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Simulations on the effects of confinement and Ni-catalysis on the formation of tubular fullerene structures from peapod precursors

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We applied the recently developed reactive force field (ReaxFF) to study the dynamics of tubular fullerene formation process starting from C60-buckyball/nanotube peapod structures. We found that the space confinement provided by the single-wall nanotube encapsulating the buckyballs is of critical importance to this coalescence reaction. We also simulated the effects of Ni particles on the coalescence process and found a significant reduction of the reaction initiation temperature in the presence of these catalysts. One important quantity is the energy barrier of forming a 4-membered ring between adjacent buckyballs. This barrier is lowered by 40% with the aid of Ni-catalysis. This research can help the community to gain a better understanding of the complicated growth processes in fullerene systems.

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A large number of experimental and theoretical studies have been reported on buckyball-containing nanotube (also known as peapod) structures since the discovery of these materials.1–3 Recent advances in peapod synthesis techniques have led to the production of peapod materials with yields close to 90%.1 Successful synthesis of chains of C60 molecules inside single-wall carbon nanotubes (SWCNs) involves depositing C60 buckyballs on the surfaces of SWCNs from the gas phase. These buckyballs subsequently self-assemble inside the nanotube in chains called “bucky-peapods” that are bound together by van der Waals interactions. Qian et al.2 demonstrated that the presence of buckyballs changes the mechanical properties of the encapsulating SWCNs. It has also been shown that the electron density of states of a SWCN is perturbed by the C60-buckyballs. Quite recently, a novel ultrahigh frequency peapod based oscillator is designed by numerical simulations.3 Furthermore, transport properties of peapod structures have been widely investigated.4 Upon high-temperature annealing, encapsulated buckyballs coalesce into interior tubes, forming pairs of nested graphene cylinders. This leads to the formation of a tubular form of carbon assembled inside the larger nanotube, which has a superior resistance to bending than a SWCN, whose elastic modulus (~1 TPa) is already the largest that has ever been measured.5 One typical geometrical feature of the peapod system is represented as self-assembled chains with nearly uniform center-to-center distances. The endofullerenes coalesce into longer capsules by either electron irradiation6 or thermal annealing.7 In this paper, we focus on thermal annealing and the role of metals in catalyzing buckyball coalescence. Although metal catalysts are often used in the production of SWCNs, the catalytic growth mechanism is not fully understood. Increased knowledge of the role of the catalyst in nanotube nucleation and production is not merely of fundamental interest, but will also assist in the quest to synthesize various forms of carbon.

In this paper, we first present our results on the interaction energy between nanotube and buckyballs. Then, we investigate how such a peapod structure can be transformed into a tubular form inside a larger tube in the absence and in the presence of a Ni catalyst. In these simulations, we employ the ReaxFF potential,8 which has been recently expanded to enable simulations on all-carbon and Ni-carbide materials.9 This method allows for high-temperature reactive dynamics simulations on relatively large (>1000 atoms) systems and thus can be used to obtain an atomistic-scale picture of the reactive events leading to the formation of tubular forms of carbon.

The ReaxFF potentials applied in this work are fitted against a large quantum chemistry (QC) database containing relative energies, geometries, and relevant reaction pathways for hydrocarbon,8 all-carbon, and nickel-carbide systems.9 Of specific importance to the application described here, ReaxFF gives excellent structural and sublimation energy data for graphite, diamond, and buckyball solids, agreeing well with experimental measurements and results from specialized nonreactive force fields. Furthermore, ReaxFF gives a good reproduction of the QC-derived stabilities for a wide range of small (<C20) acyclic, monocyclic, and polycyclic all-carbon fragments and can successfully describe Ni atoms interacting with methyl, benzene, and benzyne groups.

C60-buckyballs in SWCN are synthesized by a vapor phase route, whereby the sublimation of solid C60 in the presence of open SWCNs caused the fullerenes to enter SWCNs and self-assemble into one-dimensional chains.7 The peapod formation process has been widely studied.4,10–13 Many studies on the effect of nanotube diameter on binding properties also exist.14 It is important to check the validity of ReaxFF in the nonreactive region. First, the binding energy $E_b$ is defined as

$$E_b = (E_{\text{peapod}} - E_{\text{tube}} - nE_{\text{buck}})/n,$$

where $n$ is the number of buckyballs inside the tube. It is expected that buckyball molecules are more strongly bound to a SWCN than to each other due to the greater number of carbon-carbon van der Waals interactions in the former case.
Filling SWCN with C\textsubscript{60} is exothermic or endothermic depending on the size of the nanotube. C\textsubscript{60} in (10,10) nanotubes were found to be stable (exothermic), while filling other peapods with smaller radii such as the (9,9) and (8,8) tubes is endothermic.\textsuperscript{12} Once a fullerene enters a nanotube, the van der Waals attractions keep it inside. ReaxFF predicts a binding energy of −3.53 eV for one C\textsubscript{60} inside (10,10) SWCN, which is consistent with previous results reported by Hodak and Girifalco\textsuperscript{11} and Ulbricht \emph{et al.}\textsuperscript{13} However, results of Yoon \emph{et al.}\textsuperscript{4} and Okada \emph{et al.}\textsuperscript{12} regarding binding energy (approximately −1 eV) are not consistent with the above data. This is not surprising as it is well known that van der Waals attractive interactions are not adequately described by the density functional theory (DFT) methods employed by Yoon \emph{et al.}\textsuperscript{4} and Okada \emph{et al.}\textsuperscript{12} The detailed discussion can be found in Ref. 15. The advantage of our force field method is that attractive van der Waals interactions are included in the ReaxFF parametrization.

As the interior fullerenes are still mobile, self-assembly into chains subsequently occurs by incorporation of additional fullerenes into the nanotube, thereby increasing the filling factor further and introducing attractive van der Waals interactions between the incorporated fullerenes. For a hydrogen-terminated (10,10) SWCN of length 50.05 Å (see Fig. 1), the optimal filling number of buckyballs is 5. The separation between centers of mass of buckyballs is 0.98 nm, in good agreement with the experimental value of 0.97 nm (Refs. 1 and 16) and near the (110) intermolecular separation in fcc C\textsubscript{60} solids (1.00 nm). The binding energy in this case is −3.62 eV (−83.6 kcal/mol). Compared with only one buckyball inside a (10,10) SWCN, there exists an additional energy gain, 3.4 kcal/mol,\textsuperscript{17} due to attractive interactions between each fullerene pair. Previous studies show that the interaction energy per C\textsubscript{60} pair is 0.17 eV (3.83 kcal/mol), which can be deduced from the cohesive energy of the fcc C\textsubscript{60} crystal.\textsuperscript{18} The agreement indicates the excellent capability of ReaxFF in the nonreactive regime.

Fullerene coalescence has been intensively studied.\textsuperscript{6,19,20} However, the role of catalysis has not been addressed in these studies. In a recent interesting simulation work done by Nielson \emph{et al.},\textsuperscript{9} the critical role of Co and Ni has been uncovered in the formation of carbon-nanotube-like species from a nonbranched all-carbon feedstock. In contrast, Cu leads to very little branching and results in products with no nanotube character under the same simulation conditions. Thus we choose Ni, serving as one prototype catalyst, to study the influence of catalysts on the formation of tubular forms from buckyballs inside a (10,10) SWCN. Our simulation starts with five C\textsubscript{60} molecules placed inside a SWCN.
TABLE I. Energy barriers of formation of 4-membered ring with and without Ni atoms using ReaxFF for the onset of buckyball polymerization. The reaction coordinate is represented by the separation between centers of two C–C bonds shared by two 6-membered rings. Quantum mechanics data of the same process (without Ni atoms) is reported to validate ReaxFF results.

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<th>C_{60}–C_{60}</th>
<th>Quantum mechanics</th>
<th>ReaxFF (with Ni)</th>
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<tr>
<td>E (eV)</td>
<td>2.38, 2.60</td>
<td>2.16</td>
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Table II. Energetics of selectivity between (6- and 5-) and (6- and 6-) membered rings. (a) shows the dimerization energy of C_{60} calculated by both quantum mechanics and ReaxFF, where the 4-membered ring formed by two C–C bonds shared either by (6- and 6-) or (6- and 5-) membered rings. (b) lists the heat of reaction, E(hydrogenation), of H_{2}+C_{60}→C_{60}H_{2}. See text for discussion.

<table>
<thead>
<tr>
<th>E(C_{60}–C_{60})</th>
<th>6-6 (QM)</th>
<th>6-5 (QM)</th>
<th>6-6 (ReaxFF)</th>
<th>6-5 (ReaxFF)</th>
</tr>
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<tbody>
<tr>
<td>E (eV)</td>
<td>0.27</td>
<td>2.02</td>
<td>0.34</td>
<td>0.28</td>
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<tr>
<td>E(hydrogenation)</td>
<td></td>
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<tr>
<td>6-6 (QM)</td>
<td>−0.88</td>
<td>−0.81</td>
<td>−0.03</td>
<td>−0.87</td>
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<tr>
<td>6-6 (ReaxFF)</td>
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thermodynamics of the lowest-energy (6-6) reaction in each case. Saturating a 6-6 site disrupts the π systems of two 5-membered and two 6-membered rings in the C_{60} surface, while saturating a 5-6 site disrupts one 5-membered and three 6-membered rings. This is intriguing in the sense that usually it is believed that bonds in a 5-membered ring store more strain energy. However, when the bond shared by 6- and 5-membered rings is broken, it leads to the loss of resonant energy in three 6-membered rings. This is one bond more than breaking the bond shared by 6- and 6-membered rings. This difference between 6-6 and 5-6 sites is not captured by the current ReaxFF. However, as shown by our quantum mechanics calculations and photoinduced C_{60} polymerization experiment, the bond shared by a 6-6 site is more important for the coalescence reaction, and this is well represented by ReaxFF.

ReaxFF predicts that in the presence of a Ni catalyst, the barrier for buckyball coalescence will be reduced from 2.16 to 1.54 eV (from 49.7 to 35.4 kcal/mol) (Table I and Fig. 3). As such, we can expect that the presence of a Ni catalyst will lower the temperature required for the coalescence reaction. To study the potential influence of the presence of nickel on the coalescence process, we performed a simulation in which two Ni atoms were placed between every two C_{60} molecules. We observed the initial coalescence within 20 ps for five buckyballs inside a (10,10) SWCN at T=1800 K, significantly lower than the initial coalescence temperature we observed without Ni (2500 K). After 18 ps of simulation, links are clearly established among the cages, thus resulting in a corrugated tubular structure (see Fig. 4). The reconstructed buckyball material is highly defective and consists of coalesced cages joined by polygonal rings. Our simulations clearly show that Ni particles can catalyze the coalescence process. Owing to the multiscalar characters exhibited in double-wall carbon nanotube (DWCN), DWCNs have a promising potential for application in electronic devices. The effective synthesis approach of DWCN is so appealing that various methods have been proposed. Bandow et al. have reported one particularly interesting route to grow DWCN by peapod structures. It is well known that the barrier of Stone-Wales transformation, interchanging either pentagons and hexagons or pentagon-heptagon pair with hexagons, is in the order of 7 eV. The barrier is unable to be overcome by thermal activation. It is a quite delicate process to evolve our simulated tubular structure into a perfect inner chiral zigzag nanotube form due to the limitation of the simulation time scale. Nevertheless, the salient feature of our result is to highlight the remarkable role of a catalyst in polymerizing C_{60} molecules into a tubular structure.

To summarize, ReaxFF gives a binding energy between C_{60} and a (10,10) SWCN and a pair interaction energy between C_{60} pairs which are consistent with previous studies. Furthermore, the importance of space confinement, due to SWCN, in the coalescence of buckyballs in the peapod structure has been demonstrated. The critical role of Ni as a catalyst in the coalescence process for peapod structures is manifested by the significant reduction in the reaction temperature from our simulations.

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8 A. C. T. van Duin, S. Dasgupta, F. Lorant, and W. A. Goddard,
SIMULATIONS ON THE EFFECTS OF CONFINEMENT AND...

PHYSICAL REVIEW B 75, 134107 (2007)

17 \( (5E_b^{1\text{ball}} - 5E_b^{1\text{ball}})/4 \).