Metal-deficient perovskite-like methylammonium iodo bismuthate and silicon nanocrystal hybrids for photovoltaics

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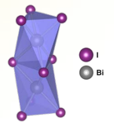
1 – Motivation

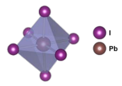
$(CH_3NH_3)_3Bi_2I_9$ - Methylammonium bismuth iodide (**MABI**)

- Perovskite-like organic-inorganic hybrid material.
- **Lead-free** and **air-stable**.
- Metal-deficient perovskite-like structure.
- Solution-processable, bandgap-tunable material.
- **Zero-dimensional network** of isolated Bi_2I_9 bioctahedra separated by CH_3NH_3.
- Excitonic behavior (binding energy >300 meV).
- We have previously demonstrated **carrier multiplication.**[1]

B_2X_9 bioctahedra in $MA_3Bi_2I_9$



Perovskite BX_6 octahedral e.g. in $MAPbI_3$

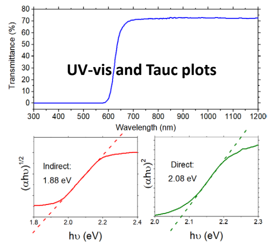


[1] C. Ni et al., *Nat. Commun.* **2017**, *8* (1), 170.

2 – Synthesis, Characterization and Device Fabrication

MABI Synthesis

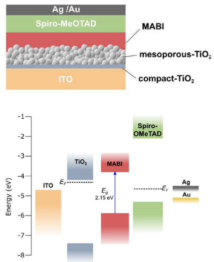
- CH_3NH_3I and BiI_3 in dimethylformamide.
- Solution stirred for 10 min at 80 °C.
- Spin coat, RPM = 1250, t = 30 s.
- Annealed at 100 °C for 30 min.

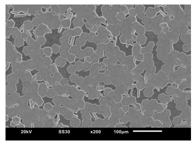


Solar Cell Fabrication

ITO/compact-TiO_2/mesoporous-TiO_2/MABI/spiro-MeOTAD/Ag or Au

- ITO cleaned by O_2 plasma.
- Compact TiO_2 layer (50 nm): spin coat (titanium (IV) isopropoxide in ethanol), RPM = 5000, t = 30 s, anneal 400 °C for 2 hours.
- Mesoporous TiO_2 layer (1 µm): spin coat (solution = Dyesol 18-NRT paste in ethanol, conc. = 1:2 ratio of paste:ethanol). RPM = 2000, t= 60 s, annealed at 400 °C for 2 hours.
- Spiro-MeOTAD layer: spin coat (0.2 g in 1 mL chlorobenzene), RPM = 1500, t = 20 s.



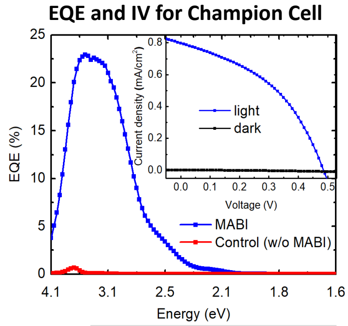


3 –Device Performance

MABI Solar Cell Devices

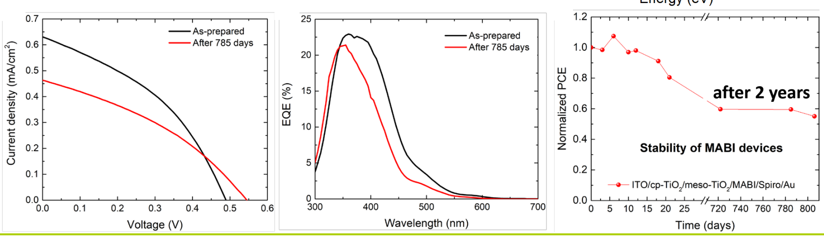
- Device performance measured under solar simulated **AM1.5G** light.
- EQE onset at approx. direct bandgap energy (**~2.1 eV**).
- EQE also shown for control device (without MABI) -> confirms photocurrent is generated by MABI.

EQE and IV for Champion Cell



Stability Over 2 Years – Champion Cell

- MABI devices with Au retain almost 60% of their original PCE **after 2 years.**
- Devices were fabricated and stored in **open-air conditions** and in the dark between measurements.

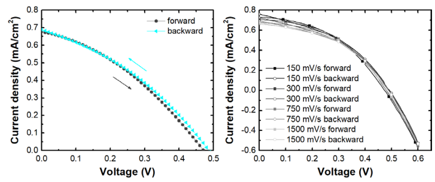


4 – MABI Hysteresis Analysis

- Hysteresis is negligible in MABI solar cells.
- Indicates low ion motion/low charge trapping at interface.
- Self-passivated surface.
- MABI forms a native **surface layer** of **BiOI** or **Bi_2O_3**.[2]

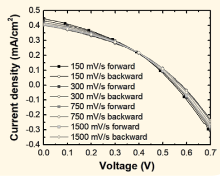
[2] R. L. Z. Hoye at al., *Chem. - A Eur. J.* **2016**, *22* (8), 2605–2610.

A) Hysteresis analysis in MABI solar cell devices



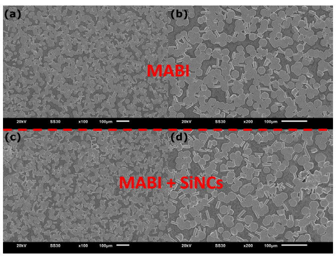
B) Hysteresis analysis after 2 years (same device)

- PCE decreases due to slight degradation.
- But hysteresis remains negligible after 2 years.
- Suggests ion migration and/or charge trapping is minimal after degradation.

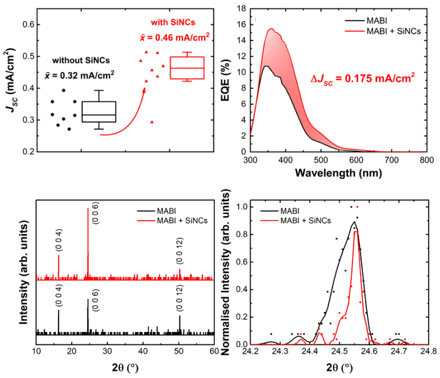


5 – MABI with SiNCs

- Silicon nanocrystals (SiNCs) introduced to explore hybrid devices.
- Exciton binding energy in MABI **>300 meV.**
- Add SiNCs -> enhance **exciton dissociation** and **carrier transport.**
- XRD -> SiNCs in MABI **improves crystallinity.**

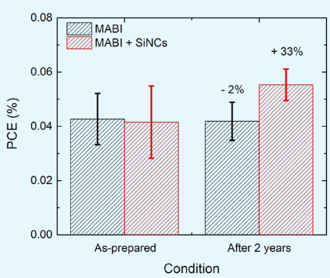


Increase in J_{SC} and **PCE** for devices with SiNCs



Device Stability with SiNCs

- Comparison of MABI stability with and without SiNCs.
- SiNCs improved stability of MABI.
- Greater crystal quality -> less defects -> greater stability -> slower degradation.
- **2 year stability.**
- SiNCs are not inducing degradation in MABI.



6 – Conclusion and Acknowledgements

MABI

- ☑ MABI has been demonstrated in a photovoltaic cell.
- ☑ Can be deposited from solution in open-air conditions and is air-stable.
- ☑ Devices were more stable when Au contacts were used.
- ☑ 2-year performance demonstrated.

MABI + SiNCs

- ☑ MABI can favorably accommodate SiNCs.
- ☑ Increase in the median J_{SC} and PCE.
- ☑ Improved crystal quality.
- ☑ Improved stability.
- ☑ SiNCs do not negatively affect stability.

Acknowledgements

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