Mapping Highly Efficient Mixed-cation Pseudohalide-perovskite Solar Cells with a Scanning Transmission X-ray Microscope

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The organic–inorganic hybrid perovskite structure has rapidly attracted much attention because of the highly efficient photovoltaic cells in which it serves as a light sensitizer [1]. The perovskites are typically metal-organic frameworks of form ABX₃, in which A is CH₃NH₃⁺ (MA) or CH₃(NH₂)₂⁺ (FA) or Cs⁺, B is Pb²⁺ or Sn²⁺, and X is I⁻ or Cl⁻ or Br⁻. For example, methylammonium lead iodide (MAPbI₃) and its analogues exhibit novel properties such as ambipolar charge transport, a large absorption coefficient and an effective electron- or hole-diffusion length, making them suitable for photovoltaic applications. Among various perovskites, the mixed-cation lead pseudohalide perovskites were particularly successful with a large power-conversion efficiency (PCE) and satisfactory stability against moisture [2-3]. The large crystalline size with few trap states, increased entropy or decreased formation of solid solution are experimentally or theoretically proposed to interpret the origin of this high efficiency and stability. The variation of film morphologies is typically examined with a conventional TEM or SEM that provides only the bulk structure in a cross-sectional view or the surface topography in a top view. The necessity arises to improve the mapping capability to inspect the multilayer structures with a scaffold of an electron-transport layer (ETL)/perovskite/hole-transport layer (HTM) in perovskite-based solar cells. We have investigated the origin of the large PCE and the stability of mixed-cation pseudohalide perovskite solar cells using a scanning transmission x-ray microscope (STXM). In our experiments to fabricate perovskite solar cells, the mixed cation with formamidinium (FA: HC(NH)₂) and Cs cations replaced methylammonium. To improve the PCE efficiency and structural stability, we used lead thiocyanate (Pb(SCN)₂) as dopant so that the thiocyanate (SCN⁻) anions replaced the halide ions in the tetragonal sites of the unit lattice of perovskite FA₀.₉Cs₀.₁PbI₃ solar cells. The cell devices with mesoscopic titania as scaffold/electron-transport layer and spiro-OMeTAD as hole-transport layer were examined for the photovoltaic performance under standard illumination conditions. PCE greater than 16 % was achieved with optimized Pb(SCN)₂ doping relative to 13.9 % for cells without Pb(SCN)₂. To understand the origin of this improved efficiency and structural stability, we used a STXM to examine the chemical structure and morphology. The samples of FA₀.₉Cs₀.₁PbI₃ cuboids and with varied Pb(SCN)₂ concentration in molar ratios 5%, and 10% were prepared in our laboratory. The NEXAFS absorption spectra and STXM images at varied absorption edges, such as the C, O, N K-edge and Ti L-edge, were recorded at BL 09A2 spectroscopy of Taiwan Light Source at NSRRC and at BL4U in UVSOR Synchrotron in Japan, respectively.

To study the effect of doping of Pb(SCN)₂ on the efficiency and stability, we prepared pristine perovskite FA₀.₉Cs₀.₁PbI₃ and Pb(SCN)₂-doped FA₀.₉Cs₀.₁PbI₃ and spin cast them on mesoporous TiO₂ layers (mp-TiO₂) that were pre-cast on SiN membranes. Figure 1 displays STXM images of the C K-edge acquired at 287.6 eV, which is attributed to a C-N σ⁺ resonance of FA (HC⁺(NH)₂) in FA₀.₉Cs₀.₁PbI₃ with Pb(SCN)₂ doped at 5 % (Fig. a) and 10 % (Fig. b). Compared to pristine FA₀.₉Cs₀.₁PbI₃ (that shows no contrast), the
5 % doped FA0.9Cs0.1PbI3 shows bright cuboids and a few black rods. In contrast, 10 % doped FA0.9Cs0.1PbI3 expresses similar bright cuboids but more black sticks and irregular blocks that show black and grey contrast, which apparently result from too much Pb(SCN)2 dopant. A comparison of chemical mapping of the C K-edge at 287.6 eV, N K-edge at 400.7 eV and Ti L-edge at 457.9 eV for 5 % Pb(SCN)2 is shown in Figure 1(e), (d) and (e), respectively. Both C and N mapping, which were acquired at characteristic absorption features of FA0.9Cs0.1PbI3 perovskite, display the same features and contrast that are not directly correlated with the distribution of mp-TiO2. The crystalline size of Pb(SCN)2 doped-FA0.9Cs0.1PbI3 perovskite are, however, significantly decreased when grown on mp-TiO2. This condition indicates that Pb(SCN)2 and mesoporous TiO2 play key important roles to affect the growth of perovskite crystallites. The optimized addition of Pb(SCN)2 is advantageous to enlarge the crystal size of FA0.9Cs0.1PbI3 on mp-TiO2. To comprehend thoroughly the distribution of heterostructure layers, we display in Figure 2 the chemical maps of the N K-edge and Ti L-edge of SiN/mp-TiO2/5% Pb(SCN)2 doped-FA0.9Cs0.1PbI3, and SiN/mp-TiO2/10% Pb(SCN)2 doped-FA0.9Cs0.1PbI3, which are maps of optical density (OD) obtained at the characteristic absorption features of FA0.9Cs0.1PbI3 and mp-TiO2. There are notable additional sticks and large aggregated blocks, as shown in red and yellow colors in the composite images determined as TiO2 nanoparticles that have a uniform diameter 2–5 μm and appear to be more uniformly dispersed in 5 % Pb(SCN)2 doped-FA0.9Cs0.1PbI3. 5 % Pb(SCN)2 doped-FA0.9Cs0.1PbI3 has hence an effective charge transfer between perovskite and TiO2. The STXM results indicate that the interaction between mp-TiO2 and perovskite plays a key role in determining the PCE performance. The morphology variation of perovskite is correlated with mp-TiO2 and Pb(SCN)2, which illustrates that the interaction between mp-TiO2 and perovskite is not favored to grow large and defect-free perovskite layers for charge transfer.

References

[4] The authors acknowledge funding from the Ministry of Science and Technology, National Synchrotron Radiation Research Center and the UVSOR-RIKEN collaboration program.