

Carbon Nanotube Scanning Tunneling Microscopy Tips for Chemically Selective Imaging

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Carboxyl-terminated single-walled carbon nanotubes (SWNTs) were successfully immobilized from solution phases onto the apexes of gold tips for scanning tunneling microscopy (STM). Gold STM tips were first modified with self-assembled monolayers of 4-mercaptopbenzoic acid, and its carboxyl groups were used to anchor carboxylated SWNTs through Zn²⁺ ion-bridged coordination. These SWNT tips gave high-resolution STM images of a diether monolayer formed on the graphite surface. In addition and more importantly, the ether oxygens of the sample molecules were selectively observed as bright spots with the SWNT tips with significantly high reproducibility, which is due to the facilitation of electron tunneling through hydrogen bond interactions between the ether oxygens and carboxyl groups at the end of the SWNT tips.

Scanning tunneling microscopy (STM) has been a powerful tool to study conducting surfaces because of its high spatial resolution.¹ It is, however, often difficult to discriminate functional groups and chemical species. We have recently found that rational chemical modification of STM tips by self-assembled monolayers (SAMs)^{2–5} or polypyrrole⁶ allows the controlled discrimination of chemical species based on chemical interaction between functional groups on the tip and sample. These chemical selectivities can be ascribed to the facilitated electron tunneling through the overlap of the electronic wave functions of tip and sample formed by chemical interactions, such as hydrogen bond or coordination bond interaction, between chemically modified tips and the samples.^{2–7} Others also have reported that the attachment of an atom/molecule onto a STM tip apex enables differentiation of chemical species.^{8–14}

Carbon nanotubes (CNTs) can be regarded as hollow cylinders with diameters of a few nanometers. Despite their tiny dimensions, they are mechanically robust and buckle reversibly. In addition, the high electron conductivity of the CNTs is one of the characteristics that makes CNT an attractive material for use as the STM tips, which probe tunneling current flowing to or from sample surfaces. In fact, two research groups have reported that CNT tips allow STM observation to reveal the atomic arrangement of the sample surfaces.^{15,16} The CNT tips are also ideal for atomic force microscopy (AFM) and have been extensively studied to improve spatial resolution of AFM.^{17–23} Furthermore, CNTs can be chemically derivatized and functionalized at their ends with various functionalities, as demonstrated in chemical force microscopy with functionalized CNT tips.^{24–26} These CNT tips were first prepared by mechanically attaching CNTs on a commercial cantilever tip by acrylic adhesive or amorphous carbon under viewing with an optical microscope or a scanning electron microscope.^{15–20,24–26} Recently, it was shown that the CNT tips can also be fabricated by in situ attachment of CNTs onto AFM tips during observation²³ or by chemical vapor deposition to directly grow CNTs on AFM tips.^{21,22}

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We report herein for the first time that the STM tips of single-walled carbon nanotubes (SWNTs), smaller CNTs than multi-walled carbon nanotubes and thus expected to allow higher resolution, can be prepared by simple wet chemistry using a reported immobilization procedure of SWNTs onto a flat solid surface.^{27,28} Carboxylated SWNTs were attached to gold tips coated with SAMs of 4-mercaptobenzoic acid through Zn^{2+} ion-bridged coordination.²⁷ This adds another method to the earlier reported ones^{15,16} for the preparation of CNT STM tips. With these SWNT tips, it is demonstrated that the ether oxygens of the sample can be selectively and highly reproducibly recognized at high resolution by facilitation of electron tunneling through hydrogen bond interaction between the ether oxygens and carboxyl groups at the apex of SWNTs. The carboxylated SWNT termini are accessible to a variety of covalent chemical modifications through amide coupling from the terminal carboxyl groups to attach molecules having desired functional groups therein.^{24–26} On the basis of our previous studies,^{2–7} the results described in this paper may indicate that the rational modification of SWNT tips allow aimed differentiation of chemical species.

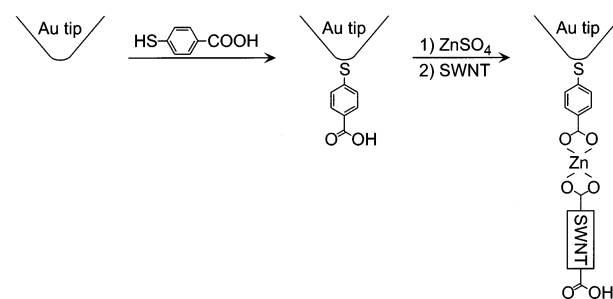
EXPERIMENTAL SECTION

Reagents. As-produced SWNT was purchased from Fruuchi Chemicals (Tokyo, Japan) and refluxed for 4 h in HNO_3 ^{29,30} or ultrasonicated in $\text{HNO}_3/\text{H}_2\text{SO}_4$ (1/3) for 8 h.³¹ It has been known that both treatments cause segmentation and carboxylation of SWNTs at their terminus.^{29–31} The sample diether, 1,11-bis-(hexadecyloxy)undecane ($\text{CH}_3(\text{CH}_2)_{15}\text{O}(\text{CH}_2)_{11}\text{O}(\text{CH}_2)_{15}\text{CH}_3$), was synthesized as described previously.⁴ Deionized water purified with a Milli-Q water system (Japan Millipore, Tokyo, Japan) was used throughout all experiments.

Tip Modification. STM tips were prepared from gold wire (0.25 mm diameter, Nilaco Co., Tokyo, Japan; 99.95%) by electrochemical etching in 3 M NaCl at AC 10 V. They were washed by sonicating in pure water and further dipping in “piranha solution” (7:3 concentrated H_2SO_4 /30% H_2O_2 . *Caution: piranha solution reacts violently with organic compounds and should not be stored in closed containers*) and finally washed again with pure water. Carboxyl-terminated SWNTs (see above) were immobilized by the three-step procedure as illustrated in Scheme 1. First, gold STM tips were immersed for more than 12 h in a 1–10 mM ethanolic solution of 4-mercaptobenzoic acid, followed by rinsing with ethanol and pure water. These tips modified with 4MBA SAMs were dipped in a saturated aqueous solution of ZnSO_4 for 5 min and further immersed in the dispersion of the carboxylated SWNTs (about 0.1 mg/mL) for more than 24 h.²⁷

STM Observation. STM measurements were performed on a Nanoscope E (Digital Instruments, Santa Barbara, CA). The diether was dissolved in 1,2,4-trichlorobenzene (near saturation), and the resulting solution was applied onto freshly cleaved highly oriented pyrolytic graphite (HOPG; Digital Instruments). Mea-

Scheme 1



surements were performed with the constant current mode under ambient conditions. Typically, a bias voltage varying from -0.5 V to -1.0 V (sample negative) and a tunneling current of 0.5 – 0.9 nA were employed. No bias dependence was thereby observed. It was also confirmed that no polarity dependence was observed by applying the reversed potential.

Transmission Electron Microscopy (TEM) Observation.

TEM observation was carried out on a HF-2000 (Hitachi, Tokyo, Japan) instrument at optimum defocus with an accelerating voltage of 200 kV. The TEM samples were prepared by gluing the SWNT tips to a single hole Cu grid. Care was taken to avoid damage during the observation by minimizing exposure of the sample to the electron beam.

RESULTS AND DISCUSSION

First, we studied the immobilization of SWNTs on STM gold tips by means of TEM. When SWNTs oxidized by ultrasonication in $\text{HNO}_3/\text{H}_2\text{SO}_4$ were used for the tip modification, we found that not only SWNTs but also the multilayer of aggregated carbon nanoparticles (CNPs) were attached to the tip (Figure 1a). Indeed, it was reported that crude SWNTs thus treated include at least 1/3 (w/w) of CNPs as impurities.³⁰ With these “dirty” SWNT tips, we often observed disruptive tunneling current during the STM observation. A most plausible explanation for this unstable tunneling current is desorption of the CNPs in the overlayers during the observation. In contrast, these CNPs were not observed on the tips when SWNTs oxidized by refluxing them in HNO_3 were used (Figure 1b). Instead, SWNT bundles of ~ 10 nm width were successfully immobilized onto the underlying gold STM tips. The absence of the CNPs in these SWNTs is probably due to favorable oxidative consumption of CNPs over SWNTs during refluxing them in HNO_3 .³⁰ With these “clean” SWNT tips, no disruption of the tunneling current was observed. This result shows that the 4MBA/Zn/SWNT assembly fabricated from the solution phases is sufficiently robust for the STM observation.

Figure 2 shows STM images of diether observed with (a) an unmodified tip, (b) a tip modified with a 4MBA SAM, and (c) an SWNT tip. Pairs of bright lines, which indicate high tunneling conductivity, were observed with 4MBA-modified tips (Figure 2b), whereas these bright lines were absent in images observed with unmodified tips (Figure 2a). We earlier demonstrated that the pairs of the bright lines in Figure 2b correspond to the two ether oxygens of the diether molecules.^{4,5} This change in image contrast selective to the ether oxygens was ascribed to the facilitation of the electron tunneling by hydrogen bond interaction between the ether oxygen of diether and the carboxyl group of 4MBA on the tip. These pairs of bright lines, which reveal the positions of the

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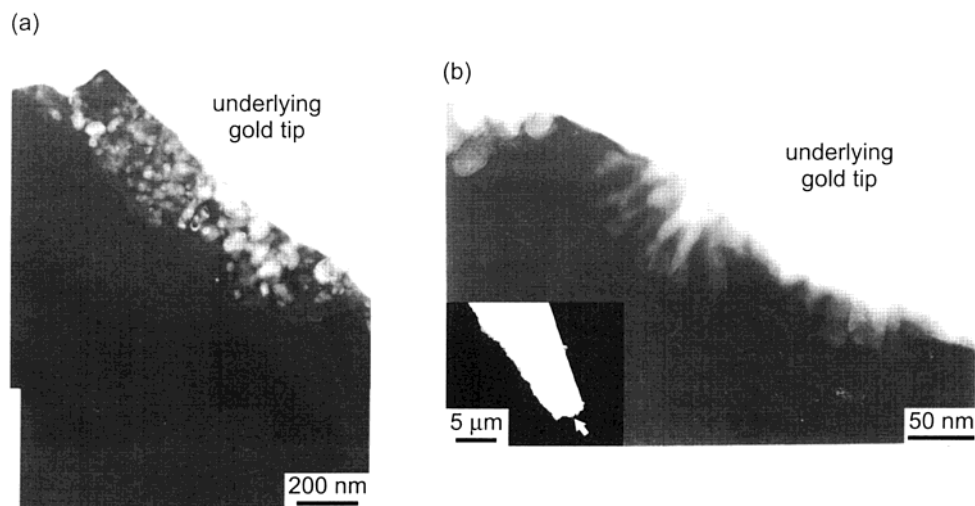


Figure 1. TEM micrographs of STM tips near their apices. (a) Modified with unpurified SWNTs. Aggregated CNPs were immobilized on the underlying gold tip. (b) Modified with purified SWNTs. SWNTs nearly free of CNPs were immobilized on the underlying gold tip. The image was taken near the tip apex marked by the arrow in Inset that shows the whole underlying gold STM tip.

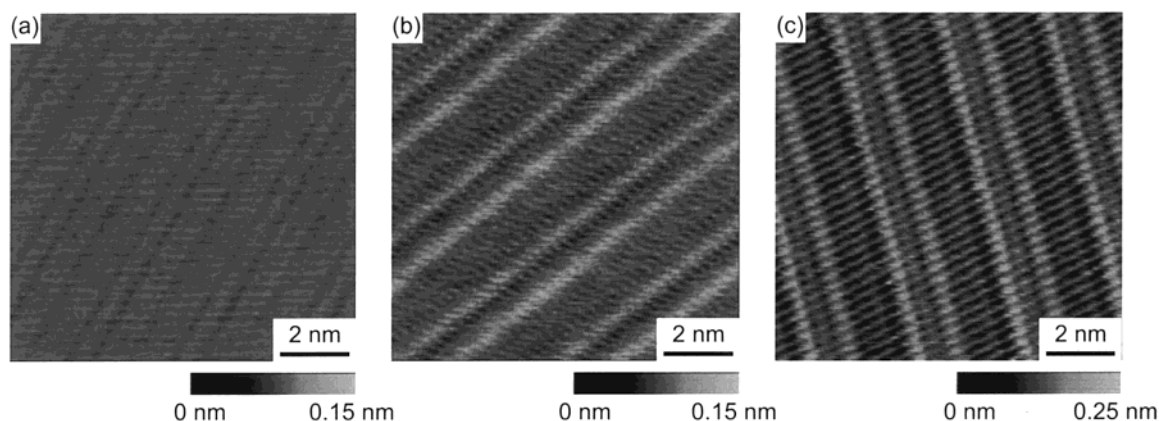


Figure 2. STM images of a diether monolayer physisorbed from a 1,2,4-trichlorobenzene solution onto HOPG. (a) Observed with an unmodified gold tip: sample bias voltage, -0.9 V (sample negative); and tunneling current, 0.7 nA. (b) Observed with a tip modified with the SAM of 4MBA: sample bias voltage, -1.0 V (sample negative); tunneling current, 0.7 nA. (c) Observed with a SWNT tip: sample bias voltage, -1.0 V; tunneling current, 0.4 nA.

two ether oxygens of the sample molecules, were observed also with an SWNT tip (Figure 2c). The similarity between the STM images obtained with 4MBA-modified tips (Figure 2b) and those obtained with the SWNT tips (Figure 2c) suggests that the contrast enhancement in Figure 2c also reflects the facilitated electron tunneling by hydrogen bond interaction between the ether oxygens of the sample and the carboxyl group at the end of the SWNT. In Figure 2c, individual hydrogen atoms of the methylene groups were resolved, in contrast to Figure 2b. The observed result suggests that this SWNT tip gave STM images with an improved chemical selectivity and a higher lateral resolution as compared with the earlier SAM-modified tip.^{2–5} In addition, the corrugation of the sample molecules is more clearly resolved in Figure 2c than it is in Figure 2b. The small diameters of SWNT or SWNT bundles on the tip are probably responsible for the improved resolution. In general, oxidatively shortened SWNTs have a broad distribution of their length, as seen in Figure 1b. Because the tunneling current flows only through the foremost part of the probe tip, this heterogeneity guarantees the high resolution achieved in this study, even if not an individual SWNT but a larger SWNT bundle is present at the tip apex. The improved

resolution would be more advantageous with highly corrugated samples, such as DNAs or proteins.

When tips modified with 4MBA SAMs were used, the number of tips that exhibited the changes in image contrasts for ether oxygens was rather limited (about 24%).^{4,5,7} This lack of contrast enhancement was explained by the removal of a 4MBA molecule from the very apex of the tip during the imaging as a result of the lateral mobility of the SAM molecules. Because of the exponential dependence on the distance between tip and sample of the tunneling current, the presence of a 4MBA molecule at the very apex of STM tips is a requisite for the contrast enhancement. In contrast, 20 SWNT tips out of 44 examined tips exhibited molecular resolution, and among this, 15 SWNT tips (75%) gave STM images that exhibited selective changes in image contrast of the ether oxygens. The van der Waals interaction between SWNTs is expected to be strong and is, in fact, evidenced by their preferential bundle formation, as seen in Figure 1b. This strong interaction probably stabilizes the SWNT layer on the underlying SAMs, resulting in the improved reproducibility of the observed contrast change observed in the present study.

SWNT is either metallic or semiconducting, depending on its diameter and chiral angle, and of these, about two-thirds are reported to be semiconducting. In this study, however, we have not observed the semiconducting behavior of the SWNT tips, such as bias or polarity dependence of the image contrast. This may suggest that not individual SWNTs, but SWNT bundles are immobilized onto the underlying gold STM tips and that the bundles show a metallic conductivity because of intertube electronic coupling.^{31,32}

The current–voltage characteristics of CNTs are of interest for fundamental understanding of their electronic structures. In principle, scanning tunneling spectroscopy (STS) using CNT tips would allow such a characterization. However, we could not perform reliable STS measurements. This may be attributed to an unstable or insufficient electrical contact at 4MBA/Zn/SWNT interfaces. This problem is quite common not only to CNT tips

for STS but also to almost all applications of CNTs.¹⁶

CONCLUSIONS

The present study demonstrates that the use of SWNT tips allows chemically selective and highly reproducible STM observation, encouraging us to develop further functionalization of the end of a SWNT tip that would tune the chemical selectivity by rationally designing the chemical interactions between the SWNT tip and the sample. STM observation selective to the metal ion based on a coordination bond has been already demonstrated with SAM modified tips.³ The chemical functionalization of SWNT tips is now in progress for chemically selective imaging based on charge-transfer interaction.

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