

Atomic-Scale Investigations of Carbon Nanotube Growth Mechanisms

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The combination of unique mechanical, thermal, optical, and electronic properties of carbon nanotubes (CNTs) make them a desirable material for use in a wide range of applications [1]. Many of these unique properties are highly sensitive to how carbon atoms are arranged within the graphene nanotube wall [2]. Precise structural control of this arrangement remains the key challenge of CNT growth to realizing their technological potential. Plasma-enhanced chemical vapor deposition (PECVD) from methane-hydrogen gas mixtures using catalytic nanoparticles enables large-scale growth of CNT films (Figure 1), however, much is still unknown about what happens to the catalyst particle during growth, the atomistic mechanisms involved, and how these dictate the final nanotube structure. To investigate the fundamental processes of CNT growth by PECVD, in addition to infrared spectroscopy, optical emission spectroscopy and Raman spectroscopy, a collection of (S)TEM-based characterization techniques were used, including, convergent-beam electron diffraction (CBED), high-resolution (S)TEM imaging, energy dispersive x-ray spectroscopy, and electron energy-loss spectroscopy (EELS).

It is found that hydrogen plays a critical role in determining the final CNT structure through controlling catalyst crystal phase and morphology. A variety of tube structures grow, via a base-growth mode, from single crystalline BCC iron and cementite catalyst particles. At low hydrogen concentrations in the plasma, well-graphitized nanotubes grow from elongated Fe₃C crystals, while at high hydrogen concentrations, poorly-graphitized nanofibers grow from BCC iron crystals. Although catalyst particles are single crystals, they exhibit combinations of small-angle (~1°-3°) rotations, twists, and bends along their axial length between adjacent locations (Figure 2). Distortions are most severe away from the base up into the nanotube where the number of walls is large. Near the attachment point to the substrate, however, where few, if any graphene walls exist, particles remain undistorted. This suggests that the stresses generated by the surrounding nanotube distort the catalyst particle during growth [3]. The much larger thermal expansion coefficient of Fe₃C compared to that of the nanotube may also play a role in shaping the crystal into the observed tear-drop morphology. No preferential catalyst orientation relative to the nanotube axis was observed, suggesting that what is required for nanotube growth is not an epitaxial relationship with the catalyst, but rather, only formation of an initial graphitic carbon seed. Z-contrast STEM images combined with atomic-scale EELS measurements, shown in Figure 3, revealed an iron-oxide shell at the very base of each BCC and Fe₃C catalyst crystal. It is unclear what role this oxide cap plays during nanotube growth.

Chemical processes occurring at the catalyst-CNT interface during growth were inferred by measuring, ex situ, changes in atomic bonding and concentration at an atomic scale with a 0.15 nm electron probe. Carbon concentration was measured as a function of position within the iron oxide base cap, and is shown in Figure 4. The observed variations of this concentration are consistent with carbon diffusing through the bulk of the crystal during nanotube growth. At the interface between Fe₃C and iron oxide, EELS analysis reveals a carbon rich region, composed of amorphous carbon. It is concluded that this is the source of additional carbon for continued nanotube growth [4].

References

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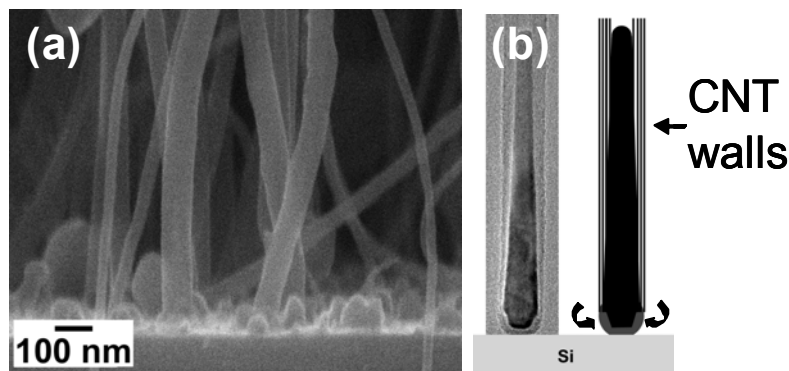


FIG 1.

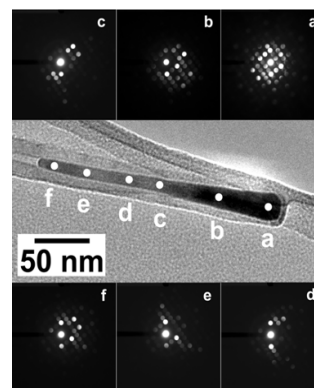


FIG 2.

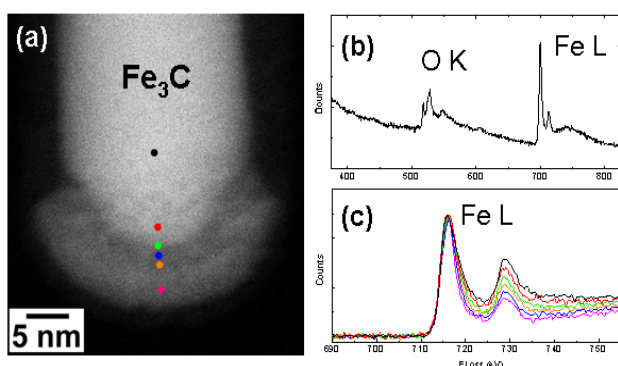


FIG 3.

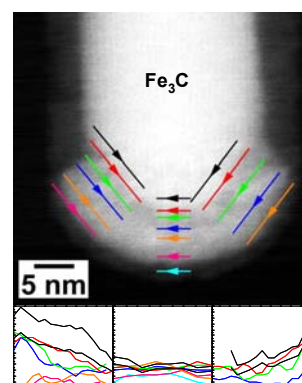


FIG 4.

FIG. 1. (a) Cross-sectional SEM micrograph of the carbon nanotube film on a silicon substrate. (b) A bright-field (BF) TEM image of a cementite catalyst crystal inside the base of a multiwall carbon nanotube, and corresponding schematic diagram of the nanotube. Arrows indicate point of carbon entry into the catalyst crystal from the gas phase.

FIG. 2. BF-TEM image (middle) of a 225 nm long cementite crystal oriented along the [101] zone axis at position 'a' and the CBED patterns obtained from positions 'a'-'f'.

FIG. 3. (a) Z-contrast HAADF-STEM image of a cementite catalyst inside the base of a carbon nanotube. The EELS spectrum in (b) confirms that the very base of the catalyst is composed of iron and oxygen. (c) Fe $L_{3,2}$ EELS spectra collected as a function of position along the length of the catalyst (positions indicated in (a)).

FIG. 4. ADF-STEM image (top) of a cementite catalyst inside the base of a carbon nanotube. Plots of carbon concentration obtained from EELS measurements as a function of position along each of the colored lines are shown in the three bottom panels.