

**EARLY STAGE IN THE NUCLEATION
PROCESS OF CARBON NANOTUBES:
DENSITY-FUNCTIONAL TIGHT-BINDING
MOLECULAR DYNAMICS SIMULATIONS
OF ACETYLENE OLIGOMERIZATION
AND CROSS-LINKING ON AN Fe₃₈
PARTICLE**

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Introduction

Catalytic chemical vapor deposition (CCVD) is typically used to synthesize carbon nanotubes (CNTs), but the exact role of metal catalysts is still unknown. Since Fe substrate is known to be highly effective for the CNT growth in the CCVD process and C₂H₂ is an excellent carbon source for high yield [1-5], we performed quantum chemical molecular dynamics (QM/MD) simulations based on the density-functional tight-binding (DFTB) method [6] to investigate the self-assembly process of carbon nanotubes from acetylene molecules on an Fe₃₈ particle. We found that oligomerization and cross-linking reactions between carbon chains with high H:C ratio were observed as initial steps, preceding any future cap nucleation.

Computational methodology

A. Density-Functional Tight-Binding method (DFTB)

The density-functional tight binding (DFTB) method is the central method adopted in the present studies. All DFTB calculations were carried out with DFTB program package developed by Frauenheim, Seifert, and Elstner [6-8]. DFTB is an approximate density functional theory method based on the tight binding approach and utilizes an optimized minimal LCAO Slater-type all valence basis set in combination with two-center approximation for Hamiltonian matrix elements. The DFTB method is approximately two orders of magnitude faster than first-principles density functional theory (DFT) but often yields comparable accuracy, therefore enables longer simulations and more adequate model systems for nonequilibrium dynamics of nano-sized clusters with quantum mechanical treatment of the electronic degrees of freedom. The molecular orbitals obey the following generalized eigenvalue equation,

$$\sum_{\nu} c_{\nu i} (H_{\mu\nu} - \epsilon_i S_{\mu\nu}) = 0$$

and the total energy is described as follows,

$$E_{tot} = 2 \sum_i f_i \epsilon_i + E_{rep} + \frac{1}{2} \sum_{\alpha\beta} \gamma_{\alpha\beta} \Delta q_{\alpha} \Delta q_{\beta}$$

Where $H_{\mu\nu}$ and $S_{\mu\nu}$ are Hamiltonian matrix and overlap matrix, respectively, f_i and ϵ_i represent fractional occupation and orbital energy of the i^{th} Kohn-Sham (KS) molecular orbital, E_{rep} denotes the distance-dependent diatomic repulsive potentials, and $\gamma_{\alpha\beta}$ represents the distance-dependent charge-charge interaction functional, which is derived from the chemical hardness (IP-EA). The Δq_{α} are induced charges on atom α . In the SCC-DFTB method, the atomic charge-charge interaction is explicitly included in the electronic energy, and the DFTB secular equation is solved iteratively until the Mulliken atomic charges of the KS orbitals become self-consistent with the Hamiltonian.

B. Molecular Dynamics simulation

The DFTB/MD approach is a Born-Oppenheimer molecular dynamics technique based on the DFTB electronic structure method, and can bridge the gap between classical and the first principle MD simulations. In the present DFTB/MD simulations, the self-consistent-charge DFTB (SCC-DFTB) method in combination with a finite electronic temperature approach [9-11] with $T_e = 10000$ K was employed to evaluate the quantum chemical potential on the fly. The electronic temperature allows the occupancy of each molecular orbital to change smoothly from 2 to 0 depending on its energy, and effectively incorporates the open-shell nature of the system due to near-degeneracy of iron d orbitals as well as carbon dangling bonds. In the molecular dynamics simulations the velocity Verlet integrator was used with a short time step of 0.5 fs. The nuclear temperature ($T_n=1500$ K) was controlled by connecting the Nose-Hoover chain thermostat [12] to the degrees of freedom of the present model system. Periodic boundary conditions were imposed with a cubic box size of 100 Angstrom³.

Results and Discussion

In our MD simulations, we first equilibrated an fcc-Fe₃₈ icosahedral magic number cluster at 1500 K for 10 ps. Then, ten structures were randomly chosen from this equilibration run between the 5 and 10 ps mark. Using these 10 Fe₃₈ initial structures, we started to “shoot” single C₂H₂ molecules every 1 ps onto the metal cluster until their total number was 30. During the beginning of these 30 ps carbon supply simulations we found that H occasionally transfers to the iron particle or other C₂H₂ units on the cluster to form C₂H₃ species, producing C₂H. Subsequently, these more reactive radical species initiate oligomerization reactions among the C₂-containing molecules. In the following, we annealed the resulting clusters for 80 ps at the same temperature. During these carbon diffusion simulations, five- (trajectories A, E, and I) or six-membered rings (Trajectory F), as well as longer carbon chains were formed from oligomerization or cross-linking. All trajectories produce

pentagons first. For trajectory E, and F, the ring formed from a single chain (C_6H_x or C_8H_x), similar to trajectory A, as shown in Fig. 1b, while for trajectory I, the ring formation mechanism results from cross-linking between C_6H_x or C_4H_y , as shown in Fig. 2. This cross-linking is similar to the mechanism proposed in Reference [1], however, we did not observe the direct formation of H_2 , and cross-linking did not form a six-membered ring network directly. We show here the analysis of trajectory A as a representative example, and give the carbon hybridization state analysis and cluster size histogram in Figs. 1 c-d. We found that the numbers of double- (sp^2) and triple- (sp) bonded carbons are of similar magnitude. Fig. 1d shows that the number of C_2H_x increases gradually until about 45 carbons are present on the metal cluster. With increasing time, larger clusters (blue, red and yellow areas) gradually consume smaller fragments.

Accompanying our QM/MD simulations, we computed the barrier heights for four kinds of reactions at the DFTB level: H-transfer to Fe (~ 40 kcal/mol), C-C bond breaking (~ 45 kcal/mol), H_2 abstraction (~ 70 kcal/mol), and C-C oligomerization (~ 23 kcal/mol). These energetics explain why C-C oligomerization occurs readily since it is an exothermic reaction (~ -10 kcal/mol). To the contrary, direct H_2 abstraction possesses a very high barrier and is an endothermic process (~ 68 kcal/mol), less likely to occur in MD.

Conclusions

During 30 ps Carbon supply simulation, some of C_2H_2 loose H or some H transfer to C to form C_2H_x and oligomerization occurs, especially the connection between C_2H_2 and C_2H (8/10 ratio), which has a lower barrier of 23.39 kcal/mol and it is an exothermic reaction (15.13 kcal/mol). During 80 ps carbon diffusion simulation, some five or six-membered rings formed from long chain C_6H_x or C_8H_x , and by cross-linking. We found pentagon-first mechanism. H_2 abstraction possesses a very high barrier and is an endothermic process, then it was consequently never observed in our 110 ps MD simulations. We hope our results can serve as a basis for future study of growth mechanism of CNT as well as catalytic decomposition of hydrocarbon on metal surface.

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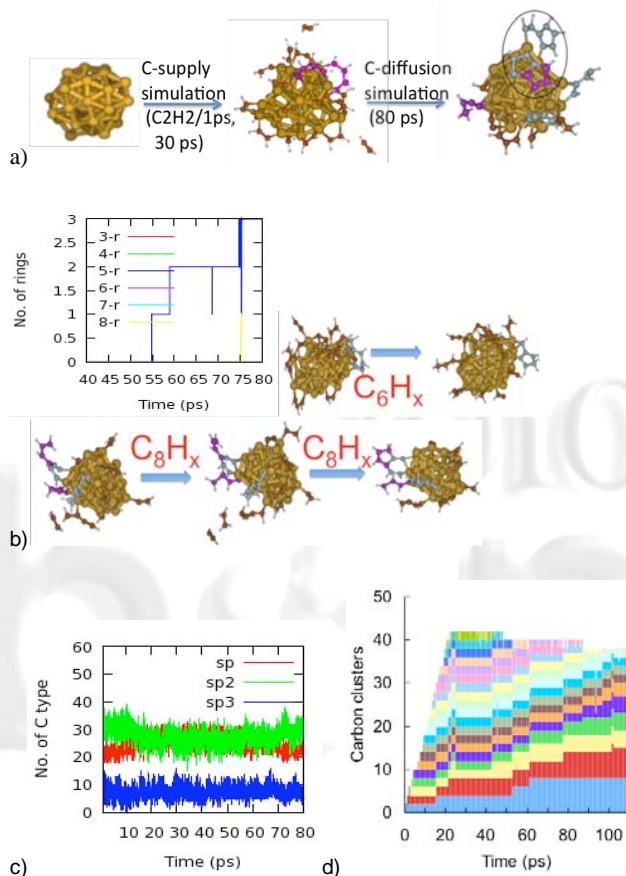


Fig. 1 Analysis of trajectory A. Carbons undergoing chemical transformations are highlighted by purple and blue spheres. a) The snapshots after carbon supply simulation and carbon diffusion simulation; b) ring count statistics as a function of time and schematic depictions of pentagons formation procession from polyene-like chains; c) carbon hybridization analysis; d) carbon cluster size count.

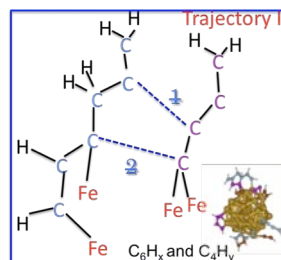


Fig. 2 Crossing Link for trajectory I. Reactive carbons are highlighted by purple and blue spheres, 1 and 2 indicate first and second connection.