

Catalyst-Support Interactions during Carbon Nanotube Synthesis

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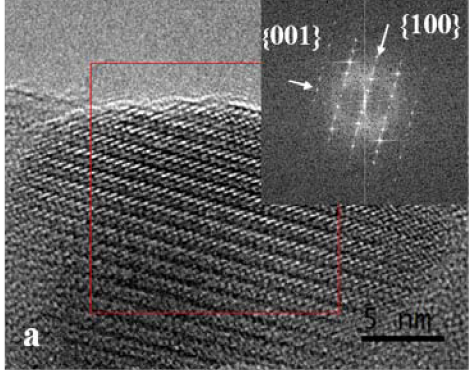
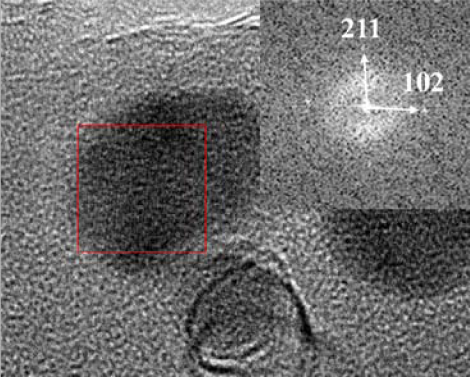
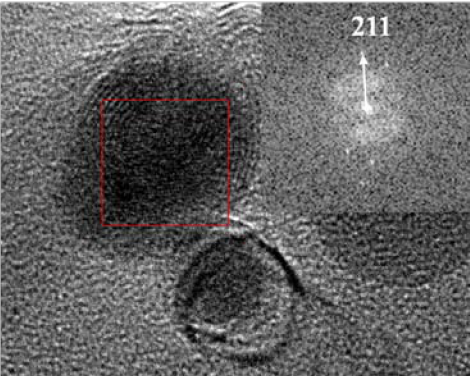
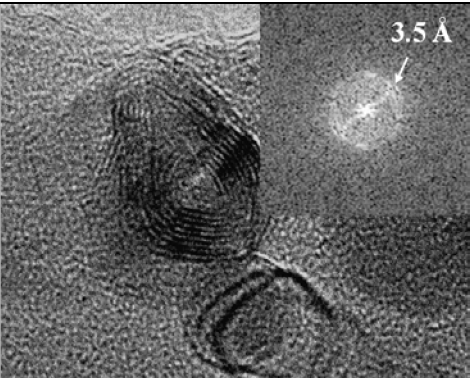
It has been shown that the catalyst-support interactions play an important role in metal-catalyzed carbon nanofiber growth, which could be due to physical or chemical interaction. [1] However, the exact nature of the catalyst-support interaction, especially for carbon nanotube (CNT) growth is still unclear. 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

- [1] Vander Wal et al., Carbon 29 (2001) 2277
- [2] H. Yoshida et al., *Nano Lett.*, 8 (7) (2008) 2082
- [3] R. Sharma et al., *Nano Lett.* 9 (2) (2009) 689.
- [4] The use of facilities in the LeRoy Eyring Center for Solid State Science at Arizona State University is gratefully acknowledged.

	<p>FIG. 1. A $(\text{Fe}_2\text{SiO}_4)_{0.546}(\text{Fe}_3\text{O}_4)_{0.454}$ 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.</p>
	<p>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_3C structure and $[\bar{2}31]$ 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_3C.</p>
	<p>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_3C phase.</p>
	<p>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.</p>