Supporting Information

Photovoltaic Enhancement of Bismuth Halide Hybrid Perovskite by

N-methyl pyrrolidone-assisted Morphology Conversion

Ashish Kulkarni, Trilok Singh*, Masashi Ikegami, Tsutomu Miyasaka*

Graduate School of Engineering, Toin University of Yokohama, 1614 Kuroganecho, Aoba,

Yokohama 225-8503, Japan.

Corresponding Author

*trilok@toin.ac.jp and miyasaka@toin.ac.jp

Electronic supplementary information:

Characterization:

The structural, morphological and optical analysis were carried out using X-ray diffractometer (D8 Discover, Brucker) with CuK α radiation source, scanning electron microscope (SU8000, HITACHI) and UV-Vis spectrophotometer (UV-Vis 1800, Shimadzu) respectively. The photovoltaic characterization was measured with Keithley 2400 source meter under 1 sun illumination (AM 1.5 G, 100 mW/cm²) using a Peccell Technologies PEC-L01 solar simulator. The active cell area was of 0.09 cm².

Device fabrication:

Device followed fabrication process was from the previous report. ¹ All the materials were purchased from Sigma Aldrich and were used as received. Transparent conductive FTO glass was cleaned by solvent washing and UV-ozone treatment. TiO₂ compact layer (CL) was deposited by repeated spin coating of titanium diisopropoxide bis(acetylacetonate) solution in 2-propanol followed by sintering at 550 °C for 30 min. After cooling down the substrates were given 80 mM TiCl₄ treatment at 70 °C for 40 min and were annealed again at 550 °C for 30 min. Mesoporous layer was deposited by dissolving the commercial available TiO₂ paste (18-NRT) in ethanol (1:4 wt. ratio) and spin coating the solution at 3000 rpm for 30 sec. After depositing the mesoporous layer, the substrates were annealed at 500 °C for 1 hr. MBI layer was achieved by spin coating the DMF solution, containing 20 wt.% bismuth iodide (Bil₃) and methylammonium iodide (MAI) (Wako) (169 mg Bil₃ and 69 mg MAI in 1 ml DMF), at 1500 rpm for 30 sec followed by annealing at 110 °C for 90 min. The HTM solution was prepared by dissolving 84 mg of 2 2' 7 7'-tetrakis-(n n-di-4methoxyphenyl amino)-9 9'-spirobifluorene (spiro-OMeTAD) (Merck), 14 µL of 4-tertbutylpyridine (TBP, Aldrich), 27 µL of a stock solution of 170 mg/mL of lithium bis(trifluoromethylsulfonyl) imide in acetonitrile in 1 mL of chlorobenzene. The prepared solution was spin coated on MBI deposited substrates at 3000 rpm for 30 sec. and the cells were left overnight in dark for air oxidation. Finally, thermal evaporation of gold was performed at 5 \times

 10^{-4} pa pressure to complete the cell. To introduce NMP treatment in the device fabrication, different concentration of NMP (12.5 μ L, 25 μ L, 50 μ L) was added to 1 ml MBI-DMF solution and after stirring for 1 hour the solution was skinned by procedure mentioned above.

(a) (b) NMP MBI in NMP **MBI** without additive Absorbance (a.u.) Absorbance (a.u.) MBI with NMP additive (25 µL/mL) 350 400 450 500 550 300 600 700 800 300 400 500 600 900 1000 Wavelength (nm) Wavelength (nm)

Fig. S1: UV-Vis spectra of (a) MBI dissolved in NMP and (b) MBI perovskite with out and with NMP (25 μ L/mL) additive



Fig. S2: Top surface SEM image (low mag.) of 12.5 µL NMP additive based MBI film.

Figures:



Fig. S3: Top surface SEM image of 50 μL NMP additive based MBI film showing smooth and non-smooth region.

References:

¹ T. Singh, A. Kulkarni, M. Ikegami, T. Miyasaka, ACS Appl. Inter. Mater. 2016, 8 (23),14542.