Unraveling the molecular structure of 2D polymers by low-dose diffraction and imaging

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Two-dimensional (2D) covalent crystals, which are laterally infinite, down to monomer-unit thin and freestanding, are promising candidates for next-generation electronics, optoelectronics, sensors, and membranes. Organic synthesis opens up an emerging route to the realization of novel 2D covalent crystals, i.e., crystalline 2D polymers (2DPs). Through self-assembly of well-defined building blocks, the crystal structure of 2DPs can be engineered at the molecular level giving rise to rational-designed functionalities [1]. In order to confirm the successful synthesis of target 2DPs with high crystallinity, as well as to reveal the structure-property correlation, it is indispensable to determine their crystal structures on molecular/atomic level. However, despite that atomic resolution imaging is readily achievable on modern aberration-corrected transmission electron microscopes, even at low voltages from 20 to 80kV [2], the structural characterization of organic 2D crystals remains a formidable task. The strong interaction between incident electrons and organic molecules, particularly with C-H bonds [3], triggers bond dissociation and various chemical reactions degrading the structural integrity of 2DPs, which hinders their structural definition.

In order to circumvent the detrimental effects of irradiation damage, we have fully explored the potential of low-dose technique for the characterization of 2DPs. By employing low-dose selected-area electron diffraction (SAED) and aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) at 300 kV, the crystal structures of various synthetic 2DPs, including, polyimide, polyamide and polyimine (atomic models in Fig. 1), have been systematically studied. Figure 2 presents the TEM data on 2D polyimide and polyamide. The unit cell dimensions and symmetry extracted from SAED patterns are in perfect agreement with the atomic models derived by density functional tight-binding calculation, demonstrating the realization of target 2DPs. AC-HRTEM further confirmed the molecular structures of 2D polyimide and polyamide. Remarkably, our AC-HRTEM results provided not only structure-proof for the synthetic 2DPs but also rich information on the single-crystalline domain size, domain edge/boundary configurations, dislocations, and stacking faults, which is scarcely reported in literature of 2D covalent crystals. Figure 3a and 3b shows the coalescence of multiple domains of 2D polyimine. The grain boundaries between tilted domains (Fig. 3c), as well as an antiphase domain boundary (Fig. 3d), have been clearly resolved.

In summary, by applying low-dose SAED and AC-HRTEM at 300kV, we have unambiguously elucidated the structures of various organic 2DPs on the molecular level. For future studies, we will further explore specimen-electron beam interactions under lower accelerating voltages (20-80kV) with the aim to minimize irradiation damage on organic specimens and to evaluate the potential for atomic-resolution imaging of 2DPs.

References

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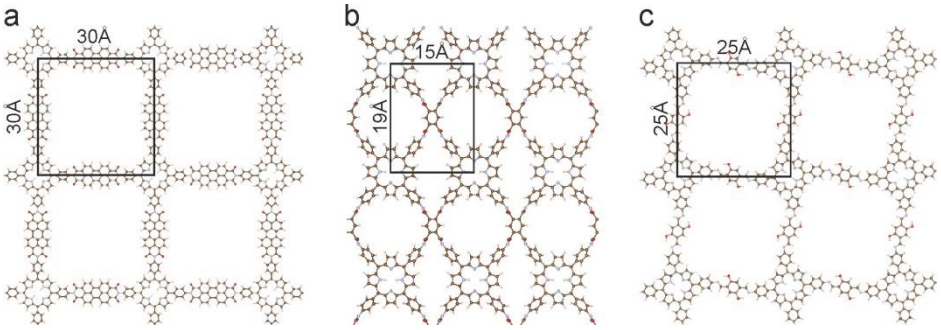

Fig. 1 (a-c) Atomic models of 2D polyimide, polyamide, and polyimine, respectively.

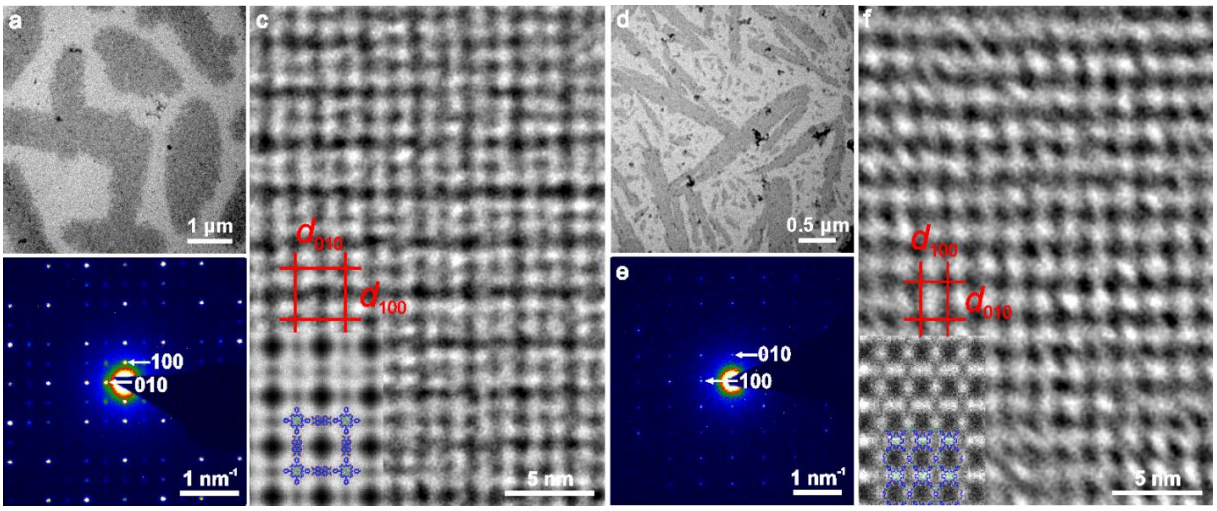

Fig. 2 (a) Bright-field TEM image showing the single-crystalline domains of 2D polyimide (dark) bridged by amorphous fragments (bright). (b) SAED pattern from the crystalline domain in (a), the 100 and 010 reflections are at 0.33 nm^{-1} (i.e., 3 nm). (c) AC-HRTEM image of polyimide (Inset: simulated TEM image with the structure model overlaid). (d) Bright-field TEM image showing the single-crystalline domains of 2D polyamide (dark) bridged by amorphous fragments (bright). (e) SAED pattern from the crystalline domain in (d), the 100 and 010 reflections are at 0.65 nm^{-1} (1.54nm) and 0.52 nm^{-1} (1.92 nm), respectively. (f) AC-HRTEM image of polyamide (Inset: simulated TEM image with the structure model overlaid).

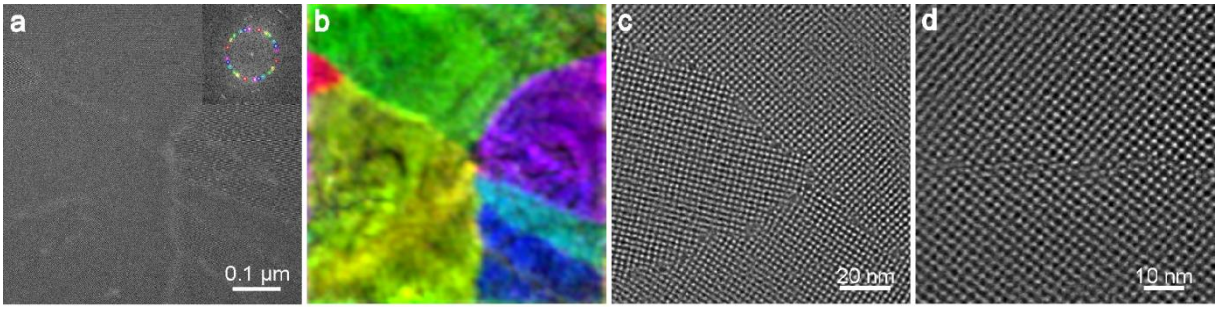

Fig. 3 (a) TEM image showing the coalescence of 2D polyimine single-crystalline domains (Inset: Fast Fourier transform pattern of the image, the colored circles indicate the Fourier masks). (b) Fourier-filtered image of (a), the single-crystalline domains have been color-coded. (c) AC-HRTEM image of grain boundaries between tilted domains. (d) AC-HRTEM image of an antiphase domain boundary.