

A molecular dynamics simulation of SWNT growth by CVD method -- Octopus and VLS modes --

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In order to explore the possible chirality-controlled growth process, the growth mechanism of single-walled carbon nanotubes (SWNTs) was studied by molecular dynamics simulations. We adopted a newly developed Tersoff-type classical potential for carbon and several metal atoms, such as Co, Ni, Pt, Fe and Ti. A genetic algorithm was employed to optimize the potential functions for various solid structures and metal-on-graphene model calculated by density functional theory [1]. A metal cluster of certain size and at certain temperature is prepared and is exposed to carbon vapor at certain vapor density (pressure) [2]. We can observe the nucleation and growth of SWNTs at certain temperature range and pressure range depending on metal species (as shown in Fig. 1).

We can observe two apparently different growth modes of SWNTs. A preferred structure at lower temperature is ‘Octopus’ mode where several carbon chains are wrapping the metal cluster as shown in Fig. 1. The preference of carbon chain structure on metal surface prohibited the transition to hexagonal structure which can lead to the full encapsulation of metal cluster. Because of this chain structure, the solid-state metal cluster can be a stable catalyst. Another structure appeared at higher temperature is ‘VLS’ mode where carbon atoms are dissolved in liquid metal cluster. The nucleation and growth of SWNTs is dynamics process depending on carbon feeding rate. The diameter of nanotube is similar to the metal cluster size for Octopus mode in contract to the VLS mode where the diameter is determined in the dynamically nucleated cap structure. These 2 modes may correspond to ‘tangential’ and ‘perpendicular’ modes observed in TEM [3].

These 2 different growth modes can explain the drastic diameter change observed in CVD by adding nitrogen in carbon precursors [3-6]. We found that reversible and repeatable growth of 1nm or 2 nm diameter SWNTs from the same catalysts [6]. The nitrogen atoms sticking on metal particle can easily hinders the pathway of carbon chain to SWNTs, hence ‘Octopus’ mode growth is completely suppressed. As a result smaller diameter SWNTs by ‘VLS’ mode prevails. The softening of metal catalyst may be caused by nitrogen atoms.

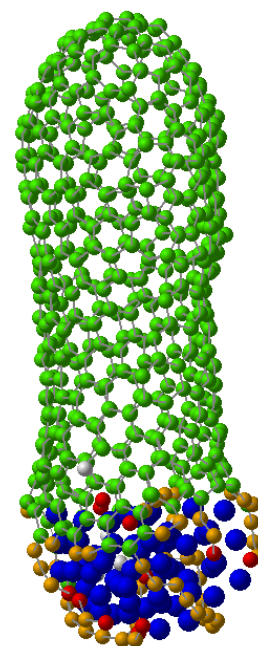


Fig. 1. Octopus mode growth from a Co₆₀ cluster at 1500K. The chirality of bottom part is close to (11, 6). Carbon density (3/10nm cell) corresponds to atmospheric pressure.

References

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