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Nanobuds Promote Heat Welding of Carbon Nanotubes at Experimentally-Relevant Temperatures

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ABSTRACT: Direct heat welding of commonly found single-walled carbon nanotubes (SWCNTs) (i.e. diameters >1 nm) requires a temperature of >4000K which is too high to be practical. This work reports a novel welding method of SWCNTs at experimentally-relevant temperature by means of nanobuds to facilitate C-C bonded junction formation between the nanotubes. Through molecular dynamics (MD) simulations, it is demonstrated that SWCNTs independent of their diameters can be welded together using the proposed method even at a temperature below 1500K.

KEYWORDS: Nanobuds, Fullerene, Carbon Nanotube, Molecular Dynamics, Heat Welding

1. Introduction

Fullerenes and carbon nanotubes (CNTs) have attracted much 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 [9-11], which have been found to possess high emission characteristics and are promising for the development of new types of vacuum electronic devices [9,12].

Carbon nanotube network based devices has been intensively studied in recent years [13-17]. Interconnected network of carbon nanotubes (CNTs) is a promising material that is able to translate the unique properties of individual CNTs to three-dimensional space. Although some novel materials based on carbon nanotube networks have been constructed; however, the extraordinary properties of the individual CNTs such as their exceptional mechanical property are often lost in these materials because the CNT junctions are formed by other chemical components instead of carbon-carbon (C-C) covalent bonds. To solve this problem, many researchers have been investigating how to join CNTs to form multi-terminal junctions, such as 'Y-,' 'T-,' or 'X-' junctions made of C-C bonds. The techniques that have been proposed include electron beam irradiation or ion irradiation [18, 19], mechanical manipulation with atomic force microscope [20], and heat welding [21–27].

Heat welding is arguably the most promising method among the techniques mentioned above. This technique not only has the capability to form junctions readily and efficiently in a network, but also preserves the carbon–carbon bond order (i.e. graphitic) at the junctions. However, it is very difficult to experimentally weld together commonly found CNTs, whose diameters are typically greater than 1 nm. Previous studies based on MD simulations have shown that the required temperature for junctions to form between CNTs of this size range is greater than 4000K, which is too high for heat welding to be feasible in practice [24, 28]. Since the chemical bonds between carbon atoms in a nanotube become stronger when its diameter increases, the required temperature for heat welding of CNTs also becomes higher.

In this study, we report a novel heat welding method for welding CNTs independent of their diameters at a sufficiently low temperature to be practical in real experiments. The method is based on using C_{60} to facilitate nanobud formation and CNT welding. First, two different techniques for forming nanobuds on CNTs will be investigated using MD simulations. Then using the formed nanobuds, we will demonstrate that CNTs tested with nanobuds can be easily welded together even at temperature below 1500K, which makes the method feasible for experimental study.

2. MD Simulation of Nanobuds Formation

Our previous study via MD simulations has shown that nanobuds can be formed by bombarding C_{60} with a perfect CNT [29]. In fact, nanobuds also can be formed by placing C_{60} in close contact with a perfect CNT under high pressure, as demonstrated by using MD simulations. For convenience, we call the first method as the ‘collision’ method, and the second one as the ‘contact’ method, where each method exhibits a different mechanism in the nanobud formation.

In the simulations of the contact method, the initial distance between C_{60} and single-walled CNT (SWCNT) is set to a certain value ranging from 1.6 to 0.5 Å. In the MD simulations of the nanobud formation (and the subsequent simulations of heat welding), the adaptive intermolecular reactive empirical bond order (AI-REBO) potential [30] 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 [31]. Because the initial distance is less than the van der Waals distance of 3.4 Å, the effect is similar to adding a pressure to make the C_{60} and CNT close [32]. Since no constraints are set, any atoms are free to move during the simulations. If interlinking bonds between C_{60} and CNT form, the structures will equilibrate at 300 K in 0.2 ns with a fixed timestep 0.5 fs using the Nosé–Hoover thermostat. All MD simulations in this study are performed using the code LAMMPS (Large-scaleAtomic/Molecular Massively Parallel Simulator) [33].

In our MD simulations, two kinds of configurations can be observed in the resulting CNT nanobud structures: (1) attaching configuration, where a pristine or imperfect fullerene attaches onto the outer wall of a pristine CNT; (2) embedding configuration, where a pristine or imperfect fullerene embeds within a carbon nanotube, whose structure is actually imperfect. By using the ‘collision’ method, nanobuds with both attaching configuration and embedding configuration can be formed; however, only attaching configurations can be observed in our MD simulations of the ‘contact’ method. Thus compared with the ‘contact’ method, a higher number of different structural configurations of CNT nanobuds can be obtained by using the ‘collision’ method with different irradiation energies. On the other hand, when generating atomistic models of interconnected CNT networks via nanobud formation, the ‘contact’ method is easier than the ‘collision’ method.

In fact, the effects of the collision and close contact between C_{60} and SWCNTs can explain the formation mechanism of nanobud by solid phase mechanochemical reactions by X. Li [12]. In that study, naobuds are synthesized by vigorously shaking a mixture of fullerenes and SWCNTs.

3. Heat Welding of Carbon Nanotubes via Nanobuds

In contrast to ultra-thin SWCNTs, heat welding of relatively large diameter nanotubes is quite challenging because the required temperature for welding the larger nanotubes together is too high to be practical [24, 28]. Here we demonstrate that nanobuds can facilitate the welding of SWCNTs at much lower temperatures.

The simulation models of heat welding of CNTs have been described in details in our previous works [23-27] and will be employed in this work as well. In a typical MD simulation setup, two SWCNTs with a nanobud are placed at a crossed angle of 90^{o}, and nanobuds are separated by 3.4 Å wall-to-wall. All four ends of the two crossed SWCNTs are constrained in order to prevent the tubes from rigid body motions during the heating process. In the first series of simulations, the pair of (10,10) SWNTs (1.356nm diameter) with nanobud excluding the constrained regions is heated from 300K to a maximum temperature ranging from 1500K to 1900K in 2ns, after which the temperature is kept at the maximum temperature for 10ns with a fixed timestep of 1fs using the Nosé–Hoover thermostat. Each junction formed by heating will then be annealed from the corresponding welding temperature to 300K in 1ns and will be kept at that temperature for 0.2ns.

In our simulations, all the (10,10) SWCNT nanobud pairs can be easily welded together to form junctions, and the junctions formed by four typical nanobuds are shown in Fig. 1. Moreover, our simulations also demonstrate that the junctions between the nanobuds are quite stable as the bonds in the junctions formed did not break after the temperature has been lowered and maintained at 300K for 1 ns.

By using nanobuds to facilitate welding, carbon-carbon-bonded junctions can be easily formed. Moreover, it should be more practical for constructing interconnected carbon nanotubes network in real experiments. Figure 2 shows the junctions formed at different temperatures for the pair of (26, 0) CNTs (2.036nm diameter) with nanobud at 1350K, 1500K and 2100K. It can be observed that nanobuds can be formed even at temperature of only 1350K, but the junction formed at that temperature contains very few bonds. At 1500K, the junctions formed between the fullerenes contain more bonds and thus are more stable. At higher temperature (i.e. 2100K), heat treatment will result in a complete coalescence of the fullerenes in the nanobuds formed as shown in Fig. 2.

The most attractive advantage of this method is that the heat welding process seems to be independent of the diameter of the CNTs. For example, we have tested the heat welding between the different pairs of (10, 0), (14, 0), (18, 0), (22, 0), (26, 0), (30, 0) CNTs (0.783nm, 1.096nm, 1.409nm, 1.722nm, 2.036, 2.349nm diameter, respectively) with nanobuds using MD simulations at 1500K. The diameters are almost in the typical diameter range of SWCNTs from 0.6 to 2nm.

The initial distance between the two CNTs with nanobuds is set to 3.4 Å. In our simulations, it can be observed that all the CNT pairs with nanobuds can be easily welded. The formation energy [24, 28] of heat-welded junctions for the pairs of (10, 0), (14, 0), (18, 0), (22, 0), (26, 0) (30, 0) SWCNTs with nanobuds are -14 eV, -37.8 eV, -13.2 eV, -34.2 eV, -34.4 eV and -30.1 eV, respectively. Ref. [28] has shown that the formation energy of X-junction by direct heat welding of SWCNT pairs is a function of diameter of crossed tube, and the formation energy for the crossed tubes increases as the diameters of the tubes increase. However, our results show no size dependence of the formation energy of X-junction via nanobuds heat welding, indicating the independence of the diameter on the welding feasibility. Meanwhile, it can be observed that the formation energies of junctions have negative values, and thus the resulting X-junctions are stable.

Moreover, two SWCNTs of different diameters and chiralities with C_{60} on the surface also can be welded together easily. Figure 3(a, b) shows the heat welded junctions of SWCNT pairs (18,0)-(30,0) and (10,10)-(26,0) via nanobuds at temperature 1500K, respectively.

4. Heat Welding of Carbon Nanotube Bundles with Nanobuds

In experiments, as-fabricated CNTs in a network are oftentimes bundled together, and here we will examine whether using nanobuds can facilitate heat welding at an experimentally-relevant temperature. To begin, the SWCNT bundles containing 2x2 (10,10) SWCNTs with nanobuds distributed on the surface of the CNTs are formed by applying pressure via MD simulation in two steps. The length of each open SWCNT (10,10) in the bundles is about 4.9nm (20 axial period length). First, similar to the nanobud formation by using the contact method, the interlinking bonds between 2x2 SWCNTs can be formed by applying pressure, which results into a SWCNT bundle. Then, to make the nanobuds distribute on the surface of the SWCNTs bundle, each C_{60} is attached onto the surface of the SWCNTs by using the 'contact' method.

At the start of an MD simulation of the heat welding of the (10,10) SWCNT pairs with distributed nanobuds, two (10,10) SWCNT bundles with nanobuds are crossed at a 90° angle and separated by a distance varying between 2 to 4 Å as shown in Figure 4(a). All ends of the two crossed SWCNTs bundles are constrained in order to prevent the tube bundles from rigid body motions during the heating process. The entire system excluding the constrained regions is heated from 300K to a maximum temperature ranging from 1500K to 1900K in 2 ns, after which the temperature is kept at the highest temperature set for 10ns with a fixed timestep of 1 fs using the Nosé–Hoover thermostat. Each junction formed by heating will then be annealed from the corresponding welding temperature to 300K in 1 ns and will be kept at that temperature for 0.2 ns.

In all the MD simulation, we find that junctions form between the two CNT bundles. Two typical heat welded CNT bundles connected through nanobuds are shown in Figure 4(b). Note that the junctions between the two CNT bundles are formed by the C_{60} molecules fusing together. In the simulations, some C_{60} molecules in nanobuds with attaching configuration can slip on the tubes; they can be trapped and combined with other C_{60} molecules attached to the CNTs at elevated temperature. Thus chains of C_{60} fullerenes [12] can be observed in the formed junction. In Fig. 4(a, b), it can be observed that the C_{60} molecule in yellow color slips and join the C_{60} chain in the junction area.

Thus we have demonstrated that the SWCNTs in bundle form can be welded together via nanobuds at experimentally-relevant heating temperature. It should be noted that the temperatures employed in these simulations are relatively high compared to experiments due to the time scale limitation of MD simulations. Hence the required temperature for heat welding of SWCNTs or their bundles via nanobuds in real experiment is expected to be much lower than 1500K.

To test the mechanical stability of SWCNTs junctions via nanobuds, MD simulations of separating the two SWCNTs bundles with junction via nanobuds are conducted. The optimal scheme S2, which is appropriate and effective for analyzing the nanotube structure and mechanical properties as described in Ref. [34], is used in the MD simulation of the loading process. Simulation time step is set to be 0.5 fs, and the wall thickness of a SWCNT is taken as 3.4 Å. The atoms of the upper 3/4 of the upper SWCNTs bundles and lower 3/4 of the lower SWCNTs bundles 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 1000 relaxation steps.

One typical simulation snapshot of the tensile deformation process is shown in Fig. 5. The bond breaking/reconstruction process and the formation of a one-atom chain can be observed in the tensile process. The tensile stress versus displacement relationships separating the two SWCNTs bundles are shown in Fig. 6. The maximum stress of separating the two SWCNTs bundles with junction via nanobuds is about 27.3 GPa, and thus the heat welded SWCNTs bundles with junction via nanobuds show good mechanical stability.

5. Conclusions

In summary, we have presented a novel method for heat welding of SWCNTs at experimentally-relevant temperatures. Our results show that these SWCNTs with nanobuds can be easily welded together even at heating temperature below 1500K. The key advantage of this method is that the heat welding process is independent of the diameter of the CNTs. This method provides a simple while effective way of joining SWCNTs together via covalently-bonded junctions to form a continuously interconnected CNTs network, which should be able to translate the extraordinary properties of individual CNTs to bulk CNT materials. It should be noted that the junctions formed by heat welding of nanobuds have never been reported before. Thus it will be interesting to investigate their various properties such as their electronic property in the future.

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Notes

The authors declare no competing financial interest.

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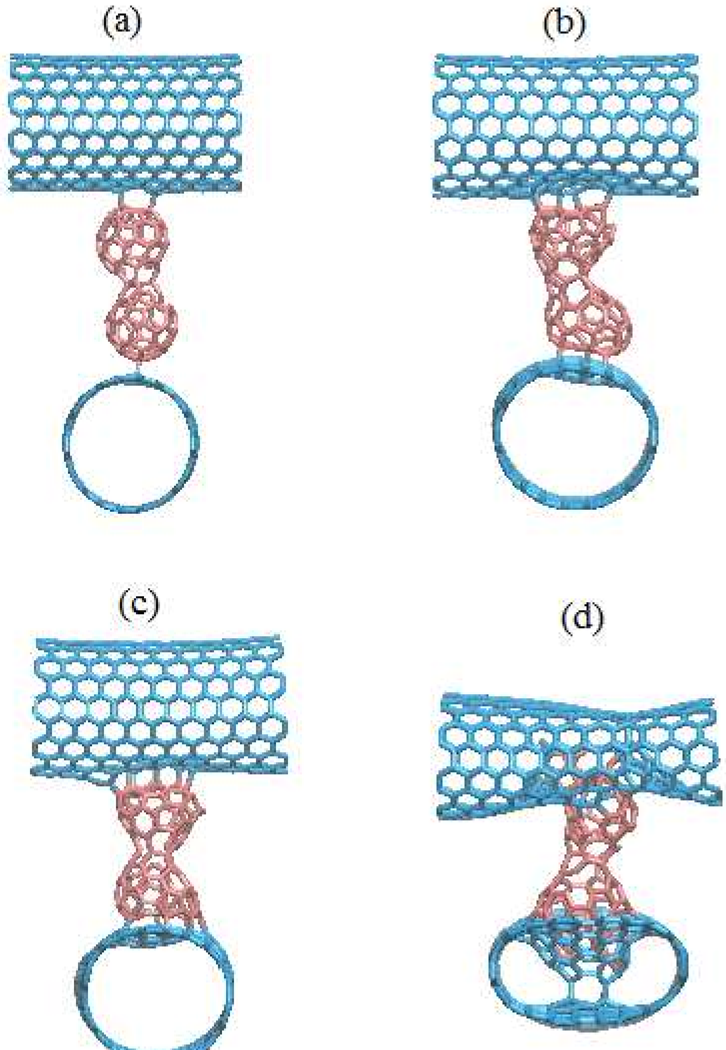


Figure 1: Typical heat-welded junction formed by nanobudes at temperature 1900K

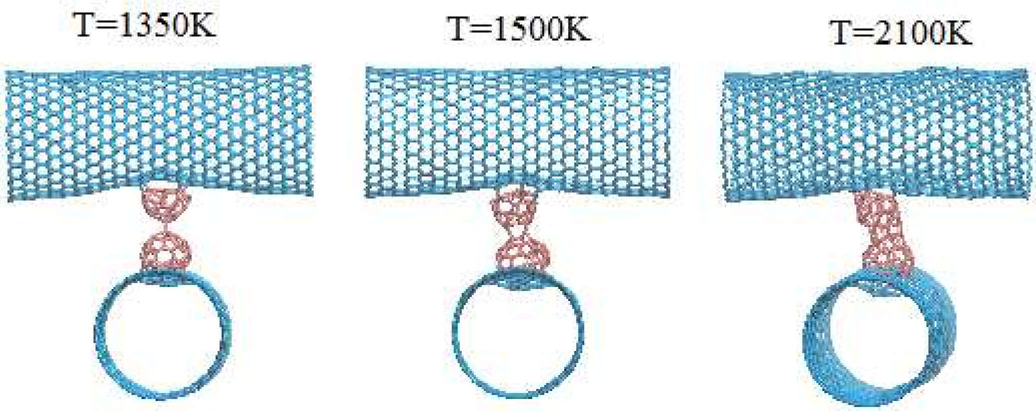


Figure 2: Heat-welded junction formed by CNT pairs (26, 0) with nanobuds at different temperatures 1350K, 1500K and 2100K

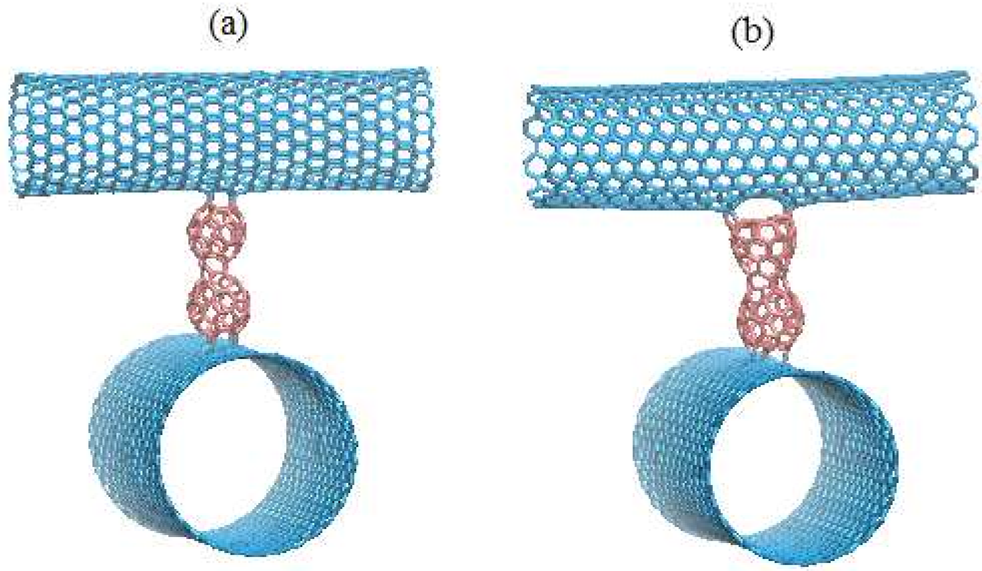


Figure 3: Heat-welded junction formed by two SWCNTs of different diameter and chiralities with nanobuds at temperature 1500K: (a) heat welded junctions of SWCNT pairs (18, 0)-(30, 0); (b) heat welded junctions of SWCNT pairs (10, 10)-(26, 0).

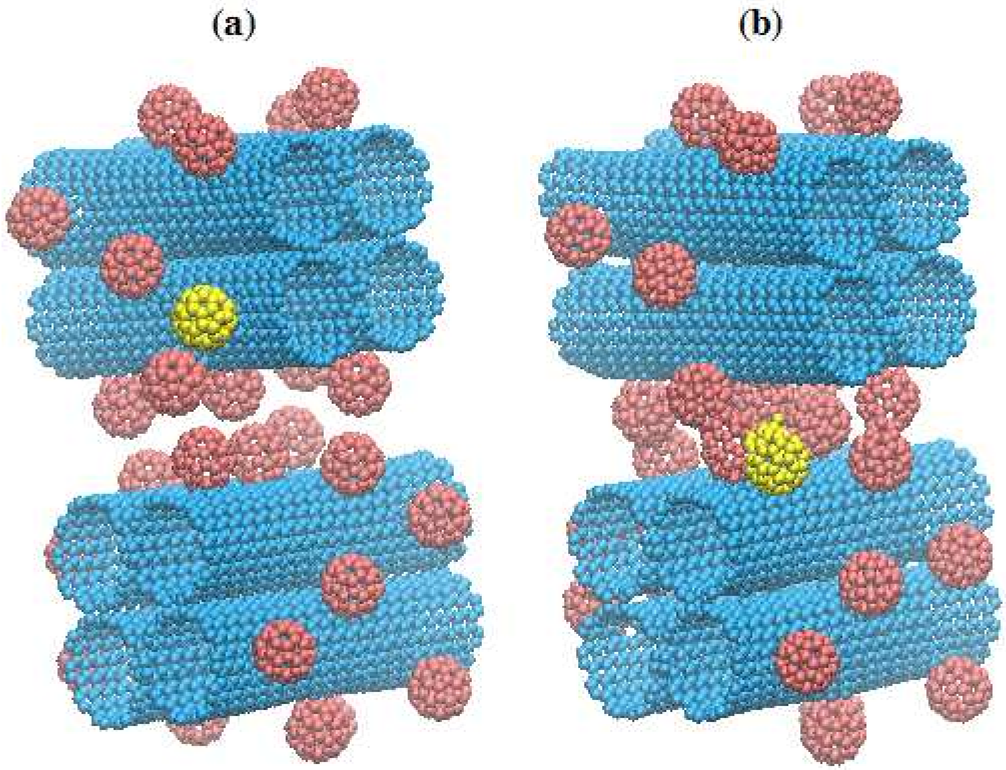


Figure 4: Heat welded carbon nanotube bundles via nanobuds: (a) two crossed SWCNTs bundles with nanobuds before heat welding. (b) two crossed SWCNTs bundles with junction formed after heat welding via nanobuds.

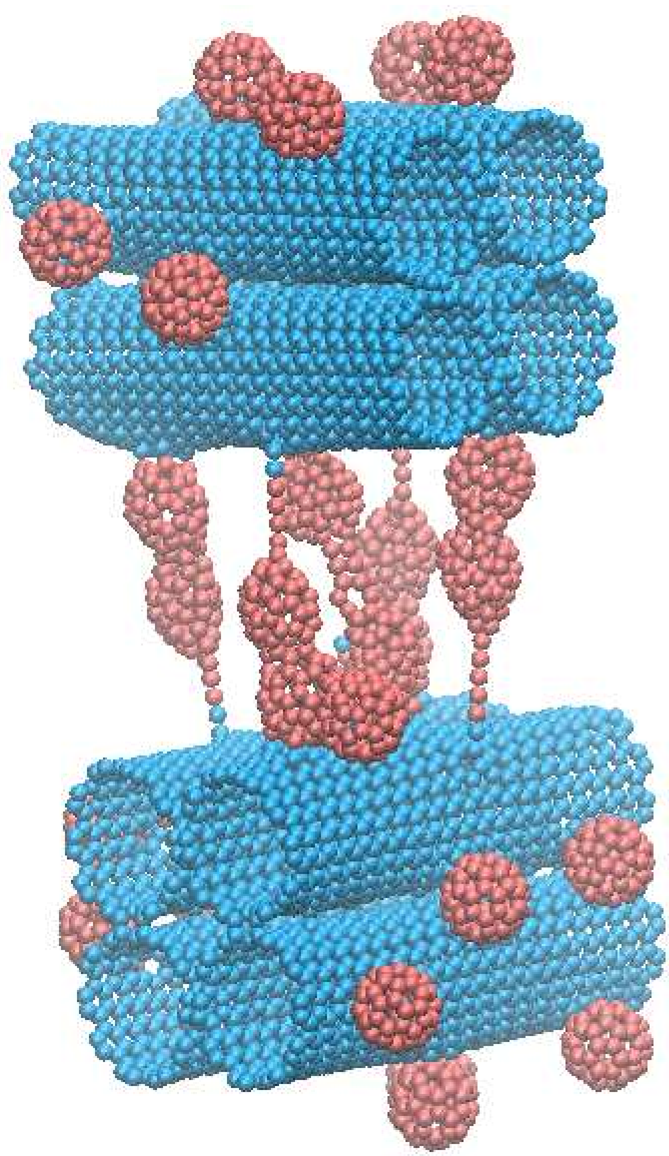


Figure 5: A typical simulation slide in the tensile process when separating the two SWCNTs bundles with junction via nanobuds

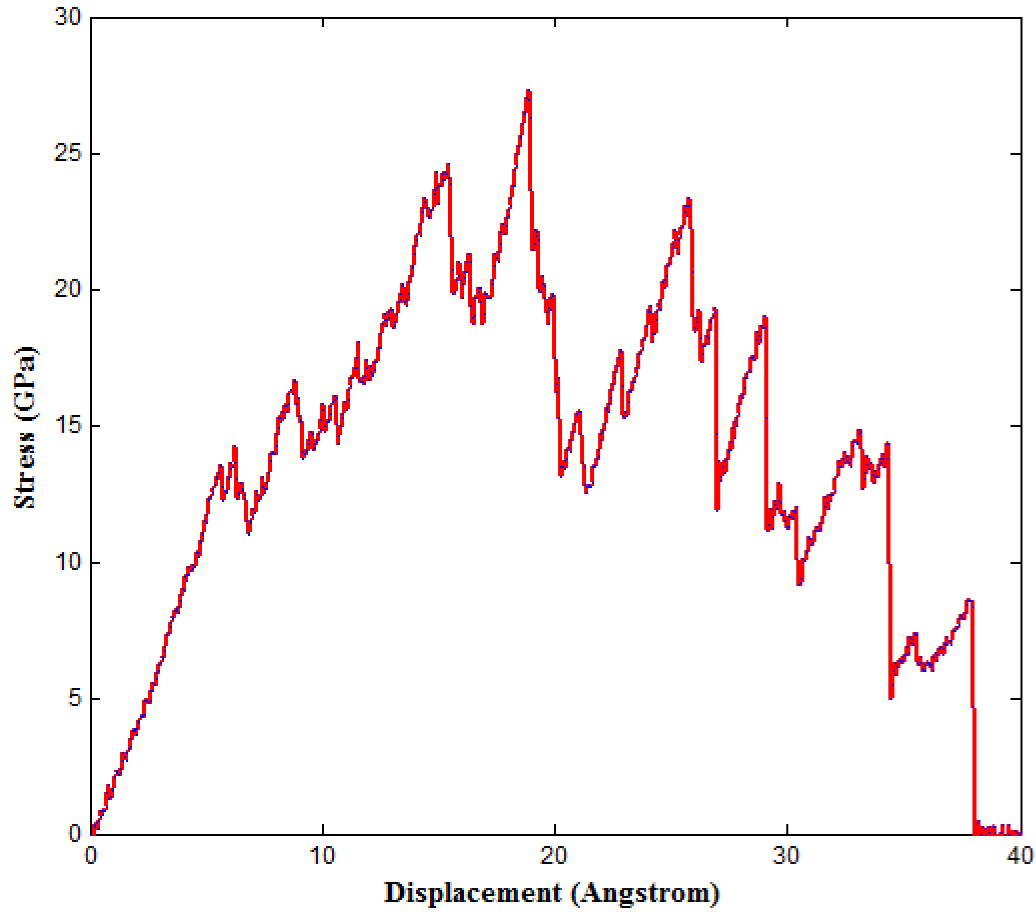
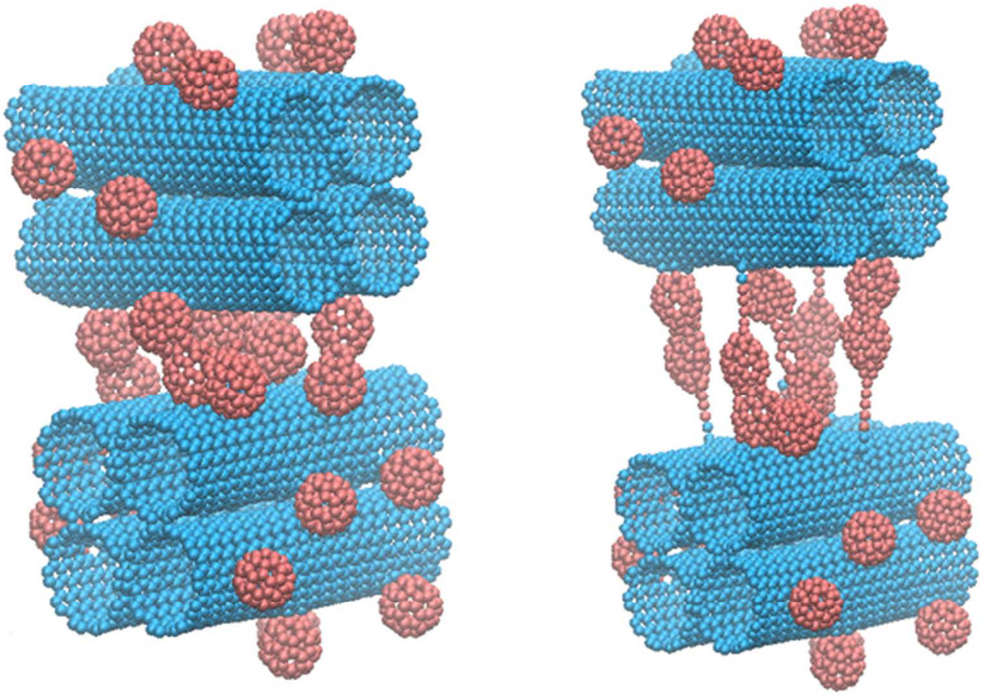


Figure 6: The tensile stress versus displacement relationships when separating the two SWCNTs bundles with junction via nanobuds



Nanobuds promote heat welding of carbon nanotubes at experimentally-relevant temperatures
24x17mm (600 x 600 DPI)