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Amorphous carbon nanowires investigated by near-edge-x-ray-absorption-fine-structures

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The structure and bonding of amorphous carbon nanowires and amorphous carbon nanowires-converted multiwalled carbon nanotubes have been investigated with carbon *K*-edge near-edge x-ray absorption fine structure using surface-sensitive total electron yield, and bulk-sensitive fluorescence yield. The results strongly support that amorphous carbon nanowire is a precursor to multiwalled carbon nanotubes. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1425462]

The recently reported preparation of bulk quantities of amorphous carbon nanowires[1] has added a new member to the already fascinating family of elemental-carbon based materials. Amorphous carbon nanowire (CNW) and carbon nanotube,[2] especially the multiwalled carbon nanotube (MWNT) are quasi-one-dimensional materials. It is of fundamental interest to investigate whether or not there is any inherent connection between them. In addition, although there have been some growth models for the formation of a MWNT, such as the scroll model[3] and the lip–lip bonds model,[4] the growth mechanism of MWNT remains elusive and awaits further experimental verification.[5] Here, we show that a CNW can be converted to a MWNT. These two phases have been identified with high-resolution transmission electron microscopy (HRTEM). The structure and bonding of the CNW and the CNW-converted MWNT have been investigated with carbon *K*-edge near-edge x-ray absorption fine structure (NEXAFS) using surface-sensitive total electron yield (TEY), and bulk-sensitive fluorescence yield (FLY). The results strongly support that CNW is a precursor to MWNT.

Figure 1 shows the high-resolution image of the CNW and CNW-converted MWNT used in the NEXAFS measurement. CNWs were prepared by thermal evaporation.[1] The MWNTs were prepared by heating a CNW with the following procedure. A quartz tube containing the CNWs was placed inside a tube furnace. Argon was fed into the tube as a protective gas after the tube had been evacuated to 4×10^{-3} Torr. The furnace temperature was kept at 900 °C for 30 min. A total pressure of 740 Torr was maintained throughout annealing. The nanowires and nanotubes were dispersed onto a carbon grid and a clean Si(100) wafer for HRTEM and NEXAFS measurements, respectively. A Philips CM 200 FEG high-resolution transmission microscope (operating at 200 kV) was used for the HRTEM. The CNW in Fig. 1(a) has a diameter of ~20 nm and a smooth surface. There are no lattice fringes inside the CNW unlike a MWNT [Fig. 1(b)], while the nearly parallel dark lines (separated by 0.34 nm) in the MWNT are clearly visible; these are the graphite

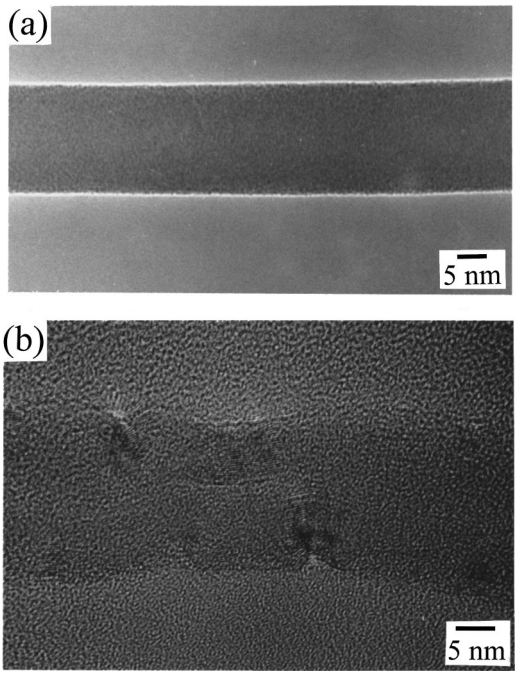

FIG. 1. HRTEM images. (a) Amorphous carbon nanowire and (b) a multiwalled carbon nanotube.

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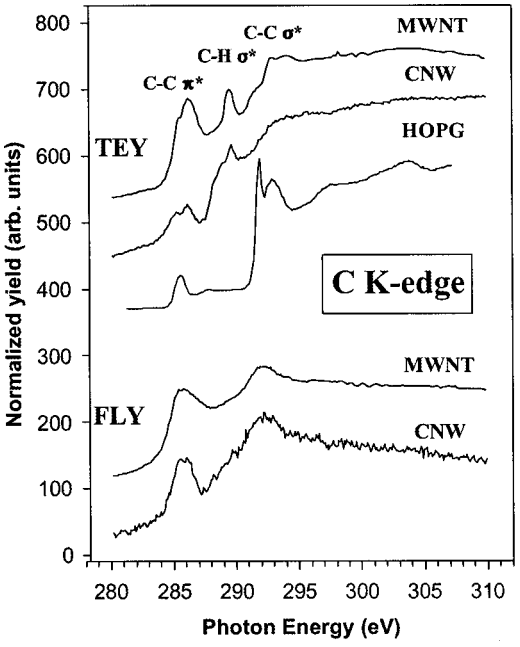

FIG. 2. C *K*-edge NEXAFS of a CNW and MWNT. HOPG NEXAFS is also shown. All were recorded at normal incidence.

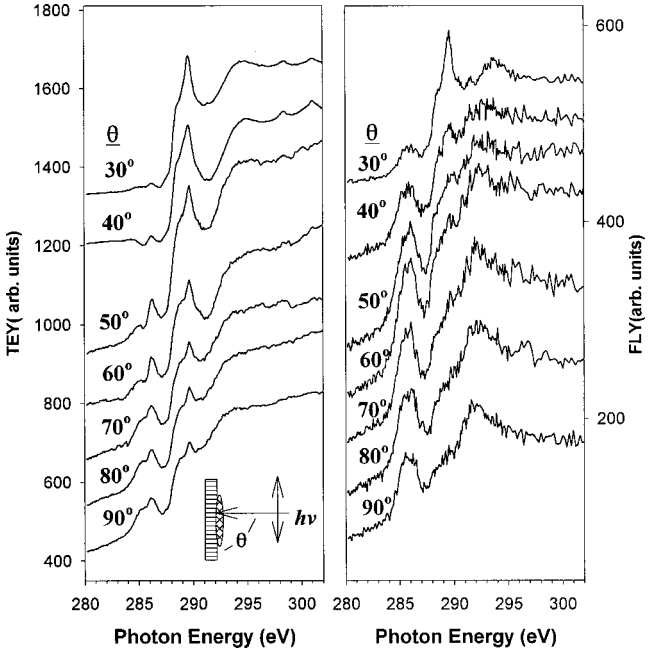

FIG. 3. Angular dependence of the C *K*-edge NEXAFS of a CNW.

basal planes. The inner and the outer diameter of a typical nanotube are 3 nm and 20 nm, respectively. Discontinuity and defects in the nanotube are also apparent.

The C *K*-edge NEXAFS of a CNW and the CNW-converted MWNT in TEY and FLY are given in Fig. 2 together with the TEY of highly ordered pyrolytic graphite recorded at normal incidence. These measurements were conducted at the spherical grating monochromator beamline of the Canadian Synchrotron Radiation Facility at the Synchrotron Radiation Center, University of Wisconsin–Madison.[6] It should be noted that TEY and FLY at the carbon *K*-edge have probing depths of the order of nm and 10^2 nm, and are hence surface and bulk sensitive, respectively. Resonances at ~285 and ~286 eV in the TEY of both a CNW and a MWNT are attributed to C 1*s* to π^* transitions which are also observed in the FLY albeit somewhat blurry due to self-absorption. These features immediately indicate the presence of unsaturated carbon–carbon interactions (sp^2 bonding),[7,8] delocalization and the presence of chemically nonequivalent carbon.[9] The π^* transitions in CNW-converted MWNT are more pronounced than that of a CNW. The most interesting observation is in the region of 287–290 eV where a CNW exhibits intense features in the TEY which are suppressed in the FLY. A similar feature is also detected at ~289.5 in the TEY of a MWNT but not in the FLY. These are σ^* resonance characteristics of C–H bonds in amorphous carbon[7–9] and are attributable to C–H bonding in both a CNW and CNW-converted MWNT (Fig. 1). The low energy shoulder in a CNW contains some sp^3 contribution that vanishes in a MWNT. Except for the C–H σ^* resonance in the TEY from the residues, the NEXAFS of the CNW-converted MWNT are in very good accord with previous MWNT results.[10,11] This observation strongly indicates that a CNW, despite its generally amorphous nature revealed by HRTEM, already contains building blocks (graphitic-like carbon) inside. These units ultimately lead to the formation of a MWNT upon annealing. Apparently, graphitization and MWNT formation did not occur at the stage of CNW formation until further annealing, otherwise, the HRTEM would have shown lattice fringes near the surface of a CNW [Fig. 1(a)].

The presence of local order and texture in the CNW is observed in the angular dependence of the NEXAFS of the CNW. Since the synchrotron light is linearly polarized horizontally, the intensity of the π^* transition is sensitive to the orientation of the π^* orbital with respect to the polarization vector. Thus, if the π^* orbitals in the nanowire specimen are partially oriented with respect to the incident photon beam, a rotation of the specimen with respect to the incoming photon will show a measurable angular dependence. A C–C or C–H σ^* orbital orthogonal to the π^* orbital will show an opposite trend. Figure 3 shows the angular dependence of the NEXAFS of a CNW in both TEY and FLY: the π^* resonance intensity decreases from normal to glancing incidence while the C–H σ^* exhibits an opposite trend. The intense C–H σ^* resonance observed at glancing angle indicates the presence of a C–H bond in the graphitic-like basal plane. The emergence of the C–H feature in the FLY at 30° can be also due to increased surface sensitivity at a glancing angle. The effect should be less dramatic since these are partially oriented samples at best. This observation indicates partial orientation (texture) of the precursor inside the CNW such that the π^* orbitals are partially oriented and orthogonal to the C–H σ^*. Hence, the MWNT building block within a CNW is likely to have the structure somewhere between a phenyl group and a graphitic-like basal plane (sp^2 bonding).

In summary, we have presented evidence from HRTEM and NEXAFS that amorphous carbon nanowire is a precursor to the formation of multiwall carbon nanotubes and can be converted to a MWNT upon annealing. This result is consistent with the chemical behavior of carbon in that graphite nanoscale onions can be formed by heating amorphous carbon film with an electron beam[12] and graphitic carbon film can be formed by heating an amorphous carbon film.[9]

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