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Refinement of Conditions of Point-Contact Current Imaging Atomic Force Microscopy for Molecular-Scale Conduction Measurements

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ABSTRACT

We have refined the measurement conditions of point-contact current imaging microscopy (PCI-AFM) to measure the electric properties along the long axes of one-dimensional structures. Using this refinement, the current image of the PCI-AFM can be used to distinguish individual single-walled carbon nanotubes in a bundled structure. The PCI-AFM will thus help further developments in nanoscience for conduction measurements in one-dimensional structures.

1. Introduction

Although there are several methods to measure conductivity on the nanoscale, each of these methods has its own weak points for measurements along the long axis of one dimensional (1D) nanostructures. Using a nanogap electrode fabricated by several different methods, for example electron beam lithography,[1)] break junctions,[2)] electrochemical growth,[3)] electromigration,[4)] it was difficult to confirm that nanoscale objects (<10 nm) within the gap actually made stable contact with the electrodes. Using scanning tunneling microscopy (STM), current can be measured through a sample sandwiched between a scanning tip and a conductive substrate with a certain gap size. In order to measure the conductivity along the long axis of a 1D structure by STM, however, the sample needs to be placed vertically on the substrate, perpendicular to the substrate surface. If not, the current passes through the diameter between the STM tip and the substrate. Contact mode atomic force microscopy is the most frequently used method to measure the conductivity of the long axis of 1D structures shown in Fig. 1(a). However, the method also has a disadvantage in that if the sample has weak or there is no interaction with the substrate, the sample can be moved by the scanned cantilever during measurements similar to the one shown in Fig. 1(b).

In order to overcome the disadvantages described above, point contact current imaging atomic force microscopy (PCI-AFM), which utilizes the precision of an atomic force probe to measure current-voltage (I-V) characteristics at specific points on a nanosystem, was developed to investigate variations in transport characteristics of 1D structures. During our development of the PCI-AFM, the conduction properties of single-walled carbon nanotubes (SWCNT),[5,6] the electric properties of porphyrin aggregation working as a nanodevice on a wired SWCNT, [7,8] DNA[9] etc. were measured along their long axes. These results proved that the PCI-AFM is a powerful technique for electrical measurements in 1D nanostructures. However, PCI-AFM also has a problem in that if the measurement conditions are slightly different from the most optimal conditions, not all of the measurements will be successful. In the present paper, we report a method for determining reproducible and optimized conditions for PCI-AFM measurements. By refining the optimized conditions, the PCI-AFM current images allow for distinguishing individual SWCNTs in a bundled structure.

2. Experimental Method

The PCI-AFM measurements were conducted using the Scanning Probe Microscope (JEOL JSPM-4210) expanded with two function generators (FG) (WF1946, NF Corporation). Pt-coated conductive cantilevers were used to measure the current. The force constant and resonant frequency of the cantilevers were 4.5 N/m and approximately 150 kHz, respectively. This measurement was performed in a nitrogen-gas-purged atmosphere to avoid humidity. When I-V measurements were carried out, the force between the cantilever and the sample was approximately 13 nN, calculated using a force curve.[6)] A bias voltage was applied to the gold electrode on the substrate and the cantilever was grounded. Each signal was stored using a storage Oscilloscope (Lecroy WaveRunner 6030).

The procedure used for the PCI-AFM method is shown in Fig.2, and a timing chart of conventional conditions for the procedure is shown in Fig. 3(a). Feedback is controlled by a transistor logic (TTL) signal. When the signal is in zone A in Fig. 3(a), feedback is active and the cantilever is oscillated at a resonant frequency for tapping-mode scanning. In this zone, the *z*-servo voltage is stored in the memory of the computer to form a topographic image. When the cantilever tip is displaced to the preset positions for I –V measurements by changing the bias for the piezo-actuator to change the height of the cantilever from the sample surface (Z-control), the lateral scan is interrupted and the feedback control signal is set to low. This high-to-low transition of the Z-control provides a trigger signal to start measurement of I-V characteristics in zone B. In this zone, the feedback system is deactivated, the cantilever excitation is stopped, and the tip-sample separation is set so that the tip and the sample come into contact under a specific loading force. Stopping the excitation enables the tip to contact the sample statically. The applied bias voltage is then ramped and I-V characteristics are stored in the computer. Finally, the tip-sample separation is reset to the previous value, the feedback system is reactivated, and tapping mode scan is restarted. These alternate operations are performed continuously, and both the topographical data and the I-V data are simultaneously obtained at 128x128 pixels. The SWCNTs used for the measurements were obtained from a commercial source (As-produced HiPco nanotubes by Carbon Nanotechnology Inc.).

3. Results and Discussion

3.1. Confirmation of Timing Condition of Bias voltage, Z-control, Cantilever Excitation and Cantilever Vibration

As described above, in the conventional PCI-AFM measurement, the Z-control is changed to the low state immediately after stopping cantilever excitation at the boundary between zones A and B in Fig.3(a),[5] even though the cantilever is still being vibrated (see arrow (i) in Fig. 3(a)). Due to the sudden height change, the cantilever crashed and kept bouncing on the sample, therefore a certain interval was needed to stabilize the contact condition. We thus focused on the V_{A-B} signal to monitor the cantilever vibration, which is controlled to be stopped before the end of the high state of Z-control (zone C’) in Fig. 3(b). The cantilever keeps vibrating for a short time period even though the bias for cantilever excitation is actually stopped at the end of zone C’ in Fig. 3(b). The cantilever vibration thus needs to be stopped until the end of the low state of Z-control. Next, the timing of each signal needs to be checked. Sweeping the sample bias should be started after the low state of Z-control has started and finished before the end (zone D in Fig. 3(b)). In the present measurement, the cantilever position is changed from the original height to the “low state” to contact the measured sample, similar to the condition shown in Fig 2(c).

In the case wherein stable contact was late for the I-V measurement, an incorrect and irregular result was obtained, as indicated by region B in Fig. 4(a). To avoid unstable contact, the cantilever displacement was controlled to be slower than the conventional condition for mild collision to the sample. The speed of height change is empirically chosen. If the slope of Z-control is smaller than that in Fig 3(b), in other words, if the cantilever moves more gently than for the refined condition, the cantilever did not bounce on the sample after started I-V measurement. By this change, the quality of the measured data was obviously improved from the previous results. If the interaction between the cantilever and sample is too strong for them to disconnect, for example, due to the presence of a sticky material, the cantilever can be retracted by a displacement large enough to disconnect the sample and the cantilever once and then returned to the original position.[10)]

3.2 Checking the PCI-AFM measurement condition in detail

The synchronizing condition can be checked by the shape of the current-bias (I-V) curves obtained. In the case wherein all the conditions were ideal, the I-V curve shown in Fig. 4(b) was obtained. In the case wherein the condition was bad, the I-V curve became irregular, as shown in Fig. 4(a). The noise shown in region B in Fig. 4(a) was observed when the I-V measurement was started without good contact, that is, when the cantilever contacted the sample before the cantilever vibration was stopped or the cantilever was bounced on the sample. The I-V curve in zone A in Fig. 4(a) was obtained when the cantilever was disconnected from the sample at -0.25 V and detected no current at the lower bias. It is to be noted that the bias voltage was swept from 1.5 V to -1.5 V in the measurements. When the I-V curve was irregular, such as in zone B in Fig. 4(a), it was always observed that the vibration of the cantilever was not stopped yet like at arrow (i) in Fig. 3(a).

The V_{A-B} signal in the 'low state' of the Z-condition also yields important information. The curves in Fig. 4(c) show V_{A-B} (vibration of cantilever) when the cantilever was in contact with the sample. The distance from Z-control at the high state increased in the order from (i) to (iv). The insets on the right in the figure indicate the cantilever shape at each condition. In chart (i) in Fig. 4(c), the cantilever approaches the sample in the attractive force region when the Z-control was in the low state. In the case of chart (iii), the cantilever shape is the same when no force is applied because the attractive and repulsive forces are balanced. The cantilever feels a repulsive force in the case of chart (iv). At point C in the chart, the cantilever started to experience the attractive force from the sample. The spiky peak, as a signal of the attractive force between the sample and the cantilever, was observed when the two were disconnected as shown in area D of the charts (ii) to (iv) in Fig. 4(c). These peaks were observed for the I-V measurements since the cantilever must contact the sample during the measurement. Using the timing of the signals, Z-control can be controlled suitably with no clash between the sample and cantilever to avoid damage to both. To obtain both good quality PCI-AFM images and I-V curves, the case shown in chart (iii) allows for the best resolution for the topography and current images. In particular, the resolution of the current image was sometimes much higher than that of the topographic image, as shown in Fig. 5. The results imply that the contact condition of the cantilever may become stable during measurement when the repulsive and attractive forces are balanced.

By setting all the conditions as described above, we were successful in distinguishing six SWCNTs on the surface of a bundle of nanotubes in a current image, as shown in Fig. 5(b). This suggests that the PCI-AFM images and I-V curves can be obtained simultaneously and reliably. From the topographic image, diameter of the bundled SWCNT is estimated about 4 nm although it looks much wider in the observed image because the curvature of AFM probes makes the width wider in AFM image. It is reasonable that 5-6 nanotubes are observed at the surface of the bundle structure. In particular, the resolution of the current image exceeded that of the topographic image. The present result is much improved when compared to that obtained by contact mode AFM previously.[11)] The present refinement was thus shown to be useful for distinguishing electric properties of 1D nanoscale structures.

4. Conclusions

We optimized conditions for using PCI-AFM to obtain the best results. This will help researchers in measuring the electric properties along the long axes of 1D structures. Using the conditions, the current image of PCI-AFM was demonstrated to show the distribution of conductivity along individual SWCNTs in a bundled structure.

Acknowledgments

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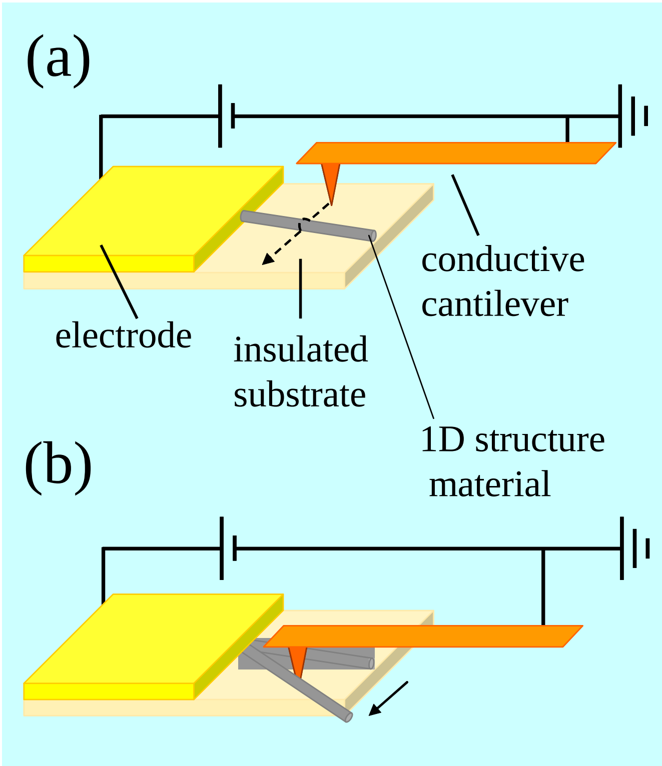

Fig.1; Problem of measurement of the conductivity of a 1D material by contact mode AFM. (a) Typical measurement. AFM probe is scanned along the dashed line, for example, and I-V curve is obtained at each pixel of an image. (b) If the 1D material has a small interaction with the substrate, the sample can be moved easily by the scanned cantilever.

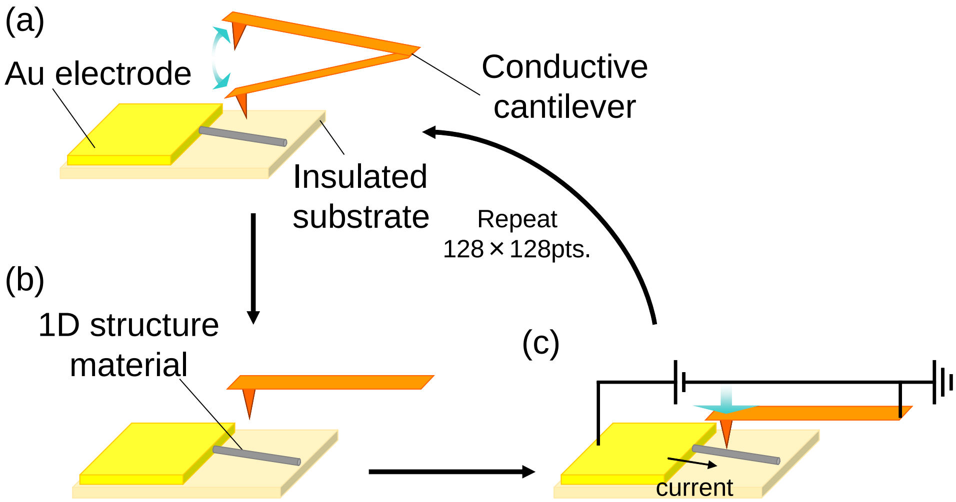

Fig. 2; Procedure of the PCI-AFM method. (a) A topographic image was obtained by tapping-mode AFM. (b) The vibration of the cantilever was stopped to measure the *I-V* curve. (c) The AFM tip was pressed to the sample to make electrical contact, and the I-V curve was then measured. Steps (a)-(c) were repeated at each of 128×128 pixels of the AFM image.

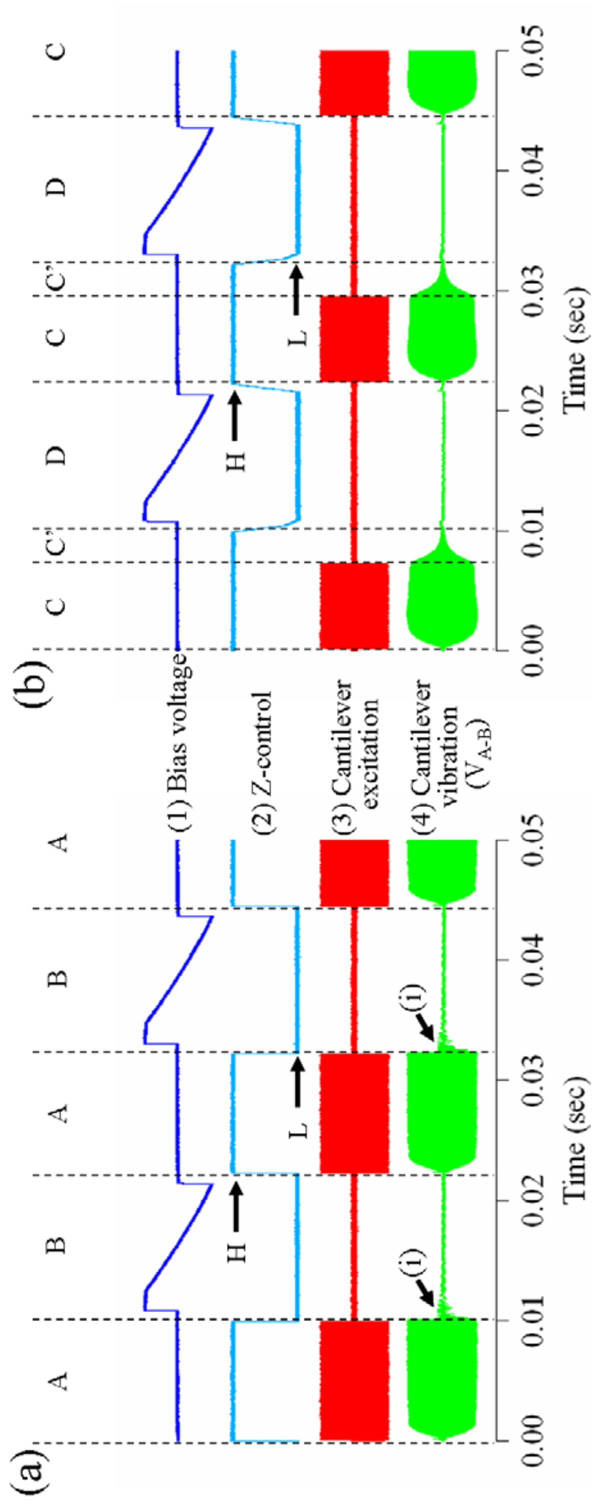

Fig. 3 Timing chart of Z-control, cantilever excitation and cantilever vibration ($V_{A\text{-}B}$) for (a) conventional condition and (b) refined condition. The cantilever vibration was

stopped when the Z-control was at a “low state”. The characters ‘H’ and ‘L’ indicate ‘high state’ and ‘low state’ of the cantilever position. Arrows (i) indicate an unstable contact condition when the cantilever crashes on the sample. In zones A and C, the excitation of cantilever was on, while in zone B, C’ and D the excitation was off.

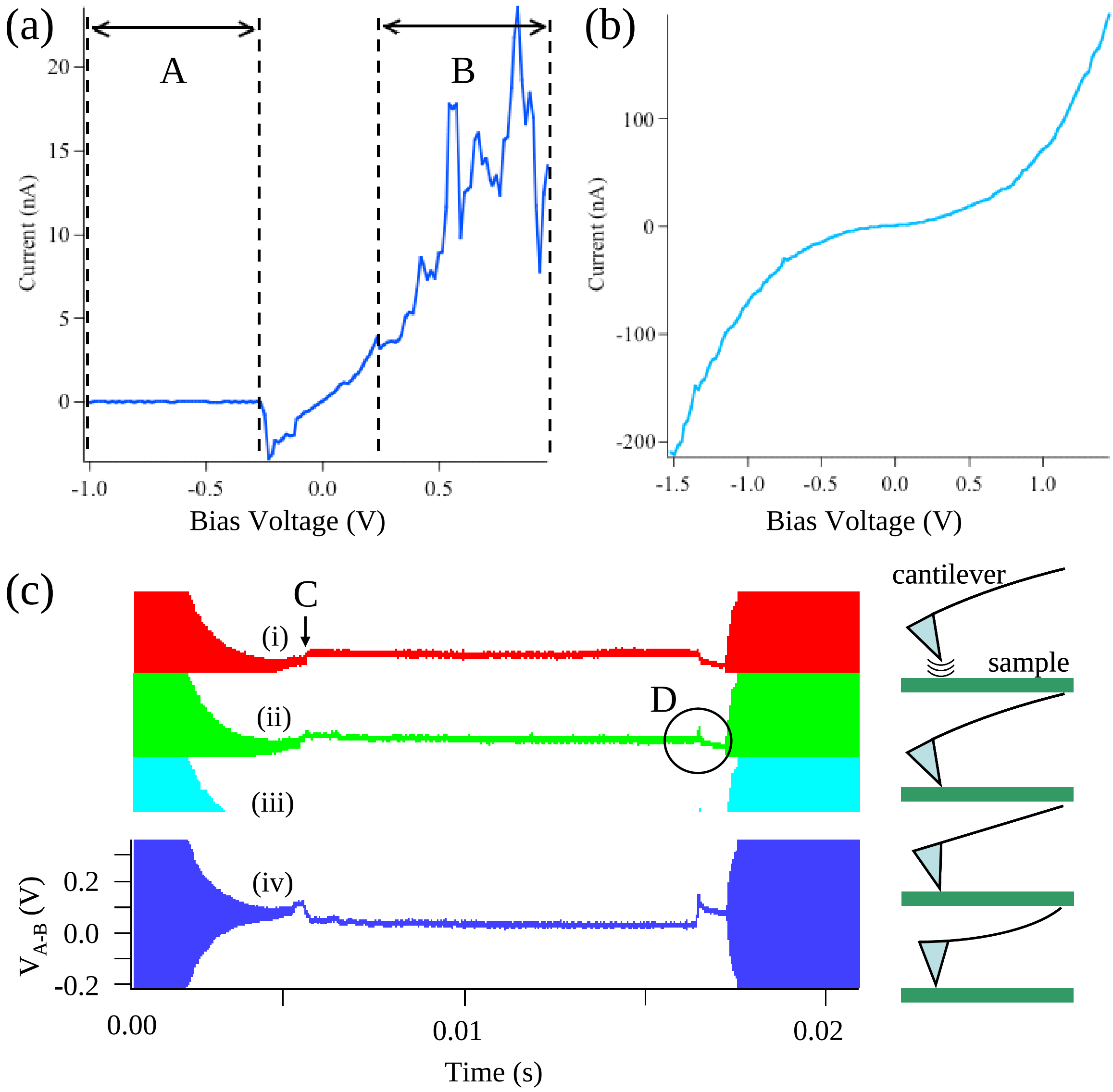

Fig. 4 I-V curves obtained by (a) unsuitable conditions for PCI-AFM and (b) optimized condition. Bias voltage was swept from 1.5 V to -1.5 V in the measurements in (a) and (b). The I-V curve in region A was obtained when the cantilever was disconnected from the sample at -0.25 V and detected no current at the lower bias. The noise shown in region B was observed when the I-V measurement was started without good contact, that is, when the cantilever contacted the sample before the cantilever vibration was

stopped or the cantilever was bounced on the sample. (c) V_{A-B} during I-V measurements for (i) attractive force region with no contact to the sample (red), (ii) first contact position (green) (iii) force balanced region (light blue) and (iv) repulsion force region (blue). The dashed lines show the average bias of the free force region. The insets on the right side show the shapes of the cantilever for each case in (c). V_{A-B} for (iii) is on the averaged line, which are same range in curves (i)-(iv). At point C, the cantilever started to experience the attractive force from the sample. The spiky peak shown in area D, as a signal of the attractive force between the sample and the cantilever, was observed when the two were disconnected. The distance from Z-control at the high state increased in order from (i) to (iv).

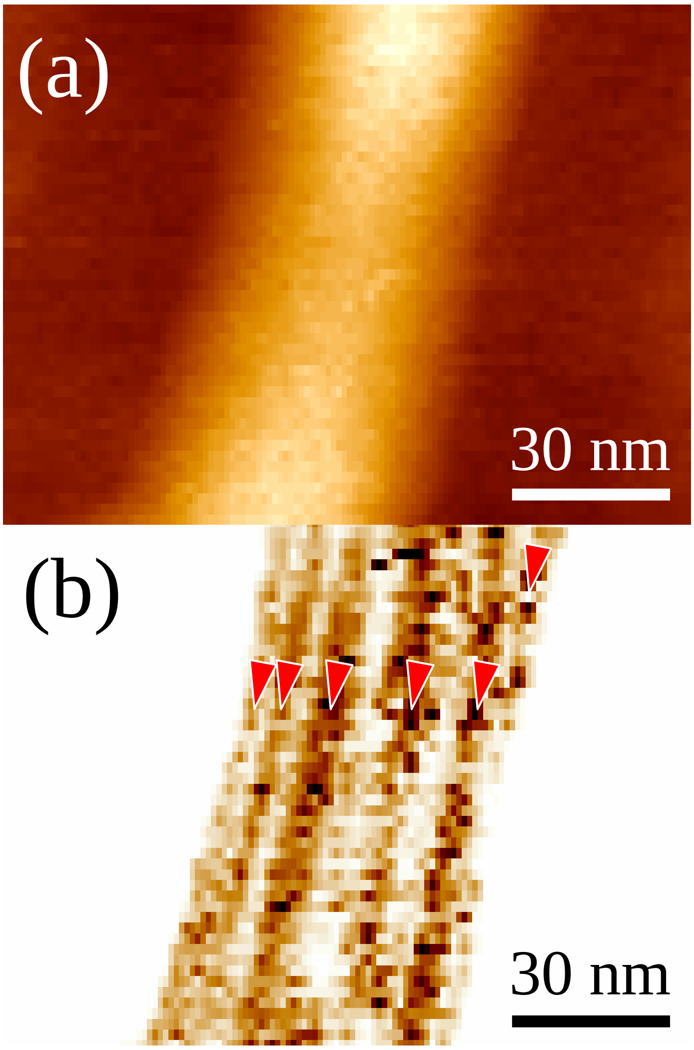

Fig.5 (a) PCI-AFM topographic image of bundled SWCNTs, and (b) current image at -1.5 V obtained in the same area. Six dark (higher current indicates darker color in the picture) strips indicated by the red triangles were observed as individual nanotubes on the surface of a bundled SWCNT wire, which can be distinguished only in the current image. Improvement in the resolution was due to the refined conditions of PCI-AFM.

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