

Preferential growth of carbon nanotubes via the carbon volume diffusion channels in Fe₃C nanoparticles.

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It is well-known that mechanical, electrical or physical properties of the carbon nanotube (CNT) depend on its crystallographic directions, which is decided by its growth directions from the catalyst particles. Although environmental transmission electron microscopy (ETEM) has been extensively used for direct observation of CNT growth with supplying precursor hydrocarbons such as methane (CH₄), acetylene (C₂H₂) gases [1-3], crystal orientation relationships between the growth direction of CNT and catalyst particles are still controversial [4, 5], due to the lack of direct experimental evidence.

In this research, Fe₃O₄ nanoparticles (average 30 nm, dispersed in ethanol, Aldrich) which are one of the most popular catalyst of CNTs [6] were deposited on an amorphous carbon film coated (~15 nm) SiC chip for *in-situ* heating experiment in a TEM as shown in Fig 1. The amorphous carbon film acts as both the support materials of catalysts for TEM observation and carbon sources for CNT formation. The aberration-corrected TEM (Titan ETEM G²) operating at 80kV and the Fusion heating holder (Protochips inc.) enable us for atomic-scale *in-situ* observation at high temperature. To minimize sample drift and electron irradiation effect, we heated gently the SiC chip with a rate of 35 °C/min until 750°C without electron irradiation.

During *in-situ* heating at 750°C, Fe₃O₄ nanoparticles are reduced and transformed into Fe₃C (iron carbide) by carbon atoms supplied from amorphous carbon film of TEM Chip. We collected a series of high-resolution TEM (HR-TEM) images to investigate the crystallographic relationship between growing CNT and a catalyst nanoparticle (Figs. 2(a)-(c)). These results indicate that morphology of the Fe₃C nanoparticle fluctuates, but maintains its crystallographic orientation as shown in a fast Fourier transform (FFT) pattern (Fig. 2d). As shown in Figs. 2(e) to (h), remarkably, CNTs are aligned abruptly and start rapid growth parallel to the wall perpendicularly to (031) plane channel direction, indicating that (031) planes of the Fe₃C particle are the one of the carbon diffusion channel during the CNT growth.

Using atomic-scale *in-situ* TEM, in this study, we provide the direct evidence of volume diffusion of carbon atoms through the specific channel in the carbonized catalyst nanoparticles.

References

- [1] S. Helveg, C. Lopez-Cartes, J. Sehested, P. L. Hansen, B. S. Calusen, J. R. Rostrup-Nielsen, F. Abild-Pedersen, J. K. Norshkov, *Nature*, **427**, 426 (2004)
- [2] S. Hofmann, R. Sharma, C. Ducati, G. Du, C. Mattevi, C. Cepek, M. Cantoro, S. Pisana, A. Parvez, F. Cervantes-Sodi, A. C. Ferrari, R. Dunin-borkowski, S. Lizzit, L. Petaccia, A. Goldoni, J. Robertson, *Nano Lett.*, **7**, 602 (2007)
- [3] H. Yoshida, S. Takeda, T. Uchiyama, H. Kohno, Y. Homma, *Nano Lett.*, **8**, 2082, (2008)
- [4] C. Y. Wen, C. C. Huang, H. Z. Cheng, H. Y. Lu, *J. Mater. Sci.*, **43**, 123 (2008)

[5] M. J. Behr, K. A. Mkhoyan, E. S. Aydil, *ACS Nano.*, **4**, 5087 (2010)

[6] H. Sato, Y. Hori, K. Hata, *J. Appl. Phys.*, **100**, 104321 (2006)

[7] This work was supported by Institute for Basic Science (IBS) (IBS-R004-G3).

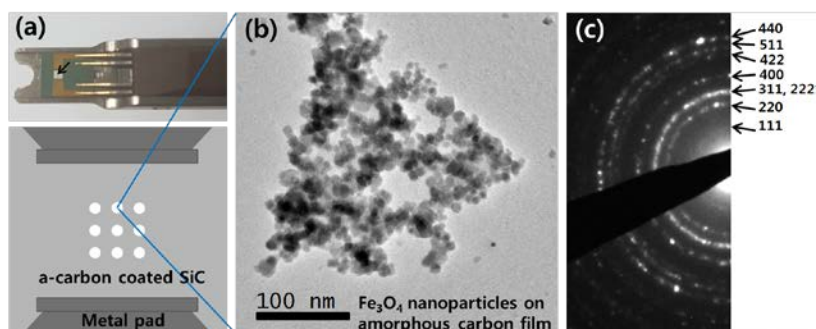


Figure 1. (a) Protochips heating holder and schematic diagram of indicated area by arrow, (b) bright-field TEM image of Fe_3O_4 nanoparticles which were deposited on an amorphous carbon film and (c) selected area electron diffraction (SAED) pattern of Fig. 1 (b)

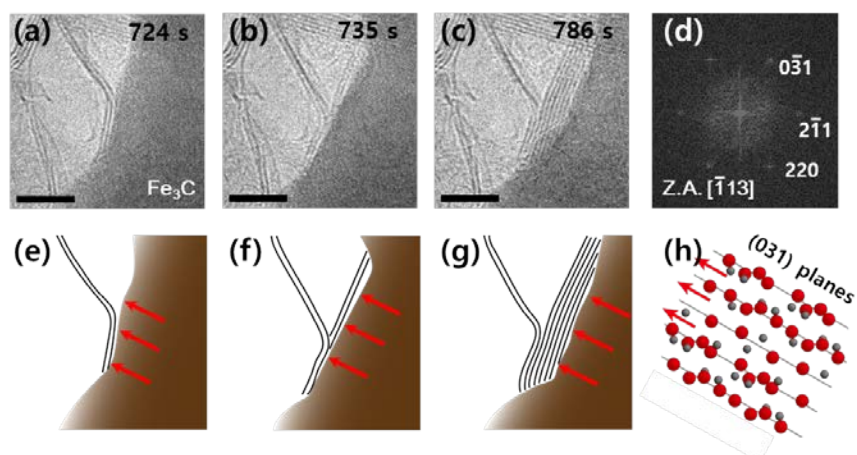


Figure 2. (a), (b) and (c) a series of HRTEM images showing the initial stages of CNT formation on Fe_3C nanoparticles, (d) a fast Fourier transform (FFT) of Fe_3C nanoparticle, (e), (f) and (g) schematic diagrams corresponding to a series of HRTEM images of (a), (b) and (c) respectively, and (h) atomic arrangement of Fe_3C crystal along the $[-113]$ zone axis.