Catalyst-Support Interactions during Carbon Nanotube Synthesis

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It has been shown that the catalyst-support interactions play an important role in metal-catalyzed carbon nanofiber growth, which could be due to physical or chemical interaction. [1] However, the exact nature of the catalyst-support interaction, especially for carbon nanotube (CNT) growth is still unclear. Here we report the dynamic observation of the structural changes occurring due to chemical interaction between the Fe catalyst and the SiO2 support during CNT growth.

The formation of CNT using Fe-containing catalysts is studied in situ in an environmental scanning transmission electron microscope (ESTEM) by depositing the catalyst nanoparticles and growing the CNT in successive steps. 20 Pa of Nonacarbonyldiiron (Fe2(CO)9) vapors were introduced in the sample area of the ESTEM and nanoparticles between 15 nm to 20 nm in diameter were fabricated by electron-beam induced decomposition of the iron precursor on a perforated SiO2 thin film at 150 °C using a focused electron beam. After the column was evacuated from the iron precursor, samples were heated to 680°C in ≈12 Pa of H2 in order to remove the co-deposited carbon and to prevent the oxidation of the iron-containing catalyst. Hydrogen was then replaced by ≈2 Pa of flowing acetylene (C2H2) at the same temperature. The formation of the catalyst nanoparticles and the growth of CNT were recorded using high resolution digital videos. The crystallographic structures were periodically sampled using fast Fourier transform (FFT’s) of frames extracted from the high resolution video.

We observed that the deposited Fe undergoes a series of reactions with the SiO2 substrate to form the intermediate phases (Fe2SiO4)0.546(Fe3O4)0.454 and Fe2SiO4. In situ monitoring reveals that these structures decompose and react with acetylene to form Fe3C, the active structure towards the formation of CNT’s. [2, 3] A particle of (Fe2SiO4)0.546(Fe3O4)0.454 with a high degree of crystallinity is shown in Fig. 1. After about 7 seconds, a structural transformation is initiated, indicated by the temporary loss of fringe contrast. The structure changes gradually to Fe3C before the particle starts forming a CNT (Fig. 2). The CNT formation reaction slows down markedly when the grown CNT completely encases the catalytic nanoparticle and the rate of supply of carbon from the acetylene gas becomes diffusion limited. At the end of the CNT formation the original complex silicide (Fe2SiO4)0.546(Fe3O4)0.454 structure has completely transformed and the structure of the active nanoparticle remains compatible with Fe3C (Fig. 3) though the overlying CNT structure on the particle prevents a conclusive determination of its structure (Fig. 4).

References
FIG. 1. A (Fe$_2$SiO$_4$)$_{0.546}$(Fe$_3$O$_4$)$_{0.454}$ nanoparticle at 680 °C in 2 Pa of acetylene gas. (Inset). Fast Fourier Transform of the particle indicating a [010] orientation. The scale bar of 5 nm applies to all real space images. Selection squares indicate the areas where the FFT were taken from.

FIG. 2. Active nanoparticle (upper) formed from the area shown in Fig. 1, at 680 °C in 2 Pa of acetylene gas; it has a F$_3$C structure and [231] orientation; the lower nanoparticle has a CNT attached to it at the beginning of the observation and remains inactive. (Inset) FFT calculated from the active nanoparticle, with reflections corresponding to (211) and (102) planes of Fe$_3$C.

FIG. 3. The same nanoparticle as in Figs. 1 and 2, after forming a CNT. The overlaying CNT structure impedes structure determination; (Inset) FFT showing reflections compatible with the (211) periodicity of the F$_3$C phase.

FIG. 4. The same nanoparticle at the end of a multi-walled CNT growing perpendicular to the image plane. Carbon shells with a periodicity of 3.5 Å can be seen surrounding the particle.