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Effect of coiling on the electronic properties along single-wall carbon nanotubes

P. Castrucci,[a),b)] M. Scarselli, and M. De Crescenzi
Dipartimento di Fisica, Unità INFM, Università di Roma "Tor Vergata," Via della Ricerca Scientifica 1, 00133 Roma, Italy

M. A. El Khakani,[a),c)] F. Rosei, N. Braidy, and J.-H. Yi
Institut National de la Recherche Scientifique, INRS-Énergie, Matériaux et Télécommunications 1650, Blvd. Lionel-Boulet, C.P. 1020, Varennes, Québec J3X-1S2, Canada

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Straight and coiled single-wall carbon nanotubes (SWCNTs) synthesized by laser vaporization were dispersed on highly oriented pyrolitic graphite. Their morphology and electrical properties were investigated by scanning tunneling microscopy (STM). STM images revealed that the SWCNTs (either straight or coiled) often self-organize into bundles of two or more tubes and are rarely found alone. The conductance measured along a periodically coiled CNT was found to increase at locations where the CNT is squeezed, while it decreases significantly in unsqueezed regions characterized by an unperturbed hexagonal network. This provides experimental evidence of significant conductance modulation along a one-dimensional system on the nanometer scale. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1809277]

One-dimensional systems such as nanowires and nanotubes[1,2] exhibit interesting properties, and represent promising building blocks for the future generations of devices. Carbon nanotubes (CNTs) are among the most widely investigated nanostructures because of their outstanding mechanical,[2] electrical,[3] and chemical[4,5] properties. In particular, their ability to transport charge carriers with high efficiency makes them highly attractive for use as components in nanoelectronics[3] and nanophotonics.[6,7] Soon after the discovery of straight CNTs made of a perfectly rolled defect-free graphitic layer,[8] other CNT morphologies were observed, namely Y branches,[9] bent,[10,11] twisted,[12] and coiled nanotubes.[13] Theoretical calculations showed that, as a result of the structural distortion, the local electronic properties of CNTs are strongly modified.[14–16] Perfectly straight nanotubes are known to act as ballistic conductors, able to carry large current densities, whereas conduction electron scattering at distorted regions may cause electron localization. Numerous theoretical and experimental studies have been performed on twisting and bending effects on metallic straight CNTs.[11,14] In particular, the opening of an energy gap has been predicted when bending exceeds a critical value or in twisted nanotubes.[14] This gap was ascribed to asymmetric compression and dilation of C–C bonds along the nanotubes. A recent theoretical study investigated the stability of CNTs constituted of several straight sections of decreasing diameter joined by topological defects, i.e., pentagon and heptagon pairs.[17] This work predicted the possibility of obtaining a sequence of metal/semiconductor junctions occurring at topological defects.[17]

In this letter, we report the experimental observations that confirm the above-described theoretical predictions.[11,14,17] Single-wall carbon nanotubes (SWCNTs) produced by pulsed laser vaporization were dispersed on highly oriented pyrolitic graphite (HOPG) and observed by scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). STM analysis reveals the presence of both straight and coiled nanotubes, generally self-organized into bundles consisting of two or more tubes. Occasionally two coiled nanotubes appear to be tightly bound (i.e., well coiled around each other in a twisted pair, like a DNA double helix). By studying the electronic properties of these twisted nanotubes with their alternating and oscillating stressed regions, we provide experimental evidence of a significant conductance modulation along these one-dimensional (1D) systems. A dramatic change in the local electrical behavior of the coiled tubes occurs in correspondence to squeezed and unsqueezed regions, thus forming a system with several junctions on the nanometer scale.

The SWCNTs[18] were produced by ablating a CoNi-doped graphite target, using a pulsed Nd:YAG laser in the superposed double pulse configuration.[19] The target, placed in a quartz tube at the center of a furnace, was ablated with a laser intensity of $\sim 2.5 \times 10^9 \mathrm{W/cm^2}$, at $T = 1150\ ^\circ\mathrm{C}$ in a flowing Ar gas.[19,20] The synthesis product was collected on a water-cooled surface at the furnace exit. A droplet of the raw synthesis product diluted in isopropyl was used to disperse the nanotubes on an HOPG substrate after its peeling-off to obtain fresh carbon atomic planes.[21,22] STM measurements were performed at room temperature in an ultrahigh vacuum chamber (base pressure $\sim 8.5 \times 10^{-11}$Torr) by using an OMICRON STM/AFM apparatus.[23]

The STM observations revealed that the SWCNTs generally self-organize into bundles of two tubes or more but some of them are found alone [as those shown in Figs. 1(a) and 1(b)]. The STM image of Fig. 1(a) displays a straight nanotube lying across several HOPG planes. An atomically resolved STM image acquired on the surface of the nanotube clearly confirms its graphitic character [inset of Fig. 1(a)]. In Fig. 1(b) we report another STM micrograph of the end of a straight small nanotube, which is found to be particularly smooth [see the line profile plotted along the tube itself, Fig.

[a)]Authors to whom correspondence should be addressed.
[b)]Electronic mail: castrucci@roma2.infn.it
[c)]Electronic mail: elkhakan@inrs-emt.uquebec.ca

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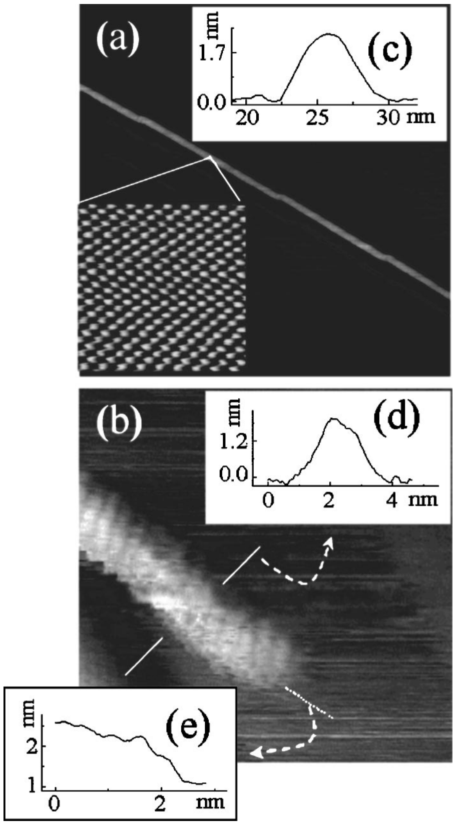

FIG. 1. (a) STM image $(180\times180\ \text{nm}^2)$ showing a straight nanotube that crosses many HOPG planes. Tunneling parameters are $I_t=1$ nA, $V_t=0.1$ V. The inset shows an atomically resolved STM image $(2.5\times2.5\ \text{nm}^2)$ of a surface area of the tube. (b) STM image $(10\times10\ \text{nm}^2)$ of the end part of a small tube. (c) and (d) Line profiles across the tubes shown in Fig (a) and (b), respectively. (e) Line profile along the tube (dashed line) shown in (b).

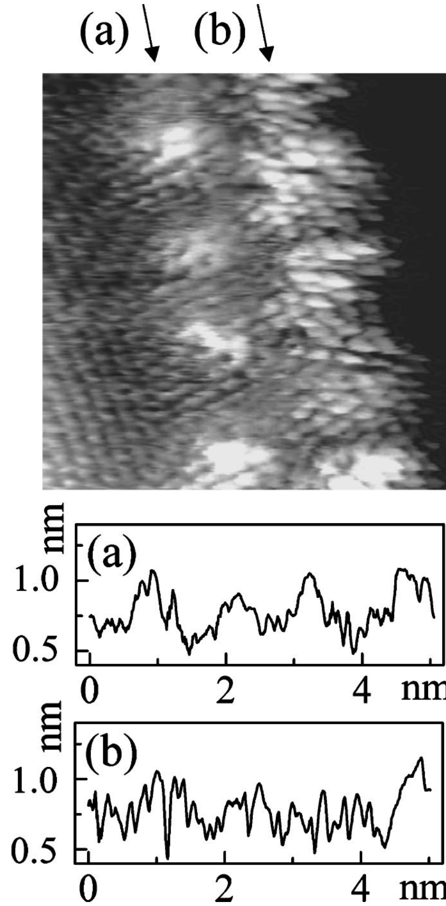

FIG. 2. STM image $(5\times5\ \text{nm}^2)$ of two coiled adjacent nanotubes ($I_t=1$ nA and $V_t=0.1$ V). The lower panel shows the line profiles obtained along the directions indicated by the arrows (a) and (b), respectively.

1(e)]. This means that the end of the tube is somehow capped.[24] The diameters of the tubes shown in Figs. 1(a) and 1(b) are about 5.0 and 1.8 nm, respectively, whereas their measured heights are much smaller [see line profiles in Figs. 1(c) and 1(d), respectively]. This behavior can be ascribed to a strong vertical compression experienced by the tubes, induced by van der Waals interactions between the nanotubes and the HOPG substrate itself (the larger the tube diameter, the stronger the vertical deformation it undergoes). This phenomenon is remarkably similar to that observed for large organic molecules deposited on metal surfaces.[25]

Like the straight tubes, coiled nanotubes frequently appear in bundles of two or more. Sometimes when they are adjacent, the swollen and coiled regions of each tube are in antiphase with respect to each other (they fit like a sort of braid). Figure 2 displays an atomically resolved STM image of two adjacent coiled nanotubes that exhibit this peculiarity. The lower part of Fig. 2 displays the line profiles of these tubes that are characterized by the same periodicity of (1.24 ± 0.05)nm, showing the antiphase behavior in the sequence of valleys and hills along the tube's axis. Figure 3 (central panel) displays another nanotube that is characterized by a double periodicity. This is visible in the line profile along the nanotube's axis (Fig. 3, upper panel), which exhibits an alternating sequence of hills and valleys with a periodicity of approximately 4.2 nm. Two consecutive hills differ in height by about 0.2 nm. We interpret this as a measurement of two coiled nanotubes twisted together. Based on molecular dynamics simulations, coiled nanotubes were predicted by Ihara *et al.*[13] as originating from the regular insertion of pentagons and heptagons in a perfect hexagonal network. By contrast, Birò *et al.*[26] interpreted coiled tubes as haeckelite structures[27] in which pentagons, hexagons, and heptagons all represent equivalent building elements. From atomically resolved STM images we obtained power spectra (not shown here) that show a hexagonal pattern. This demonstrates that the haeckelite structure can be excluded, since it would generate a completely different power spectrum. Thus we suggest that coiling is caused by a sparse distribution of few pentagons and heptagons at the coiling region.

By means of STS, we characterized the electronic properties along this atomically resolved nanotube.[28] In Fig. 3 (lower panel), we display $I-V$ curves obtained by averaging similar curves recorded around the points labeled in the STM image. Curve A corresponds to the $I-V$ signal of clean HOPG, whereas curves $B-D$ are taken at different locations along the tightly bound nanotubes. For the overprotruding regions of this 1D system the behavior is less metallic than that measured at the squeezed regions. This is even more evident in the dI/dV curves obtained by differentiating the I/V curves in Fig. 3. This position-sensitive variation is a peculiar feature of these squeezed nanotubes, in contrast to the conductance of straight nanotubes which was not found to vary significantly along the tubes. This behavior is qualitatively ascribed to the scattering effect that electrons undergo inside the hills, which locally affects their transport properties.[29,30]

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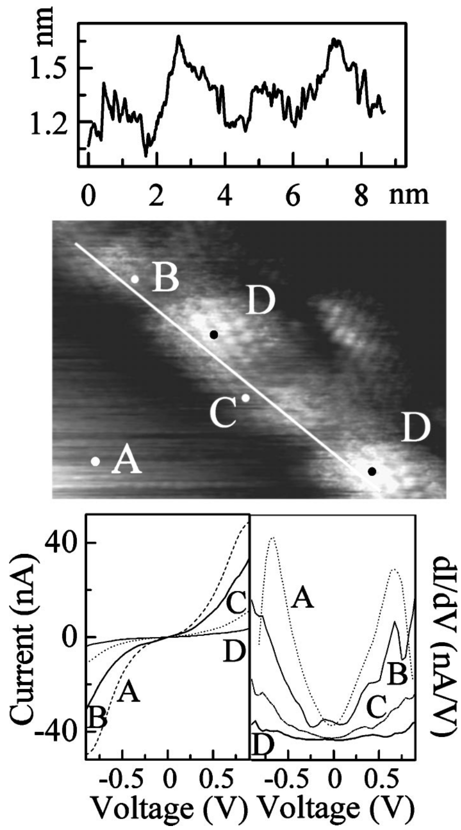

FIG. 3. STM image $(5\times5\ \text{nm}^2)$ showing two coiled nanotubes twisted together. The upper panel shows the line profile along the white line drawn on the STM image. The lower panels show the $I-V$ curves recorded around points A,B,C, and D, respectively, and the corresponding dI/dV curves obtained by differentiation.

In conclusion, coiled and straight CNTs synthesized by laser ablation were dispersed on HOPG and characterized by STM. Straight tubes were found to undergo large squeezing induced by van der Walls forces with the underlying HOPG substrate, and to exhibit a uniform conductance along their axis. By contrast, we measured a significant conductance modulation along the axis of two tightly bound and coiled nanotubes in correspondence to the hills and valley-like regions. This 1D system can therefore be thought of as a sequence of junctions with alternating metallic/semiconducting behavior.

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[1]H. Dai, Surf. Sci. **500**, 218 (2002).
[2]*Carbon Nanotubes: Synthesis, Structures and Applications*, edited by M. S. Dresselhaus, G. Dresselhaus, and Ph. Avouris (Springer, Berlin, 2001).
[3]A. Bachtold, P. Hadley, T. Nakanishi, and C. Dekker, Science **294**, 1317 (2001).
[4]K. Kamaras, M. E. Itkis, H. Hu, B. Zhao, and R. C. Haddon, Science **301**, 1501 (2003).
[5]H. Oudghiri-Hassani, E. Zahidi, M. Siaj, J. Wang, and P. H. McBreen, Appl. Surf. Sci. **212–213**, 4 (2003).
[6]J. A. Misewich, R. Martel, Ph. Avouris, J. C. Tsang, S. Heinze, and J. Tersoff, Science **300**, 783 (2003).
[7]J. Lefebvre, Y. Homma, and P. Finnie, Phys. Rev. Lett. **90**, 217401 (2003).
[8]S. Iijima, Nature (London) **354**, 56 (1991).
[9]A. L. Macky and H. Terrones, Nature (London) **352**, 762 (1991).
[10]M. R. Falvo, G. J. Clary, R. M. Taylor II, V. Chi, F. P. Brooks Jr., S. Washburn, and R. Superfine, Nature (London) **389**, 582 (1997).
[11]T. Hertel, R. E. Walkup, and Ph. Avouris, Phys. Rev. B **58**, 13870 (1998).
[12]W. Clauss, D. J. Bergeron, and A. T. Johnson, Phys. Rev. B **58**, R4266 (1998).
[13]S. Ihara, S. Itoh, and J. Kitakami, Phys. Rev. B **48**, 5643 (1993).
[14]A. Rochefort, Ph. Avouris, F. Lesage, and D. R. Salahub, Phys. Rev. B **60**, 13824 (1999).
[15]C. L. Kane and E. J. Mele, Phys. Rev. Lett. **78**, 1932 (1997).
[16]In fact, while in straight tubes the states accessible for electrical conduction are essentially pure $C(2p_\pi)$ states, the increased curvature induced by bending, twisting, or coiling makes them acquire a $C(2p_\sigma)$ character.
[17]V. Meunier, M. Buongiorno Nardelli, C. Roland, and J. Bernholc, Phys. Rev. B **64**, 195419 (2001).
[18]Raman spectroscopy (using Ar^+ excitation at 514.5 nm) characterizations of these nanotubes revealed the presence of an intense radial breathing mode absorption band centered at 184 cm^{-1}, corresponding to SWCNTs with a diameter of $\sim$1.2 nm, in accordance with high-resolution TEM observations [see Refs. 19 and 20 cited hereafter].
[19]N. Braidy, M. A. El Khakani, and G. A. Botton, Carbon **40**, 2835 (2002).
[20]N. Braidy, M. A. El Khakani, and G. A. Botton, Chem. Phys. Lett. **354**, 88 (2002).
[21]C. Balasubramanian, S. Bellucci, M. De Crescenzi, P. Castrucci, and S. V. Bhoraskar, Chem. Phys. Lett. **383**, 188 (2004).
[22]M. De Crescenzi, P. Castrucci, M. Scarselli, P. S. Chaudari, C. Balasubramanian, T. M. Bhave, S. V. Bhoraskar (unpublished).
[23]The effect of convolution induced by the tip's finite size is estimated to be negligible (less than 0.1 nm), since measurements of HOPG monoatomic steps were very accurate. Typical tunneling parameters were $I_t = 0.2-1.0$ nA and $V_t = 100-200$ mV (bias voltage applied to the sample).
[24]E. Bengu and L. D. Marks, Phys. Rev. Lett. **86**, 2385 (2001).
[25]F. Rosei, M. Schunack, Y. Naitoh, P. Jiang, A. Gourdon, E. Laegsgaard, I. Stensgaard, C. Joachim, and F. Besenbacher, Prog. Surf. Sci. **71**, 95 (2003).
[26]L. P. Birò, R. Ehlich, Z. Osvath, A. Koos, Z. E. Horvath, J. Gyulai, and J. B. Nagy, Mater. Sci. Eng., C **19**, 3 (2002).
[27]H. Terrones, M. Terrones, E. Hernandez, N. Grobert, J.-C. Charlier, and P. M. Ajayan, Phys. Rev. Lett. **84**, 1716 (2000).
[28]J. A. Stroscio and R. M. Feenstra, in *Scanning Tunneling Microscopy*, edited by J. A. Stroscio and W. J. Kaiser (Academic, New York, 1993), p. 95.
[29]A strong modulation of the conductance has been very recently measured by AFM on a bent carbon nanotube: M. Stadermann, Science **301**, 1473 (2003).
[30]M. Ouyang, J.-L. Huang, C. L. Cheung, and C. M. Lieber, Science **291**, 97 (2001).

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