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Direct Measurement of Active and Inactive Iron Catalysts Nanoparticles during the Carbon Nanotube Synthesis

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Catalytic chemical vapor deposition (C-CVD), using a transition metal catalyst (Ni, Fe, Co, etc.) on SiO_2 or Al_2O_3 support and a carbon-containing precursor (C_2H_2, C_2H_4, CH_4, CO, etc.), is commonly employed for large scale synthesis of carbon nanotubes (CNTs). However, controlling the synthesis conditions to obtain CNTs with desired structure and morphology for a specific application has still not been demonstrated. Recently, the effect of synthesis conditions on the structure and morphology of CNTs has been revealed from dynamic observations using environmental scanning-transmission electron microscopy (ESTEM) [1]. *In situ* observations show that the catalyst remains crystalline during the growth [2,3], while both *in situ* and *ex situ* observations have confirmed that not all catalyst particles are active for CNT growth. Here we report a detailed structural analysis of active and inactive particles, subjected to same experimental conditions during dynamic observations, and show that the structure and orientation of the catalyst particles play an important role in their activity for CNT growth.

Iron catalyst particles were synthesized by electron beam induced decomposition (EBID) of di-iron nonacarbonyl ($Fe_2(CO)_9$) on perforated SiO_x thin films supported on Mo TEM grids at 150 °C in the ESTEM [3]. Samples were then heated in 12 Pa (90 mTorr) of H_2 up to 680 °C to (a) burn off any carbon co-deposited during EBID and (b) keep the metal catalyst from oxidizing [3]. H_2 was then replaced by 4 Pa (30 mTorr) of C_2H_2 while keeping the sample at 680 °C. Digital videos were recorded during the CNT nucleation and growth. The structure and orientation of individual active and inactive particles was identified by careful analysis of the fast Fourier transforms (FFTs) calculated from the high resolution images extracted from the video sequences. Previous reports have shown that the Fe_3C structure is formed during CNT growth from Fe catalyst particles [3,4], but not much has been reported about the inactive nanoparticles (NPs). High resolution images, extracted from a video sequence (Fig. 1) show the apparent nucleation and growth of an iron-rich nanoparticle from an inactive particle encased in graphitic shell. Both particles remained inactive during the observation time of about two minutes. The measured spacings and angles between the lattice planes for both particles matched those of Fe_5C_2 [5]. This structure was commonly found in other inactive particles. On the other hand, most of the active particles, growing CNTs were identified as Fe_3C, as shown in Fig. 2. The time elapsed since the starting of the recording is shown in the top left corner of each frame in both Fig. 1 and Fig. 2.

These observations show that both the structure and orientation of the catalyst NPs are important for CNT growth: carbon atoms may be bound by surfaces that do not provide easy diffusion paths or a nucleation plane for graphite layers. Complete analysis and models explaining the role of orientation and the formation of carbon coatings on the catalytic activity of such NPs will be presented.

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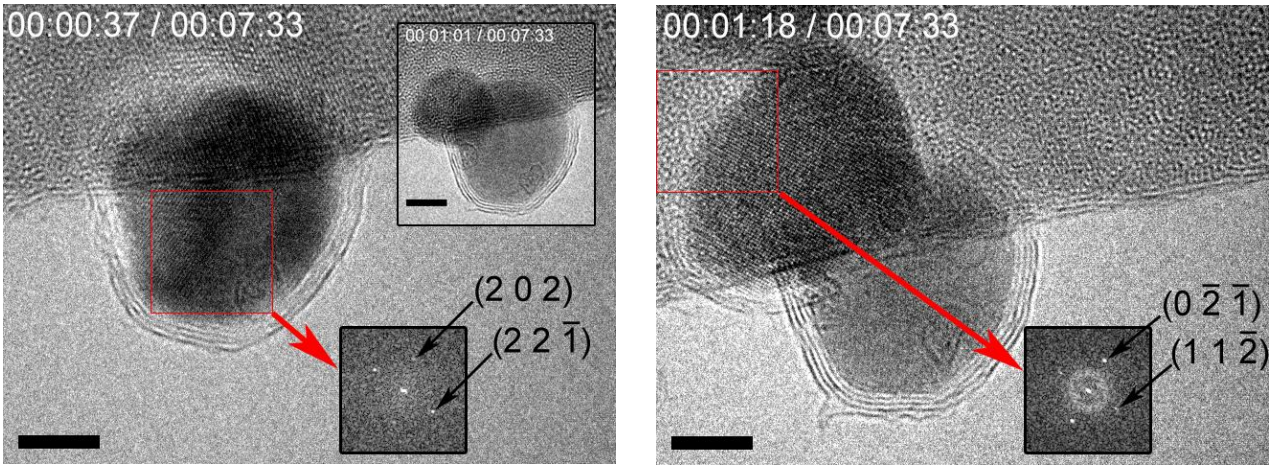

FIG. 1. Individual frames extracted from the *in situ* observation of inactive iron catalyst NPs.; the scale bar is 5 nm. Left: First NP encased in a carbon shell; the upper inset shows the start of the nucleation of the second NP. Right: second NP formed from first NP. The lower insets show the FFTs calculated from the marked squares. Observed lattice spacings from the first NP and from the second NP could be indexed as (202) and $(22\bar{1})$ planes, $(0\bar{2}\bar{1})$ and $(11\bar{2})$, respectively for Fe_5C_2 structure.

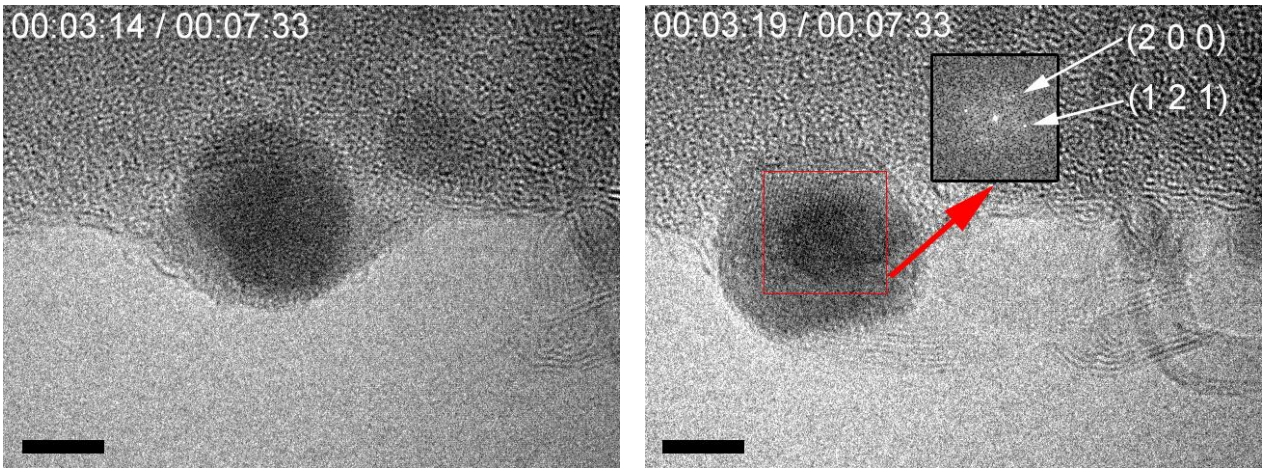

FIG. 2. Frames extracted from the *in situ* observation of active iron catalyst NPs right before (left), and during (right) CNT growth. Lattice spacings measured from FFT (right inset) could be indexed as (200) and (121) for Fe_3C structure.

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