

Low-dose Transmission Electron Microscopy of Highly-Oriented Polyacetylene

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Recent advances in the synthesis of highly-oriented polyacetylene (HOPA) have demonstrated that well-defined supramolecular architectures with combined advanced mechanical and electronic properties can be designed and produced at a massive scale [1]. In order to understand the structure-property relationship of these electrically conducting polymers, characterization techniques at the subnanometre scale is critical because the macroscopic properties of these fibers are closely related to the local structures and the isomerism. However, direct observation of the atomic structures of polymeric fibers through electron microscopy remains a challenge as these soft materials are very sensitive to electron beam damage.

Using low-dose transmission electron microscopy and microanalysis techniques, we identified highly-oriented polyacetylene (HOPA) synthesized via high-pressure and observed that the resulting product of the solid-state polymerization is primarily composed of *trans*-polyacetylene (*trans*-PA). Direct observation of the atomic structure of HOPA is complicated by the modest structural stability of delocalized conjugated π -electron systems under the electron beam [2]. Therefore, a controlled dose rate is required to minimize the radiolysis damage on the sample during imaging and analysis. Similar to carbon nanotubes, we observed that HOPA is susceptible to electron beam damage, which leads to the loss of long-range ordering and preferred orientation under irradiation. Graphitic nanostructures were obtained from the HOPA film upon e-beam radiation with the accelerating voltage of 80-200kV, which suggests that e-beam radiation of conjugated π -electron systems might be an alternative post-synthetic alteration in order to make carbon nanostructures in addition to pyrolysis [3]. High-resolution images of HOPA and their corresponding Fast Fourier Transforms (FFTs) in Figure 1 demonstrate the dose effect. Figure 1a shows the graphitic carbon nanostructures from the HOPA sample subjected to high electron dose, which is indicated by the nano-onion like structures. Figure 1b presents a schematic of the structure of *trans*-PA along the $\langle 1-30 \rangle$ axis. A low-dose image along with the corresponding Fourier-filtered image, which is indexed to the $\langle 1-30 \rangle$ zone of *trans*-PA, are presented in Figure 1c. In this study, the structural transformation of HOPA sample under the electron beam was further examined in situ through Electron Energy Loss Spectroscopy (EELS), which is intended to monitor the gradual loss of the well-aligned, linearly delocalized π electrons in HOPA as an alternative approach in order to determine the critical dose [4].

References:

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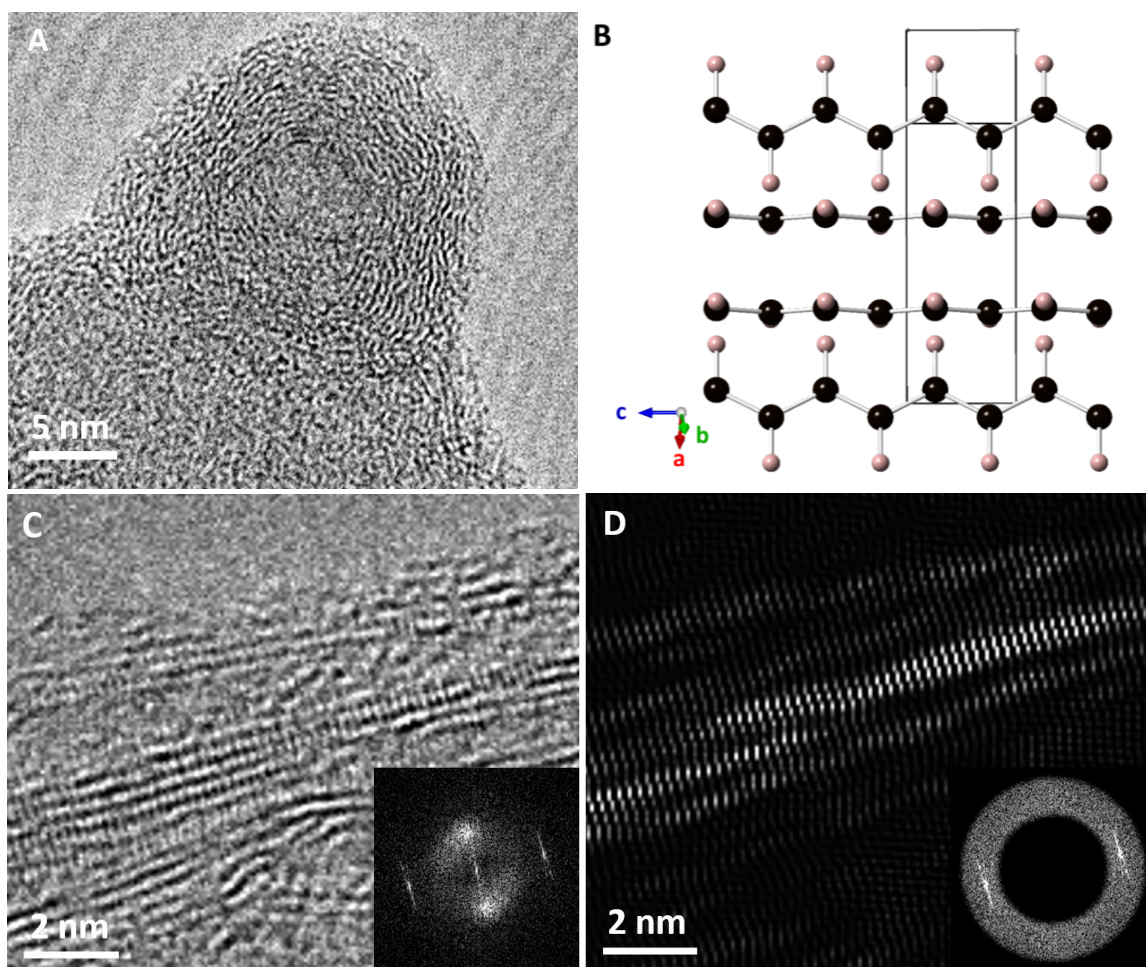


Figure 1. (A) A typical high-dose HRTEM image of HOPA sample taken at the fluence of 941 electrons/ $\text{\AA}^2\text{s}$ shows graphitic carbon nano-onions like structures embedded in hydrogenated amorphous carbon matrix. (B) A schematic shows the crystal structure of *trans*-PA along the $\langle 1-30 \rangle$ axis. (C) A low-dose HRTEM image, taken at the fluence of 181 electrons/ $\text{\AA}^2\text{s}$, shows the presence of HOPA along with few-layer graphene. The inset FFT shows the HOPA characteristic asymmetric pattern which is indexed to the $\langle 1-3\ 0 \rangle$ zone of *trans*-PA and (D) the corresponding Fourier filtered image further accentuated the wavy striation of the *trans*-PA chains.