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Carbon Nanotube-Fullerene Hybrid Nanostructures by C60 Bombardment: Formation and Mechanical Behavior

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Abstract

This study reports the investigation on C_{60} bombardment on the carbon nanotube (CNT) by molecular dynamics (MD) simulations. We found carbon nanotube nanobuds or nanotube-fullerene hybrid nanostructures can be formed by C_{60} bombardment. Different from the nanobuds in earlier studies, more structure patterns are found in the bombardment formed nanobuds and nanotube-fullerene hybrid nanostructures. In addition, the attaching strengths of the carbon nanobuds are explored, and results indicate that the junction between C_{60} and CNT in the nanobuds is very stable. Moreover, we also found the bombardment formed nanobuds and nanotube-fullerene hybrid nanostructures will generally decrease the maximum tensile strength and Young's modulus of carbon nanotube.

Keywords: Nanobuds, Fullerene, Carbon Nanotube, Molecular Dynamics

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1. Introduction

Fullerenes and carbon nanotubes (CNTs) have drawn great attention due to their unique physical and chemical properties [1–8]. Recently there have been research efforts attempting to combine fullerenes and CNTs into nanobuds [9-12], in which fullerenes covalently bond to the outer wall of a carbon nanotube. It was suggested that nanobuds pose high emission characteristics and are promising for the development of new types of vacuum electronic devices [9, 13]. Additionally, C_{60}^{+} and C_{60} have been considered to be a good candidate for potential application in three-dimensional imaging in cluster ion beams. Reports have shown that C_{60}^{+}, as a polyatomic projectile, can enhance the secondary ion yield with a relatively small amount of damage to the surface because of the small energy per atom [14-27].

There exist very few experimental techniques to synthesize nanobuds. The two techniques proposed for combining fullerenes and CNTs into a single structure include one-step continuous process by Albert G. Nasibulin et al. [9-11] and solid phase mechanochemical reactions by X. Li [12]. Up to date, it is still quite challenging to probe the mechanism of the nanobud formation and the structure of the nanobuds through experiments. Meanwhile, though some theoretical work has discussed the structure of nanobuds and their properties [29-31]; unfortunately, how the nanobuds are formed physically has not been discussed. Nanobuds have also been suggested for different engineering applications; for example, besides as promising materials in field emission and nano-device, they also are seen as a good candidate to replace CNTs in polymer nanocomposites due to their better ability to prevent interfacial slippage with the polymer matrix [9, 13].

Based on the above discussion, this paper will examine the formation and mechanical properties of nanobuds formed by C_{60} bombardment on the carbon nanotube (CNT). A series of

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molecular dynamics (MD) simulations will be conducted to simulate C_{60} bombardment on carbon nanotube (CNT). We will first show that different types of nanobuds and carbon nanotube–buckyball nanostructures can be formed by C_{60} bombardment. Then, the attaching strength of the C_{60} in the nanobuds on the CNTs and the effects of nanobuds on the tensile strength of CNT will be presented and discussed in details.

2. MD simulations of Nanobuds Formation by C_{60} Bombardment on CNTs

The initial setup of the MD simulations of C_{60} bombardment on a CNT is shown in Fig. 1. In the MD simulation of the bombardment process, the adaptive intermolecular reactive empirical bond order (AI-REBO) potential [32] is used to describe realistically the atom interactions in one CNT as well as the van der Waals-type interactions between the C_{60} and SWCNT [33].

The irradiation energies of C_{60} are calculated as $E = \frac{1}{2} m v^2$, where E is the irradiation energy, m is the mass of C_{60}, and v is the bombardment velocity of C_{60}. The velocity-Verlet algorithm [34] is used for integration of the classical equations of motion that govern the motion of the atoms. All MD simulations are performed using the code LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [35].

Taking (10, 10) carbon nanotube (CNT) as an example, in the first step of the bombardment simulation, the velocity of C_{60} particle is set to zero and the system is equilibrated at 300K under canonical (NVT) ensemble for 100ns. Then simulation is continued under the microcanonical (NVE) ensemble, and the bombardment velocity of C_{60} particle is to set to a certain value v. When C_{60} particle impacts the surface of a (10, 10) SWCNT with ends fixed, the tube will vibrate for a while, and the bombardment result is not examined until the tube vibration disappears.

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When the irradiation energy is above 0.38 keV, the C_{60} particle is captured by the tube of the CNT. As shown in Fig. 2, different types of carbon nanotube-fullerene hybrid nanostructures formed by C_{60} bombardment can be observed. The corresponding number of bonds in a junction with respect to the irradiation energy is shown in Table 1 for various irradiation energies. Different from the studies of C_{60} keV bombardment for applications of cluster ion beam imaging, in which a key issue is the depth resolution achievable under bombardment of molecular surfaces, here we only focus on the nanobuds formation and their configuration with different irradiation energies. Thus the required irradiation energies in this work are much lower than that in the studies of C_{60} keV bombardment for applications of cluster ion beam imaging, eg. 1~20 keV in Refs. [17, 24, 25], and 40 keV in Ref. [26].

For Nanobuds A and B, due to the small irradiation energy, both the shape and configuration of C_{60} and CNT do not change, which is similar to those synthesized by chemical functionalization. For Nanobud C, the surface of the CNT is dented by collision with the C_{60} and its cross section deforms into a heart shape; however, the configuration of fullerenes and CNT in the formed nanobud does not change.

For Nanobuds D, E, and F, with the increased irradiation energy, the configuration of the C_{60} in the nanobud changes. As an example, defects such as heptagon or nonagon appear in the configuration of the C_{60} in some of the nanobuds formed by C_{60} bombardment. In Nanobud D, 2 heptagons appear in the configuration of the C_{60}, which has 22 hexagons, 6 pentagons and 2 heptagons, but no defects appear in the CNT. The C_{60} in Nanobud E has 18 hexagons, 10 pentagons and 2 nonagons, but no defects appear in the CNT. For NanoBud F, as shown in Fig. 3, heptagons and nonagons can be observed in $C_{60,}$ and successive gap shaped defects appear in the CNT.

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When the irradiation energy is above 0.46 keV, the fullerene molecule is broken and embeds in the CNT. The configuration of both the CNT and the fullerene molecule has changed apparently. It may be more reasonable to call them a new kind of nanotube-buckyball hybrid nanostrauctrue rather than nanobuds. This is because nanobud is defined as a nanostructure in which fullerene covalently bonded to the outer wall of a carbon nanotube. For nanotube-buckyball hybrid nanostructures G, H, and I, both C_{60} and the surface of CNT are broken, and the cross section of CNT becomes flat because bonds form between the incident and back surfaces.

When using the MD model in which the CNT is placed on a virtual substrate, as shown in Fig.1(b), the types of the hybrid nanostructures obtained by C_{60} bombardment are similar to those of the CNT model with ends fixed; however, the cross section of the CNT in most of the nanobuds obtained deforms into flat ellipse (instead of heart shape).

As mentioned in Ref. [31], CNT nanobuds have two kinds of structural patterns: (1) Attaching configuration, where a perfect fullerene attaches onto the outer wall of a CNT; (2) embedding configuration, where an imperfect fullerene embeds within a carbon nanotube, whose structure is actually imperfect. Here we should note is that there are more structural patterns shown in our work than these two structural patterns presented above. Nanobuds A, B and C are in the attaching mode and Nanobud F is in the embedding mode. However, for Nanobuds D and E, defects appear in their configuration of the C60 rather than in the CNT, and thus Nanobuds D and E are new kinds of nanobuds which have not been reported previously.

Bond length and bond order of the bonds in the junction of the nanobuds formed are shown in Table 2, the method for determining the hybridization of the bonds in the junctions is based on an empirical equation, fitted to DFT calculations, for carbon–carbon bonds [36]:

$$\mathrm{BO}_{ij} = \exp\left[-0.097 \cdot \left(\frac{r_{ij}}{1.399} \right)^{6.38} \right] + \exp\left[-0.26 \cdot \left(\frac{r_{ij}}{1.266} \right)^{9.37} \right] + \exp\left[-0.391 \cdot \left(\frac{r_{ij}}{1.236} \right)^{16.87} \right] \quad (1)$$

where the variable r_{ij} is the bond length between atom *i* and *j*.

Compared with the bond length and bond order of the bonds in the CNT junction [37], the value of bond length in the junction of nanobuds is relative large. Thus it seems to be questionable if the bonds in the junction of nanobuds are strong enough. In the next section, the mechanical properties of carbon nanotube-fullerene hybrid nanostructures formed by C60 bombardment will be investigated via MD simulations.

3 Mechanical Properties of Carbon Nanotube-fullerene Hybrid Nanostructures Formed by C60 Bombardment

For easy comparison with previous results of mechanical properties of CNTs available in the literature [38], the Reactive Empirical Bond Order (REBO) potential proposed by Brenner [39] is used in our MD simulation. First, simulations which pull the C_{60} away from the Nanobuds A, B, C, D, E and F are conducted. The simulation system is shown in the subfigure of Fig. 4. The optimal scheme S2 as described in Ref. [38] is used in the MD simulation of the loading process. The length of the open SWCNT (10, 10) is about 4.9nm (20 axial period length), and the wall thickness of a SWCNT is taken as 3.4 Å. Simulation time step is set to be 0.5 fs. The first layers of atoms on both ends of a CNT and the upper half of the fullerene molecule were held rigid, and all atoms except the boundary ones rigidly held are treated as thermostat atoms. Each displacement step is set to be 0.05 angstrom and is followed by 50 relaxation steps. The Tensile stress versus displacement relationships when separating the C_{60} from the nanobuds are shown in

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Fig. 4. The tensile strength of pulling the C_{60} away from the Nanobuds A, B, C, D, E, F are 11.2GPa, 16.0GPa, 16.3GPa, 25.0GPa, 24.8GPa, and 21.8GPa, respectively. Results indicate that the junction between C_{60} and CNT in the nanobuds is very stable.

The mechanical properties of the hybrid nanostructures formed by C_{60} bombardment also need to be investigated to determine their effects on the strength of the CNT. In the MD simulations, the first layers of atoms on both ends of a CNT were held fixed and all atoms except the boundary ones fixed are attached to a Nose-Hoover thermostat.

The stress-strain curves for carbon nanotube-fullerene hybrid nanostructures under uniaxial tensile strain are shown in Fig. 5. Young's modulus versus irradiation energy relationship in carbon nanotube-fullerene hybrid nanostructures is also examined, as shown in Fig. 6. With the irradiation energy increasing, Young's modulus of these carbon nanotube-fullerene hybrid nanostructures obtained will generally decrease.

The maximum stress of SWCNT (10, 10) is about 300.1GPa around a strain of 0.4, which is in agreement with Refs [38] when using the wall thickness of SWCNT 3.4 Å. The maximum stress of the nanotube-fullerene hybrid nanostructures formed by C_{60} bombardment is less than the original CNT, meaning that the strength of the CNT is reduced by some structural changes. Moreover, we can observe that tensile strength of the CNT with carbon nanotube-fullerene hybrid nanostructures formed by C_{60} bombardment is decreased with increased irradiation energy.

4 Conclusions

In summary, we have found that carbon nanotube-fullerene hybrid nanostructures can be formed by C_{60} bombardment, including different types of nanobuds and nanostructures by C_{60} embedded in CNT. With the irradiation energy increasing, both the maximum strength and

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Young's modulus of these carbon nanotube-fullerene hybrid nanostructures obtained will generally decrease. It has been expected that nanobuds could be used as molecular anchors to prevent slipping of SWNTs in composites, thus improving the composite’s mechanical properties; however, our work shows the nanobuds may also cause the degradation of strength of the CNTs.

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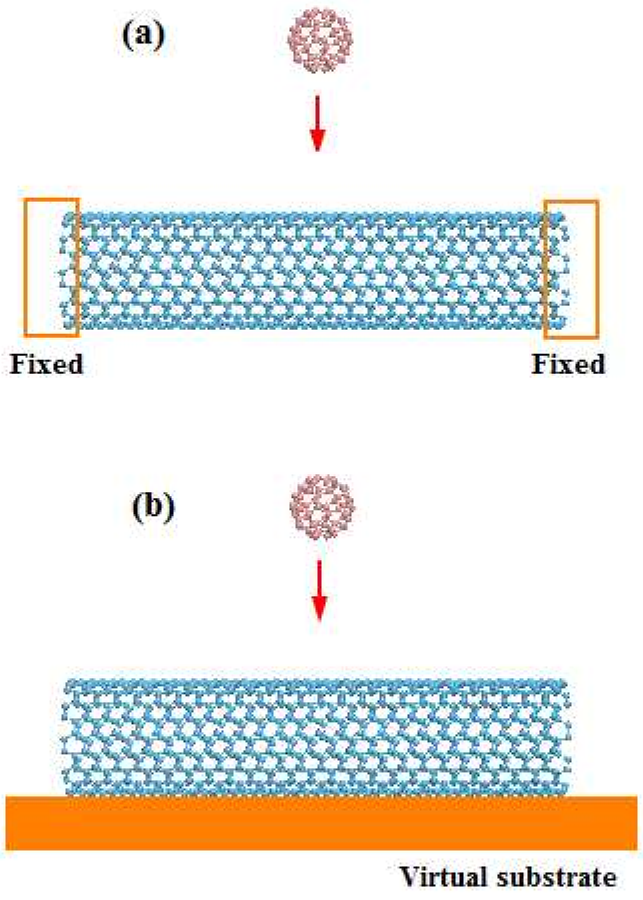

Figure 1: Initial setup of C_{60} bombardment on the carbon nanotube

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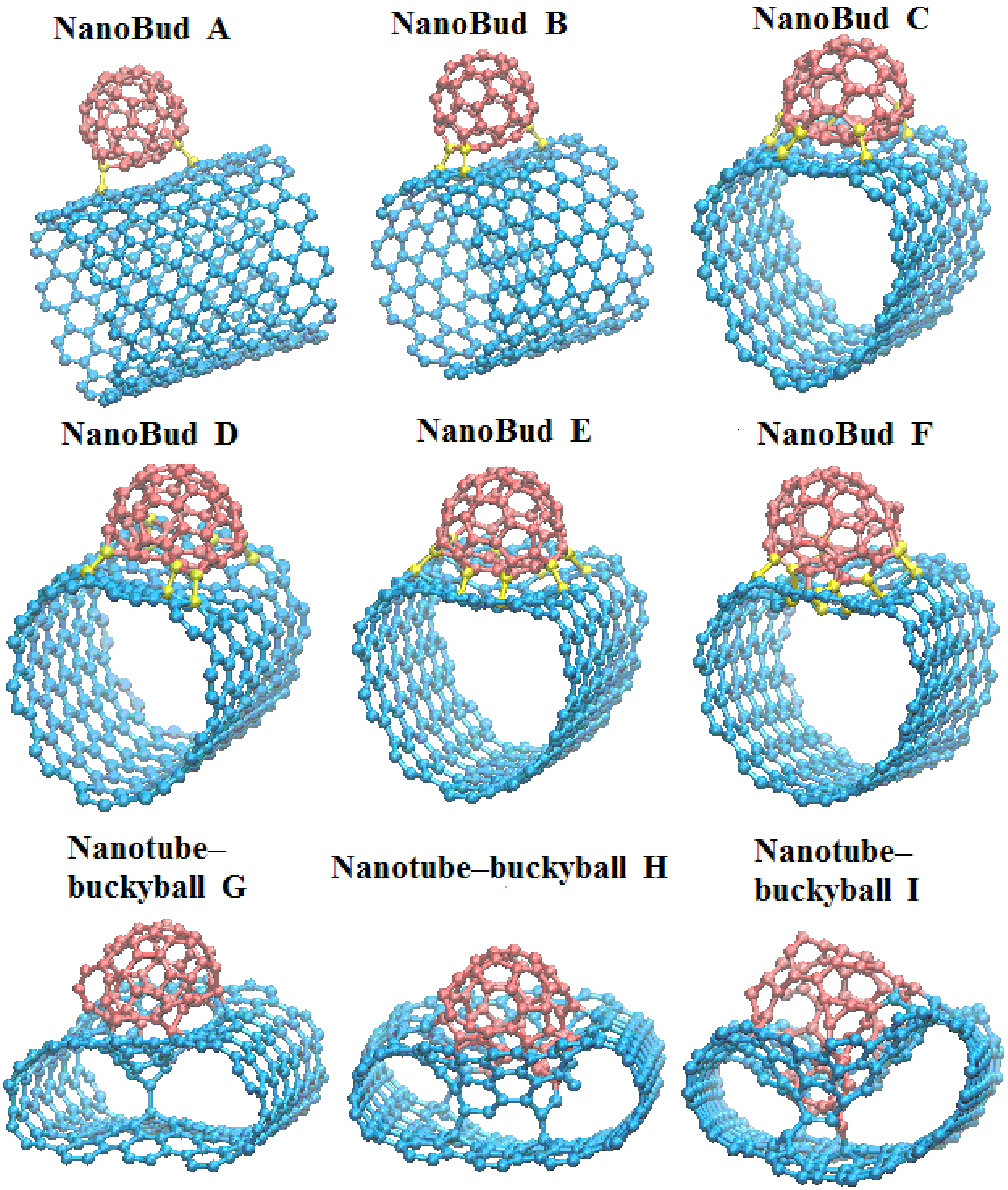

Figure 2: (1) NanoBud A, B, C, D, E, F with interconnected bonds number 2, 3, 5, 7, 8, 10 and irradiation energy 0.38, 0.40, 0.41, 0.42, 0.44, 0.46 keV respectively; (2) Nanotube-buckyball hybrid nanostrauctrue G, H, I by irradiation energy : 0.51, 0.57, 0.60 keV.

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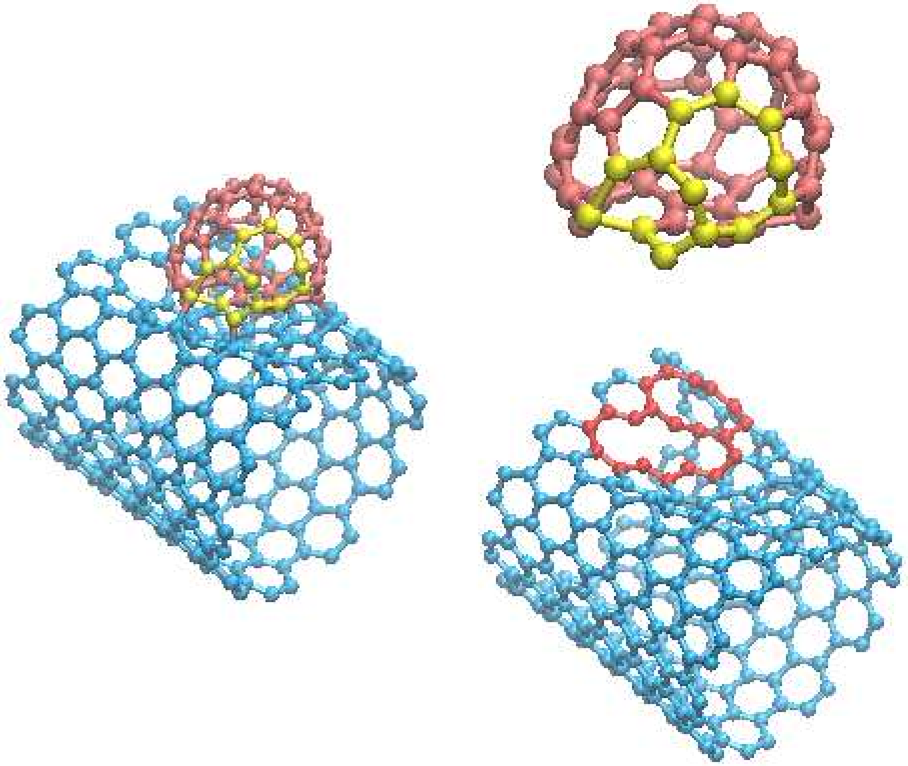

Figure 3: Nanobud F with topological defects highlighted.

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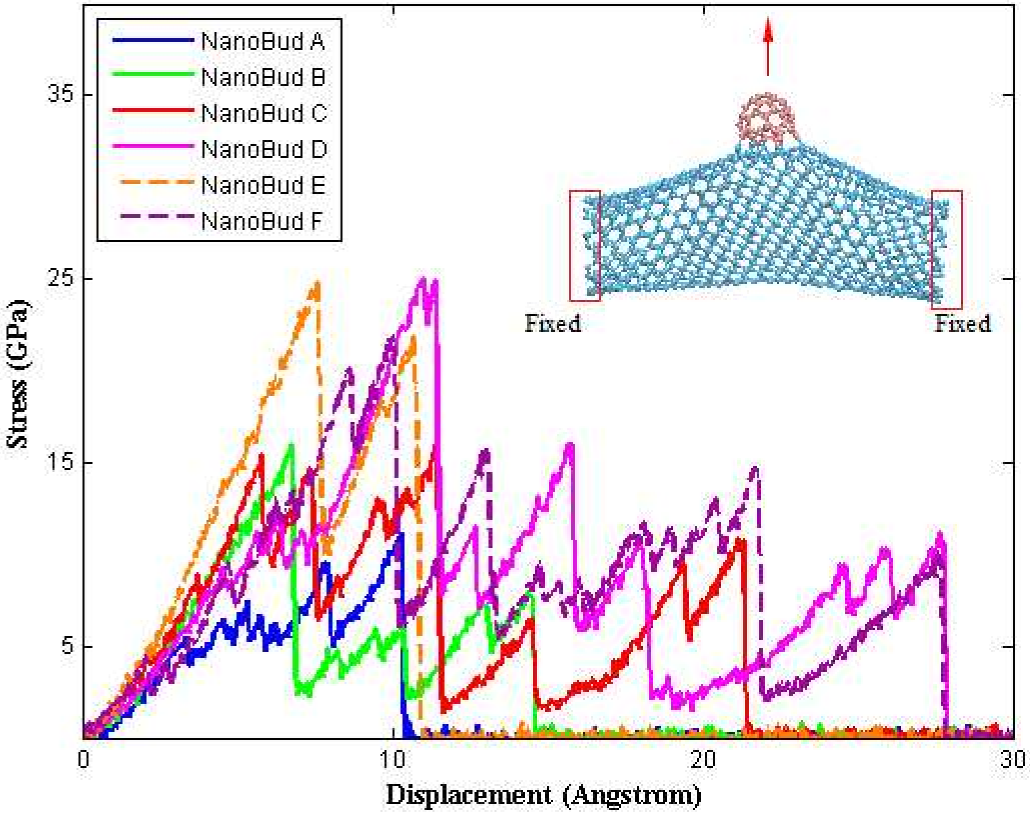

Figure 4: Tensile stress versus displacement relationships when separating the C_{60} from the nanobuds

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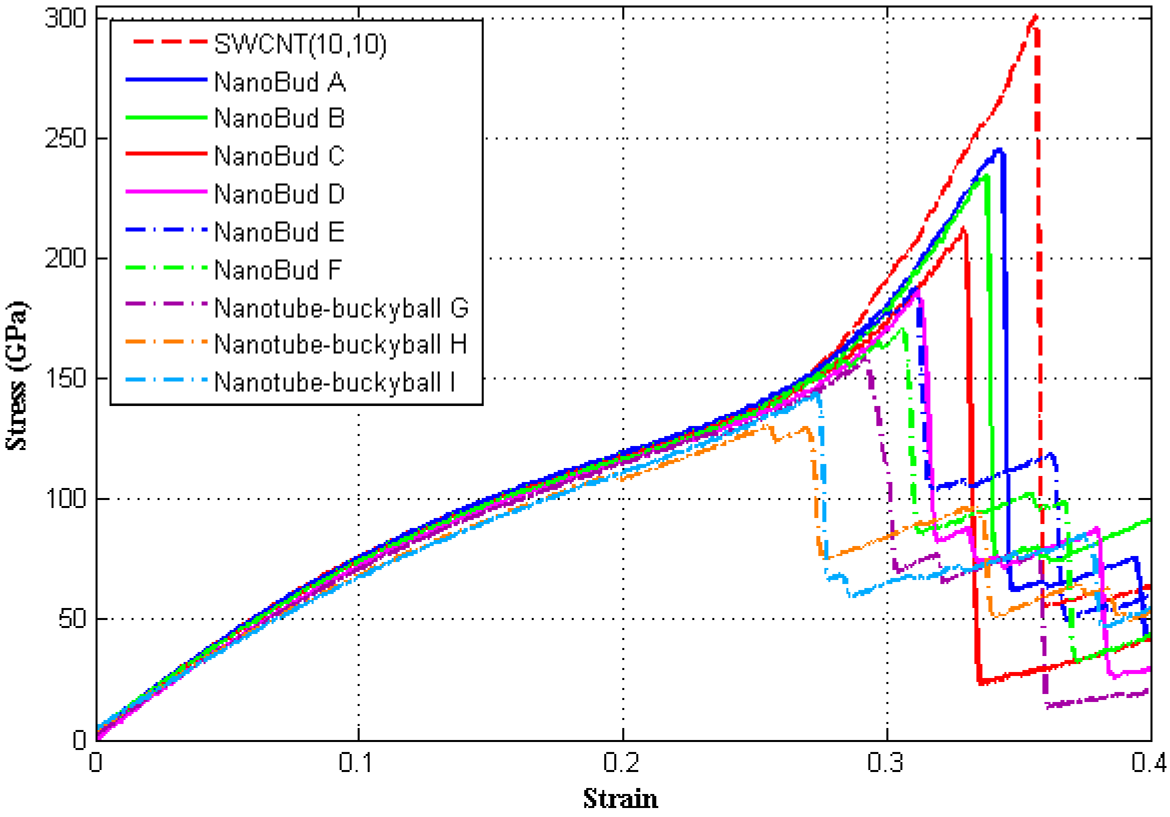

Figure 5: Tensile stress versus strain relationships for CNT(10,10) with carbon nanotube-fullerene hybrid nanostructure

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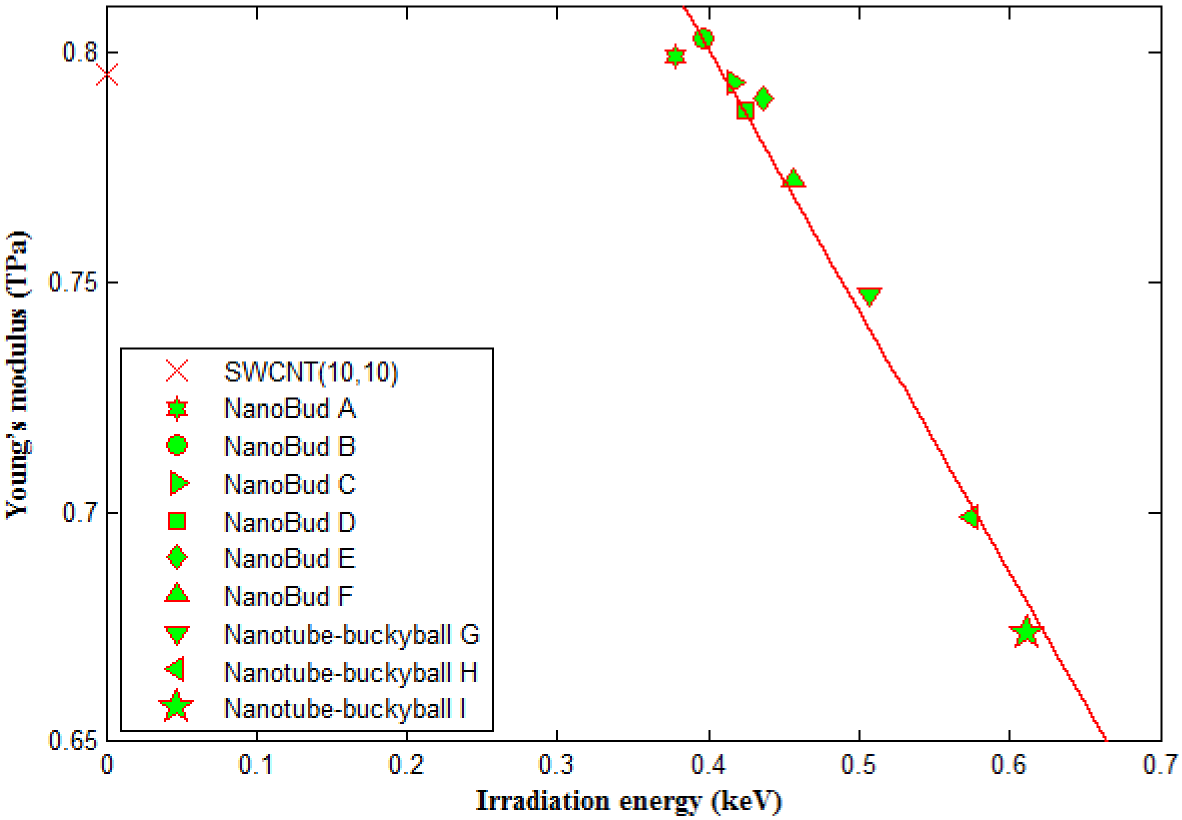

Figure 6: Young's modulus versus irradiation energy relationships for CNT(10,10) with carbon nanotube-fullerene hybrid nanostructure

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Tables

TABLE 1. Bonds number in the junction of NanoBuds and corresponding irradiation energies

	Bond number	irradiation energies (keV)
NanoBud A	2	0.38
NanoBud B	3	0.40
NanoBud C	5	0.41
NanoBud D	7	0.42
NanoBud E	8	0.44
NanoBud F	10	0.46
Nanotube-buckyball G	_	0.51
Nanotube-buckyball H	_	0.57
Nanotube-buckyball I	_	0.60

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TABLE 2. Bond length and bond order of the bonds in the junction of NanoBuds.

	Bond length	Standard deviation of bond length	Bond order	Standard deviation of bond order
NanoBud A	1.7002	0.0038035	0.73052	0.004834
NanoBud B	1.6886	0.027078	0.74707	0.037468
NanoBud C	1.7059	0.005724	0.72332	0.0070962
NanoBud D	1.6643	0.061245	0.79172	0.097712
NanoBud E	1.653	0.067299	0.81238	0.10855
NanoBud F	1.5528	0.1002	1.0338	0.22501