Pulling long linear atomic chains from graphene: Molecular dynamics simulations

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Experimental methods for preparing long linear atomic chains from graphene and for using the chains to connect nanodevices are proposed based on classical and first-principles molecular dynamics simulations. We show that these methods are promising to pull out long monatomic chains, to dope other atoms, such as boron, nitrogen, silicon, and phosphorus in the chains, and to build the smallest and ultra-highly-integrated nanoelectron circuits in the near future.

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In the past few years, a great deal of attention has been focused on monatomic layers and chains. As the thinnest materials, graphene, a stable two-dimensional lattice exfoliating from graphite, challenges the theoretical predication proposed by Landau *et al.* 70 years ago, and shows room-temperature quantum Hall effect and remarkable conductivity due to the relativistic charge carriers with vanishing mass, which make it a promising candidate to replace silicon in future solid-state devices.[1–4] Linear atomic chains (LACs), which are more intensely rejected by Landau's theory, began to show its birth in recent experiments. Although the longest metallic LAC consists of only several gold atoms, and cannot survive for seconds,[5–7] carbon LAC of about ten atoms in vacuum can stands for 100 s even under the electron irradiation inside a transmission electron microscope,[8] besides the existence of carbon LACs involving 20 atoms in solution,[9–11] and up to 100 atoms inside a multiwall carbon nanotube[12] or attached to a nanotube.[13] Since carbon LACs have demonstrated some quantum effects, such as the conductance oscillating with even or odd number of atoms, or changing significantly by doping atoms,[14–18] we may speculate more novel properties, just like the case for graphene of micron in size, belonging to long carbon LACs, which are ideal one-dimensional conducting wires to transmit quantum information or common signals in nanocircuits. Furthermore, if it is possible to dope other atoms in the long carbon LACs, its conductance and other properties could be greatly modified, resulting in many kinds of LACs with specific features. Unfortunately, freestanding long carbon LACs involving more than 20 atoms in length are yet unavailable experimentally at the present, though our previous work showed via molecular dynamics (MD) simulations that much longer carbon LAC can be pulled out from graphene as long as the pulling speed is much lower than 30 m/s,[19] which was proven to be right by a recent experiment.[20]

In this work, we first put forward a more practical method to pull out long carbon LACs from graphene, and then search for approaches to dope other atoms in the chains, followed by exploring possible ways to attach the (doped) carbon LACs to nanostructures to connect nanodevices.

Our suggestion for pulling long LAC from graphene can be implemented as follows: the prefabricated graphene is dropped onto a grid of two arms separated by a microgap, and main body of the graphene is attached to two arms of the grid [Fig. 1(a)]. This grid is then put into a vacuum chamber, and electron beam is used to irradiate the graphene sample till a thin nanoribbon or a short carbon LAC is formed [Fig. 1(b)], followed by pulling one arm of the grid at speeds much lower than 30 m/s [Fig. 1(c)].

The above pulling process was first explored by classical MD simulations with Brenner potential.[21] Initially, a graphene with its left and right side fixed [Fig. 2] was allowed to relax at a given temperature T_i for 100 fs, and then the right side was pulled away from the fixed left side at the speed of 30 m/s. During the simulation process, motion of the atoms was integrated by the standard Verlet method with a fixed time step of 0.2 fs. Considering that both ends of the graphene were contacted with the grid, a thermal bath was applied on some atoms of the graphene (atoms in columns 2 to 4 from both the left and right sides) to make the system stay around at T_i.[19,22] To avoid using heating or cooling devices in the experiments, we mainly performed the MD simulations at room temperature (T_i=300 K) in this work.

Our MD simulations showed that a LAC can be pulled out from the short carbon chain or thin ribbon generated by the electron irradiation [Fig. 2(a)], and continuously elongated with the atoms coming off the graphene, just like unraveling a knitted scarf [Fig. 2(b)]. Finally, nearly all the carbon atoms joined in the LAC, and a monatomic chain involving about 300 atoms was obtained. However, if the initial graphene was replaced with a perfect one without preexisting chain or ribbon [Fig. 2(c)], the edge of graphene may be torn off randomly during the pulling process [Fig. 2(d)], resulting in uncontrollable pulling processes. Our further simulations showed that, if the prefect graphene was much longer along the pulling direction, abrupt rupture and

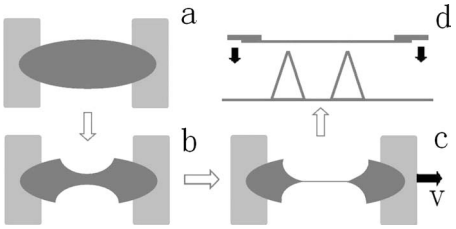

FIG. 1. Schematic view of (a)–(c) the preparation process of carbon LAC from graphene and (d) the connection process of nanostructures with the LAC.

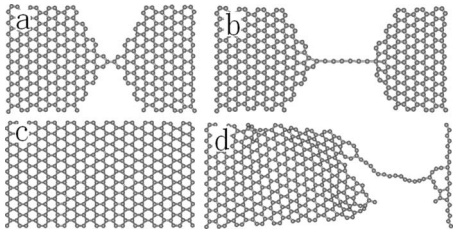

FIG. 2. Snapshots of (a) a graphene with defects that irradiated by electron beam, (b) a LAC formed from the defective position of the graphene, (c) the configuration of a perfect graphene, and (d) a LAC formed at a random position of the graphene.

rapid shrinking of the whole graphene frequently took place without formation of any LACs as mentioned in Ref. 19 because large amount of potential energy, which was accumulated in graphene layer gradually as the pulling proceeded before the graphene was ruptured, may transfer to kinetic energy of the carbon atoms as long as the graphene split.

To further confirm the feasibility and reliability of the pulling method, Car-Parrinello MD simulations[23] were performed starting from a smaller graphene sample as shown in Fig. 3(a). The simulations were carried out by the CPMD plane-wave density-functional theory code[24] and Becke, Lee, Yang, and Parr exchange-correlation density functionals,[25] with a plane-wave kinetic-energy cutoff of 60 Ry and norm-conserving pseudopotentials used.[26] The initial temperature was set to be 300 K and confined in the range of 270–330 K during the pulling process. Three atoms on the left side indicated by a rectangle in Fig. 3(a) were fixed, and three atoms in the other rectangle were pulled away from the left side at the speed of 30 m/s. At the beginning, the distance between atoms 3 and 7 was set a little shorter than the length of three carbon bonds so the short carbon LAC between atoms 3 and 7 was flabby. The pulling first broke off the bond

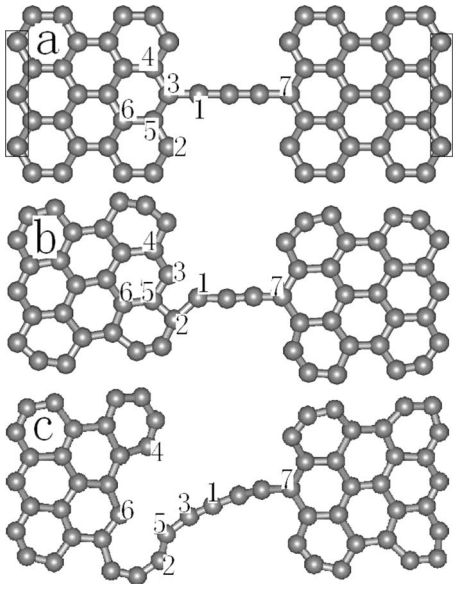

FIG. 3. Snapshots of (a) the initial configuration, (b) one end of the chain jumped from one graphene atom to another, and (c) a carbon LAC with eight atoms was formed, i.e., the final configuration of this simulation.

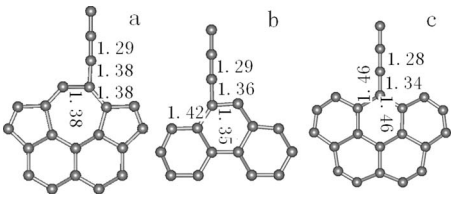

FIG. 4. The optimized geometries of (a) reconstructed zigzag edge, (b) armchair edge, and (c) zigzag edge. Some bond lengths are shown in the unit of Å.

between atoms 1 and 3, followed by atom 1 bonded with atom 2 [Fig. 3(b)]. With increase in the distance between atoms 3 and 7, atom 1 bonded with atom 3 again. This chain-jumping process due to thermal fluctuation, always occurred in our first-principles simulations, and has been observed in the experiment of Ref. 8. During the chain jumping, its end atom is free and needs sufficient time to encounter an atom in the graphene to form a bond again. So the faster the pulling speed, the fewer probabilities for the chain to bond with the graphene again, and therefore, much lower pulling speeds are beneficial to prevent the chain from breaking.

As the pulling proceeded, the bond between atoms 3 and 4 broke, followed by breaking of the bond between atoms 5 and 6, and a carbon LAC with eight atoms was formed [Fig. 3(c)], when the pulling process was terminated. It can be deduced that similar bond-breaking processes will repeat if the simulation is continued, and a much longer carbon LAC could be obtained.

Considering that besides the zigzag edge shown in Fig. 3, an armchair edge [Fig. 4(b)] is another important edge of graphene and the reconstructed zigzag edge [Fig. 4(a)] was reported to be the most stable edge of graphene,[27] we also performed similar first-principles MD simulations with the LAC attached to these structures, and successfully obtained carbon LACs. It should be noticed that these three kinds of edge structures (Fig. 4) were the most stable and probable ones,[27] and the other high-energy edges can be expected to be unraveled to form carbon LAC more easily. For some other edge structures unraveled difficultly, if the pulling speed is much slower, such as 1 μm/s in the experiment, there may exist enough time for these edge structures to transfer via self-passivating processes[27] to other stable structures that can be easily unraveled.

Figure 4 illustrates the CPMD optimized structures of the above three representative edges with a short LAC. To save the optimizing cost, all geometries are strictly confined in plane, and only a part of every graphene edge was optimized. The bond lengths of the carbon LAC, which are all less than 1.3 Å, are shorter than those of the graphene, which are around 1.4 Å, indicating that carbon bonds of the LAC are stronger than those of the unraveled graphene. The lengths of carbon bonds that connect the LAC and graphene are longer than those of the LACs and close to or a little shorter than those in the graphene, that is why the chain-jumping process always happened there.

Now we turn to preparing doped carbon LACs. Our first-principles MD simulations show that directly adding impurity atoms into a pre-existing carbon LAC is very difficult so we suggest dope other atoms to graphene first, and then

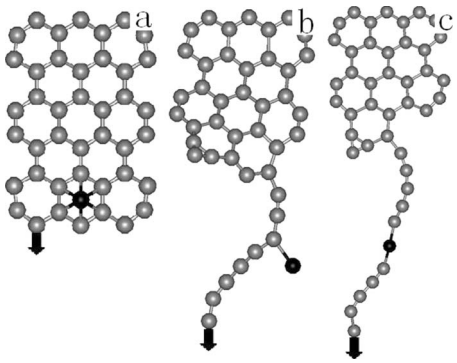

FIG. 5. Snapshots of (a) the initial configuration for pulling doped LAC, (b) the impurity atom hang on the LAC, and (c) the impurity atom join in the LAC. The black atoms are impurities and the gray ones are carbon.

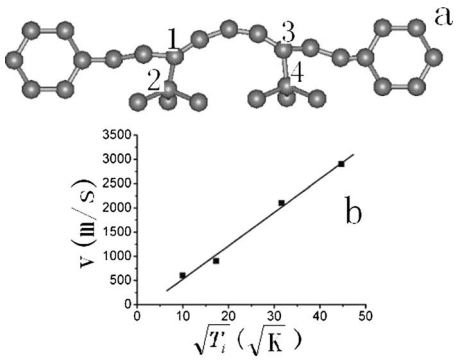

FIG. 6. (a) Snapshots of a carbon LAC that connected two carbon tips (2) and (4). (b) The threshold speed v, above which the atoms that applied forces directly can be removed from the system, was proportional to $\sqrt{T_i}$.

doped carbon LACs may be pulled out in the same way as shown in Fig. 1 from the doped graphene. Impurity atoms can be inserted into graphene by replacing an atom[28] or be placed on the graphene.[29,30] Since placing the doped atoms on graphene is much easier, our simulations started from the configuration shown in Fig. 5(a), where an impurity atom (B, N, Al, Si, or P), which is neighboring element of carbon in the periodic table, takes its local minimum on the graphene initially at 300 K. All the impurity atoms expect for aluminum can stay on the graphene stably, which can also be understood by the weak binding energy between aluminum atom and graphene.[30] With unraveling of the doped graphene, the impurity atoms, boron, nitrogen, aluminum, silicon, and phosphorus, evolves to either hang on the LAC [Fig. 5(b)] or join in the LAC [Fig. 5(c)]. In many simulations, the impurity atom mainly joins in the LAC by two ways: one is a direct process that the impurity atom is pulled out to join in the LAC while the other is an indirect process that the impurity atom first hangs on the LAC [Fig. 5(b)], and then joined the LAC under pulling. Doped LAC can be produced more probably through the indirect process because the bond between a carbon atom and the impurity atom are weaker than the carbon bond of the LAC, and new carbon atoms are a little difficult to be pulled out from graphene by the impurity atom. Our further simulations show that the main results of the above simulations are independent of the initial position of the impurities on the graphene, such as above the center of the hexagon, above the carbon bonds of graphene, and in the substitutional site because our pulling speed is slow enough for the impurity atoms finding their preferable positions.

After the (doped) carbon LAC was prepared by the above methods, it can be used as conducting wire to connect nanodevices[31] by moving together with the grid as shown in Fig. 1(d). In our simulations, a carbon LAC was moved with the ends of two hexagons toward two fixed carbon tip as shown in Fig. 6(a), and atoms 1 and 3 bonded with atoms 2 and 4, respectively, when the carbon LAC got close to the carbon tip. If there were only several atoms between the nanodevices and the unraveled graphene, the redundant atoms also can be removed by pulling the graphene at very high speeds. By this way, the graphene can be pulled away with bond breaking at the joint of the LAC and the graphene, and a few redundant atoms may be left with the nanodevices. In our simulations, the right hexagon in Fig. 6(a) was pulled at 3000 m/s and 300 K, and the six atoms of the hexagon were pulled out without obviously impacting other atoms. Unfortunately, the pulling speed of 3000 m/s was difficult to realize in experiments so we further explored the threshold speed v, above which only the atoms that applied forces directly can be pulled out, i.e., the bond broke at the joint of the LAC and the hexagon in our simulations, and below which the bond broke elsewhere. The simulations were performed at T_i=100, 300, 1000 and 2000 K, and the results indicated that the threshold speed v was proportional to $\sqrt{T_i}$ as shown in Fig. 6(b). That is, at lower temperatures, lower speed was needed to pull out the redundant atoms. For example the threshold speeds were 900 m/s for 300 K and 600 m/s for 100 K. Therefore, if the experiment was performed at very low temperatures, for example, at liquid helium, the redundant atoms may be removed by this method.

In summary, preparation of long monatomic chain is of great importance for both scientific and technical research. Here, an experiment method for pulling freestanding and long pure or doped carbon LACs from graphene is designed and proved by MD simulations. Much lower pulling speed was beneficial for making longer LACs from graphene. The process for using these LACs as electronic wire to connect nanodevices was also demonstrated by first-principles MD simulations. For further topics, preparing more kinds of doped carbon LACs by pulling, finding more structures that can be connected with the LACs, and exploring the novel properties of long carbon LACs with different structures and impurities can be researched theoretically and experimentally in the future.

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