



Deriving Carbon Atomic Chains from Graphene

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(Received 3 January 2009; published 18 May 2009)

Stable and rigid carbon atomic chains were experimentally realized by removing carbon atoms row by row from graphene through the controlled energetic electron irradiation inside a transmission electron microscope. The observed structural dynamics of carbon atomic chains such as formation, migration, and breakage were well explained by density-functional theory calculations. The method we reported here is promising to investigate all-carbon-based devices with the carbon atomic chains as the conducting channel, which can be regarded as the ultimate basic component of molecular devices.

DOI: 10.1103/PhysRevLett.102.205501

PACS numbers: 81.07.Vb, 68.37.Og

The motivation for the miniaturation of electronics has continuously pushed the research via the top-to-down approach into low-dimensional systems, and even atomic scale. As one of the most promising candidates, carbon-based nanostructures, either two-dimensional graphene [1] or quasi-one-dimensional carbon nanotubes [2] have opened entirely new perspectives towards the carbon-based electronics. As an ideal covalent one-dimensional (1D) system, a rigid monatomic linear chain of carbon atoms, such as polyynes ($\cdots C \equiv C - C \equiv C \cdots$) or cumulenes ($\cdots C = C = C = C \cdots$), has been long expected to function as the component of molecular devices due to its exceptional physical and chemical properties predicted by theoretical studies [3–7]. However, the 1D carbon chain has been little studied experimentally mainly due to the lacking of a reliable and effective way to produce it [8–13].

Here we introduce a new approach to realize freestanding carbon atomic chains by employing energetic electron irradiation inside a transmission electron microscope (TEM). A graphene nanoribbon (GNR) was continuously thinned from its two open ends by removing carbon atomic rows. This thinning process stops when the number of carbon atomic rows becomes two or one. Therefore, single and double freestanding carbon atoms chains were reproducibly fabricated. These chains show a remarkably good stability with a length up to a few nanometers even under the irradiation of energetic 120 keV electron beams.

We have chosen the graphite nanoflakes (typically with 4–20 layers) as the starting materials, which are readily found as the byproducts in the commercially available multiwall carbon nanotube specimens made from the arc discharge process. The pristine sample containing graphite nanoflakes were dispersed in ethanol by ultrasonication, and the suspension was dropped onto a carbon microgrid, before inserted into a TEM-JEOL 2010F for further manipulations and observations. The microscope is equipped with a postspecimen image corrector (CEOS) to achieve a better spatial resolution, and a CCD camera

(Gatan 894) is used for image recording with an exposure time of 0.5 s.

In the first step of our *in situ* experiment, an electron beam irradiation induced thinning process was conducted to produce a single layer graphene locally on a selected graphite nanoflake. In order to facilitate the thinning process, the acceleration voltage was set at either 80 or 120 kV, which was known to be close to the knock-on damage threshold of carbon nanostructures [14]. A high beam intensity of about 100 A/cm² was then obtained by focusing the incident electron beam and used for thinning the sample. After a prolonged irradiation, holes (or vacancy aggregates [15]) were induced on the graphite, and a GNR was formed between two large holes. The length of the as-prepared GNR is determined by the size of the area between the two adjacent holes, which can be roughly controlled by the focused electron beam irradiation through the *in situ* sputtering process.

After a GNR with a reduced width was formed, the beam intensity was immediately reduced to about 4 A/cm² in order to slow down the thinning process and to avoid overirradiation damage. Then the HR-TEM characterization was carried out *in situ*. Reproducible experiments to fabricate one or two carbon atomic chains were summarized in Fig. 1. The whole process was similar to that used for the fabrication of metallic quantum wires [16,17].

A detailed analysis of the carbon atomic chain behavior has been carried out in the case shown in Fig. 2. At the beginning of the thinning process [Fig. 2(a)], a GNR formed between two adjacent holes of the graphene had a neck width of about 1.7 nm, corresponding to about 6 to 7 rows of carbon chains. The GNR edges at both sides became partly disordered due to prolonged intense irradiation. Through further thinning process, 1D freestanding carbon atomic chains were finally prepared [Figs. 2(a) and 2(b), and see also movie S1 [18]]. Interestingly, the formation of a double chain was frequently observed [Fig. 2(c)] in our numerous attempts. The as-formed car-

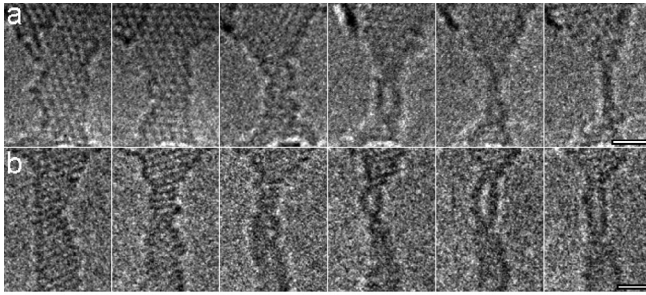


FIG. 1. Formation of free-standing carbon atomic chains. An image gallery shows two examples for the dynamics for formation of free-standing carbon atomic chains from GNR through the controlled electron beam irradiation induced sputtering. Scale bar = 1 nm.

bon atomic chains were rigid but quite flexible, and they were occasionally twisting with each other and vibrating with a variable separation [Figs. 2(c) and 2(d), see also movie S1 in Ref. [18]]. No obvious link was found between these two chains. Interestingly, there is a knot found on the left chain of Fig. 2(d) (marked by the black arrow), which should correspond to a residual carbon hexagon or other polygons (see inset). Soon after, this hexagon disappeared and became a linear chain, either through the further carbon loss or a local conformation change [Fig. 2(e)]. It was also found that the chain at the right-hand side broke and detached from the graphene edge at its chain end (marked by the white arrow). This broken chain migrated along the left-hand side neighbor before a local connection was made with the upper edge [Fig. 2(f)] and finally a linear monatomic carbon chain was sustained.

The single carbon atomic chain shown in Fig. 2(f) has a length of about 2.1 nm (corresponds to about 16 carbon atoms) and behaved like an elastic string with a quasi-linear arrangement, which is consistent with the theoretical studies [7]. No abrupt junction corresponding to the zigzag- or armchairlike configuration was ever found. Contact between the chain end and the graphene edge was not stable, and occasionally the chain end migrated discretely along the edge with atomic steps as if swapping the bonding atoms at the edge of the graphene [see Figs. 2(g) and 2(h)]. Under the typical experimental condition (an acceleration voltage of 120 kV and a beam intensity of 4 A/cm²), this carbon chain survived for more than 100 s before the breakage happened in its lower end [Fig. 2(i)]. It should be noted that the carbon atomic chains never break in the middle. Again here, this broken end jointed to the graphene edge and kept migrating along the graphene edge (see movie S1 [18]).

A surface atom sputtering mechanism should dominate the thinning process. The carbon atoms and/or clusters were selectively removed from the edges of the GNR, not from the central region. This is quite reasonable because the edge carbon atoms are typically doubly coordinated and have dangling bonds that surely induce

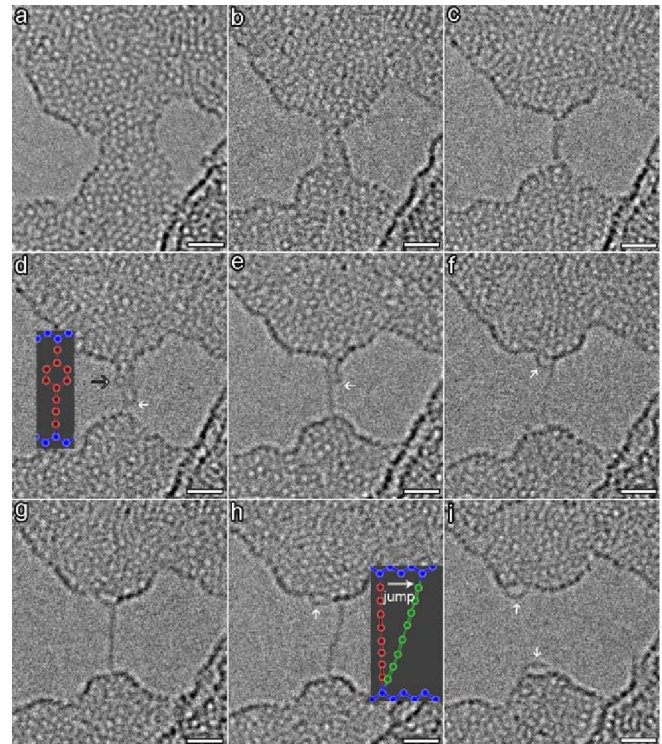


FIG. 2 (color online). Consecutive HR-TEM images showing the dynamics for the formation, breakage of freestanding carbon atomic chains through continuous electron beam irradiation. (a) A GNR with a width of about 1.7 nm was formed between two holes on the graphene. (b) The GNR was thinned row-by-row under the continuous irradiation. (c) A carbon chain consisting of double strands was formed, and there was a knot remained on the left chain (marked as the black arrow). Inset is a representative scheme. The right chain broke from its bottom end (marked as white arrow) and detached with the graphene edge. (d)–(f) The broken chain (on the right) migrated along the left chain, and finally made a connection with the edge belonging to the upper graphene. (g) The carbon was found to be linear and flexible. (h) The carbon chain made a jump along the graphene edge with a changing of edge bonding. The inset is a representative scheme. (i) The carbon chain broken from its upper head. Again it was able to migrate along the graphene edge. Scale bar = 1 nm.

instability of these edge atoms. The thinning process should therefore be initiated by removing the doubly coordinated carbon atoms at the two edges of the GNR, which was followed by the further sputtering of the adjacent carbon atoms. In this way the carbon atoms and clusters were removed row by row. The number of hexagon arrays was continuously reduced from 6 to 2 in this experiment [Figs. 2(a)–2(c), and movie S1 [18]]. The bond breakage and carbon loss from the GNR edges are associated with the momentum/energy transfer from the incident high energy electron through the so-called knock-on mechanism [14].

It is well known that the linear carbon chains can possess either cumulene (characterized by double C-C bonds) or

polyynes (with alternative singlet and triplet bonds) structures with sp hybridization, and the sp^2 bonded graphene can be regarded as a network of zigzag or armchair chains. Therefore a transformation from either zigzag or armchair arrangement to linear chain either cumulene or polyyne type should be possible. Unfortunately, due to the limitation of the spatial resolution of our TEM and the mechanical instability of the specimen, we were unable to resolve individual carbon atoms and to measure precisely the C-C bond length. Therefore the type of carbon atomic chain, cumulene or polyyne, could not be experimentally determined here.

In order to understand the formation mechanism and the dynamic behaviors of linear carbon atomic chains, a series of density-functional theory (DFT) calculations were performed. We employed the generalized gradient approximation for exchange correlation functional [19] and projector augmented waves for the C($2s2p$) electrons [20], as implemented in VASP package [21] using the plane waves with 400.0 eV cutoff. More than ten k points were used to sample the periodic direction, and the spaces for aperiodic directions were set ≥ 10.0 Å. The climbing nudged elastic band method (CNEB) [22] was used to determine the activation energy barrier for the migration process.

Since the carbon atomic chains were derived from the GNRs in our experiments, we first compared their stabilities with the corresponding GNRs by the formation energies. After optimizing the GNR geometries with zigzag, reconstructed 5–7 and armchair edges [Fig. 3(a)] [23], the formation energies of the carbon chains (ϵ_{form}) were calculated (in referring to the graphene) and compared with the edge formation energies of GNRs with the various edge geometries [24,25]:

$$\epsilon_{\text{form}} = [E_{\text{chain/ribbon}} - N\epsilon_{\text{graphene}}]/L, \quad (1)$$

where $E_{\text{chain/ribbon}}$ and $\epsilon_{\text{graphene}}$ are, respectively, the total energy of carbon chain or GNR and the energy per carbon atom for the graphene, N is the number of carbon atoms in the carbon chain or the GNR, and L is the length of the carbon chain or the GNR edge. The calculated formation energies of carbon chains and GNRs are plotted versus the width of the GNR in Fig. 3(b). The dependence of the formation energies on the GNR width agrees well with the

previous reports on GNRs [24,25]. The results suggest that the edge atoms of a GNR should bear in relative high energy states in comparison with other atoms of the GNR. Therefore, the edge atoms especially the doubly coordinated atoms should be knocked off from the GNR under electron irradiation first, and the GNR is thinned narrower by sputtering edge atoms row by row. When the GNR becomes 2–3 atoms wide, edge atoms become dominating and result in large structural transformations. We found that the narrowest zigzag and 5–7 edge GNRs give relative small formation energies of carbon chains by dissociating into two isolated atom chains. For example, the formation energy of a carbon atomic chain from a narrow zigzag edge GNR is about 1.09 eV/Å, which is 0.13 eV/Å lower than that of a thicker GNR (about 1.23 eV/Å). And this process is assisted by additional 0.33 eV/Å in releasing the strain of the carbon atomic chain [see Fig. 3(b)].

The frequently observed formation of double-chain structures can now be understood as follows. Taking the GNR with mainly zigzag edges as an example. This GNR could be continuously thinned down to a serial of hexagons which can be regarded as two interlinked zigzag carbon chains. This structure has a formation energy of about 1.22 eV/Å which is higher than that of the carbon atomic chain (0.76 eV/Å). Therefore, it would be reasonable for this narrow GNR to become a double-chain structure by separating its two zigzag edges. The same mechanism also applies to other cases, such as armchair and reconstructed GNRs. Such a transformation should be initiated by the breakage of cross-linking bonds under the electron beam irradiation, and assisted by the release of strain energy in transforming from a carbon nanoribbon into 1D chain.

The stability of the various observed carbon chains can also be understood from their optimized structures (see Fig. S1 [18]). The average bond length of the carbon chains (sp hybridization) is smaller than that of the GNR edge (mainly sp^2 hybridization), and the shorter bond length leads more valence electrons distributed around bonds and corroborate the bond strength. While the edge carbon atoms of the GNR were easier to be sputtered through the local bond breakages, the relatively higher stability of the carbon chain may help it to sustain under the electron beam irradiation. This might be a reason that the thinning

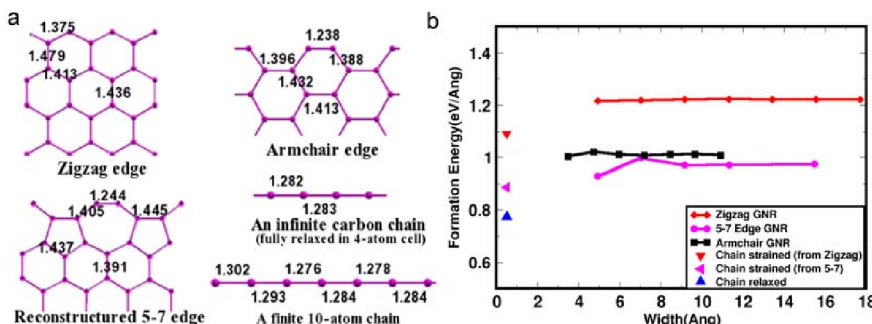


FIG. 3 (color online). (a) The optimized geometries of GNRs (with different types of edges) and carbon atomic chains. (b) The formation energies of different carbon atomic chains (strained or relaxed) and their corresponding GNRs were plotted versus their widths. The unit for bond length is Å.

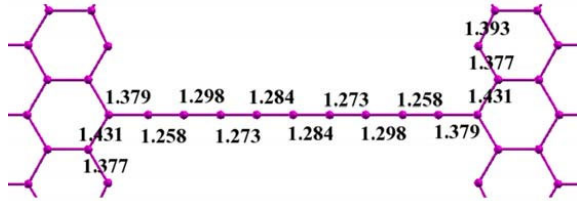


FIG. 4 (color online). Optimized geometries of a carbon chain constrained by two GNRs with zigzag edges. The unit for bond length is Å.

process stops when the number of carbon atomic rows becomes two or one. Also there should be a slight expansion in the total length associated with the transformation from the GNR edge to the carbon atomic chain, accompanied with an expansive strain on the chain

The DFT calculation results also explain the interesting observation that a carbon chain tends to break at its ends (contact with the graphene), instead in its middle. This is mainly due to the difference in C-C bond length with sp and sp^2 hybridizations, which is clearly clarified by the optimized geometrical configuration as shown in Fig. 4 (and Fig. S1 [18]). The C-C bonds at the ends connecting the carbon chain and the graphene are slightly longer than the others within the chain. Our further calculations found that the bond breakage in the middle of the chain costs a higher energy than that at its ends by ~ 1.0 eV for all the configurations examined, suggesting that the bonds at two ends are less stable and relative easier to break.

The structural transformation from the GNR to the carbon atomic chain would result in strain accumulating along the chain. When a carbon chain breaks at its end, the strain release can make the chain become longer which possibly helps it to hop to a nearby edge site. This process could account for the frequently observed “jump” phenomena (Fig. 2). We then performed the CNEB calculations to examine the migration of carbon atomic chain along the edge which may also occur in the experiment. One of the possible migration pathways was shown in Fig. S2 [18]. For a slightly strained chain ($\sim 3\%$) bridged by two graphene monolayers, the energy barrier for the migration to occur is about 0.58 eV. But the migration would help releasing the strain and reducing the total energy of the system.

To summarize, we have introduced a novel method to prepare free-standing carbon atomic chains derived from graphene through a well-controlled energetic electron irradiation induced sputtering process. The formation energies, migration, and breakage behaviors of these chains were also investigated by the DFT calculations. The method reported here gives us a route towards the all-carbon devices, and it would be very intriguing to explore the electrical transport properties on such a system: sp -hybridized carbon atomic chains as the conducting

channel, bridged by the sp^2 -hybridized graphene as the leads.

The work on microscopy is partly supported by CREST project and a Grant-in-aid for Scientific Research in MEXT (19054017). C.J. thanks JSPS and the International Balzan Foundation through AIST and Meijo University, respectively. The authors in Beijing would like to acknowledge support by the Ministry of Science and Technology (Grant No. 2006CB932401) and the National Science Foundation of China (Grant No. 90606026). We thank the referees for the fruitful suggestions which motivated the DFT calculations.

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- [1] A. K. Geim and K. S. Novoselov, *Nature Mater.* **6**, 183 (2007).
- [2] S. Iijima, *Nature (London)* **354**, 56 (1991).
- [3] N. D. Lang and Ph. Avouris, *Phys. Rev. Lett.* **81**, 3515 (1998); **84**, 358 (2000).
- [4] B. Larade *et al.*, *Phys. Rev. B* **64**, 075420 (2001).
- [5] Z. Crljen and G. Baranovic, *Phys. Rev. Lett.* **98**, 116801 (2007).
- [6] S. Tongay *et al.*, *Phys. Rev. Lett.* **93**, 136404 (2004).
- [7] S. Okano and D. Tomanek, *Phys. Rev. B* **75**, 195409 (2007).
- [8] R. J. Lagow *et al.*, *Science* **267**, 362 (1995).
- [9] V. Derycke *et al.*, *Phys. Rev. Lett.* **81**, 5868 (1998).
- [10] X. L. Zhao *et al.*, *Phys. Rev. Lett.* **90**, 187401 (2003).
- [11] T. D. Yuzvinsky *et al.*, *Nano Lett.* **6**, 2718 (2006).
- [12] H. E. Troiani *et al.*, *Nano Lett.* **3**, 751 (2003).
- [13] J. R. Heath *et al.*, *J. Am. Chem. Soc.* **109**, 359 (1987).
- [14] F. Banhart, *Rep. Prog. Phys.* **62**, 1181 (1999).
- [15] C. H. Jin, K. Suenaga, and S. Iijima, *Nano Lett.* **8**, 1127 (2008).
- [16] Y. Kondo and K. Takayanagi, *Phys. Rev. Lett.* **79**, 3455 (1997).
- [17] J. Bettini *et al.*, *Nature Nanotech.* **1**, 182 (2006).
- [18] See EPAPS Document No. E-PRLTAO-102-058919 for two HR-TEM movies showing the formation process of carbon atomic chain and two figures related with the DFT calculation results. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.
- [19] J. P. Perdew *et al.*, *Phys. Rev. B* **46**, 6671 (1992).
- [20] P. E. Blochl, *Phys. Rev. B* **50**, 17953 (1994).
- [21] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993); G. Kresse and J. Furthmuller, *ibid.* **54**, 11 169 (1996).
- [22] G. Henkelman, B. P. Ubergaga, and H. Jonsson, *J. Chem. Phys.* **113**, 9901 (2000).
- [23] Note here, under the present experimental conditions, the edges of the GNRs were found to be mostly of a zigzag type, rather than an armchair one. The formation of stable reconstructed edges was seldom observed.
- [24] P. Koskinen, S. Malola, and H. Hakkinen, *Phys. Rev. Lett.* **101**, 115502 (2008).
- [25] S. Okada, *Phys. Rev. B* **77**, 041408 (2008).