

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.¹⁻⁷ 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 investi-

gate 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

$$E_b = (E_{peapod} - E_{tube} - nE_{ball})/n, \quad (1)$$

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.

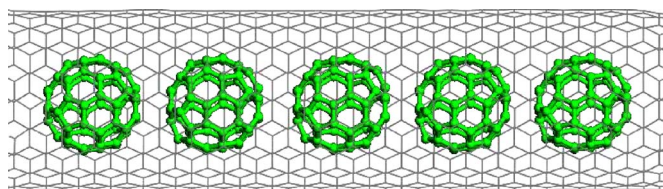


FIG. 1. (Color online) Peapod structure model of five buckyballs inside (10,10) SWCN.

Filling SWCN with C_{60} is exothermic or endothermic depending on the size of the nanotube. C_{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.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_{60} inside (10,10) SWCN, which is consistent with previous results reported by Hodak and Girifalco¹¹ and Ulbricht *et al.*¹³ However, results of Yoon *et al.*⁴ and Okada *et al.*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 *et al.*⁴ and Okada *et al.*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 $\langle 110 \rangle$ intermolecular separation in fcc C_{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,¹⁷ due to attractive interactions between each fullerene pair. Previous studies show that the interaction energy per C_{60} pair is 0.17 eV (3.83 kcal/mol), which can be deduced from the cohesive energy of the fcc C_{60} crystal.¹⁸ The agreement indicates the excellent capability of ReaxFF in the nonreactive regime.

Fullerene coalescence has been intensively studied.^{6,19,20} However, the role of catalysis has not been addressed in these studies. In a recent interesting simulation work done by Nielson *et al.*,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_{60} molecules placed inside a SWCN.

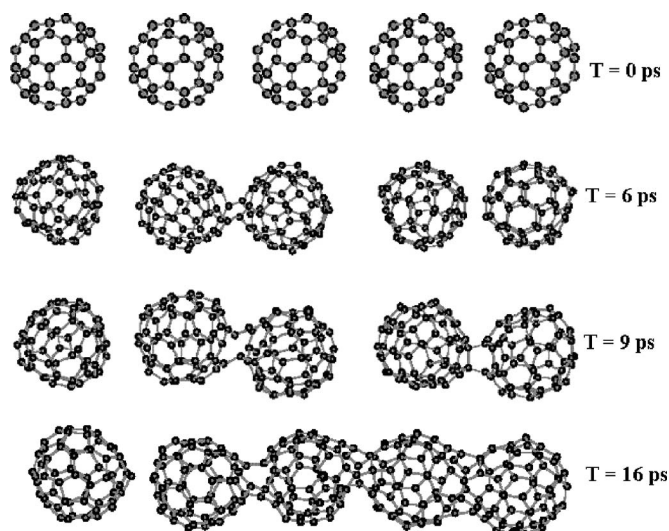


FIG. 2. Snapshots of ReaxFF dynamic simulations of five C_{60} balls coalescing inside a (10, 10) nanotube (diameter approximately 1.38 nm) at 2500 K without catalysis. The SWCN is not shown here for clarity.

The unit cell contains 820 carbon atoms for the nanotube and 300 carbon atoms for the encapsulated fullerenes; a time step of 0.2 fs is used in the molecular-dynamics simulations.

We have run ReaxFF molecular-dynamics simulations starting from a peapod structure made of a (10, 10) nanotube with five uniformly distributed buckyballs inside for a 20 ps simulation at 1800, 2000, 2200, 2400, and 2500 K. Among them, we have only observed that polymerization occurs at 2500 K (Fig. 2). Besides the limitation of time scale, note that C_{60} in our simulation is in the gas phase with ambient pressure, which is largely different from the experimental condition of polymerizing a one-dimensional orthorhombic C_{60} chainlike structure, i.e., in solid phase under very high

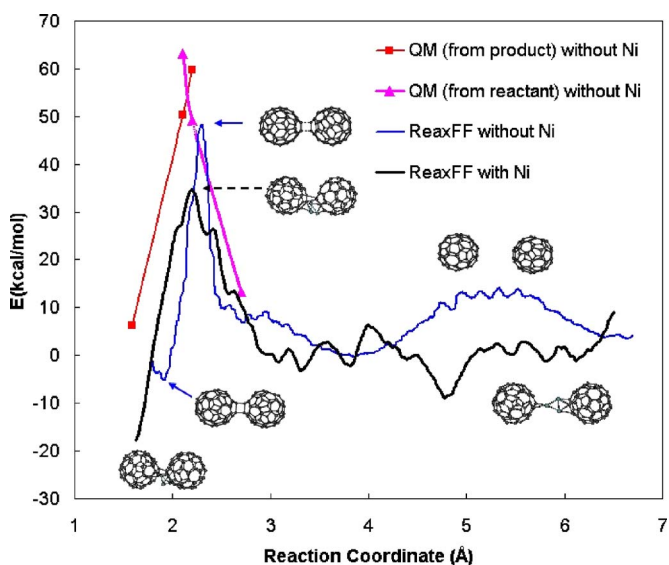


FIG. 3. (Color online) Computed reaction barriers, using quantum mechanics and ReaxFF, of (2+2) cycloaddition reaction between two C_{60} molecules with and without catalyst (Ni).

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.

	C ₆₀ –C ₆₀		
	Quantum mechanics	(ReaxFF)	ReaxFF (with Ni)
<i>E</i> (eV)	2.38, 2.60	2.16	1.54



pressure,²¹ so we cannot compare this simulation polymerization temperature to experimental value directly. Interestingly, at the same temperature and time scale we do not observe coalescence of five buckyballs in a supercell ($3 \times 3 \times 8 \text{ nm}^3$). This gives direct support for the decisive role of the tube, as it acts as a trap (energy well with 3.53 eV) for the buckyballs imposing a space confinement. The simulations show that at a high enough temperature, neighboring C₆₀ molecules have the probability of colliding with sufficient kinetic energy to cause coalescence within the time frame of the simulations. We think that the space confinement effect is the key factor in this process. The surrounding SWCN basically acts as a reaction container, ensuring a near-zero impact parameter, templating the fused product into a tubular form.

To validate these ReaxFF results, we performed DFT calculations [B3LYP (Refs. 22 and 23) with the 6-31G** (Refs. 24 and 25) basis²⁶] to locate key points on the potential-energy surface of two free buckyballs reacting to form a dimer bridged by a shared 4-membered ring. If the atoms forming this ring are shared by adjacent 6-membered rings in both C₆₀'s, this reaction is calculated to be endothermic by 0.27 eV (6.2 kcal/mole). (DFT energies do not include zero-point energy or temperature corrections.) Since this “2+2” reaction is symmetry forbidden,²⁷ the reaction coordinate does not pass through a traditional transition state on a single

potential surface. Instead, one surface (corresponding to the wave function in which the C–C sigma bonds bridging the dimer are intact) describes the system at small distances (bridging C–C bonds of less than $\sim 2.15 \text{ \AA}$). A second surface (corresponding to the wave function of two unbound C₆₀ molecules repelled by Pauli repulsion) describes the system at larger separations. To estimate the lowest-energy intersection of these surfaces, the bridging C–C bonds were constrained to various lengths and all other coordinates were relaxed. In this way the intersection, and the practical transition state for the reaction, was found between C–C bond lengths of 2.1 and 2.2 Å and energies of 2.38–2.60 eV (55–60 kcal/mole) (see Fig. 3). This barrier height is matched by the ReaxFF simulation of the uncatalyzed dimer formation (Table I and Fig. 3). Recently, the energy barrier of the same 2+2 cycloaddition reaction was reported as 0.7 eV,²⁸ but this value seems too low as it will lead to the unreasonable consequence that this 2+2 reaction can occur at very low temperatures.

If the 4-membered ring of the dimer is, instead, composed of carbon atoms which are shared by adjacent 5- and 6-membered rings, the dimerization reaction is predicted by DFT to be 2.02 eV (46.7 kcal/mole) endothermic [Table II(a)]. We also calculated the reaction energy of adding H₂ across a 6-6 or 5-6 site on a single C₆₀ to be -0.88 eV (-20.4 kcal/mole) or -0.03 eV (-0.7 kcal/mole), respectively [Table II(b)]. The difference in energy upon hydrogenating a single 6-6 or 5-6 site (0.85 eV) is evenly half the difference of the 6-6 and 5-6 dimerization reactions (1.76 eV), in which two sites are saturated. We note that the energy difference between the 6-6 and 5-6 hydrogenation reactions obtained when the carbon atoms of the buckyballs are frozen at their free-C₆₀ coordinates and with only the hydrogen atoms allowed to relax (1.15 eV) is similar to the value obtained when all atoms are relaxed (0.85 eV). We conclude that 5-6 sites are intrinsically 0.88 eV more difficult to saturate than 6-6 sites, due primarily to electronic factors rather than the relief of geometric strain. This is consistent with the fact that ReaxFF fails to predict any distinction between the 6-6 and 5-6 sites for either the hydrogenation or dimerization reactions, and instead reproduces the

TABLE II. Energetics of selectivity between (6- and 5-) and (6- and 6-) membered rings. (a) shows the dimerization energy of C₆₀ 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, $E(\text{hydrogenation})$, of $\text{H}_2 + \text{C}_{60} \rightarrow \text{C}_{60}\text{H}_2$. See text for discussion.

$E(\text{C}_{60}\text{--C}_{60})$	6-6 (QM)	6-5 (QM)	6-6 (ReaxFF)	6-5 (ReaxFF)
<i>E</i> (eV)	0.27	2.02	0.34	0.28
<i>E</i> (hydrogenation)	(a)		(b)	
				
	6-6 (QM)	6-6 (ReaxFF)	6-5 (QM)	6-5 (ReaxFF)
<i>E</i> (eV)	-0.88	-0.81	-0.03	-0.87

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,²⁹ 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 multicarrier characters exhibited in double-wall carbon nanotube (DWCN), DWCNs have a promising potential for application in electronic devices.³⁰ The effective synthesis approach of DWCN is so appealing that various methods have been proposed. Bando *et al.* have reported one particularly interesting route to grow DWCN by peapod structures.³¹ 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.³² 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 form³¹ due to the limitation of the simulation time scale. Nevertheless, the salient feature of

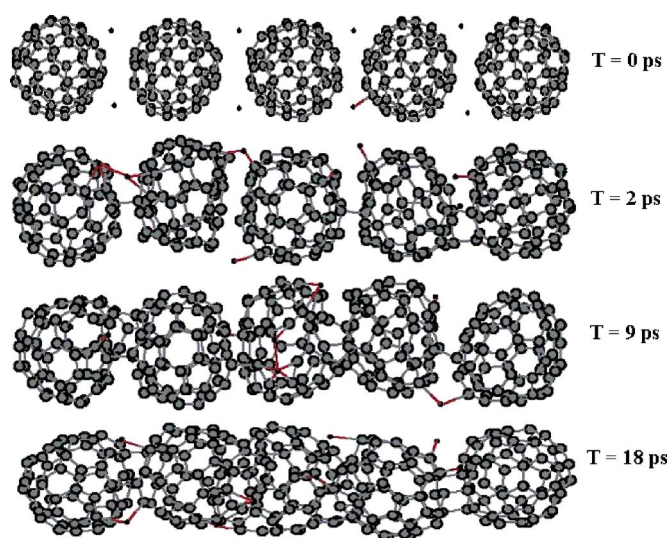


FIG. 4. (Color online) Snapshots of ReaxFF dynamic simulations of five C_{60} balls coalescing inside a (10, 10) nanotube (diameter approximately 1.38 nm) at 1800 K with two Ni atoms between each C_{60} pair. The SWCN is not shown here for clarity.

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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