Unzipping of Functionalized Multiwall Carbon Nanotubes Induced by STM

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ABSTRACT Carbon nanotubes (CNTs), functionalized by a cycloaddition reaction, were studied by ultrahigh vacuum scanning tunneling microscopy (STM). The STM images provided evidence for partial or total unzipping of the outer CNT layer. The formation of graphene ribbons was triggered by the STM tip, under specific operating conditions. A model for the unzipping is proposed, based on the perturbation of the π-conjugation along the CNT surface induced by the cycloaddition reaction.

KEYWORDS Carbon nanotube, graphene, cycloaddition reaction, scanning tunneling microscopy

Carbon nanotubes (CNTs) are extraordinary nanomaterials that carry unique functional properties. The sp[2] carbon structure of their concentric cylindrical graphene layers provides them with excellent electrical and thermal conductivity, and high elastic modulus.[1,2] CNTs can withstand high compressive forces and accommodate large deformation levels, all of this without permanent damage to the unique nanotube structure. Furthermore, they have the ability to heal when damaged, or reform, when subjected to specific conditions.[3] Although CNTs are extraordinary by themselves, only a few applications have been reported where they were used as raw materials. Most applications require manipulation, interaction/bonding of the CNTs with other materials, dispersion in solvents or in high-viscosity matrices, with or without orientation, and so forth.[4] These operations are hampered by the chemical inertness of the CNTs surface and by their highly entangled form. Therefore, chemical modification of the outer layer of nanotubes is an approach often used to overcome these problems.[5−9] In a recent application of CNT functionalization, extensive oxidation of CNTs was used as a means to strip graphene ribbons from nanotubes, through unzipping of the outer graphene CNT layer.[10] Here we report on the functionalization of CNTs through a cycloaddition reaction, present scanning tunneling microscopy (STM) evidence of the surface reaction, and demonstrate the potential of this functionalization method for the unzipping of the CNT outer graphene layer under STM conditions, resulting in clean, nonoxidized graphene nano-

ribbons. Our results reveal a general method of producing graphene nanoribbons under well-controlled clean conditions. The absence of oxidation or incorporation of contaminants is of utmost importance for the preservation of the electronic properties of the graphene for further applications.

The functionalization method presented in this work was based on the solvent-free reaction of an α-amino acid, *N*-benzyloxycarbonylglycine (Z-gly-OH) with formaldehyde.[11] This functionalization route reduced the reaction time from five days[5] to two hours, eliminated the use of hazardous solvents and allowed the homogeneous treatment of large batches of tens of grams of CNTs. Recently, Brunetti et al.[12] reported the modification of nanotubes using this functionalization route, assisted by microwaves. This approach reduced the reaction time to one hour, but it was still limited to small scale science related production. In the present work the reaction mixture (amino acid + paraformaldehyde + CNTs) was heated in the solid state, generating a 1,3-dipole that reacts with the CNT surface to originate the cyclic protected amine (**1**), as represented in Scheme 1. Above 453−473 K, partial thermal cleavage of the protecting group leads to the pyrrolidine (**2**). The product ratio obtained (compound **2** to compound **1**) increases with reaction temperature.

The CNTs used in this study were functionalized under solvent-free conditions at 483 K for seven hours and were analyzed by thermogravimetric analysis (TGA). The observed weight loss was mainly due to the degradation of the organic groups bonded to the CNTs, since, under nitrogen atmosphere, the CNT structure is stable in the temperature range of 323−973 K. An increase in weight loss of approximately
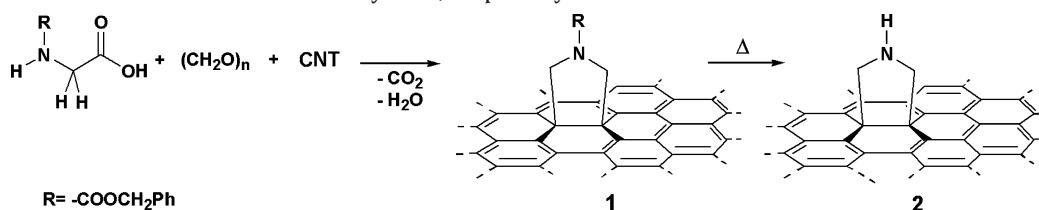

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SCHEME 1. Functionalization of the CNT Surface by the 1,3-Dipolar Cycloaddition Reaction

R= -COOCH₂Ph

20% for the functionalized CNTs relative to the nonfunctionalized was observed.

The X-ray photoelectron spectroscopy (XPS) studies of the nonfunctionalized CNTs showed that they were formed by carbon and residual oxygen (0.008 O atomic ratio). The XPS studies revealed that the chemical functionalization of the CNTs resulted in the incorporation of nitrogen and oxygen atoms (0.028 N atomic ratio and 0.036 O atomic ratio).[13] Correcting for the initial O content of the nonfunctionalized CNTs evidenced that a similar amount of oxygen and nitrogen, in terms of atomic ratio, was added to the surface. This finding implies that approximately half of the functionalization groups were in the form of product (**1**), still bearing the protecting group of the original amino acid, and the other half were in the form of product (**2**) in the cyclic amine form, considering the protected amine and the pyrrolidine as the main reaction products.

The usual goal of the chemical modification of the CNTs surface is to introduce the right chemical functionality to provide reactivity toward certain compounds, polymers, molecules with biological activity, and so forth. This is expected to facilitate the disentanglement of CNT bundles inside the matrix material, to establish a strong interface, and thus to improve the transfer of the extraordinary properties of the CNTs to the composite. It is also a general consequence of the chemical modification of the CNT surface that the sp² C−C structure will be disrupted to sp³ geometry, thereby weakening the corresponding C−C bonds. This change in the hybridization state of some C atoms of the CNT surface can be detected by STM.

The atomic-scale structure of the CNTs deposited on highly oriented pyrolytic graphite (HOPG) surfaces was revealed by STM. The detailed STM studies were carried out with the Aarhus STM[14] operated under ultrahigh vacuum (UHV) conditions. A typical STM image of a bare CNT region, without chemical functionalization, is depicted in Figure 1. The perfect graphene surface of the CNT with a diameter of approximately 7 nm appears very smooth and featureless in the STM images.

The functionalized regions along the CNT could be identified directly from the STM images by the presence of bright protruding patterns along the CNT surface as revealed in Figure 2. STM observations of functionalized CNT described in the literature comprise acid treated CNT, showing bright spot patterns;[15] after nucleophilic addition of *t*-BuLi to the CNT sidewalls, large protruding areas were observed that

were assigned to the *t*-butyl groups bonded to the CNT surface;[16] images of noncovalently functionalized CNT presented protrusions identified as the adsorbed molecules at the CNT surface.[17] In the present work the patterns observed are tentatively interpreted as resulting from the chemical modification of the CNT surface.

As a consequence of covalent bonding to the outer graphene layer of the CNT, the bond order of the functionalized C atoms decreases, changing the geometry of the C molecular orbitals, resulting in an increase in the bond length and decreasing the bond strength. Under these conditions a functionalized nanotube sidewall will "swell" away from the inner, unmodified part of the tube. The high electrical conductivity of the graphene layer is interrupted at the
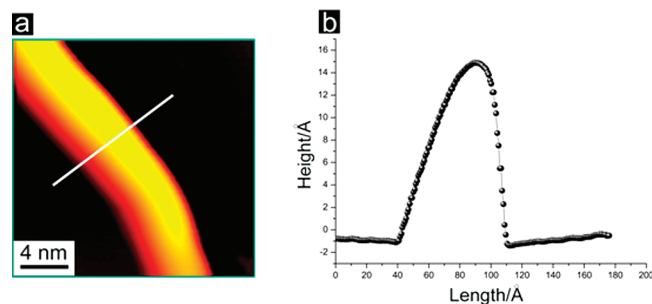

FIGURE 1. (a) STM image of a nonfunctionalized area of a CNT and (b) corresponding line profile, indicating a diameter of approximately 7 nm (scanning condition: It = −2.59 nA, Vt = −320.7 mV).

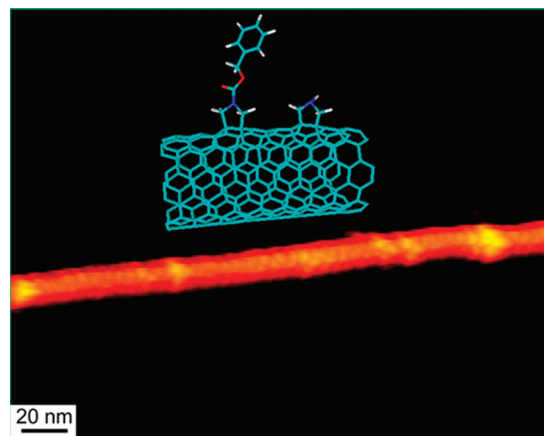**FIGURE 2.** CNT showing evidence of chemical functionalization of the nanotube wall (scanning condition: It = −1.88 nA, Vt = −1444.1 mV).
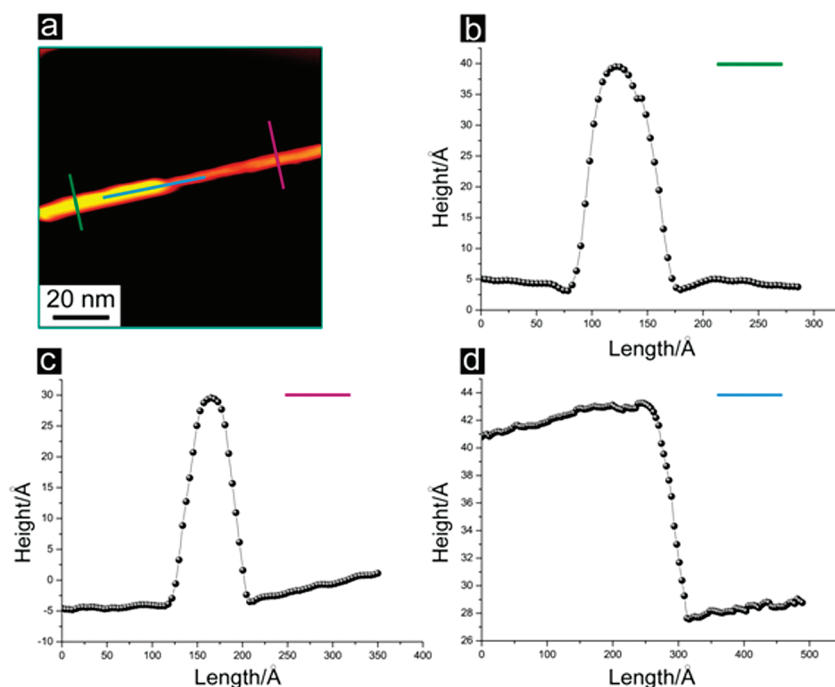
FIGURE 3. (a) Functionalized CNTs showing a discontinued outer graphene layer; (b−d) the nanotube dimensions along the green, purple, and blue lines drawn on image (a), as measured by STM (scanning condition: It = −0.98 nA, Vt = −508.4 mV).

functionalized regions as depicted by the bright patterns observed by STM.

The covalent cycloadduct formed on the CNT sidewall may alter the conjugation pattern of the carbon layer, rendering the CNT prone to physical damage under specific stimuli. Figure 3 depicts an STM image of a functionalized

CNT with a discontinued outer layer. The diameter difference between the thicker and thinner parts of the CNT was determined to be approximately 7.5 Å, representing an interlayer spacing of 3.75 Å, a value close to the interlayer spacing in graphite. This type of irregularities has been observed previously by STM on nonfunctionalized CNTs.[18]
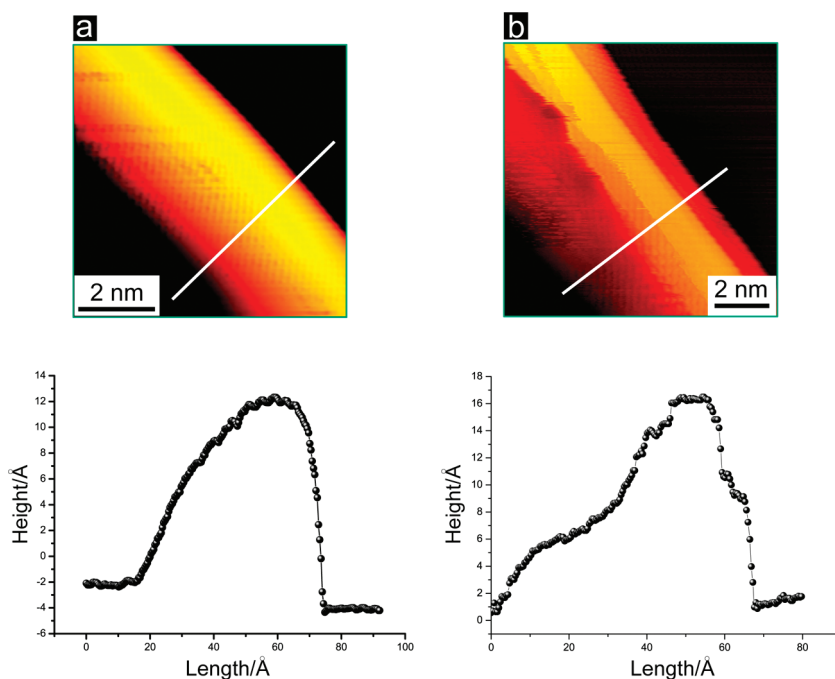

FIGURE 4. (a) STM image of a nonfunctionalized region of a CNT; (b) the "unzipping" of the outer graphene layer of a functionalized CNT; below the images (a) and (b) the dimensions of the nanotube profile along the white line are provided (scanning conditions: (a) It = −2.2 nA, Vt = −7 mV; (b) It = −2.2 nA, Vt = −29 mV).
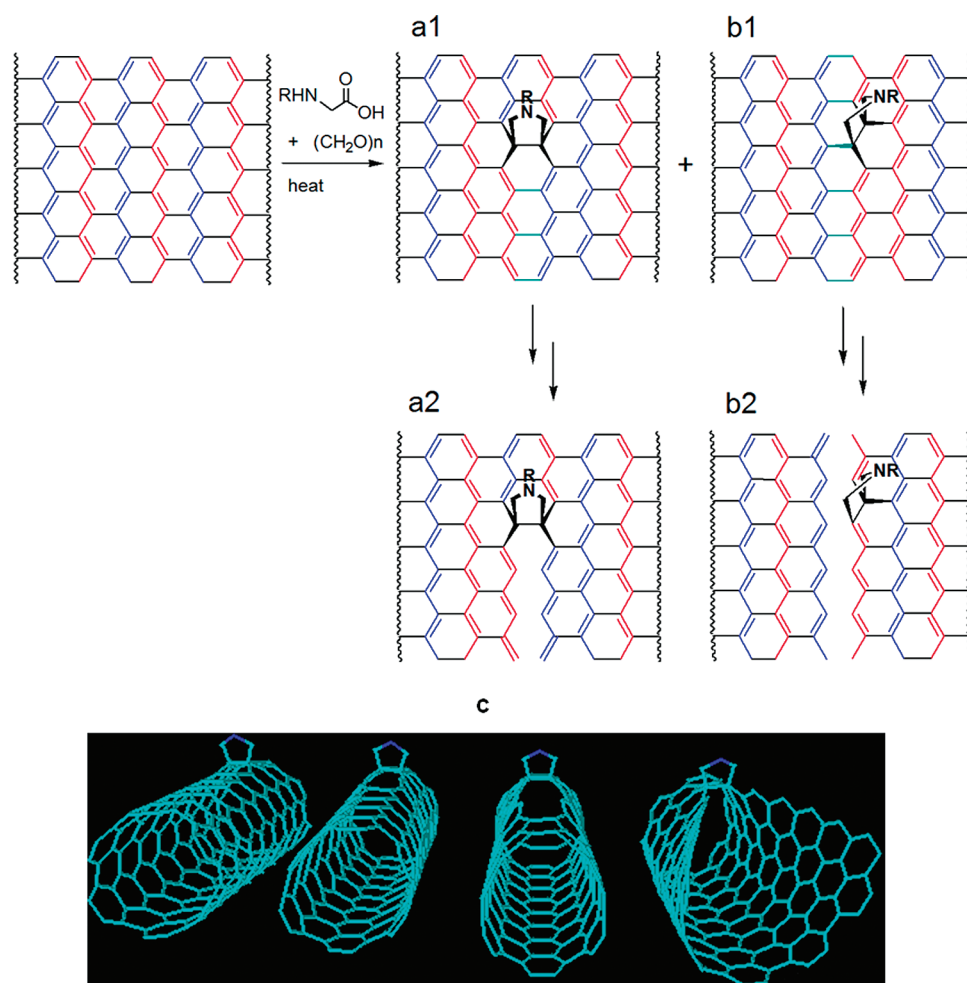
FIGURE 5. Representation of the chemical mechanism for (a) partial and (b) total unzipping of the outer wall of a functionalized CNT and (c) 3D representation of the partial unzipping depicted in (a).

Very interestingly, we demonstrate in Figure 4b that unzipping of the outer graphene layer of the functionalized CNTs induced during the in situ STM manipulation is feasible. The external graphene layer was peeled away from the CNT, exposing the layer underneath. As a comparison, the nonfunctionalized CNT (shown in Figure 4a) was still stable under the manipulation process. Notice that the unzipping process could only be induced under the conditions required for atomic resolution STM imaging of the CNT (i.e., at high tunnel current and low bias voltage). The STM image shown in Figure 4b demonstrates that the whole segment of the CNT was unzipped (propagating about 15 nm along the CNT in the observed region) rather than at the defect points only. Thus we consider that the unzipping process under the STM manipulation is not a local process and should occur along the whole tube.

Recently, the formation of graphene ribbons by unzipping of CNTs was described,[10] and a mechanism based on the graphene oxidation by $KMnO_4/H_2SO_4$ treatment was proposed. Theoretical calculations supported this unzipping mechanism, triggered by permanganate addition to a C—C bond of the CNT surface. This defect weakens the neighboring C—C bonds, making them more prone to further oxidation reactions that cascade along the length of the CNT and ultimately result in bond breaking.[19]

In the present work the observed unzipping of the outer layer of the functionalized CNT was triggered by the interaction of the STM tip with the two tetrahedral sp^3-hybridized carbon atoms in adjacent positions, formed by the cycloaddition reaction. A possible interpretation of this unzipping process is that the two adjacent sp^3-hybridized carbon atoms disrupt the π-conjugation along the CNT, originating a row of slightly elongated carbon—carbon bonds along the CNT length. This perturbation may act along one side of the functionalized C atoms (Figure 5, a1) or along both sides (Figure 5, b1), depending on the original position of the cycloadduct on the CNT surface. This new set of slightly elongated carbon—carbon bonds along the CNT is more susceptible to cleavage if enough energy is supplied by an external source, such as under the STM conditions, leading to preferential lines of partial or total unzipping (Figure 5, a2 and b2, respectively). A clear consequence of partial unzipping is the elimination of part of the outer graphene layer, as observed in Figure 3a.

The use of a high energy ultrasonic tip in a solution/suspension of functionalized CNT may have a similar unzipping effect. In fact, the STM samples prepared by this technique using functionalized CNTs could not be observed by STM due to the presence of large amounts of an unidentified "debris" (as described in the Supporting Information) that could be due to the formation of large amounts of graphene ribbons.

In summary, CNT nanotubes were functionalized by a cycloaddition reaction, and the functionalized CNT surface was imaged by STM. By means of in situ STM manipulation, we have shown that it is possible to unzip graphene layers of functionalized CNTs. A model for the unzipping mechanism was proposed, based on the perturbation of the π-conjugation along the CNT, induced by the cycloadduct and its interaction with the energy supplied by the STM tip. This model is applicable to any cycloaddition reaction to the CNTs, opening a new purpose for this type of CNT functionalization, and a new way of producing graphene ribbons of controlled size. In the present work, the CNT unzipping was achieved under clean reaction conditions, without oxidation of the graphene edges or the presence of contaminants. This is an important requirement for the preservation of the electronic properties of the graphene.

Supporting Information Available. The experimental procedure for the functionalization of the carbon nanotubes, for the STM sample preparation method, and STM analysis conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

(1) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787.

(2) de Heer, W. A. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 355.

(3) Jin, C.; Suenaga, K.; Iijima, S. Plumbing carbon nanotubes. *Nat. Nanotechnol.* **2008**, *3*, 17.

(4) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95.

(5) Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* **2002**, *124* (5), 760.

(6) Holzinger, M.; Vostrowsky, O.; Hirsch, A.; Hennrich, F.; Kappes, M.; Weiss, R.; Jellen, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 4002.

(7) Delgado, J. L.; Cruz, P.; Langa, F.; Urbina, A.; Casado, J.; Navarrete, J. T. L. *Chem. Commun.* **2004**, 1734.

(8) Proença, M. F.; Araújo, R. F.; Paiva, M. C.; Silva, C. J. R. *J. Nanosci. Nanotechnol.* **2009**, *9*, 6234.

(9) Saito, T.; Matsushige, K.; Tanaka, K. *Physica B* **2002**, *323*, 280.

(10) Kosynkin, D. V.; Higginbotham, A. L.; Sinitskii, A.; Lomeda, J. R.; Dimiev, A.; Price, B. K.; Tour, J. M. *Nature* **2009**, *458*, 872.

(11) Araújo, R. F.; Paiva, M. C.; Proença, M. F.; Silva, C. J. R. *Compos. Sci. Technol.* **2007**, *67*, 806.

(12) Brunetti, F. G.; Herrero, M. A.; Munoz, J. M.; Diaz-Ortiz, A.; Alfonsi, J.; Meneghetti, M.; Prato, M.; Vazquez, E. *J. Am. Chem. Soc.* **2008**, *130* (25), 8094.

(13) Novais, R. M.; Ferreira, T.; Oliveira, B. A.; Paiva, M. C.; Pötschke, P.; Pleul, D.; Simon, F. *Chemical functionalization of carbon nanotubes by the 1,3-dipolar cycloaddition reaction: the effect of temperature*, Carbon 2009 Conference Proceedings, T6−845: Biarritz, France, 14−19 June 2009.

(14) Laegsgaard, E.; Osterlund, L.; Thostrup, P.; Rasmussen, P. B.; Stensgaard, I.; Besenbacher, F. *Rev. Sci. Instrum.* **2001**, *72*, 3537.

(15) Nemes-Inczea, P.; Tapasztó, L.; Darabont, Al.; Lambinc, Ph.; Biró, L. P. *Carbon* **2009**, *47*, 764.

(16) Graupner, R.; Abraham, J.; Wunderlich, D.; Vencelová, A.; Lauffer, P.; Röhrl, J.; Hundhausen, M.; Ley, L.; Hirsch, A. *J. Am. Chem. Soc.* **2006**, *128* (20), 6683.

(17) Lauffer, P.; Jung, A.; Graupner, R.; Hirsch, A.; Ley, L. *Phys. Status Solidi B* **2006**, *243* (13), 3213.

(18) Méndez, A.; Freitas, M. M. A.; Villar-Rodil, S.; Paredes, J. I.; Martínez-Alonso, A.; Tascón, J. M. D.; Figueiredo, J. L. *Mater. Lett.* **2007**, *61*, 4787.

(19) Rangel, N. L.; Sotelo, J. C.; Seminario, J. M. *J. Chem. Phys.* **2009**, *131*, No. 031105.

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