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Electron Spectroscopic Imaging of DNA Molecules along Carbon Nanotubes by Aberration-Corrected Transmission Electron Microscopy

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Single-stranded DNA molecules (ssDNA) can effectively disperse bundled carbon nanotubes into individuals in aqueous solution for the synthesis of carbon-nanotube-supported platinum catalysts [1], and carbon nanotubes can be used as transporters for the delivery of DNA molecules into cells [2]. For these and other potential applications, it is critical to understand structure-property correlations of the nanotube/DNA hybrids. However, there remains a lack of systematic observations regarding the interfacial structure between the DNA and the nanotube surface. In this study, we used aberration-corrected transmission electron microscopy (TEM) to investigate the morphology and interfacial structures of the nanotube/DNA hybrids using energy-filtered TEM (EFTEM) and electron energy-loss spectroscopy (EELS).

In a typical experiment, 1 mg of nanotube powder was suspended in 1 ml ssDNA solution (TTTGGAGTGACCTGGTGT, 1 mg/ml, 0.1 M NaCl). After sonication and centrifugation, the supernatant was dialyzed using cellulose ester membranes with a 100k molecular weight cutoff to eliminate free DNA molecules [1-2]. Several drops of hybrid solution were transferred onto carbon films supported by the TEM grids. EFTEM and EELS data were acquired with aberration-corrected FEI TEAM 0.5 and TEAM 1.0 TEM at 80 kV [3]. The three-window method was used to remove EFTEM backgrounds. The window conditions for phosphorus mapping were as follows: pre-edge 1 image, 90-110 eV; pre-edge 2 image, 110-130 eV; and post-edge image, 160-180 eV. The exposure time was 20 s per image.

FIG.1a demonstrates that a number of DNA molecules envelop a three-walled carbon nanotube with various morphologies. Since DNA molecules contain relatively low concentrations of phosphorus, special attention must be given to subtracting core edge signal from the background. As shown in FIG.1b, clustered DNA molecules generated more signal for phosphorus than other portions of the same DNA molecules attached to the nanotube; the phosphorous backbones of individual DNA molecules are indicated by arrows. There could be two components to the EFTEM maps: one is the chemical map and the other one is motion of the DNA.
In order to confirm the phosphorous signal, EELS analysis was conducted on more than twenty nanotube/DNA hybrids. As given in FIG.2, the EELS spectrum obtained from a portion of two-nanotube/DNA hybrids (inset: analysis area indicated by the circle) clearly exhibits phosphorus $L_{2,3}$ and carbon K characteristics. Our results demonstrate that TEM/EFTEM/EELS at 80 kV are capable of giving structural and chemical information about a biomolecule with a spatial resolution to the atomic level.

References

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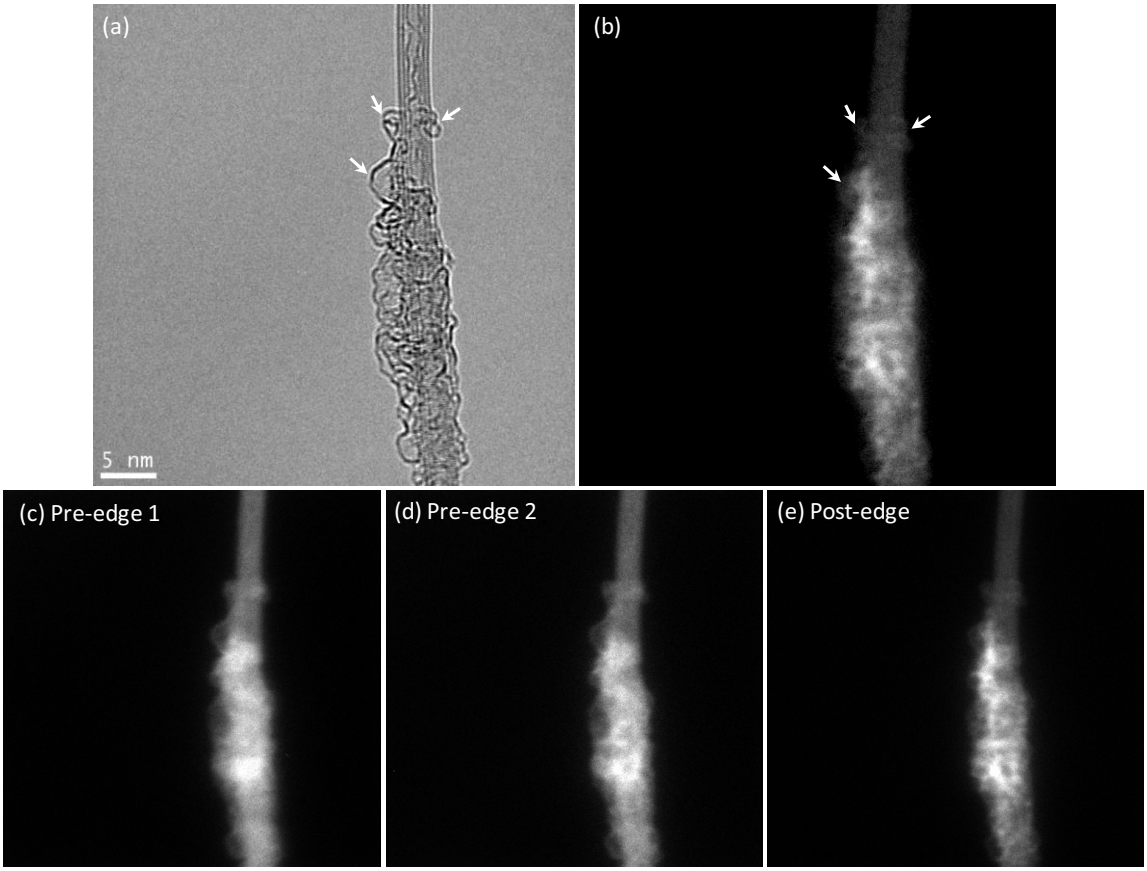

FIG.1. (a) Unfiltered TEM image and (b) phosphorus mapping image of a three-walled carbon nanotube enveloped by DNA molecules demonstrates the presence of phosphorus around the nanotube: (c) 1st pre-P $L_{2,3}$ edge image, (d) 2nd pre-P $L_{2,3}$ edge image, and (e) post-P $L_{2,3}$ edge image.

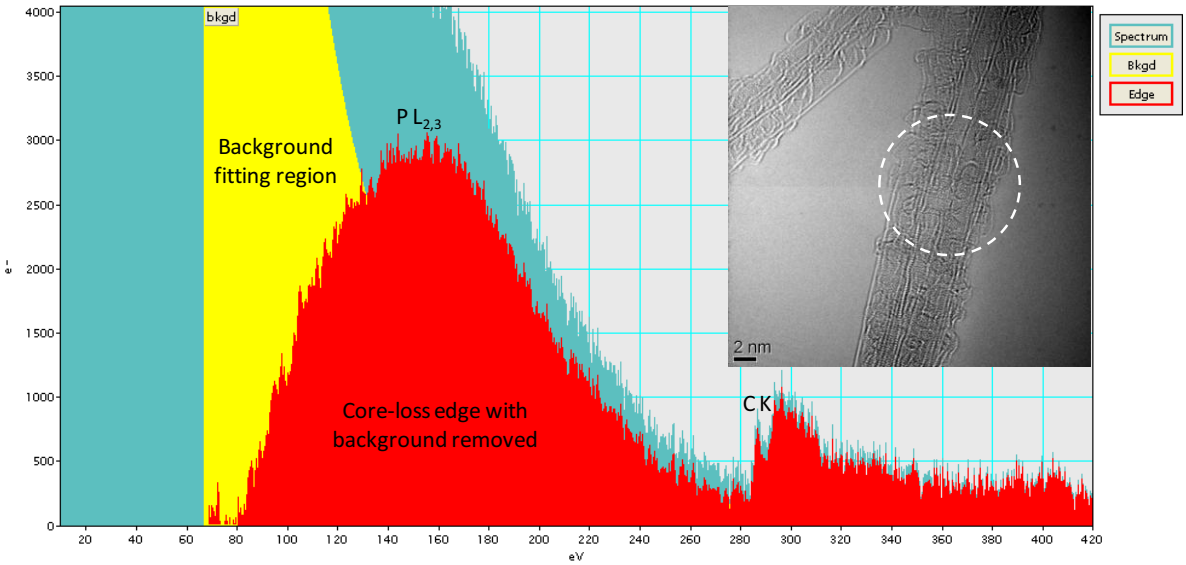

FIG.2. Phosphorus *L*-loss spectrum and Carbon *K*-loss spectrum obtained from two nanotubes wrapped with ssDNA molecules (labeled with a dashed-line circle in the inset). The spectra were computed by fitting the pre-edge spectrum according to an inverse power law and subtracting the extrapolated background from the spectrum above the edge.

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