Monochromated Low-Dose Aberration-Corrected Transmission Electron Microscopy of Diamondoid Carbon Nanothreads

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Carbon nanothreads are the first in a new class of one-dimensional sp³ carbon nanomaterials that was recently discovered through compression-induced polymerization of benzene in a Paris-Edinburgh cell [1]. Their diamond-like structure is predicted to have interesting mechanical properties that are on par with or greater than carbon nanotubes [2]. In addition, the solid-state synthesis is entirely driven by kinetic control and devoid of waste, which may open up new routes to fabricate efficient carbon nanomaterials [3,4]. Therefore, it is important to probe the atomic and chemical structure of nanothreads to elucidate the reaction mechanisms that result in their synthesis and determine their macroscale physical and chemical properties.

X-ray diffraction (XRD) studies and density functional theory (DFT) calculations strongly suggest that carbon nanothreads form a well-aligned, hexagonally-packed structure with an inter-thread spacing of ~6.5 angstroms [1]. Likewise, electron diffraction patterns reveal higher order reflections that agree with these experimentally and theoretically-derived models. Direct observation of the atomic structure of nanothreads is complicated by the low threshold of carbon nanomaterials for beam damage in the electron microscope [5]. Similarly, carbon nanothreads' one-dimensional tetrahedral structure is akin to polymers, which makes them susceptible to electron beam damage. In this study, the structural degradation of carbon nanothreads is examined through selected-area electron diffraction, and the critical dose is determined. An electron gun monochromator is then employed to reduce the electron dose and minimize beam irradiation and damage [6] while imaging the nanothreads on a high-resolution aberration-corrected transmission electron microscope. High-resolution images and their Fourier transforms in Figure 1 demonstrate the effect of electron dose on the sample. Figure 1a shows the structural degradation of the nanothreads when exposed to a high electron dose, which is indicated by the amorphous morphology. Figure 1b presents a low-dose image of the highly-oriented nanothread structure, which displays 6.4angstrom inter-thread spacing and large-scale crystallinity in the sample. These direct observations agree with the predicted 6.5-angstrom hexagonally-packed lattice shown in Figure 1c. This study further employs low-dose imaging techniques to explore a variety of sample preparation techniques, which are intended to separate individual nanothreads in order to determine their atomic and chemical structure.

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References:

- [1] T.C. Fitzgibbons, M. Guthrie, E.S. Xu, V.H. Crespi, S.K. Davidowski, G.D. Cody, N. Alem, and J.V. Badding, "Benzene-Derived Carbon Nanothreads". *Nature Materials* 14, 43-47 (2015)
- [2] R.E. Roman, K. Kwan, and S.W. Cranford, "Mechanical Properties and Defect Sensitivity of Diamond Nanothreads". *Nano Lett.* 15 (3), 1585-1590 (2015)
- [3] B. Chen, R. Hoffmann, N.W. Ashcroft, J. Badding, E.S. Xu, and V. Crespi, "Linearly Polymerized Benzene Arrays as Intermediates, Tracing Pathways to Carbon Nanothreads". *J Am Chem Soc* 137 (45), 14373-14386 (2015)
- [4] E. Xu, P.E. Lammert, and V.H. Crespi, "Systematic Enumeration of sp³ Nanothreads". *Nano Lett.* 15 (8), 5124-5130 (2015)
- [5] R.F. Egerton, P. Li, and M. Malac, "Radiation damage in the TEM and SEM". *Micron* 35 (6), 399-409 (2004)
- [6] B. Barton, B. Jiang, C.Y. Song, P. Specht, H. Calderon, and C. Kisielowski, "Atomic Resolution Phase Contrast Imaging and in-Line Electron Holography Using Variable Voltage and Dose Rate". *Microscopy and Microanalysis* (2012)

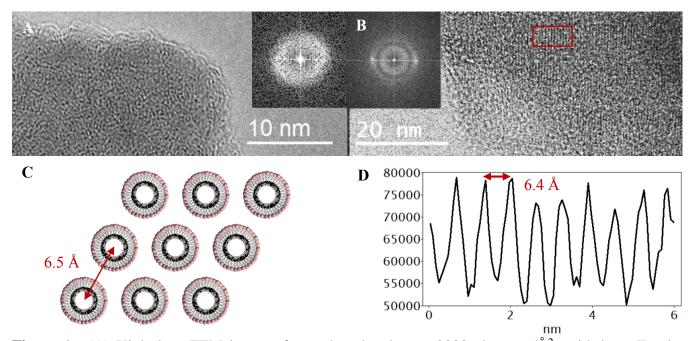


Figure 1. (A) High-dose TEM image of nanothreads taken at 2000 electrons/Å²s with inset Fourier transform shows amorphous morphology, even though (B) a nanothread model predicted from x-ray diffraction data suggests highly-oriented hexagonal packing. (C) A low-dose TEM image taken at 50 electrons/Å²s and (D) a line profile show thread-like features with 6.4 Å spacing, which correlates to the anticipated 6.5 Å interthread spacing.