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Density-functional tight-binding molecular dynamics simulations of the self-capping process in open-ended (n,n) SWCNTs (n=3 to 10)

([1]Graduate school of science, [2]Graduate school of information science, Nagoya University)

○[1]Hironori Hara, [2]Genki Ichinose, [1]Stephan Irle

Introduction

Although many important and fundamental studies of CNTs have been conducted so far, there are still many unknows about these wondrous molecules. Especially, their formation and transformation mechanism at high temperatures such as the here investigated self-capping mechanism has not been completely revealed yet today. Since CNTs consist of graphitic material, π-conjugation effects are important. Previously used calculation methods such as semiclassical reactive empirical bond-order (REBO) interatomic carbon-carbon molecular mechanics (MM) force fields are computationally cheap but do not include π-conjugation or aromaticity at all. Accurate quantum chemical methods such as Moller-Plesset or Density Functional Theory (DFT) approaches are computationally too expensive. The density-functional tight-binding molecular dynamics (DFTB/MD) method, which allows the study of the time evolution of molecules using potentials and gradients from quantum mechanical electronic structure calculations, has proven to be a very useful approach to investigate the formation and transformation processes of carbon nanomaterials over the course of ~100 ps. Using this method, we previously elucidated the mechanism of fullerene formation starting from short open-ended SWCNT models [1,2]. According to these previous studies, a suitable temperature range for self-capping is 3000 K to 3500 K, and it was discovered that small-diameter armchair-type SWCNTs are able to anneal relatively faster than zigzag-type SWCNTs. In the present study, we tried to answer whether and how larger-diameter tubes are also able to anneal, namely how they form half-hemisphere-like caps, and to find a correlation between the tube diameter and the self-capping time at temperatures of 3000 K and 3500 K.

Simulation Details

Using canonical (constant temperature, NVT) DFTB/MD simulations, we studied the self-capping processes of 35 Å-long, open-ended armchair (n,n) single-walled carbon nanotubes (SWCNTs) (n=3 to 10, the diameter ranges from 4 Å for n=3 to 13.5 Å for n=10) during annealing at temperatures of 3000 K and 3500 K, using 3 trajectories for each (n,n) SWCNT type and temperature. These systems are far more large than the ones studied in [1,2] and have diameters closer to real SWCNTs. The open ends were modeled by simply cutting the tube perpendicular to the tube direction and leaving dangling bonds in one set of model systems (CUT), and by saturating the resulting dangling bonds with carboxyl groups and atomic hydrogen in a 1:1 ratio in another set of model systems (OX).

Results and Discussion

We find that the open ends tend to lose mostly C_2 units in case of CUT models, and in

addition CO_2, CO, C_n, C_nH, OH and so forth in case of OX models, in dependence on temperature. With the exception of the (3,3) SWCNT the all-carbon ends of the open-ended armchair SWCNTs are able to self-cap during simulation times on the order of 100 ps. The time required for self-capping increases steeply with the tube diameter beyond an "optimal" diameter which depends on the temperature and corresponds to roughly n=5 to 6 at 3000 K and 3500 K. The self-capping process for smaller diameter tubes is less efficient, presumably due to the higher ring strain associated with the resulting caps and their therefore more difficult creation. The very small (3,3) tube is highly strained and typically falls apart at the present temperatures. Ring statistics show that the initial hexagon-only SWCNT structures begin to incorporate between 10 to <20 pentagons (associated with positive curvature) during the self-capping process as a natural consequence of the buildup of cap curvature. Heptagons (associated with negative curvature) are rarely to never seen during the dynamics, in agreement with expectation and previous fullerene self-assembly studies.

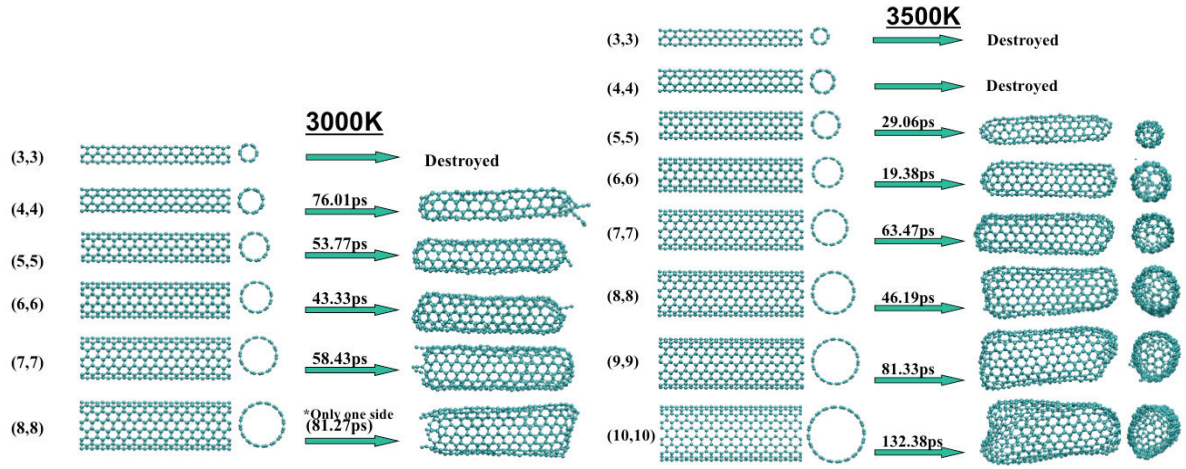

Fig.1 The initial structures and both-sides self-capped structures and simulation time length to obtain them are shown. Times are the average of 3 trajectories for the same n and temperature.

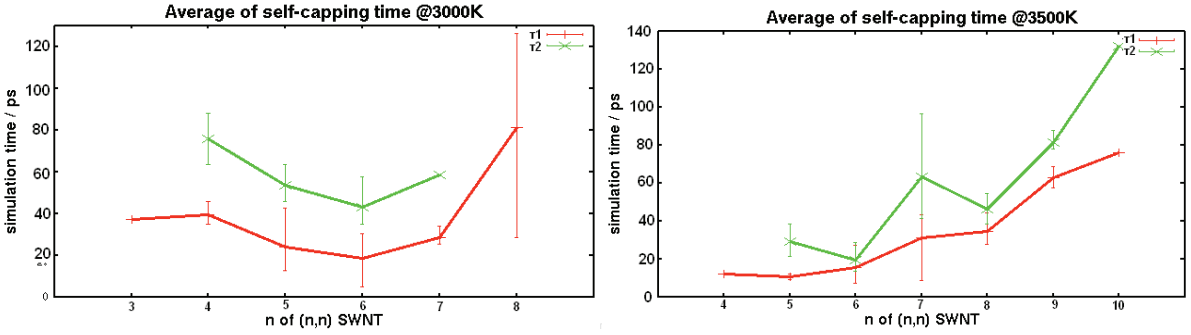

Fig.2 Average time length of self-capping. τ_1 is the time of closing of the first end, and τ_2 is that of the other end.

Reference

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[2] Zheng, G.; Irle, S.; Elstner, M.; Morokuma, K., *J.Phys. Chem. A* (2004), **108**, 3182-3194.