absorbance was noted on a Shimadzu UV 3600, UV-visible NIR instrument. Steady state photoluminescence was recorded on Hitachi F-7000 spectrofluorometer using an excitation wavelength of 450 nm.

GIWAXS Analysis

Grazing incidence wide-angle X-ray scattering (GIWAXS) was recorded using a XEUSS SAXS/WAXS equipment under different conditions. For GIWAXS measurements, perovskite film was fabricated on a Si substrate in optimized conditions as for solar devices.

SEM Analysis

Scanning electron microscope (SEM) analysis of perovskite films with different doping levels of AnBr spin coated on Glass/ITO/PEDOT:PSS as we described earlier. Analysis was carried out on SU 8200 scanning electron microscope made by Hitachi.

AFM and KPFM Study

For topographic analysis and surface potential estimation, using atomic force microscopy, perovskite layer was spin coated on Glass/ITO/PEDOT:PSS as we described earlier. The tapping mode AFM (Asylum Research MFP-3D Infinity) with non-conductive tip (AC240TS-R3) was used to acquire the topographic image. Secondly, KPFM with conductive probe (ASYLEC-01, Tip was coating by Ti/Ir material) was used to map the surface potential^{1,2} of the perovskite films. KPFM mappings were characterized by using two-pass technique: the first pass same as tapping mode was used to explore the topographic image, while the second pass was used to explore the V_{CPD} by keeping the tip at a selected lift height. The V_{CPD} value can be measured by applying VDC and VAC between the tip and sample. Output signal is nullified and F_{ω} reaches to the zero ($F_{\omega}=0$). Because if the F_{ω} reaches minimum, the V_{CPD} can be acquired which shows surface potential of sample.³ In our study, the conductive probe was kept at a lift height (ΔH) of -20nm to avoid the topographic artefacts.

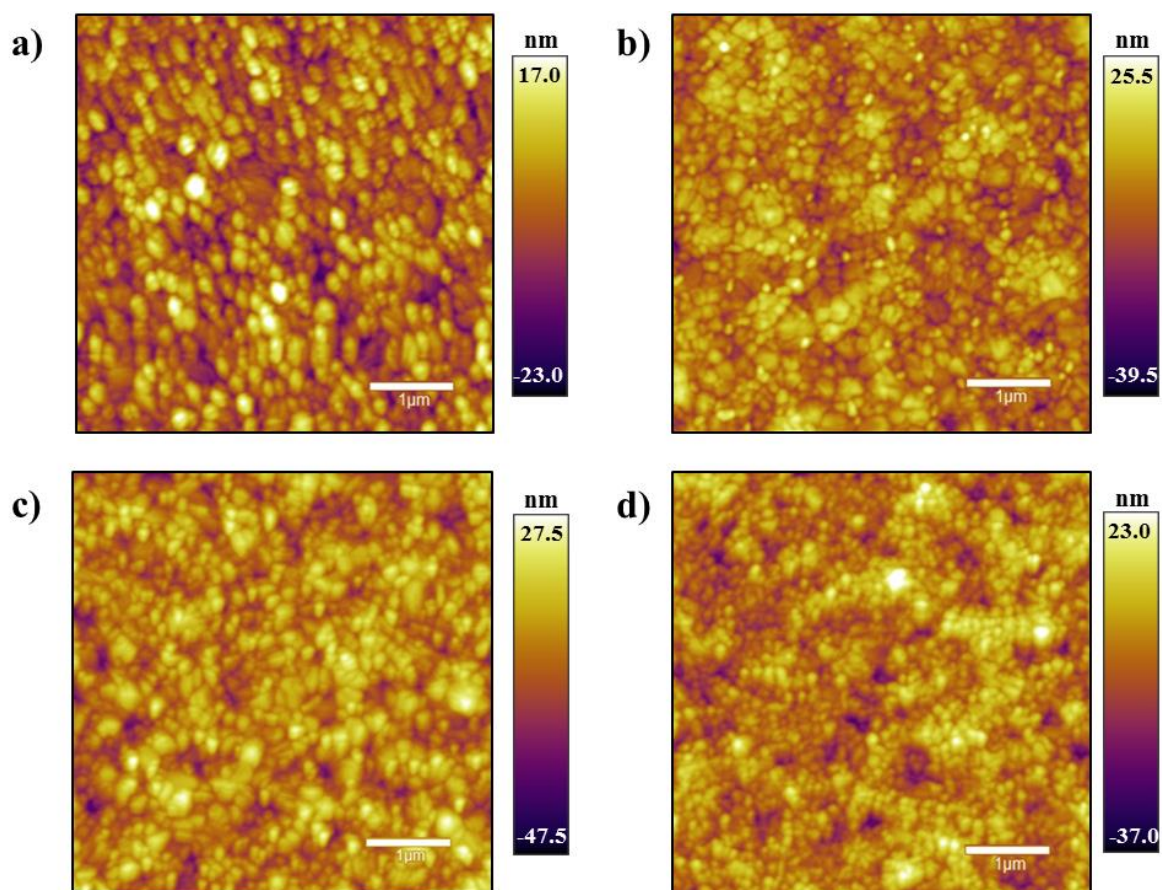


Figure S1: AFM (Tapping mode) images of 3D Perovskite (S1a) and 2D/3D perovskite (S1b-S1d) with different molar ratio of MAI:AnBr, with 0.9:0.1, 0.8:0.2, and 0.7:0.3 respectively. Perovskite films were spin coated on ITO/PEDOT:PSS surface and annealed for 10 minutes at 120 °C.

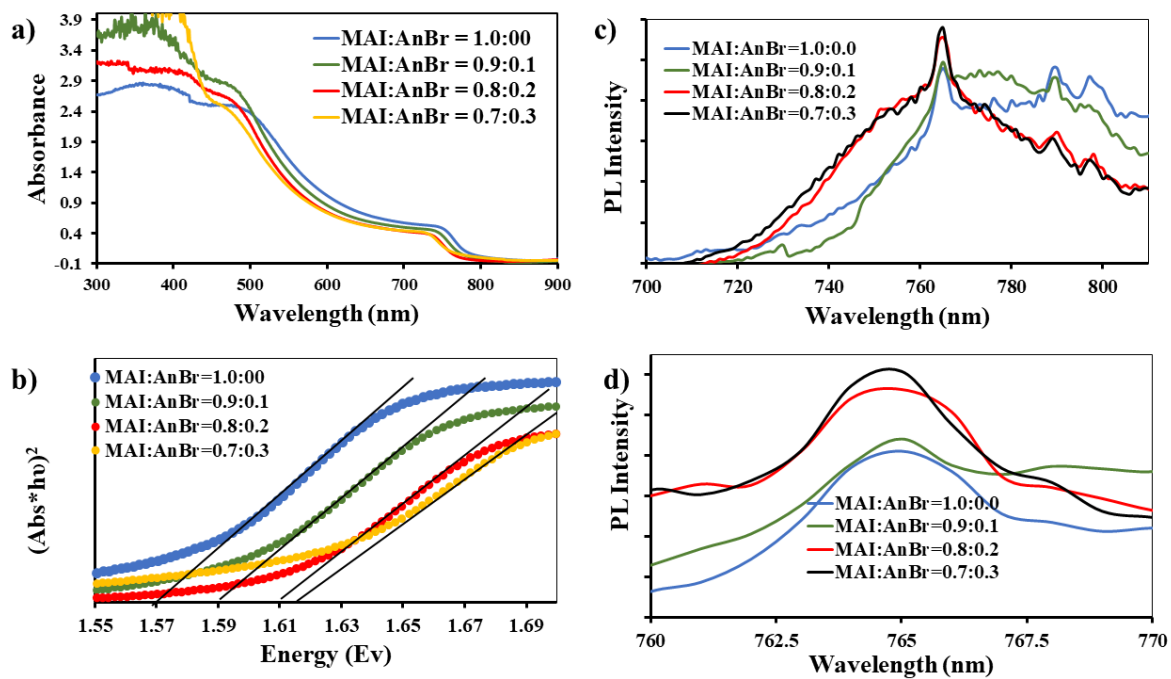


Figure S2: a) UV-visible absorbance spectra of 3D and 2D/3D perovskite with different molar ratio of MAI:AnBr. b) Tauc Plot c) PL emission spectra, d) Magnified PL Spectra

Table-S1: J_{sc} values measured from solar cell simulator and calculated from EQE and resultant PCE from calculated J_{sc} .

S. No.	3D:2D	J_{sc} (mA/cm ²)	J_{sc} (mA/cm ²) Integrated from EQE	PCE% With integrated J_{sc}
1	1:0	23.09	17.02	9.84
2	0.9:0.05	22.05	16.17	8.25
3	0.8:0.1	27.56	20.50	12.96
3	0.7:0.15	21.77	16.03	8.43

References

- [1] R. Xu, X. Wang, Z. Zheng, S. Ye, K. Xu, L. Lei, S. Hussain, F. Pang, X. Liu, Y. Li Y, Y. Sugawara, *Nanotechnology* **2018**, 30, 205702.
- [2] R. Xu, S. Ye, K. Xu, L. Lei, S. Hussain, Z. Zheng, F. Pang, S. Xing, X. Liu, W. Ji, Z. Cheng, *Nanotechnology* **2018**, 29, 355701.
- [3] S. Hussain, K. Xu, S. Ye, L. Lei, X. Liu, R. Xu, L. Xie and Z. Cheng, *Front. Phys.* 2019, 14, 33401.