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STM investigation of carbon nanotubes connected by functional groups

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Abstract

Chemical functionalization of carbon nanotubes (CNTs) is essential for many applications. Attachment of functional groups to nanotubes can dramatically increase the solubility of the nanotube material. Sidewall functional groups should react with polymers and improve the mechanical properties of nanocomposites. Tubes interconnected by chemical bonds will have a reduced contact resistance and can be used for interconnection purposes in nanoscale circuits. Carbon nanotubes covered with functional groups attached to their exterior wall were analyzed using scanning tunneling microscopy (STM) and TEM. The functionalization was carried out in three steps: acid treatment in H_2SO_4/HNO_3 (3:1) mixture, reaction with $SOCl_2$ and reaction with diaminopropanol (DAP). The binding force between the nanotubes connected by functional groups and the mechanical stability of the connection was investigated.

Keywords: Carbon nanotube; Functional groups; Scanning tunneling microscopy

1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 [1], many potential applications have been suggested due to their extraordinary mechanical [2–5] and electronic properties [6–9]. The functionalization of carbon nanotubes may extend the range of their potential applications. The electric properties of CNTs can be modified using chemical functionalization and the contact resistance between the interconnected tubes can be reduced by chemically binding functional groups. Suitable functionalization enables the linking of individual carbon nanotubes to form complex networks for nanoscale electronic circuits [10]. The functionalization solubilizes the nanotubes in a variety of solvents [11,12], allows chemical manipulations and improves the dispersion in composite applications. In nanocomposites, the functional groups attached to the walls of CNTs can form strong chemical bonds with the surrounding polymer matrix, increasing the binding force between the nanotube and polymer [13,14]. In recent papers, the first successful interlinking of functionalized MWCNTs were reported [10,15]. In the present paper, we investigate MWCNTs completely covered with functional groups. Because of the complete coverage with functional groups the probability of interconnections is increased. The functionalization of sidewalls is a difficult task because there are not reactive dangling bonds on the walls. Scanning tunneling microscopy (STM) and spectroscopy (STS) was used to investigate the efficiency of the functionalization method and the influence of functional groups on the electronic properties of nanotubes, respectively. The presence of connected nanotubes was examined using TEM. The strength of the binding force between the connected nanotubes was investigated by manipulation with the STM tip.

2. Experiment

MWCNTs were synthesized by catalytic decomposition of acetylene on alumina supported Co/Fe catalyst as described in Ref. [16]. The purified nanotube sample was functionalized using a three-step chemical treatment [17]. In the first step, the sample was treated in H_2SO_4/HNO_3 (3:1) mixture for 24 h at room temperature. This treatment attaches –COOH groups to the CNT surface. After this

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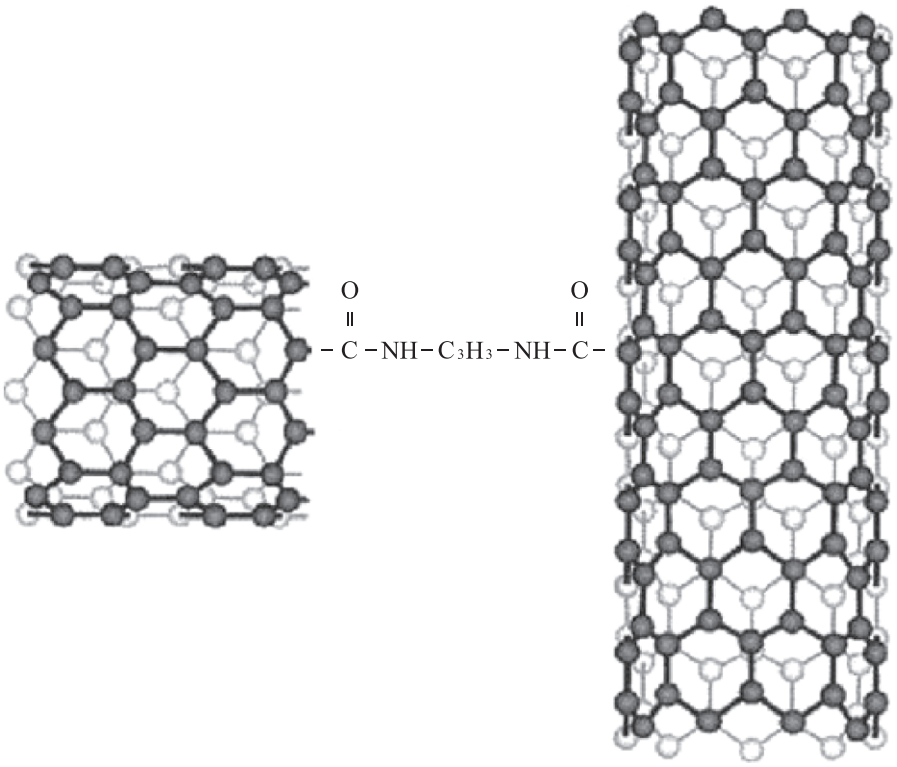

Fig. 1. Schematic representation of an end-to-side junction. The nanotubes are connected via diaminopropane.

treatment, the MWCNTs were mixed in $SOCl_2$ overnight, in order to transform the –COOH groups connected to nanotube surface in –COCl groups. Finally, the nanotube sample was mixed in diaminopropane (DAP) at for 24 h. The diaminopropane connects the functional groups attached to the nanotubes, and in this way interconnects the nanotubes. Fig. 1 shows the schematic representation of an end-to-side junction.

The STM investigation was performed with a DI Nanoscope E STM/AFM instrument in air using commercial Pt/Ir tips with set point currents of 200 pA at a bias of 1 V. The nanotubes were ultrasonicated in isopropanol and droplets

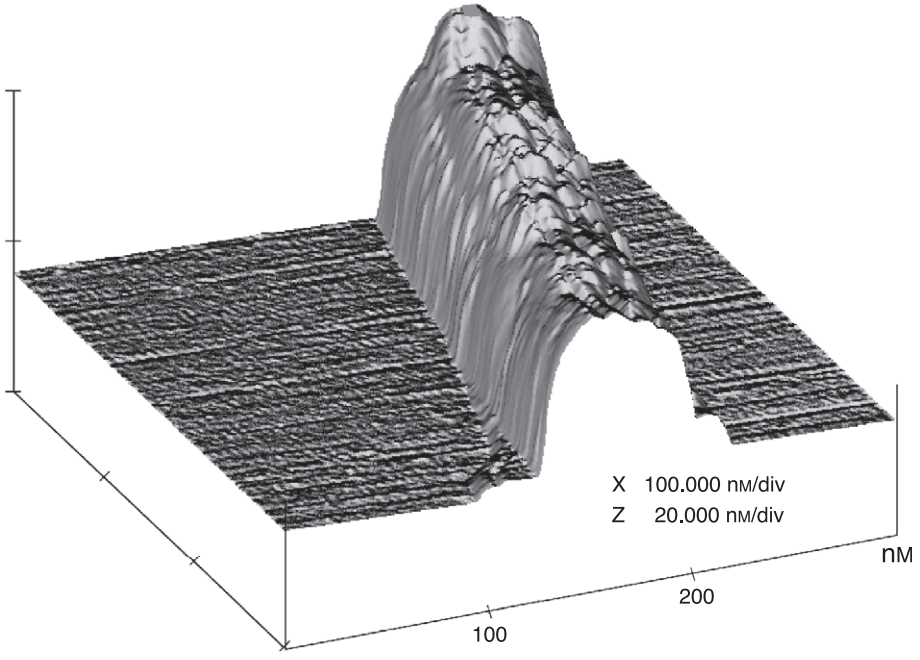

Fig. 2. 3D topographic STM image of MWCNTs covered with functional groups.

of the suspension were placed on highly oriented pyrolytic graphite (HOPG) or Au evaporated onto mica. The connected nanotubes were investigated with a Philips CM 200 (200 kV) TEM.

In order to get insight in the way in which the functionalization took place, the surface of the nanotubes was investigated by STM [18]. Our previous investigations showed that in case of nanotubes functionalized by ball milling in reactive atmosphere the functional groups are attached to defects on the surface in a grouped-together way [19]. The STM investigation of nanotubes after the three-step chemical treatment showed that, opposite to ball milling, the whole surface of the nanotubes was covered with functional groups. The continuous coverage is the consequence of the high density of defect sites on the nanotube surface. Some of these defects may originate from the CVD growth itself, but we have no reason to assume that this would be significantly different from the defect density of the carbon nanotubes used for ball milling experiments. The number of anchoring points for the functional groups incorporated during the CVD process was significantly increased by the applied chemical treatment. The average distance between the defects decreased to a few nanometers; therefore, the "islands" of functional groups are touching each other. A typical nanotube from this sample is shown in Fig. 2.

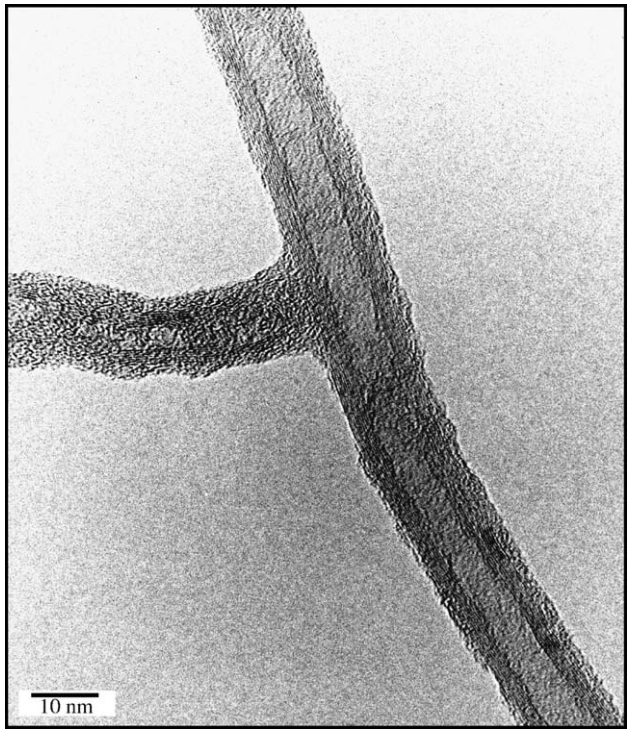

Fig. 4. TEM image of two T-connected nanotubes.

Using STS we investigated the changes in the electronic properties of CNTs. Fig. 3B shows an STS curve recorded on the nanotube shown in Fig. 3A. In order to reduce the noise, 10 current–voltage curves were averaged and after numerical derivation the resulting dI/dV curve was Fourier filtered. The apparent tube diameter determined from Fig. 3A is $d = 13$ nm. The nanotube has metallic behavior because the STS curve shows a nonzero density of states at the Fermi energy. For chemically unmodified nanotubes, the distance between the Van Hove singularities should depend only on the diameter [9]. For metallic SWCNTs the singularities appear at energies $E_1 = \pm 3\gamma_0 a_{C-C}/d$, $E_2 = \pm 6\gamma_0 a_{C-C}/d$ and $E_3 = \pm 9\gamma_0 a_{C-C}/d$, where $\gamma_0 = 2.7$ eV is the C–C tight-binding overlap energy, $a_{C-C} = 0.142$ nm is the nearest neighbor C–C distance and d the tube diameter [9,20–22]. Because the interaction between the layers in MWCNT is weak the distance between the Van Hove singularities is not significantly changed compared with SWCNTs [23]. In

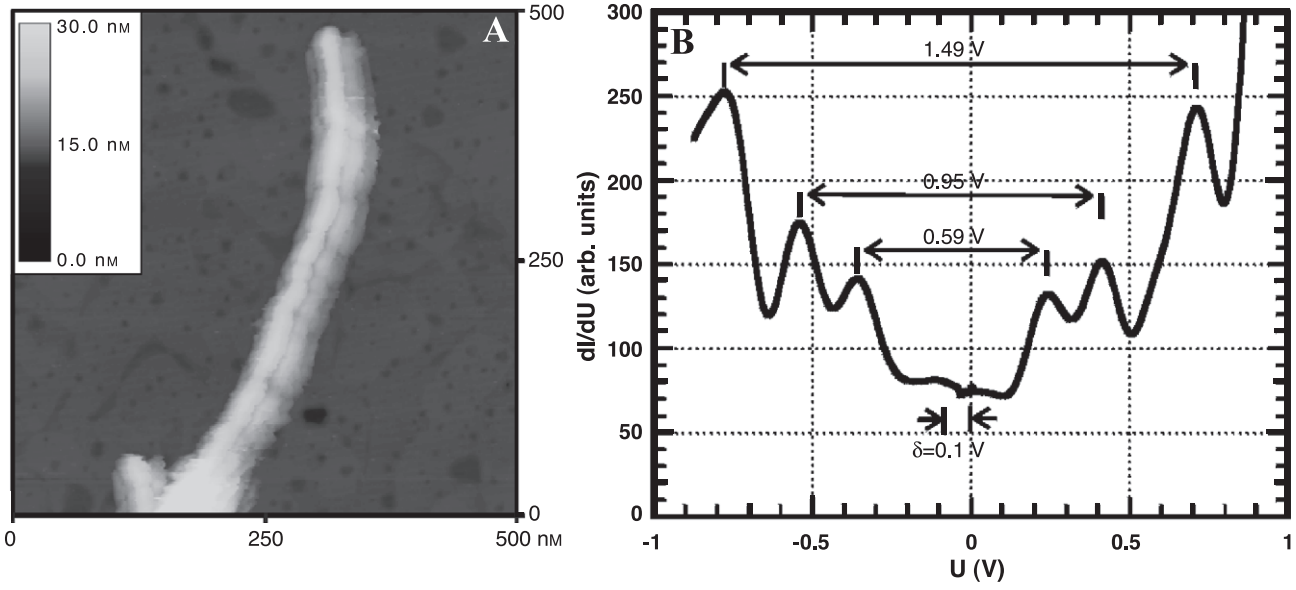

Fig. 3. STM image of a functionalized MWCNT on Au (A) and the STS curve on this tube (B).

our case, the calculated energy gap should be $\Delta E_1 = 0.18$ eV, $\Delta E_2 = 0.35$ eV and $\Delta E_3 = 0.53$. The measured energy gaps are 0.59, 0.95 and 1.49 eV for ΔE_1, ΔE_2 and ΔE_3, respectively, wider than twice the calculated value. Assuming that the functional groups cover the nanotube in one layer only, and they are short as compared with the diameter of the nanotube; this result indicates that the theoretical model used to calculate the position of Van Hove singularities has to be modified in case of functionalized nanotubes. The difference between the calculated and measured energy gaps could be explained only with a significant change in the electronic structure of the nanotube. Furthermore, the Van Hove singularities on the STS curve are not symmetrically positioned around zero bias, the tubes may be doped by the functional groups and possibly by the charge transfer from the Au substrate. The energy levels of not functionalized metallic nanotubes placed on Au surface is shifted by 0.3 eV towards lower energy [9]. The Van Hove singularities on the STS curve are shifted by $\delta = 0.1$ eV to higher energies, which is another difference from the behavior of not functionalized nanotubes. Consequently, functionalization may be used to produce CNTs with modified electronic properties as predicted by theoretical models [24,25].

Because the whole surface of CNTs is covered with functional groups, the probability of interconnections between the nanotubes is higher than in the case of nanotubes functionalized only at their end. The presence of connected nanotubes in the sample was investigated with TEM. A large number of connected nanotubes were found. Approximatively, 10% of the nanotubes were connected in one way or another. Fig. 4 shows a T-like connection of two nanotubes.

The strength of the bonds between the nanotubes was checked using manipulation with the STM tip. This method is able to compare the binding force between the connected nanotubes and the van der Waals interaction between the nanotubes and the HOPG substrate. Fig. 5 shows two consecutive STM images taken in the same region (the same HOPG cleavage step appears on both images). The group of nanotubes on the upper part of the images is moved about 200 nm, while the nanotube on the lower part of the images is rotated with 30°. The nanotubes on the upper part of the images are moved together without the alteration of their global arrangement. This indicates that the binding force between them is larger than the van der Waals interaction between the nanotubes and the substrate. Taking into account that the "dragging force" exerted by the STM tip was acting on only one tube of the group, this indicates a strong enough chemical connection between the nanotubes.

3. Conclusions

The applied functionalization method was able to cover the whole surface of MWCNTs with functional groups. The large number of functional groups on the CNTs surface facilitates the formation of connections between nanotubes; therefore, a large number of connected nanotubes were observed by TEM. This treatment may be useful to improve the mechanical interaction between the nanotubes and the surrounding matrix in composites, too. The functionalization produces significant modifications in the electronic structure of the nanotubes and makes possible to produce nanotubes with modified electronic properties. The binding force between the connected nanotubes was found stronger than the van der Waals interaction between the nanotubes and the graphite substrate, indicating that the electric circuit built from connected nanotubes will be mechanically stable. The carbon nanotube networks connected with functional groups may be used in nanoelectronics.

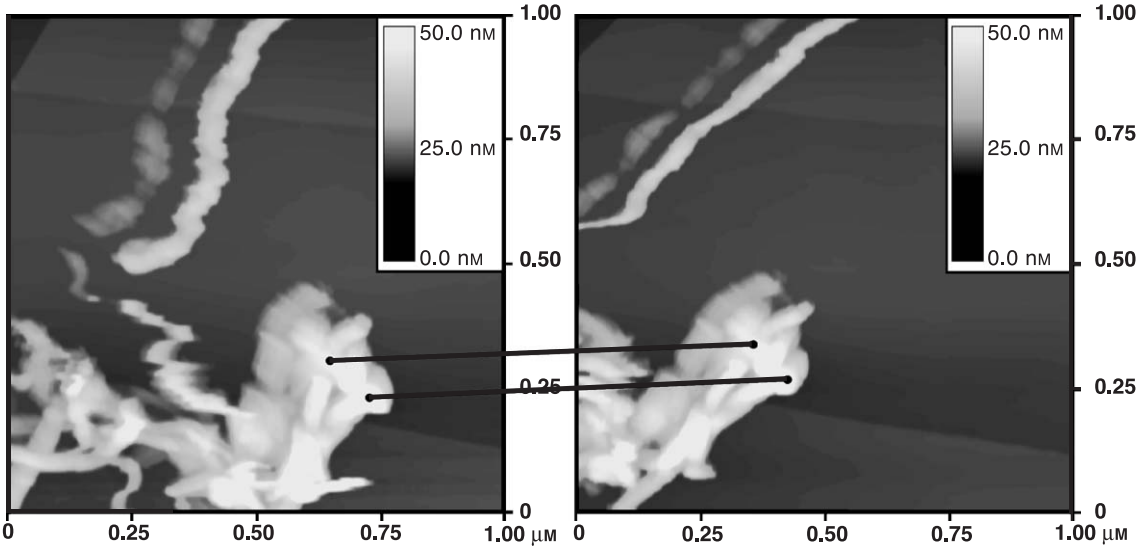

Fig. 5. Consecutive STM images taken in the same region. The nanotubes are moved together without the alteration of their global arrangement.

Acknowledgements

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