Electronic Supplementary Information

Selective Visualization of Point Defects in Carbon Nanotubes at the Atomic Scale by an Electron-Donating Molecular Tip

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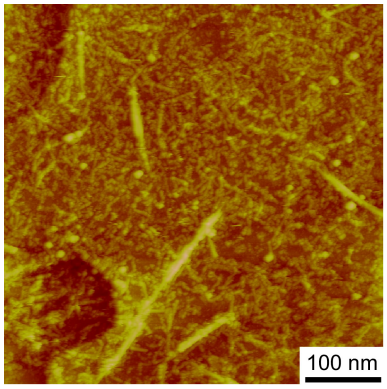

Fig. S1 A large-scale STM image of individual and bundled SWNTs on a Au(111) surface observed with an unmodified metal tip. Bias voltage (V_b) +1.3 V, tunneling current (I_t) 0.54 nA. A large amount of the SWNT solution (approximately 100 μL) was applied onto the Au(111) substrate in order to increase the number of immobilized SWNTs. The bundles were found to align nearly 120° to one another, reflecting the three-fold symmetry of the underlying Au(111) substrate. This result indicates a very high degree of cleanliness along the SWNT surface because it has been reported that such an alignment was seen only with well-purified carbon nanotubes.[1]

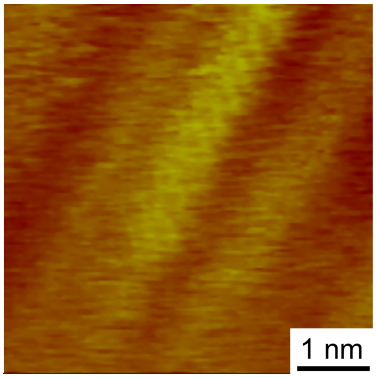

Fig. S2 An atomically resolved STM image of SWNT terminal observed with an unmodified metal tip. V_b= +0.75 V, tunneling current I_t = 0.3 nA.

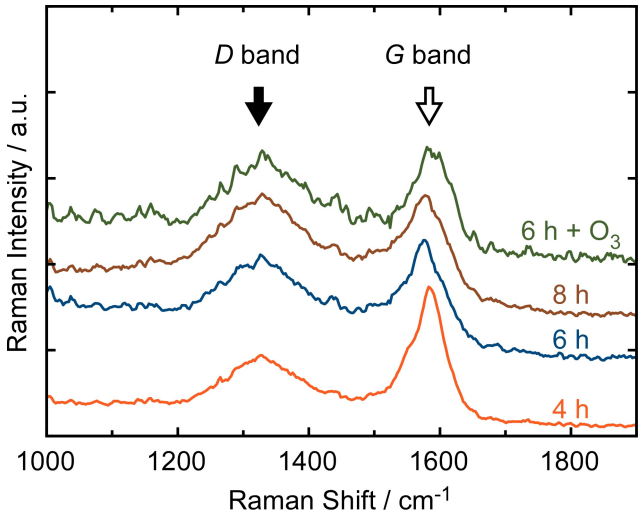

Fig. S3 Raman *D*- and *G*-bands (black and white arrows, respectively) of 4-h, 6-h, and 8-h oxidized SWTNs, and SWNTs oxidized in the mixed acid for 6 h and further exposed to UV-ozone for 1 min.

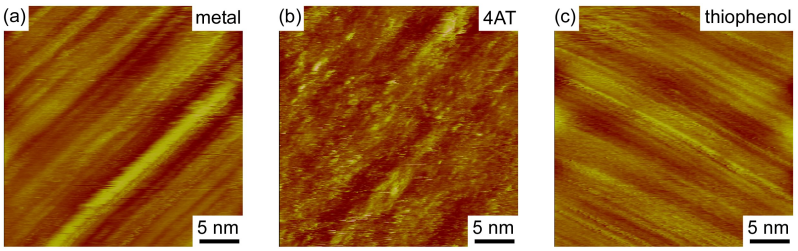

Fig. S4 STM images of SWNTs oxidized in the mixed acid for 6 h and further exposed to UV-ozone for 1 min. (a) Observed with a metal tip. V_b = 0.61 V, I_t = 0.57 nA. (b) Observed with a 4AT tip. V_b = 0.68 V, I_t = 0.44 nA. (c) Observed with a thiophenol tip. V_b = 0.70 V, I_t = 0.55 nA.

Evaluation of Au Tips

We have developed molecular tips for STM. Au tips are chemically modified with self-assembled monolayers of organosulfur compounds in order to construct the molecular tips. Although it is demonstrated that these molecular tips enable chemically selective imaging at the single molecule level, one might suspect that the gold is not ideal material for the use of (underlying) STM tips. Therefore, we investigate whether this is correct. Atomic resolution is easily achieved for highly oriented pyrolytic graphite (HOPG, Fig. S5a). Observation of monatomic steps of a Au(111) surface (Fig. S5b, c) revealed sufficient and accurate vertical resolution of the Au tips. No artificial image caused by, e.g., a multiply protruded tip was observed with all the investigated tips (over 30). Furthermore, we observed no discernible change in the image quality during continuous imaging of the Au(111) terrace-step structure for a couple of hours, showing sufficient stability of the Au tips. These results confirm the reliable STM imaging performed with the Au tips.

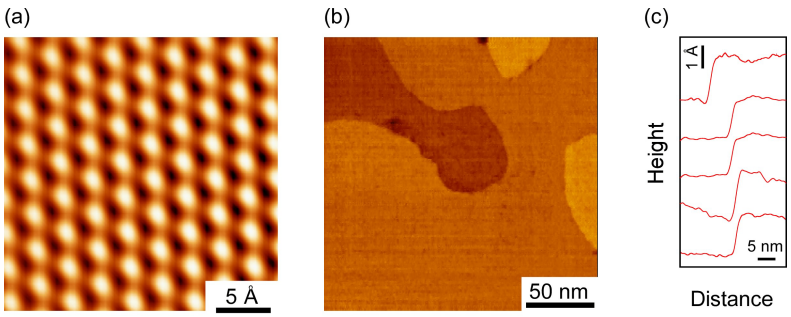

Fig. S5. (a) STM image of HOPG observed with a Au tip. V_b = +0.2 V, I_t = 1.0 nA. (b) STM image of Au(111) observed with a Au tip. V_b = +0.5 V, I_t = 0.5 nA. (c) Representative cross-sectional profiles of Au(111) monatomic steps. Each profile was measured with STM images taken with different Au tips.

Experimental Procedures

General. The reagents were purchased from Tokyo Kasei Kogyo (Tokyo, Japan) otherwise specified and of the highest grade available. De-ionized water purified with a Milli-Q water purification system (Japan Millipore, Tokyo, Japan) was used throughout the experiments.

Oxidation of SWNTs. Thoroughly purified HiPco SWNTs were purchased from Carbon Nanotechnologies Inc. Typically, 10 mg of as-received SWNTs was added to 40 mL of a 3:1 mixture of concentrated H_2SO_4/HNO_3 in a 100-mL test tube, and ultrasonicated for 4, 6, or 8 hours. The resultant dispersion was then diluted with 200 mL of water, and oxidized SWNTs were collected on a 100-nm pore PTFE membrane filter (Advantec, Tokyo, Japan). After thorough wash with water, the SWNTs on a filter were dried in vacuum overnight. The dried SWNTs were pealed off and added into DMF or *N*-methylpyrrolidone (0.1 mg/mL), and ultrasonicated.[2] Appropriate amount of the acid-oxidized and dried SWNTs was placed on a PTFE membrane filter, further oxidized by exposure to UV-ozone for one min with a PL16-110 photo surface processor (Sen Lights Co., Osaka, Japan) and successively dispersed in *N*-methylpyrrolidone (0.1 mg/mL) by ultrasonication.

Preparation of 4-Aminothiophenol (4AT) Molecular Tips. Small pieces of gold wire (0.25 mm diameter, Nilaco Co., Tokyo, Japan; 99.95%) were electrochemically etched in 3 M NaCl at AC 10 V. They were washed by sonicating in water and further dipping in "piranha solution" (7:3 concentrated H_2SO_4/H_2O_2. *Caution: piranha solution reacts violently with organic compounds and should not be stored in closed containers*), and finally rinsed thoroughly with water. 4AT molecular tips were prepared by

self-assembly of 4AT molecules onto underlying gold tips. For the formation of the self-assembled monolayer, 4AT was dissolved in ethanol at a typical concentration of 5 mM, and the gold tips were immersed in the solution overnight. The modified tips were successively rinsed with ethanol and water prior to use.

Preparation of Ultraflat Au(111) Substrates. An atomically flat Au(111) thin layer, 200 nm thick, was prepared by thermal evaporation of Au (Nilaco) onto mica (Nilaco) under vacuum. The microscope glasses (8 mm × 8 mm) were glued onto the Au layer with Epotek 377 (Epoxy Technology, Billerica, MA, USA), and these assemblies were heated at 150ºC in an electric oven for 1.5 h. The mica sheet was stripped off to expose an ultraflat clean Au(111) surface. [3]

STM Observation. Immediately after the exposure of the Au(111) surface by stripping mica, the Au surface was washed with water, and dried under a dry stream of Ar. Then, 7.5 μL of SWNT suspension was applied thereon. The Au surface was blown by an Ar stream to remove excess suspension and observed with STM (Nanoscope E; Digital Instrument, Santa Barbara, CA) operated at room temperature in air. Alternatively, SWNTs were immobilized onto 4AT-modifid Au(111) surface by spin coating according to literature.[4] Similar STM images were obtained irrespective of the immobilization process. The images were recorded in the constant current mode at a bias voltage of +0.5 to +1.0 V and tunneling current of 0.2–0.5 nA. We observed almost no facilitation of electron tunneling at the defects when a sample negative bias voltage was used, being consistent with our earlier study.[5]

References

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