Molecular Junctions by Joining Single-Walled Carbon Nanotubes

M. Terrones,[1] F. Banhart,[2,*] N. Grobert,[3] J.-C. Charlier,[4] H. Terrones,[1] and P. M. Ajayan[5]
[1]*Department of Advanced Materials, IPICyT, Venustiano Carranza 2425-A, 78210 San Luis Potosí, SLP. México*
[2]*Universität Ulm, Zentrale Einrichtung Elektronenmikroskopie, 89069 Ulm, Germany*
[3]*Sussex Nanoscience and Nanotechnology Centre, University of Sussex, Brighton BN1 9QJ, UK*
[4]*Université Catholique de Louvain, PCPM & CERMIN, B-1348 Louvain-la-Neuve, Belgium*
[5]*Department of Materials Science & Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180-3590*
(Received 30 January 2002; published 29 July 2002)

Crossing single-walled carbon nanotubes can be joined by electron beam welding to form molecular junctions. Stable junctions of various geometries are created *in situ* in a transmission electron microscope. Electron beam exposure at high temperatures induces structural defects which promote the joining of tubes via cross-linking of dangling bonds. The observations are supported by molecular dynamics simulations which show that the creation of vacancies and interstitials induces the formation of junctions involving seven- or eight-membered carbon rings at the surface between the tubes.

DOI: 10.1103/PhysRevLett.89.075505 PACS numbers: 61.46.+w, 68.37.Lp, 81.07.De

Single-walled carbon nanotubes (SWNT) have shown to possess most remarkable electronic and mechanical properties [1–3]. Various applications in nanoscale devices have been described [2–11]. However, little progress has been reported on techniques related to connecting such tubular structures. Although a connection between SWNTs would constitute a novel type of molecular junction, it remained unknown whether such junctions exist at all and if they are stable. This is a key issue because both electronic devices and strong nano-mechanical systems need molecular connections among individual SWNTs. In view of possible applications, theory predicts that, for example, a "Y" or a "T" junction of SWNTs could act as a multiterminal electronic device [12–16].

Although branched multiwalled tubular carbon fibers, these being rather multistacked cones than tubes, have been synthesized earlier [17–21], the manipulation and formation of real molecular junctions on the basis of SWNTs have not been reported hitherto. The task of joining two SWNTs appears nontrivial since it is intuitively clear that two individual perfect tubes (consisting of just a cylindrically rolled sheet of hexagonal carbon rings) are more stable than the complicated arrangement of sp^2-bonded carbon atoms within the topology of a tubular junction. In the present work, it is shown experimentally that "X", "Y", and "T" molecular junctions between SWNTs exist and can be created by controlled electron beam exposure of crossing tubes at elevated temperatures. In addition, tight binding molecular dynamics calculations demonstrate that vacancies and interstitials, formed under electron beam exposure, trigger the formation of the junctions.

In the present experiments, SWNTs [22,23] were dispersed ultrasonically in ethanol and deposited onto holey carbon grids for transmission electron microscopy (TEM) observations. The experiments were carried out in a high-voltage TEM with accelerating voltage of 1.25 MV (Jeol ARM-1250, located at the Max-Planck-Institut für Metallforschung in Stuttgart). Observations were performed at specimen temperatures of 800 °C using a Gatan heating stage. Images were recorded with a slow-scan CCD camera. The nanotube behavior was monitored under controlled electron irradiation and usual imaging conditions (1.25 MeV electron energy and beam intensity of ca. $10\ \mathrm{A/cm^2}$).

From the random crisscrossing distribution of individual nanotubes and nanotube bundles on the specimen grid, several contact points could be identified where tubes were crossing and "touching" each other. These arrangements were selected and observed under controlled electron beam conditions. After a few minutes of irradiating two crossing tubes, their merging was observed at the point of contact, resulting in the formation of a junction with an "X" shape (Fig. 1). In other words, the tubes were welded together under the influence of electron irradiation and annealing at their contact region. As depicted schematically in Fig. 1, during the formation of the present junction, the upper "arms" of the X junction cross over and protrude out of the plane.

The ready-formed X junctions can be manipulated in order to create Y- and "T"-like molecular connections (Figs. 2 and 3). It has been established from earlier work [24] that continuous sputtering of carbon atoms from the nanotube body takes place during irradiation, leading to dimensional changes and surface reconstructions. By using careful conditions of irradiation, we are able to remove one of the "arms" of an X junction in order to create a Y or T junction (Figs. 2 and 3). This indicates that controlled electron irradiation can tailor the transformation of the junction geometry; this tool may be used to generate arrangements with three, four, or even more terminals if the precursor crossing configurations of SWNTs can be prepared. As shown in Figs. 1 and 2, the tube diameters within the junction can be different. It needs to be pointed out that the angle between the tubes cannot be measured

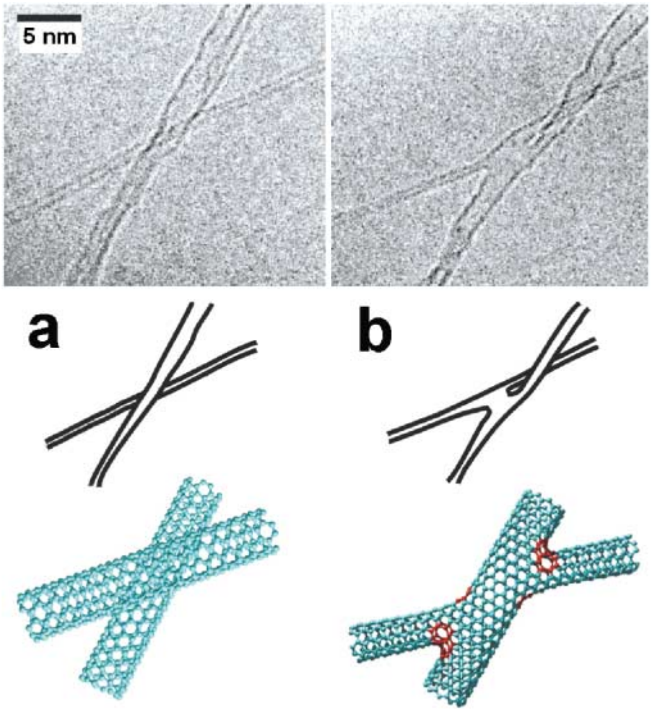

FIG. 1 (color). (a) A SWNT of ca. 2.0 nm diam (running from bottom-left diagonally towards top right) crossing with an individual SWNT of ca. 0.9 nm diam. (b) 60 sec of electron irradiation promotes a molecular connection between the thin and the wide tube, forming an "X" junction. Schematics show that this junction is twisted out of the plane. Molecular models of each image are provided; heptagonal rings are indicated in red.

directly here because we obtain only a projection of the junction in the image plane. It is noteworthy that these molecular geometries remain stable over a surprisingly long period of irradiation (Fig. 3). In some cases, when the junctions are not attached to their surroundings, the arrangements are observed to rotate, for example, into a mirror geometry (Fig. 3). Although the experimentally obtained junctions appear to a certain extent defective and their atomic arrangement might deviate slightly from the idealized molecular models shown in Figs. 1–3, the observed junctions show the expected topologies.

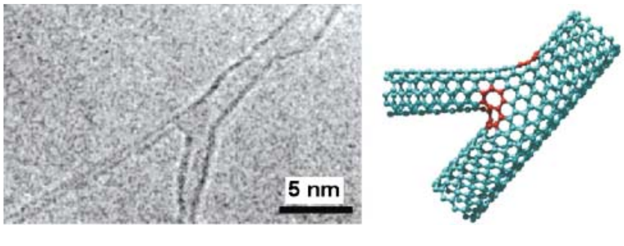

FIG. 2 (color). High-resolution transmission electron microscopy image and molecular model of a Y junction created following electron irradiation of an "X" structure. One of the arms of the "X" junction vanished due to continuous sputtering under the electron beam, and a three-terminal junction remained. The junction exhibits tubes of different diameters which are molecularly joint.

Since the merging of crossing tubes did not occur in the absence of irradiation, we conclude that electron beam effects are responsible for the formation of the junctions. It is well known that knock-on displacements of carbon atoms, i.e., the formation of vacancies and interstitials, induce rearrangements within graphitic structures under high-energy particle irradiation [25]. At the high specimen temperature of 800 °C in these experiments, carbon interstitials are highly mobile, leading to the annealing of vacancy-interstitial pairs before interstitial agglomerates can form. It is important to emphasize that electron irradiation at room temperature would rapidly lead to heavy radiation damage of the tubes. It has already been demonstrated that the coalescence of individual SWNTs placed in parallel within a bundle can occur when vacancies are present in the tubes [26]. Thus, we assume that the presence of irradiation-induced vacancies within the tubes is also responsible for the formation of junctions (see theoretical results below). Dangling bonds around vacancies at the point of contact of the two tubes can serve as bridges for the merging process. Rearrangement of carbon atoms occurs so as to form heptagonal or octagonal rings at the common surfaces, thus introducing negative curvature (shown in red in Figs. 1–3) [12–16,27].

It is remarkable that irradiation with energetic particles, which is generally believed to create more damage than order, can induce self-assembly processes in graphene cylinders such as to form a ramified network. As has been shown in earlier work [25], irradiation of graphitic

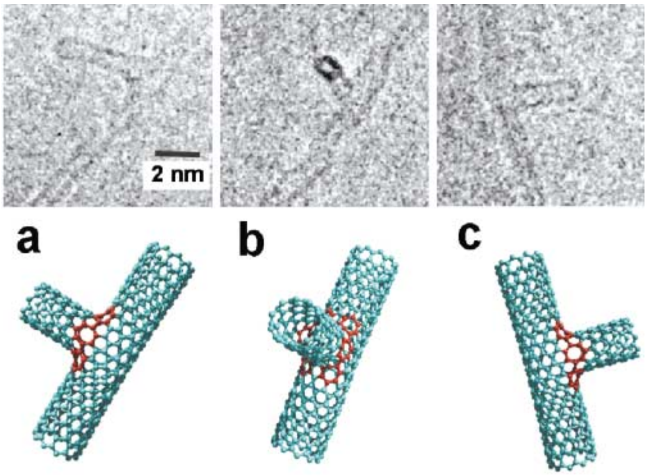

FIG. 3 (color). (a)–(c) HRTEM images of a "T"-like" junction formed after irradiating a preformed Y junction. This junction may not be a perfect "T" (90° angle between the crossing tubes) because we observe the projection of the object. The sequence shows the motion of this junction and the rotation by 180° under the electron beam; note the circular cross section in one of the tubes (b). Atomic models of the junctions are depicted below.

nanoparticles such as tubes or onions can lead to the self-organized formation of ordered structures, in particular, at high specimen temperatures where radiation defects anneal during the irradiation period. Although the regions of the tubes just around the junction are unavoidably affected by the irradiation, preliminary local density of states calculations on perfect and defective junctions [28] indicate that the altered tubes would still show semiconducting or metallic behavior.

In order to understand the formation mechanism of these molecular junctions, tight binding molecular dynamics (TBMD) calculations [29] were carried out. An energy functional and a parametrization, which has proved successful in the modeling of various carbon nanostructures [30], were used. The simulation of two crossing tubes under irradiation at 1000 °C reveals the nanotube merging process, resulting in an almost perfect molecular junction (Fig. 4). In the present experiments, each carbon atom is displaced by knock-on collisions with the high-energetic electrons approximately every 100 sec. In order to include these irradiation effects, 20 atoms [Fig. 4(a)] were removed randomly from the lattices of two (8,8)-nanotubes, thus creating vacancies in the crossing region. The unit cell contains 860 carbon atoms (white, yellow, green, blue, and red spheres, illustrating an atomic coordination of 0, 1, 2, 3, and 4, respectively). Periodic boundary conditions are imposed along both nanotube axes. TBMD calculations were performed using a time step of 0.7 fs to assure optimal integration of equations of motion and energy conservation. The total simulation time is 220 ps. The two nanotubes were heated up to a temperature of 1000 °C in order to accelerate the creation of interlinks and surface reconstruction. After 10 ps, the crossing tubes approach each other and the dangling bonds start to connect via carbon chains [Fig. 4(b)]. After 100 ps, the connection between the crossing tubes is clearly established, although both sp^3-atoms and dangling bonds are still present at the intersection [Fig. 4(c)]. After 220 ps, a complete surface reconstruction takes place, leading to the creation of an X junction, mainly constituted by sp^2-carbons [Fig. 4(d)]. Both heptagons and octagons are present in the reconstructed surface. The key role played by these rings is certainly to increase the energetic stability of the structure when compared to that shown in Fig. 4(c), as well as to introduce a smooth negative curvature. The present simulation provides a clear picture of an intermediate state of the ‘‘welding’’ process. However, the experimentally observed merging occurs on time scales of seconds or even minutes, and the calculation of the whole process, until the arrangement has reached a final and stable configuration, is too extensive to be carried out within a reasonable time scale. The energy of the system is found to decrease during the formation of a junction. The final arrangement of the merged tubes as obtained in the MD calculation [Fig. 4(d)] is 189 eV lower than the starting configuration, i.e., two individual (8,8) tubes, containing together 20 vacancies [Fig. 4(a)]. The lowering in energy of the system can thus be regarded as a driving force to promote the formation of a junction.

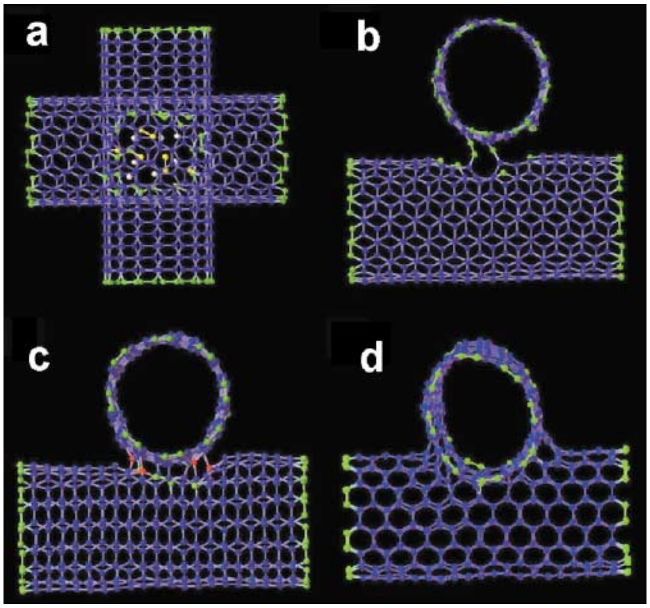

FIG. 4 (color). Sequences of merging between two crossing (8,8) carbon nanotubes (diameter ca. 1.1 nm) into a unique X-like junction. (a) The TBMD simulation starts with the random creation of 20 vacancies in the lattices of two tubes in the localized neighboring region (top view). (b) After 10 ps, two links between the two defective carbon structures are formed via carbon chains (side view). (c) After 100 ps, the connection between the two tubes is established, although some sp^3-carbon atoms (red) and dangling bonds (green) are still remaining. (d) After 220 ps, surface reconstruction occurs and the carbon system approaches an X junction. The reconstructed surface contains six heptagons, one octagon, one pentagon, and two dangling bonds.

To conclude, the *in situ* experiments demonstrate that junctions can be established between individual SWNTs and can be fabricated by using high-temperature electron beam ‘‘nano-welding’’ of crossing tubes. This technique can be regarded as an alternative to possible chemical functionalization, which, on the other hand, has limitations to provide epitaxial SWNT junctions that are mechanically robust. The junctions described here are created via vacancies and interstitials, induced by the focused electron beam, that promote the formation of internanotube links. The results suggest that it may now be possible to construct nanotube networks by growing cross-linked SWNTs followed by controlled electron irradiation at high temperature. The electrical characterization of SWNT junctions is imperative and remains a challenge for future experiments. In the present study, an electron beam with a rather large diameter (several 100 nm) was used; however, field emission electron guns available nowadays could permit controlled irradiation of small specimen regions on the nanometer scale and, hence, to prevent drastic alteration of the tubes outside the junction and to tailor SWNT junctions with higher selectivity. The geometrical perfection of the junctions could be further increased by high-temperature annealing after the welding process.

We thank the Royal Society (N. G.), the JFCC-Japan (N. G.), CONACYT-Mexico Grants No. W-8001-millennium initiative, No. G-25851, No. 36365-E, No. 37589-U (H. T., M. T.), the FNRS of Belgium and the European Union: COMELCAN project Contract No. N HPRN- CT-2000-00128 (J. C. C.), and CNT-NET project Contract No. N G5RT-CT2001-05026 (M. T.), for financial support. We are indebted to M. Rühle, F. Phillipp, and R. Höschen for the hospitality, assistance, and facilitating the use of the electron microscope based in Stuttgart. P. M. A. acknowledges funding from focus center for Interconnects at Rensselaer Polytechnic Institute funded by DARPA, MARCO, and NY state, and the NEDO international joint research grant on nano-integration system.

---

*Corresponding author.
Email address: Florian.Banhart@physik.uni-ulm.de

[1] P.M. Ajayan and T.W. Ebbesen, Rep. Prog. Phys. **60**, 1025 (1997).
[2] M. Terrones, W.K. Hsu, H.W. Kroto, and D.R.M. Walton, Top. Curr. Chem. **199**, 189 (1999).
[3] M.S. Dresselhaus and P. Avouris, Top. Appl. Phys. **80**, 1 (2001).
[4] S.J. Tans *et al.*, Nature (London) **386**, 474 (1997).
[5] J.W.G. Wilder *et al.*, Nature (London) **391**, 59 (1998).
[6] T.W. Odom, J.-L. Huang, P. Kim, and C.M. Lieber, Nature (London) **391**, 62 (1998).
[7] Z.K. Tang *et al.*, Science **292**, 2462 (2001).
[8] M.M.J. Treacy, T.W. Ebbesen, and J.M. Gibson, Nature (London) **381**, 678 (1996).
[9] M.R. Falvo *et al.*, Nature (London) **389**, 582 (1997).
[10] S.J. Tans, A.R.M. Verschueren, and C. Dekker, Nature (London) **393**, 49 (1998).
[11] Z. Yao, H.W.C. Postma, L. Balents, and C. Dekker, Nature (London) **402**, 273 (1999).
[12] L.A. Chernozatonskii, Phy. Lett. A **170**, 37 (1992).
[13] G.E. Scuseria, Chem. Phys. Lett. **195**, 534 (1992).
[14] G. Treboux, P. Lapstun, and K. Siiverbrook, Chem. Phys. Lett. **306**, 402 (1999).
[15] M. Menon and D. Srivastava, Phys. Rev. Lett. **79**, 4453 (1997).
[16] A.N. Andriotis, M. Menon, D. Srivastava, and L. Chernozatonskii, Phys. Rev. Lett. **87**, 6802 (2001).
[17] J. Li, C. Papadopoulos, and J. Xu, Nature (London) **402**, 253 (1999).
[18] B.C. Satishkumar, P.J. Thomas, A. Govindaraj, and C.N.R. Rao, Appl. Phys. Lett. **77**, 2530 (2000).
[19] X.C. Ma and E.G. Wang, Appl. Phys. Lett. **78**, 978 (2001).
[20] P. Nagy, R. Ehlich, L.P. Biro, and J. Gyulai, Appl. Phys. A **70**, 481 (2000).
[21] J.-M. Ting and C.-C. Chang, Appl. Phys. Lett. **80**, 324 (2002).
[22] C. Journet *et al.*, Nature (London) **388**, 756 (1997).
[23] P. Nikolaev *et al.*, Chem. Phys. Lett. **313**, 91 (1999).
[24] P.M. Ajayan, V. Ravikumar, and J.-C. Charlier, Phys. Rev. Lett. **81**, 1437 (1998).
[25] F. Banhart, Rep. Prog. Phys. **62**, 1181 (1999).
[26] M. Terrones, H. Terrones, J.-C. Charlier, F. Banhart, and P.M. Ajayan, Science **288**, 1226 (2000).
[27] A.L. Mackay and H. Terrones, Nature (London) **352**, 762 (1991).
[28] J.-C. Charlier *et al.* (to be published).
[29] S. Goedecker and L. Colombo, Phys. Rev. Lett. **73**, 122 (1994).
[30] C.H. Xu, C.Z. Wang, C.T. Chang, and K.M. Ho, J. Phys. Condens. Matter **4**, 6047 (1992).