Molecular Dynamics Simulation of Nucleation and Growth of Single-Walled Carbon Nanotubes

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Developments of large scale and high-purity generation technique of single-walled carbon nanotubes (SWNTs) [1] are desired for the practical applications of this fascinating new material. In addition to previously known laser-furnace [2] and arc-discharge [3] techniques, catalytic chemical vapor deposition (CCVD) methods [4] have been developed for the possible larger amount production with lower cost. In addition to the supported catalyst method, so-called HiPco process [5] can be regarded as an un-supported catalytic CVD process. In addition, we have developed a high-quality production technique of SWNTs at low-temperature by using alcohol as carbon source [6]. For the further optimization of the generation process, understanding of the formation mechanism is inevitable. Furthermore, the formation mechanism is really critical for the future development of synthesis techniques of SWNTs with controlled diameter and even chirality.

Here, the nucleation and growth process of SWNTs were studied with classical molecular dynamics simulations. The Brenner potential [7] in its simplified form [8,9] was used for the carbon-carbon interaction. The metal-carbon potential was constructed with the covalent term based on the coordination number of metal atom and the Coulomb term due to the charge transfer from metal to carbon cluster [10].

The formation mechanism in the laser-furnace method and CCVD method should be considerably different at least at the nucleation stage of SWNTs. In the former method, carbon atoms and catalytic metal atoms are vaporized at the same time by the intense laser ablation. In the later, the catalytic metal clusters are present before the assembly of carbon atoms. Hence, 2 different simulation conditions, 'co-vaporization' and 'CCVD' are compared below.

Generation conditions of SWNTs by the laser-furnace or by the arc discharge techniques are almost the same as for fullerene and endohedral metallofullerene except for the doped metal species. Hence, the same molecular dynamics simulation condition as for our previous empty fullerene [8,9] and for endohedral metallofullerene [10] except for the catalytic Ni atoms was employed. As the initial condition, the completely random vapor mixture of 2500 carbon and 25 Ni atoms were allocated in a 58.5 nm cubic fully-periodic simulation cell [11,12]. After 6 ns molecular dynamics calculation, many

relatively large clusters up to about 200 carbon atoms and a few metal atoms were observed. Carbon clusters tended to be spherical random cage structure with a few metal atoms at around the defect vacancy, which prevented the cage structure from the complete closure. These imperfect carbon cage structure with several metal atoms outside were partially confirmed by the FT-ICR reaction experiments of laser vaporized clusters [13]. In the later stage, the periodic cell size was slowly reduced to enhance the collision events in order to further accelerate the simulation. A large tubular structure was obtained after coalescence of clusters. Ni atoms were slowly assembling to form Ni clusters, and they were diffusing around until finding the most stable position at the hemi-half-fullerene cap area. Given the enough time for diffusion of metal atoms and network annealing, it is expected that the structure becomes a straight SWNT with metal clusters at each end.

The 'CCVD' molecular dynamics simulations started from randomly distributed carbon atoms and a Ni cluster. In real CCVD process, supported or non-supported catalytic metal clusters are preformed before the assembly of carbon atoms. For the simplicity of the simulation, the floated catalyst condition similar to HiPco process was employed. Assuming that the carbon source such as methane and methanol decomposed to solid carbon only at the catalytic metal surface, specially designed van der Waals potential in the simulation prohibited clustering of carbon-carbon atoms, even though hydrogen or oxygen atoms were not explicitly included. Disproportional reaction of CO was also regarded as the similar deposition of a carbon atom on the metal surface. Here, the chemical reaction process such as decomposition of hydrocarbon or disproportional reaction of CO was completely neglected in this simple simulation. Upon arrival of a carbon-containing molecule to the bare metal surface, it was assumed that such reaction would immediately take place. Hence, such reaction barrier was included in the net flux of carbon-containing molecules. As the initial metal cluster size, Ni_{32}, Ni_{108} and Ni_{256}, corresponding to about 0.8 nm, 1.3 nm and 1.6 nm were prepared. In addition to the metal cluster, completely random vapor mixture of carbon-containing molecules was allocated in 20 nm cubic periodic cell. At the earlier stage, all carbon atoms were absorbed in the metal cluster. When saturated, hexagonal carbon networks were observed inside the metal-carbon binary cluster. Depending on the initial Ni cluster size and on temperature, the formation of various nanotube cap structures was demonstrated with the continuous supply of carbon. The rate of the decomposition of carbon source was also important. Though the density of carbon source was much higher than the experimental condition for enhancement of the simulation time, we could qualitatively summarize that optimum rate existed for the nucleation of the cap structure and the higher decomposition overwhelms the rate of annealing process resulting in the overcoat of amorphous carbons.

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