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Operando Injection of Oxygen Ions to Organometal Halide Perovskite ($CH_3NH_3PbI_3$) under *In-Situ* Electrical Biasing STEM-EELS

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Organometallic halide perovskites, such as $CH_3NH_3PbI_3$ (methylammonium lead iodide, herein called MAPbI) continue to draw great attention to the photovoltaic field as a promising candidate material for its cost-effectiveness and fast growing efficiency [1, 2]. Especially, Methyl-ammonium lead trihalide as light absorber ($CH_3NH_3PbX_3$, where X is a halogen atom such as I, Br or Cl) with a bandgap of 1.5~2.3 eV depending on halide content has been studied intensively in many different types of platforms in recent years, in search for further breakthroughs in conversion efficiency [3]. However, the studies of long-term stability of such organic perovskites and their behavior under applied bias and extended photo-exposure, etc. have hitherto not been investigated at necessary details. In this study, we have probed the following configuration of the halide perovskite solar cell platform; going from the bottom to top in order is; glass, FTO, compact TiO_2, mesoporous TiO_2 with filled MAPBI, MAPBI, Spiro-OMeTAD, and top gold electrode.

Herein, we present forward biasing condition of MAPBI (i.e. a negative bias to bottom FTO and positive bias to Au) to mimic light-absorbing condition in TEM using an *in-situ* electrical biasing holder (Nanofactory). In addition to imaging and diffraction, we also monitored elemental distribution with EELS, After applying +1V to MAPBI, STEM-EELS line profile revealed measurable oxygen edge signal from MAPBI, which was notably absent before biasing; as can be seen in Fig. 1. From the forward biasing condition, the origin of injected O ions into MAPBI is likely due to mesoporous TiO_2. Indeed, we could observe alteration of Ti L and O K peaks in Fig 2-a, indicating that TiO_2 transforms to nominal Ti_2O_3 , when we compare our data with the previous EELS reference for Ti-O compounds [4]. To provide added details, we note that Ti $L_{2,3}$ peak is shifted lower by ~ 1eV, a shoulder at Ti extended energy loss of fine structure (EXELFS) is diminished, and oxygen K doublet peaks changes to a single peak. Correspondingly, MAPBI region exhibits strong feature of oxygen K edge after +1V biasing for 1~2 hours, in Fig. 2-b. In case of low loss region of TiO_2, it is no big difference in overall except for a shoulder before the plasmon peak is weakened in Fig. 2-c. Most interestingly, the bulk plasmon of MAPBI after biasing, defined in the previous report from CH_3NH_3PbICl [5], appears significantly reduced and overall shape changes close to that of metallic Pb, implying that MAPBI may have lost the property of original MAPBI probably due to the existence of oxygen ions. However, the nature of this oxygen signal needs further scrutiny. The presentation will cover additional experiments, analyses, and will argue the stability and reliability of the emerging organic halide perovskite materials.

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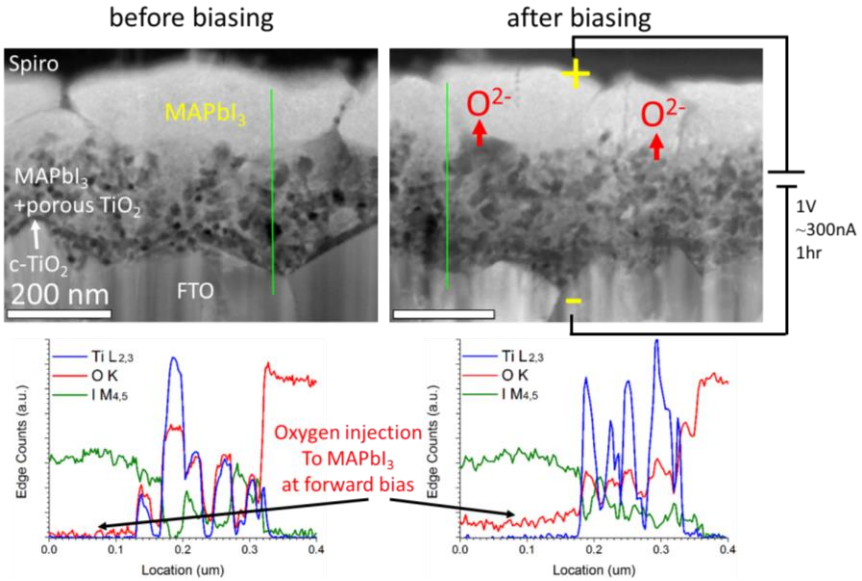

Figure 1. HAADF images of MAPBI solar cell before (left) and after (right): STEM-EELS line profiles (green line on images) display background-subtracted edge signals from Ti, O, and I at each bottom.

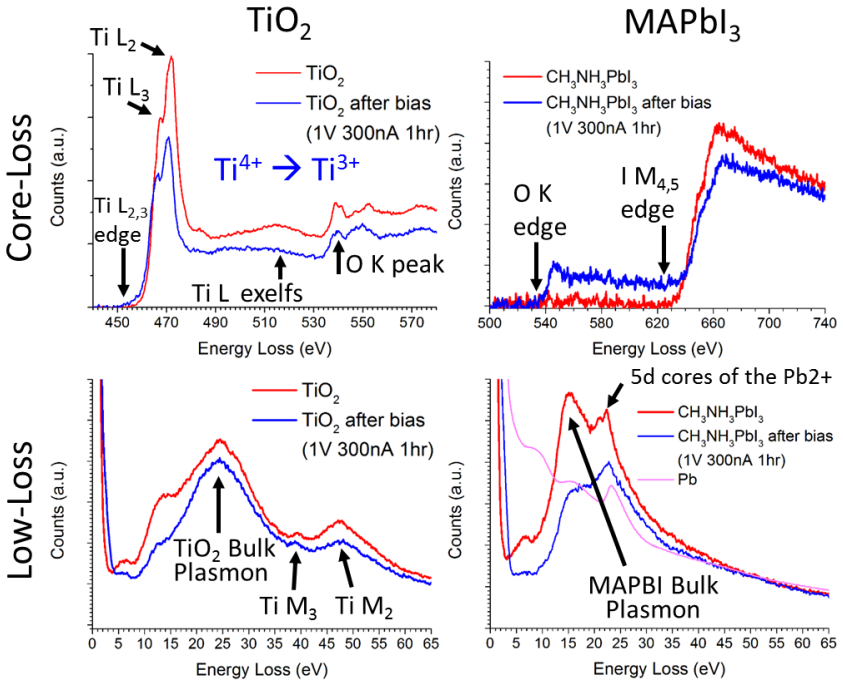

Figure 2. Core-loss (top) and low-loss (bottom) of TiO_2 (left) and MAPBI (right) are shown comparing before (red) and after (blue) biasing at forward +1V to MAPBI.

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