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Environmental Transmission Electron Microscopy Study on the Role of Impurities in Carbon Nanotube Growth

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Environmental transmission electron microscopy (ETEM) is one of the most promising experimental techniques to study solid-gas reaction at atomic scale. Along with the ETEM image simulation [1, 2], we have developed an ETEM based on a conventional 200 kV FEG TEM (FEI Tecnai F20). Using the ETEM, we have investigated the Fe-catalyzed growth of carbon nanotubes (CNTs) by chemical vapor deposition (CVD). CNTs have extraordinary properties that are structure sensitive. The key to the structure-controlled growth is deep understanding of their growth mechanism. Our previous ETEM observations have shown that nanoparticle catalysts are solid state iron carbide (Fe_3C) in the CVD condition [3]. In this work, we have elucidated the role of Mo in Fe-catalyzed CVD growth of CNTs by ETEM [4].

As catalysts, Fe and/or Mo were deposited on a Si substrate covered with a thin SiO_2 surface layer by vacuum evaporation at the room temperature. After the deposition, the substrate was set on a heating specimen holder and transferred to the ETEM operated at 200 kV. The sample was heated to 600 ˚C, and then a mixture of C_2H_2:H_2=1:1 of 10 Pa was introduced into the ETEM for the CVD process.

It is well-known that the yield of CNTs is increased by adding a certain amount of Mo to Fe, Co and Ni though pure Mo shows low catalytic activity for the growth of CNTs. Our experiments have also shown that the addition of Mo increases the yield of CNTs as shown in Fig. 1. We estimate that the yield is at least three times larger than that without Mo. The electron diffraction patterns show that compositions are different between these two samples. Fe_2SiO_4 is only formed on the only Fe deposited substrate. By observing the Fe-Mo catalyzed growth of CNTs at atomic-scale, we have found that nanoparticles of $(Fe,Mo)_{23}C_6$-type carbide are formed and act as catalysts (Fig. 2). The crystal orientation changes as shown in Fig. 2. This means that the structure of nanoparticle catalyst is fluctuating during the growth of CNTs. In summary, roles of Mo in Fe-catalyzed CVD growth of CNTs are as follows. (1) Mo leads to the formation of $(Fe,Mo)_{23}C_6$ nanoparticle catalysts in addition to Fe_3C. (2) Mo suppresses the nucleation of Fe_2SiO_4 which is catalytically inactive for the growth of CNTs, and therefore active nanoparticle catalysts of Fe_3C and $(Fe,Mo)_{23}C_6$ form efficiently.

Our conventional ETEM demonstrates that it is possible to observe the growth of CNTs at atomic scale. Recent ETEMs with a Cs corrector will be useful for the further study in this field.

References

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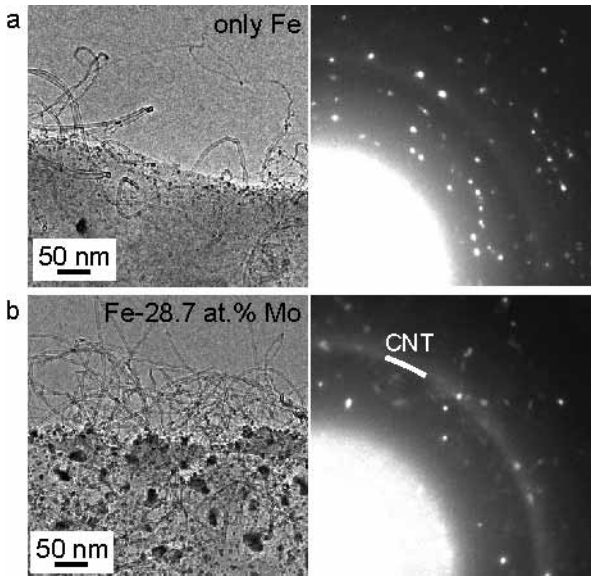

Fig. 1. ETEM images and electron diffractions of (a) only Fe and (b) Fe-Mo co-deposited substrate during the CVD process. The yield of CNTs on the Fe-Mo co-deposited substrate (b) is larger than that on the only Fe-deposited substrate (a), and a diffraction ring from CNTs is clearly visible in electron diffraction. Fe_3C and Fe_2SiO_4 are identified in the electron diffraction in (a). Fe_3C, $(Fe,Mo)_{22}C_6$, and $Fe_2Mo_3O_8$ are identified in the electron diffraction in (b).

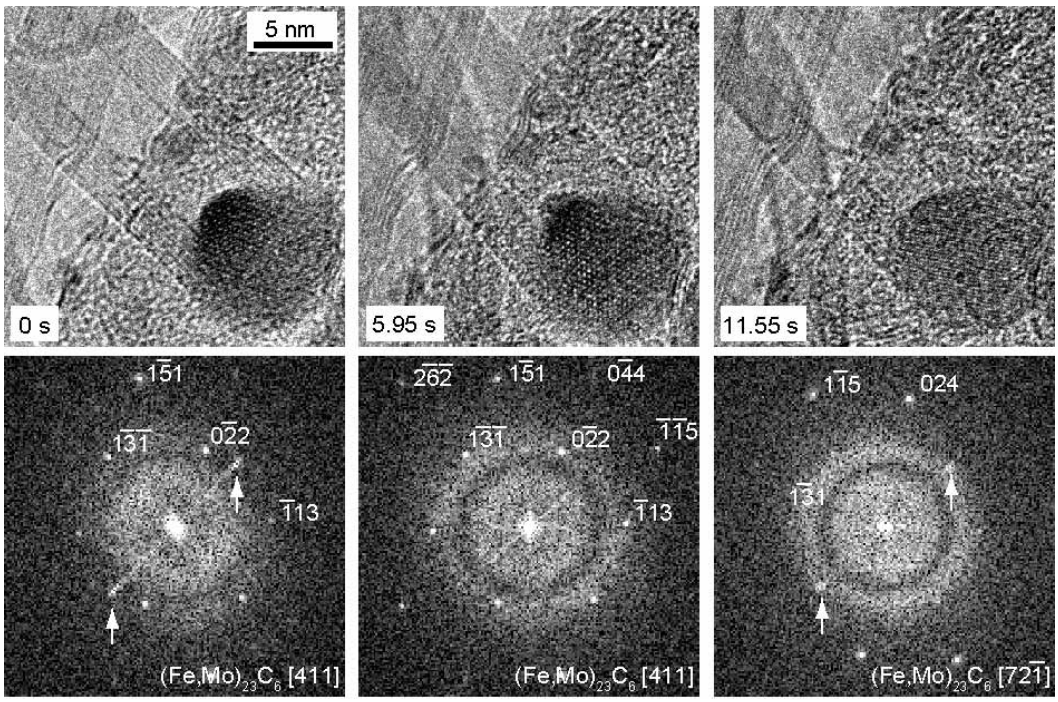

Fig. 2. Growth of a CNT from a $(Fe,Mo)_{23}C_6$-type carbide nanoparticle catalyst. ETEM images and the corresponding Fourier transforms are shown. The spots from the CNT are marked by the arrows.

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