Atomic-Scale Imaging of Organic-Inorganic Hybrid Perovskite

Subjects: Materials Science, Characterization & Testing
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Transmission electron microscope (TEM) is thought as one powerful tool to imaging the atomic-level structure of organic inorganic hybrid perovskite (OIHP) materials, which provides valuable and essential guidance toward high performance OIHP-related devices.

Keywords: organic-inorganic hybrid perovskites ; transmission electron microscopy

1. Application Status of Transmission Electron Microscope (TEM) in Organic-inorganic Hybrid Perovskites (OIHPs)

The unusual optoelectronic properties and performance of OIHPs are closely related to their unique crystal structure and microstructure, e.g., the crystal symmetry, the vibration and ordered arrangement of the organic groups, and the tilt of the $[PbI_6]^-$ octahedra [1]. Therefore, in recent years, TEM has been widely employed to reveal the atomic-level structure and image of OHIP materials, which promotes deeper understanding to their material properties and related device performance [2][3].

When OIHPs are imaged using conventional TEM, the structure of the perovskites might be destroyed in several seconds, which is sorted as the irradiation damage. Chen et al. noticed severe irradiation damages in the $MAPbI_3$ perovskite polycrystalline film when being imaged via conventional TEM at a high electron dose rate of ~9870 e/(Å^2·s), where nanoparticles were precipitated quickly within the irradiated area [4]. Kim et al. revealed the generation and expansion of “bubbles” by a series of TEM images through continuous irradiation on $MAPbI_3$ perovskite single crystals [5]. The above results indicate that it is difficult to obtain the low-magnification morphology of OIHPs films via traditional imaging mode of TEM, which should be caused by electron beam induced electrical field [4] and the direction-selectivity of the electron beam damage in OIHPs [5]. The electrical field will be formed when there occurs the accumulation of positive charges in irradiated sample regions, following the emissions of Auger and secondary electron into vacuum. The beam periphery damage in the images has been unraveled in previous related literature, where various electron doses and different accelerate voltages were attempted [4].

The structural instability of OIHP materials under various conditions (e.g., high temperature, oxygen, humid environment, light) becomes a vital issue to hamper the commercialization of PSCs [6][7][8]. By employing the SAED technique, Chen et al. investigated the decomposition mechanism of OIHPs under electron beam irradiations [9][10]. A possible decomposition way was thus proposed. Under continuous beam illumination, researchers observe structure evolution of $MAPbI_3$ (along the [110] zone axis) and MAPbBr3 (along the [001] zone axis) as exhibited by SAED patterns. With the increased electron beam dose, the loss of methylamine and halogen ions could eventually cause the collapse of perovskite structure to PbX_2 (X = I, Br), and the atomic resolution images can be seen. The structure illustrations for decomposition from tetragonal $MAPbI_3$ (viewed along its [110]) to PbI_2 and cubic $MAPbBr_3$ (along its [110]) to $PbBr_2$ can be seen. Their results indicated that the tetragonal $CH_3NH_3PbI_3$ and the cubic $CH_3NH_3PbBr_3$ may lose some halides during the irradiation, which then formed an intermediate product of perovskite superstructure with ordered vacancies (i.e., $CH_3NH_3PbX_{2.5}$, X = I, Br). The structural degradation behaviors of perovskites under various experimental conditions were also investigated via low-dose electron diffraction and imaging techniques, which optimized the operating conditions of TEM for characterizing OIHPs [9]. a TEM cryogenic holder (Gatan 636) was employed to study the SAED patterns of $MAPbI_3$ at different temperatures, which are reported to be orthorhombic phase below −(111 ± 2) °C, tetragonal phase between −(111 ± 2) and (58 ± 5) °C, and cubic phase over (58 ± 5) °C [10]. The $MAPbI_3$ is grown to be a tetragonal phase, whose SAED pattern matches with the simulated one. The acquired SAED pattern at −180 °C shows no superstructure diffraction spots of the orthorhombic phase, highlighted by the circle on the simulated ED pattern, suggesting that a low temperature in vacuum will not cause the transition from tetragonal to orthorhombic phase for the single crystal $MAPbI_3$. The phase at a high temperature and the SAED pattern at 90 indicates either a [110] direction of cubic phase or a [100] direction of the tetragonal phase, making people unable to identify the specific phase. A liquid nitrogen side-entry specimen holder was applied to cool down the specimen temperature. When the temperature is at −180 °C, a rapid crystalline-to-amorphous phase transition was observed under low doses (129 to 150 e$Å^{-2}$). Interestingly, a large electron beam dose (450–520 e$Å^{-2}$) is required to induce the transition from $MAPbI_3$ to PbI_2 at higher temperatures. Such phenomenon suggests that lowering the temperature may not hinder the decomposition of OIHPs, but rater leads to rapid undesirable phase transformation.

2. Main Issues of TEM in Characterizating OIHPs

Despite the importance and necessarily of TEM in OIHP characterizations have been gradually realized, major challenges still remain, i.e., these perovskite materials are electron beam sensitive [11][12], which limit the practical application of TEM. Taking the well-known $MAPbI_3$ as an example, due to the negligence of electron beam-sensitive property, the decomposition products, such as PbI_2, Pb and other intermediates have widely misidentified as perovskite in TEM characterizations, which negatively influenced the development of perovskite field.

In general, the electron dose value of normal HRTEM is within 800–2000 e$Å^{-2}$ s^{-1}, which is much higher than the critical value of $MAPbI_3$ (~150 e$Å^{-2}$) [11][12]. Meanwhile, several interplanar spacings and angles of the decomposition product (e.g., PbI_2) are similar with $MAPbI_3$.

Due to the inaccurate recognize of crystal planes, some researchers may identify PbI_2 as $MAPbI_3$ [13][14][15][16][17][18][19][20][21] even using low-dose electron diffraction (ED) technology. For instance, in contrast to the $MAPbI_3$ perovskite, the structures of decomposition products were misidentified as 'pseudo' perovskite. The FFT was consistent with the simulated ED pattern along [441] zone axis, which was identified as the perovskite. In fact, the HRTEM image and Fast Fourier Transform (FFT) of intrinsic $MAPbI_3$ along [001] zone axis at a total dose of 1.5 e$Å^{-2}$ at room temperature were obtained [22]. Obviously, (1$\underline{1}$0), (110) planes with 0.62 nm interplanar spacing can be seen in images, matching the ED pattern and XRD data of the intrinsic $MAPbI_3$ [21][23]. Comparing the simulated ED of PbI_2 along [4$\underline{4}$1] zone axis with that of intrinsic perovskite along [001] zone axis, it was found that they were very similar, but (11 □□□□□□□0), (110) planes missing and only (2$\underline{2}$0), (220) planes remained, which results in the misidentified of the perovskite structure.

The crystal planes that could be observed in other Bragg's law-based characterization tools, such as SAED and XRD [23][24][25][26], were missed in TEM results, which is attributed to the excessive electron beam irradiation in $MAPbI_3$, damaging its original structure. Particularly, if {2h, 2k, 0} diffraction spots along the [001] direction is observed while the {2h + 1, 2k + 1, 0} reflections [e.g., (110)] are absent, it is reasonable to presume that the perovskite structure has already been decomposed into PbI_2 [12]. Therefore, when using HRTEM images to identify phases, it seems incidental to misidentify perovskite phases by merely comparing interplanar spacing and angles. During phase identification, misidentification may occur due to the similarity of certain crystal parameters, missing crystal planes, measurement errors, and other reasons. It is thus necessary to combine with other relevant diffractograms, simulated ED, nanodiffractions, or XRD specimen data [27] to conduct accurate phase identification.

3. Strategies to Improve the Compability of TEM in OIHPs

3.1. Sample Protection

Sample protection, as its name indicates, could directly protect the material and improve its stability [28]. By coating carbon about 6–10 nm thick on $MAPbI_3$, Chen et al. revealed that the decomposition of OIHPs could be significantly suppressed, due to the thin carbon coating layer served as a diffusion barrier, reducing the escape rate of the volatile species (e.g., halogen atom and CH_3NH_2), which helps to maintain the structure framework of perovskite [9]. However, for one-side coated specimen with half of shielding, the degradation was not slowed down, likely because the volatile species can escape from the other uncoated side. Furthermore, hexagonal boron nitride thin films were deposited as an encapsulation layer, which successfully extend the stability of $MAPbI_3$, successfully reducing radiation damage induced by electron beam [14].

3.2. Low-Temperature-Based Technologies

To mitigate electron beam damage, low temperature-based technologies were also developed, which could effectively reduce mass loss and the heat damage [29][30]. Indeed, cryo-electron microscopy (cryo-EM) has already been applied for characterizing electron beam sensitive materials such as lithium-ion battery materials [31][32][33][34]. Efforts have also been devoted to investigate the effect of low temperature on the structural stability of OIHPs under electron beam irradiation [12][35][36][37][38]. It was found that the intrinsic structure of $MAPbI_3$ could be maintained at room temperature when the total electron dose is at ~1.5 $eÅ^{-2}$ [22]. When the total dose reaches 5.95 $eÅ^{-2}$, superlattice will be formed, which will damage the original perovskite structure. by employing Cryo-TEM, the critical dose of $MAPbI_3$ increases to 12 $eÅ^{-2}$, which is much higher than that at room temperature [10]. As a result, a more "stable" OIHP is achieved, which allows the use of higher electron dose to increase the signal-to-noise ratio of the image. However, conflicted results were reported in Rothmann's research, which suggests that low temperatures may lead to rapid amorphization [26]. Chen et al. [10] also found that low temperature (−180 °C) would cause rapid crystal-to-amorphous transition even at low doses (129 to 150 $eÅ^{-2}$), suggesting that low temperature may not be helpful to reduce electron beam damage. The above inconsistent might source from the specimen properties or the discrepancy between the cryo-holder and cryo-microscope methods, which needs to be investigated in the near future.

The third approach refers to low-dose imaging technology, which is also an effective strategy to obtain atomic-level resolution images for electron beam sensitive materials [39]. By combining low-dose LAADF-STEM imaging with simple Butterworth and Bragg filters, atomic-level high resolution pictures of the $FAPbI_3$ perovskite film with only minor damages were acquired [40], which unraveled some unique phenomena of these perovskite materials that may not be feasibly measured using other techniques.

The invention of the DDEC camera provides an alternate solution towards high-resolution TEM images for OIHPs. Early in 2018, Han and coworkers reported the employment of DDEC cameras in TEM, which exhibit high detective quantum efficiency, thus enabling HRTEM with ultralow electron doses that is suitable for imaging OIHPs [41]. Moreover, the intrinsic structure of $MAPbI_3$ has been revealed successfully at a total electron dose of only 3 $eÅ^{-2}$ by using DDEC cameras [10][27]. Li et al. obtained Cryo-TEM images of $MAPbBr_3$ and $MAPbI_3$ at different cumulative electron doses via DDEC camera, and investigated their electron dose thresholds at cryogenic temperatures. The resultant electron doses of $MAPbI_3$ and $MAPbBr_3$ were approximately 12 $eÅ^{-2}$ and 46 $eÅ^{-2}$, respectively [11]. Song et al. also used a DDEC camera to obtain a set of high-resolution images of $MAPbI_3$ along the [001] zone axis, which matched well with the expected structure [22]. Nevertheless, despite the employment of DDEC is one of the prerequisites for HRTEM to probe sensitive OIHP materials, the DDEC camera alone is insufficient to gain high-quality images. There still remains several obstacles. First, the desired zone axis must be aligned with the electron beam in a very fast period to prevent the crystalline structure from damage. Second, the successive short-exposure low-dose frames must be precisely aligned to avoid any loss of resolution. Last but not least, the accurate defocus value should be known to obtain an interpretable image by image processing. Han and co-workers developed a simple program to achieve a one step, automatic alignment of the zone axis, as well as an "amplitude filter" to retrieve the high-resolution information hidden in the image stack, and a method to determine the defocus value of the image. By applying such methods, they successfully acquired the first atomic-resolution (≈1.5 Å) HRTEM image of hybrid $CH_3NH_3PbBr_3$ at 300 kV with a total electron dose of 11 $eÅ^{-2}$ [41].

At the same time, researchers may also reduce the exposure dose of electron beam sensitive materials through some other techniques during the testing process, such as zone-axis auto-alignment and adjusting parameters of TEM in non region of interest (ROI). Instead of real-time observation, automatic zone-axis alignment utilizes one diffraction pattern to judge and rotate the sample to the desired zone-axis blindly using of programming control for parameter adjustment, which could save a lot of avoidable exposure. Moreover, focusing on the adjacent region of interest (ROI) instead of directly on the ROI and restoring the parameters in advance can further eliminate the electron irradiation. These dose-control strategies are able to diminish unnecessary electron exposure [42].

For electron beam sensitive materials, such as OIHPs, low-dose technology is required to obtain atomic level resolution images, however, there are problems such as sample drift during imaging processing, low signal-to-noise ration of images, and difficulty in data processing due to a large amount of data. Therefore, in order to precisely observe the atomic structure of OIHPs, processing data more efficiently and increasing the input-output ratio is also an indispensable point in practical HRTEM imaging. A combination of machine learning and development of algorithms for drift correction, denoising, and image reconstructor would benefit low-dose imaging.

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