

A-6-1 (Invited)

Probing carbon nanostructures growth mechanism using an *in-situ* UHVTEM

Y. L. Foo

Institute of Materials Research and Engineering, 3 Research Link S117602, Singapore

1. Introduction

Carbon based nanostructures can be grown by arc discharge, laser ablation and chemical vapor deposition (CVD). Amongst them, CVD is the most attractive candidate for industrial adoption due to its scalability and low cost. Most CNT formation mechanisms have been studied by theoretical calculations (1-3) or post-deposition high-resolution transmission electron microscopy (TEM) (4-11). Often, CVD growth using same experimental growth condition yields 'different' types of structures (e.g. SWNT, double-walled nanotubes (DWNT), multi-walled nanotubes (MWNT), sheets, cages and amorphous tubes) (12-16), making complete and detailed understanding of reactions difficult. This is further aggravated by the ambient/low vacuum growth conditions that convolute data with contaminants. At present there is no concerted effort to correlate the type of carbon nanostructure (single, double or multi-walled tubes, sheets, cages or onions) to growth temperature, flux and catalyst *in situ*. The *in-situ* ultra-high vacuum (UHV) TEM operating in both direct and reciprocal space, is thus an ideal platform for conducting these experiments due to its capability for real time observation on the nanometer scale. This enables quantitative investigation of the reaction pathways and growth kinetics of carbon nanostructures at elevated temperatures to be possible.

2. Results and discussions

Recently, with the modification made by setting up a gas line which feed directly into the TEM column, our research group was able to observed the growth of single-walled carbon nanotube (SWNT) in *real-time*. The experimental results for the growth of SWNT growth was conducted using a Ni-MgO supported catalyst by the catalytic decomposition of acetylene (C_2H_2). The C_2H_2 was passed into the TEM column through a leak valve and the microscope had a backfilled pressure of $\sim 4 \times 10^{-6}$ Torr during the reaction and the temperature of the catalyst was maintained at $650^{\circ}C$. Three important observations were made which warrants further investigations.

Figure 1 shows that SWNTs was found to preferentially grow on smaller sized catalyst

particles, while nanocages were observed on larger Ni catalysts. Furthermore the active spherical Ni particles for the growth of SWNTs are mainly non-faceted particles.

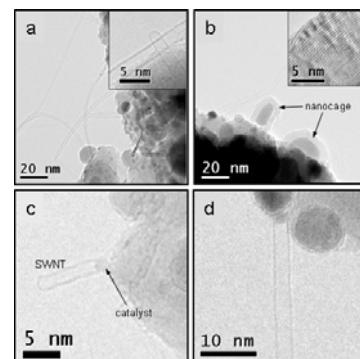


Figure 1

To gain insight into the dynamical growth of SWNTs, a sequence of bright field (BF) images was used to follow the growth process of a single SWNT as shown in Fig. 2a. When the C_2H_2 valve was opened, we observed the growth of an SWNT with a diameter ~ 3.3 nm, as shown in Fig 2b-d, on a 4 nm Ni catalyst. The growth of these SWNT however does not occur instantaneously as illustrated in Fig. 3.

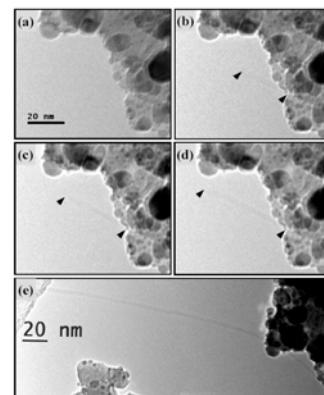


Figure 2

The implications of the above preliminary study are as follows (i) the evolution of carbon nanostructures (i.e. SWNT or nanocages) appears to be dependent on the catalyst size; (ii) active

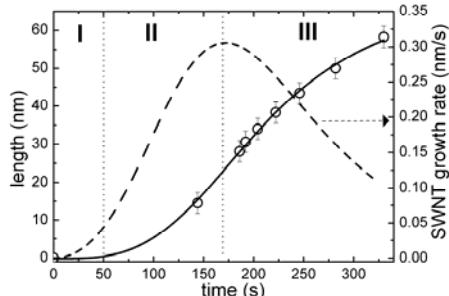


Figure 3

spherical Ni particles for the growth of SWNTs are mainly non-faceted particles; (iii) the growth rate as determined by direct measurement of the length of the nanotube as a function of time clearly show that the formation of these structures does not occur spontaneously.

The reactivity of a nanoparticle is highly dependent on its size, shape, surface composition and atomic arrangement. Our preliminary data have clearly established that active spherical Ni particles for the growth of SWNTs are mainly non-faceted particles. We will extend our study for other known catalyst such as Co and Fe to map out the phase space of the growth of carbon nanostructures, particularly from the growth mechanism perspective. We aim to similarly establish the nature of the catalyst during growth and determined whether a similar selection rules exist.

In separate series of experiments, we also observed the growth of MWNT and shape transition of catalyst. We are probing the growth mechanism such carbon nanostructures.

3. Acknowledgement

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