Carbon nanotubes

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In Situ Tailoring and Manipulation of Carbon Nanotubes**

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Multiwalled carbon nanotubes (MWNTs), with their excellent properties,[1–5] have long been considered as a model material for realizing the potential of nanotechnology. Several techniques[6–8] have been developed to tailor and manipulate MWNTs, and they have shown promise in the construction of nanobalances,[2] nanosensors,[9] SPM probes,[10,11] nanoelectronics,[12] fuel cells,[13] and so on. In order to achieve their full capability, MWNTs need to be modified in length, diameter, and shape to atomic-scale precision. Therefore, the synergy of various techniques and sequential operations in real time is often required. Here we report on an in situ method that combines several tailoring and manipulation techniques using an ultra-high-vacuum transmission electron microscope/scanning tunneling microscope (UHV TEM/STM) system. We demonstrate nanoscale precision in the engineering and fabricating of a MWNT with two examples; a probe for investigating single nanoparticles and a balance with single-atom mass resolution.

We carried out our experiments in an ultra-high-vacuum transmission electron microscope (UHV-TEM, JEOL JEM-2000V) combined with a scanning tunneling microscope (STM; built inhouse) riding on a nanopositioning system. The nanopositioning system provided coarse mechanical motions in three dimensions and the fine adjustments were performed with a piezo-tube scanner. The MWNTs (Alfa, 3–24 nm in diameter, stock #43197) were first attached to a gold knife edge electrode using the electrophoresis technique (applying a 6 MHz AC voltage of 8 V).[11] The assembly was then loaded into the electron microscope. A pre-inserted gold STM tip was aligned and connected with a chosen MWNT under TEM observation at an operating voltage of 200 kV. The bottom of Figure 1a shows such an initial MWNT with 15 walls and about 1.87 nm inner diameter attached to the STM tip. To the top (not shown in the figure) is a gold knife-edge electrode holding MWNTs of various diameters. When an MWNT is brought into contact with the knife-edge electrode, the current passing through the MWNT is maintained at a suitable bias voltage in order to assure an electric contact between them. After applying a voltage of 4 V across the tube, it often breaks in the middle, and the broken ends form a telescopic structure,[13] with the inner layers protruding from the outer layers (Fig. 1b). This telescopic structure is a great benefit, as it allows for control of the inner diameter of the MWNTs, by gradually exposing the different shell of the nanotube at the end. If one desires to extract an MWNT structure layer by layer, a telescopic structure with a single extending layer should be obtained first. Figure 1c is a TEM image displaying the telescopic nature of an MWNT. When a threshold voltage was applied to the MWNT, the electrical breakdown was initiated. At the same time, a large current passed through the outermost layer of the MWNT, causing the evaporation of the outer shell. With careful control of the voltage, a telescopic structure can be fabricated with single-layer precision, as demonstrated in Figure 1d.

Figure 2 displays TEM images of a MWNT at different stages in successive inner peeling processes. Figure 2a presents the formation of a new contact between the broken tube and the knife-edge (at the right). A voltage of ≈1 V was applied across the contact to secure it and to enable the subsequent extraction. When the gold knife edge was pulled away, the attached inner tubes were extracted from the MWNT. Figure 2b shows inner tubes pulled halfway out of the outer tubes. After extraction, the inner diameter of the remaining tube is 4.59 nm, compared to the original 1.87 nm, indicating the removal of 4 layers of graphite wall, as shown in Figure 2c.

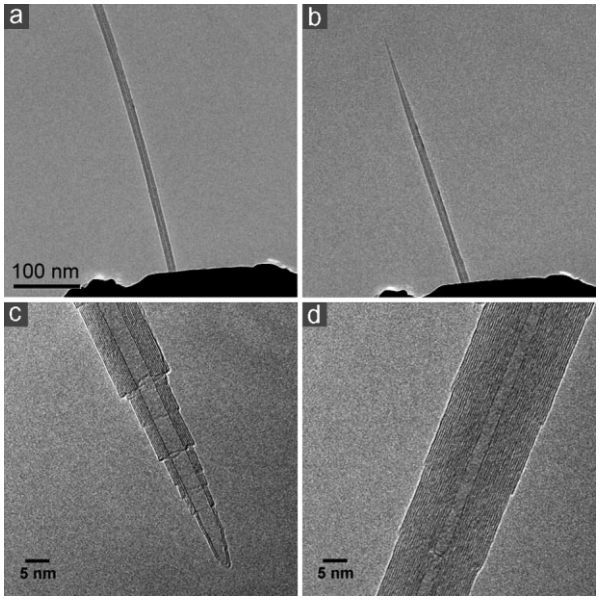

Figure 1. Transmission electron micrographs depicting the formation of the telescopic structure of a MWNT at different stages. a) The MWNT is placed between an STM tip (bottom) and a knife-edge electrode at top (not shown). b) One of the two telescopic tips formed by applying a voltage of 4 V. c), d) The close-up images of the MWNT telescopic structures.

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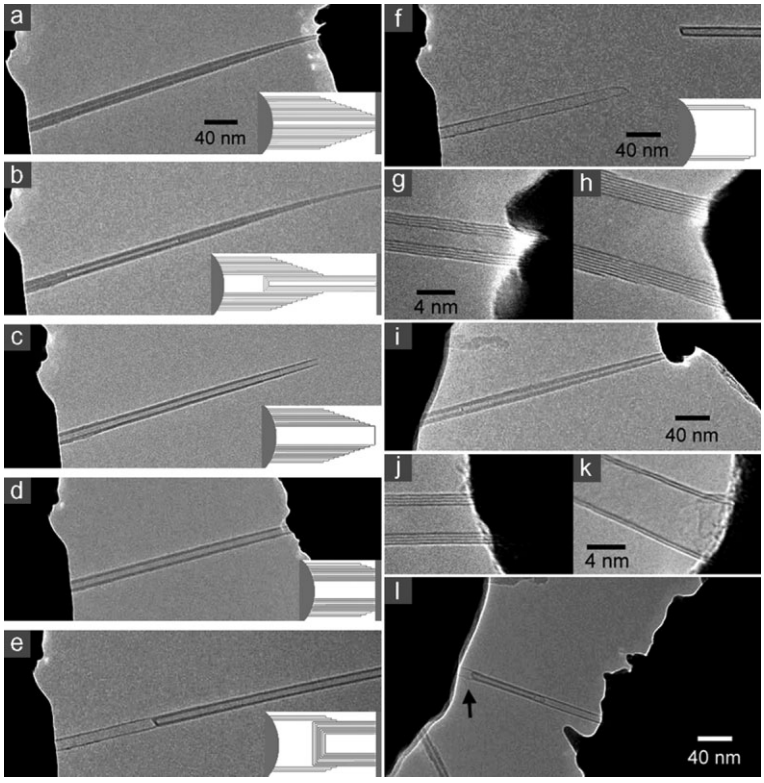

Figure 2. Transmission electron micrographs of a MWNT at different stages of the inner peeling process. Schematic drawings are inset to illustrate the process. a) Tip of the telescopic MWNT attached to the knife edge. b) The knife-edge is withdrawn, carrying several inner tubes with it. c) The remaining tube, with an enlarged inner diameter of 4.59 nm. d)–f) Further enlargement of the inner diameter can be achieved by repeating the process from (a) to (c). The final tube has only three layers left with an inner diameter of 10.04 nm. g), h) High resolution TEM images of the extracted nanotubes after the processes of (b) and (e), respectively. i)–l) Another peeling experiment which produced an artificial single-walled nanotube with an enlarged inner diameter. i) A telescopic MWNT with a base of seven walls (left) and the extracting electrode (right). j) A four-wall tube pulled out after the first peeling process. k) A two-wall tube pulled out after the second peeling process. l) The remaining single wall nanotube on the base (indicated by the arrow) obtained by two internal peeling processes.

The extracted shell of the MWNT normally has a capped end rather than an open end. This is because the end of extracted MWNT is exactly the same as the end of original MWNT from the gold electrode. A clean area of the knife-edge was moved to the tip of the MWNT and the same process was repeated to pull out more inner layers, as shown in Figure 2d and e. The final tube (Fig. 2f) has only three layers left, and has an inner diameter of 10.04 nm. Figure 2(g and h) displays high-resolution TEM images showing the extracted nanotubes after the successive first and second peeling processes; these well-formed wall images attest to a high MWNT quality. Since this process is highly reproducible, it suggests that the shear strength of the MWNT layers is easily overcome by the stronger bonding (from electrostatic forces) between the ends of the MWNT and the electrodes. The relatively weak van der Waals interactions between the MWNT layers[14–16] and the variable electric conductivity present during the telescopic deformation of the MWNT[17,18] have in fact been measured before. In principle, repeating this process should render it possible to fabricate a single-wall carbon nanotube (SWNT) of enlarged diameter; these SWNTs are difficult to harvest from presently available growth processes. This is demonstrated (Fig. 2i–l) with another extraction experiment, intended to achieve an individually tailored SWNT with an enlarged inner diameter. A telescopic MWNT with a base of seven walls and the extracting electrode are shown in Figure 2i, on the left and right, respectively. During the first peeling process, a four-walled tube was pulled out (Fig. 2j). Two more walls were pulled out in the second peeling process (Fig. 2k). Figure 2l depicts the peeling process, with the pulled-out portion with two walls on the right, and the remaining single wall nanotube on the left (indicated by the arrow), which has much weaker contrast. The final single wall tube is obtained with a diameter of 8 nm and a length of 16 nm.

The extraction of a SWNT from an MWNT was performed by Hong and co-workers[7] using atomic force microscopy. The benefits of our combined TEM/STM approach in this study include real-time measurements, increased resolution, and sequential operations. Here we present the following manipulation to illustrate the advantage of our approach. An extracted inner tube can be reinserted into its original casing and moved along the axis of the tube like a piston rod in a cylinder ring, as shown in Figure 3. In order to achieve this, the positions of the rod and ring were adjusted to almost the same level, within a few angstroms, using the standard focus determination rule of TEM. This was possible because the pulled-out tube had a capped end that is not very reactive. We also believe that it is likely to do with a potential well created at the center of the open large tube, which subsequently guided and pulled in the small tube. The similar attractive potential may also work for the growth of fullerenes into carbon-nanotube peapods where the actual mechanism used is not fully understood. The piston not only provides an interior space with adjustable dimensions but also, as it may be possible to introduce a new molecule or nanoparticle into the tube, it may be useful in various experiments. Recently, a high-resolution TEM image of a single molecule was obtained; this was made possible by growing the molecule in an SWNT.[19]

Here, we provide two potential applications employing the MWNTs that have been tailored and manipulated in sequence and in real-time. The first is the fabrication of a size- and shape-specific nanostructure, to allow further research on its physical properties. For example, if we want to study the polarized surface plasmon effect (an optical excitation effect) of a metallic nanoparticle, we need to design and fabricate a suitable nanostructure. Since the characteristic length for the excitation of surface plasmons occurs at a particle size of roughly 10 nm, we attempted to fabricate an elongated Ag particle close to this size inside a nanotube, so that the excitation was polarized along the tube axis. The inner peeling

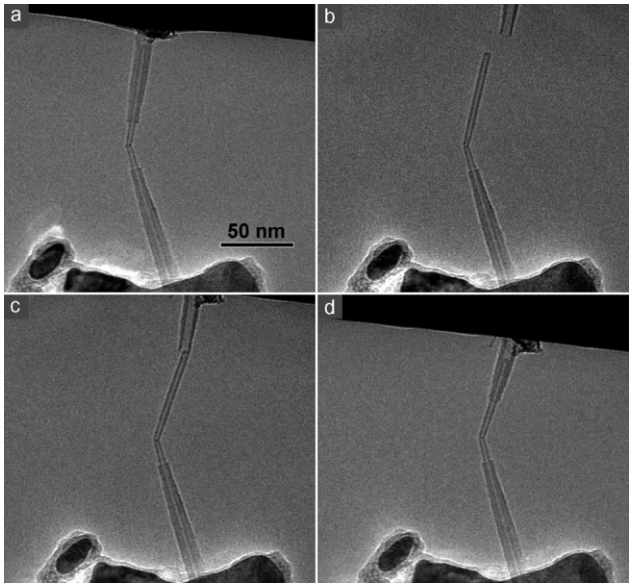

Figure 3. The extraction and reinsertion of a piston. From (a) to (d), TEM images showing the process of extraction of inner shell of MWNT and reinsertion of the withdrawn nanotube by pure mechanical force.

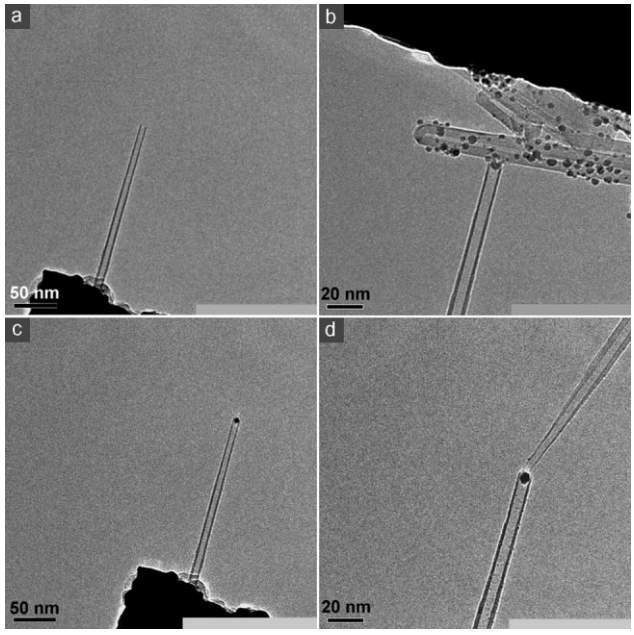

Figure 4. Transmission electron micrographs showing the insertion of Ag clusters into a peeled MWNT. a) A MWNT with a defined inner diameter (≈6nm) after the peeling process. b) This tube making contact with a chosen Ag cluster. Ag clusters of various sizes deposited on the nanotubes were formed by electron-beam evaporation under UHV. c) The Ag cluster transferred to the tube by pure mechanical force. d) The transferred Ag cluster pushed slightly into the tube by the piston rod.

process was repeated until a desired diameter of ≈6 nm was reached (Fig. 4a). This tube was then withdrawn from the central region where the evaporation of Ag atoms then took place. After Ag clusters of various sizes were formed on some of the nanotubes on the knife edge, the previously tailored tube was brought back to engage the transfer of a chosen Ag cluster (Fig. 4b). By simply contacting the cluster with the open-ended nanotube and retracting, the transfer was made as the peeled nanotube with an exposed dangling bond around the rim offered a stronger interaction. The incipient Ag cluster appeared to be round and had a diameter larger than 6 nm (Fig. 4c). This particle could be further pushed in by the piston rod to secure its position, as illustrated in Figure 4d. Once inserted into the tube, its shape was elongated, with a length now close to 9 nm. The above process can be repeated to produce nanostructures of other sizes and shapes for study. Considering applications, Ag nanostructures are able to induce the phenomenon of surface enhanced Raman scattering, which is an optical method for providing vibrational structures of a molecules or nanomaterials.[20] We suggest that this kind of Ag-nanotube structure can also be used as a new type of scanning probe to enhance Raman scattering.

The second potential application is the employment of the peeled nanotube as a super nanobalance to weigh a small nanoparticle. The resonance frequency of an MWNT increases with its outer diameter (OD) and is inversely proportional to its mass,[17] among other factors. Thus, choosing a wider MWNT (larger OD) and performing internal layer extraction on it (thus reducing its mass) actually gleans a nanotube which is better suited to application as a sensitive balance than an SWNT. Furthermore, this process is accompanied by the shortening of the tube, adding an extra factor that increases the resonance frequency. Figure 5a illustrates this idea with a three-wall nanotube of 6 nm in OD and 80 nm in length, with mass calculated to be 3.1×10^{-18} g. A small Ag particle of

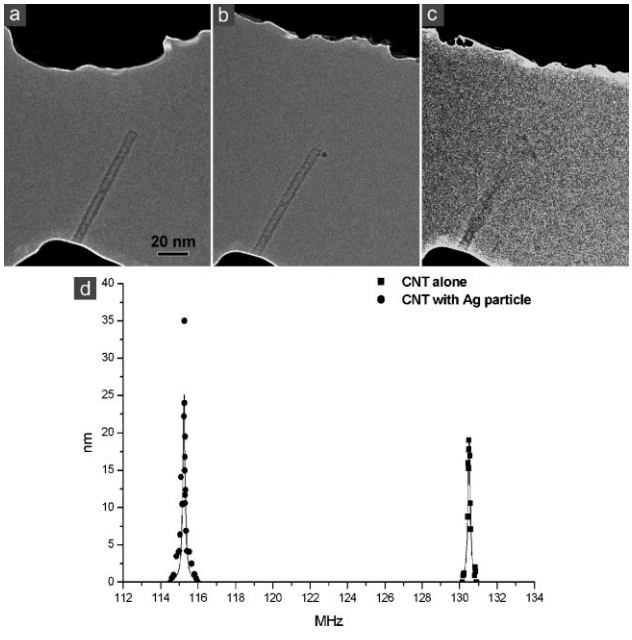

Figure 5. Transmission electron micrographs showing the application of a peeled MWNT as a nanobalance. a) A three-wall MWNT with an outer diameter of 6 nm after the extraction process. b) This tube with an Ag particle attachment, 3 nm in diameter. c) The same tube, with the Ag particle, driven into resonance. d) The shift in resonance frequency measured for tube with and without the Ag particle.

about 3 nm in diameter was attached to its top end. The resonance frequency of the original tube was 130.5 MHz (data shown by squares in Fig. 5d), and was shifted to 115.3 MHz (data shown by circles in Fig. 5d) after the attachment of the particle. By simple calculation using a previously described formula,[2] the mass of the Ag particle was estimated to be 1.8×10^{-19} g, which is close to the mass of 1000 atoms, roughly a 3 nm Ag particle. Although, in a recent report, a mass resolution of 7 zeptograms was obtained with a nano-electromechanical system (NEMS),[21] in terms of mass reduction and chemical reactivity we feel that the nanotube should have an intrinsic advantage, and the potential to achieve an even better resolution. Based on the shape of the curve in Figure 5d, it exhibited a very high Q factor (≈1000). The ultimate mass resolution is determined by this factor and, for the current tube, the mass sensitivity is about 10^{-22} g. With this mass resolution, this tube can be called an ''atom-balance'' for heavy atoms, and may be used to measure the mass of a large molecule.

In summary, we have reported on an in situ method that combines several manipulation and tailoring techniques, including precise control of both the inner and outer diameters of an MWNT, reinsertion of an extracted MWNT rod to its casing, transfer of a nanoparticle from one tube to another, and the induction of a tailored tube into mechanical resonance. We have also provided two examples to demonstrate the potential and strength of this method. Looking ahead, this method may create a new dimension for nanotube technology and offers greater opportunities to achieve higher goals for both research and applications.

Keywords:
carbon nanotubes · nanobalances · nanoscale manipulation · scanning tunneling microscopy

[1] S. Iijima, *Nature* **1991**, *354*, 56.
[2] P. Poncharal, Z. L. Wang, D. Ugarte, W. A. de Heer, *Science* **1999**, *283*, 1513.
[3] D. Mann, A. Javey, J. Kong, Q. Wang, H. Dai, *Nano Lett.* **2003**, *3*, 1541.
[4] M. Zhang, S. L. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, K. R. Atkinson, R. H. Baughman, *Science* **2005**, *309*, 1215.
[5] J. Y. Huang, S. Chen, Z. Q. Wang, K. Kempa, Y. M. Wang, S. H. Jo, G. Chen, M. S. Dresselhaus, Z. F. Ren, *Nature* **2006**, *439*, 281.
[6] J. Cumings, P. G. Collins, A. Zettl, *Nature* **2000**, *406*, 586.
[7] B. H. Hong, J. P. Small, M. S. Purewal, A. Mullokandov, M. Y. Sfeir, F. Wang, J. Y. Lee, T. F. Heinz, L. E. Brus, P. Kim, K. S. Kim, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 14155.
[8] A. V. Krasheninnikov, F. Banhart, *Nat. Mater.* **2007**, *6*, 723.
[9] S. Ghosh, A. K. Sood, N. Kumar, *Science* **2003**, *299*, 1042.
[10] S. S. Wong, E. Joselevich, A. T. Woolley, C. L. Cheung, C. M. Lieber, *Nature* **1998**, *394*, 52.
[11] Y. C. Chang, D. C. Wang, C. S. Chang, T. T. Tsong, *Appl. Phys. Lett.* **2003**, *82*, 3541.
[12] S. J. Kang, C. Kocabas, T. Ozel, M. Shim, N. Pimparkar, M. A. Alam, S. V. Rotkin, J. A. Rogers, *Nat. Nanotechnol.* **2007**, *2*, 230.
[13] G. L. Che, B. B. Lakshmi, E. R. Fisher, C. R. Martin, *Nature* **1998**, *393*, 346.
[14] M. F. Yu, B. I. Yakobson, R. S. Ruoff, *J. Phys. Chem. B* **2000**, *104*, 8764.
[15] S. Akita, K. Nakayama, *Jpn. J. Appl. Phys.* **2003**, *42*, 4830.
[16] A. Kis, K. Jensen, S. Aloni, W. Mickelson, A. Zettl, *Phys. Rev. Lett.* **2006**, *97*, 025501.
[17] S. Akita, K. Nakayama, *Jpn. J. Appl. Phys.* **2004**, *43*, 3796.
[18] T. Kuzumaki, Y. Mitsuda, *Carbon* **2005**, *43*, 2227.
[19] M. Koshino, T. Tanaka, N. Solin, K. Suenaga, H. Isobe, E. Nakamura, *Science* **2007**, *316*, 853.
[20] S. Nie, S. R. Emory, *Science* **1997**, *275*, 1102.
[21] Y. T. Yang, C. Callegari, X. L. Feng, K. L. Ekinci, M. L. Roukes, *Nano Lett.* **2006**, *6*, 583.

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