

AFM and STM characterization of thiol and thiophene functionalized SWNTs: pitfalls in the use of chemical markers to determine the extent of sidewall functionalization in SWNTs†

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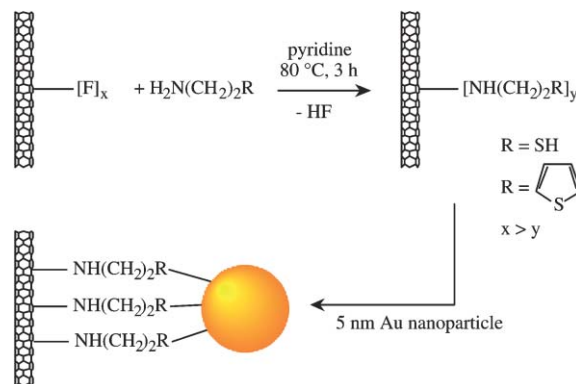
Thiol- and thiophene-functionalized SWNTs prepared *via* the reaction of a substituted amine with fluoronanotubes show similar levels of sidewall functionalization, however, the use of Au nanoparticles as chemical markers for AFM gives misleading results for substituent distribution since STM shows the thiol substituents grouped in bands while the thiophene substituents uniformly distributed along the SWNTs.

The unusual electrical and mechanical properties of single walled carbon nanotubes (SWNTs) have been the subject of much investigation,^{1,2} however, it is the functionalization, in particular of the sidewalls, that has recently become a key area of SWNT chemistry.³ A wide range of reactions has been developed, including, but not limited to: oxidation of the side walls,⁴ reactions with aryldiazonium salts,⁵ carbenes and nitrenes,⁶ and free radicals.⁷ The extent of sidewall functionalization is often demonstrated by thermogravimetric analysis (TGA) and spectroscopically by IR and Raman. In particular, the occurrence and magnitude of the D (disorder) mode at 1330 cm⁻¹ in the Raman spectrum has been previously used to indicate the presence and extent of functionalization.⁸ However, except where the substituents are significantly larger than the SWNT diameter allowing for AFM measurements, the distribution of substituents along the tubes length is difficult to ascertain. With this problem in mind, Green and co-workers have shown that sidewall functionalization of SWNTs with a sulfur containing substituent as a “chemical marker” allows for the indirect AFM imaging of the substituents upon binding of gold nanoparticles.⁹ This simple, but effective, method should allow for confirming the presence as well as distribution of substituents. We have been interested in reactivity of fluorinated SWNTs with amines and other strong nucleophiles.¹⁰ The resulting fluorine displacement reaction results in functionalized SWNTs in which the number of substituents is significantly lower than the number of F atoms on the original fluoronanotube.¹¹ STM measurements have shown fluorine is present in long bands along the length of the SWNT,¹² thus,

subsequent functionalization will occur in these areas. As part of our investigations we have prepared the SWNT substituted with the thiol and thiophene terminated moieties in order to determine the distribution of the functional groups along the sidewalls. However, during characterization there appeared a disparity between TGA analysis and the AFM images over the extent of functionalization. In order to clarify this we have attempted to correlate the AFM images of gold nanoparticle decorated SWNTs with the STM images to study distribution of functional groups. These results are reported herein.

HiPCo SWNTs produced at Rice University were purified to remove iron and other impurities,¹³ and subsequently fluorinated, to a C : F ratio of approximately 2.4 : 1, by direct fluorination at 150 °C by a previously reported procedure.¹⁴ The fluoronanotubes were functionalized by reaction with the appropriate amine in the presence of a base catalyst (Scheme 1).¹⁵ The IR spectra of thiol-SWNT (**1**) and thiophene-SWNT (**2**) derivatives show bands associated with the substituents.

The Raman spectra using 780 nm (red laser) show peaks typical of functionalized SWNTs (Fig. 1). If the relative intensity of D (disorder) mode at ~1290 cm⁻¹ *versus* the tangential G mode (1500–1600 cm⁻¹) is a measure of the level of substitution,⁸ then the thiophene-SWNT (**2**) should have significantly greater functionalization than the thiol-SWNT (**1**), however, from the TGA weight loss data the SWNT-C : substituent ratios may be calculated to be 19 : 1 (**1**) and 17.5 : 1 (**2**). Thus, contrary to the Raman data the TGA suggest that the number of substituents per C (in the SWNT) is actually similar for both substituents.



Scheme 1 Synthesis of functionalized SWNTs and the introduction of “chemical markers” for AFM visualization.

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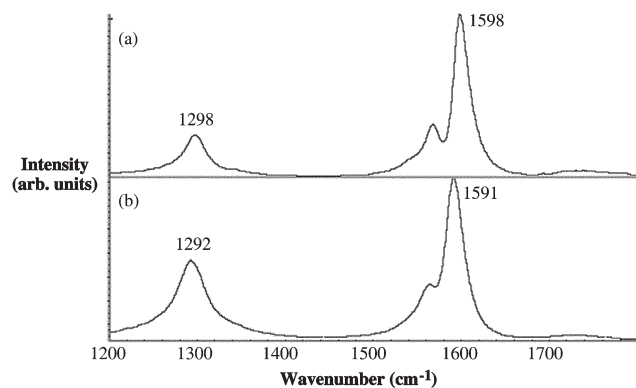


Fig. 1 Raman spectrum of (a) thiol-SWNT and (b) thiophene-SWNT using 780 nm excitation, showing the relative intensity of the D (disorder mode) at *ca.* 1300 cm^{-1} versus the tangential G mode at *ca.* 1590 cm^{-1} .

Since both thiol and thiophene substituents should allow binding to gold, we have used the method of Green and co-workers⁹ to “tag” the functional groups *via* their coordination of gold nanoparticles (Scheme 1).¹⁶ Fig. 2 shows representative AFM

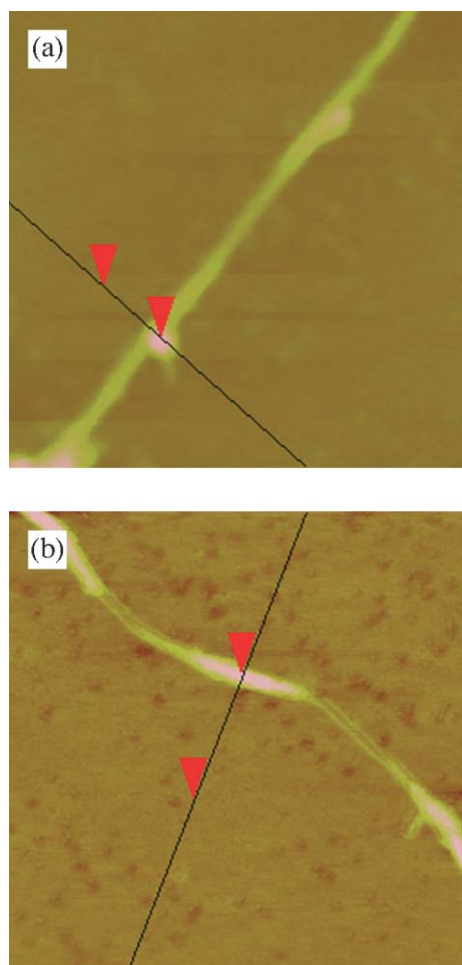


Fig. 2 Representative tapping mode AFM images and height profiles of (a) thiol-SWNT and (b) thiophene-SWNT decorated with pre-formed 5 nm colloidal gold nanoparticles.

images of thiol-SWNT and thiophene-SWNT decorated with gold nanoparticles (*i.e.*, Au-thiol-SWNT and Au-thiophene-SWNT, respectively). The AFM images and height measurements of the Au-thiol-SWNT (Fig. 2a) show the presence of individual gold nanoparticles decorating the side of the SWNTs. The gold nanoparticles appear spaced along the length of the SWNT such that the most of the sidewalls of the SWNTs are unfunctionalized. In contrast, the AFM images of the Au-thiophene-SWNT show long bands of continuous gold-functionalized and unfunctionalized regions. We can estimate that there are approximately 8–10 times more Au nanoparticles per SWNT for the thiophene functionalized SWNT. If it is assumed that each gold nanoparticle is bound by the same number of substituents, this result would suggest that the thiophene-SWNT are more highly functionalized than the thiol analogs. While this conclusion would agree, in part, with Raman measurements, it is not supported by TGA data.

In order to directly image the presence of the substituents on the SWNTs we have undertaken an STM analysis of the

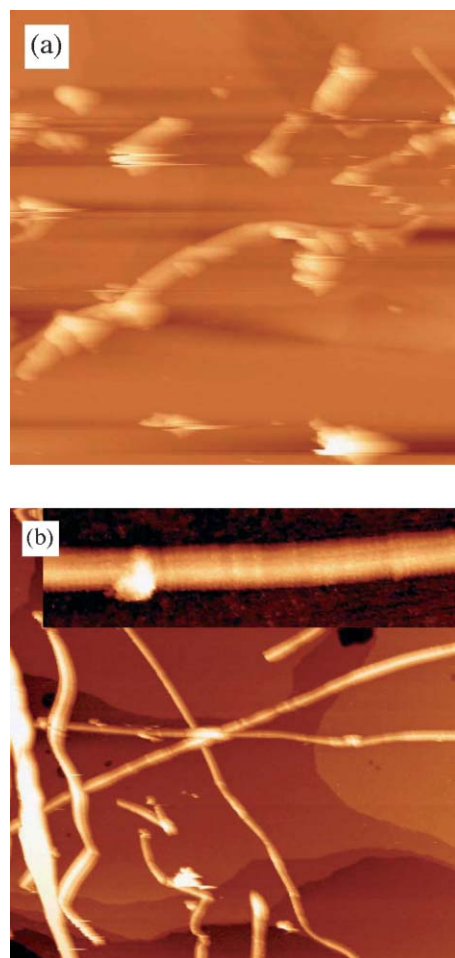
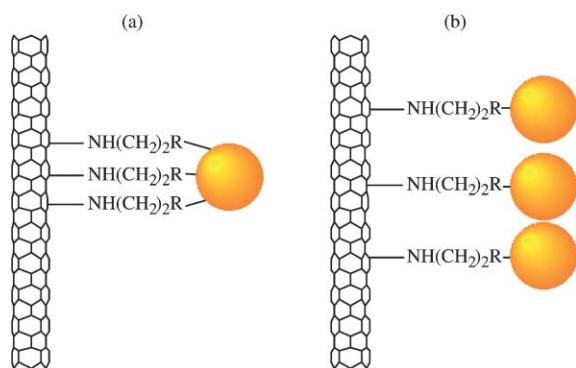


Fig. 3 Representative STM images of (a) thiol-SWNT [$4560 \times 4560\text{ \AA}$, $I_t = 3.25\text{ pA}$, $V_{\text{bias}} = -498\text{ mV}$] and (b) thiophene-SWNT [$3460 \times 3460\text{ \AA}$, $I_t = 5.66\text{ pA}$, $V_{\text{bias}} = -800\text{ mV}$] inserted into hexanethiol self-assembled monolayers on gold surfaces. Inset in (b) is a higher resolution image of the local defects on the thiophene nanotubes [$550 \times 140\text{ \AA}$, $I_t = 25.5\text{ pA}$, $V_{\text{bias}} = -800\text{ mV}$].



Scheme 2 Schematic representation of the functional group distribution and binding of gold nanoparticles for (a) thiol-SWNT and (b) thiophene-SWNT.

functionalized SWNTs on gold surfaces; representative images are shown in Fig. 3.¹⁷ STM images of thiol-SWNTs (Fig. 3a) show that multiple functional groups are present on the SWNT in tight bands of approximately 5–25 nm in length. In contrast, the STM images of thiophene-SWNT (Fig. 3b) show narrow bands (<1 nm in width) of functionalization spread out uniformly along the whole length of the SWNT. The spacing between these bands is approximately 4 nm, coincidentally, comparable to the diameter of the gold nanoparticles.

Based upon the forgoing, it appears that while thiol and thiophene functionalization of SWNTs *via* the reaction of fluoronanotubes with the appropriate amine (Scheme 1) results in similar levels of functionalization, the distribution of the functional groups is quite distinct. The functional groups on the thiol-SWNT are grouped together and each group is of a size that binds to a single gold nanoparticle. The wide distribution of, possibly individual, functional groups in the thiophene-SWNTs allow for the binding of large groups of gold nanoparticles. These groups occupy the regions of the SWNT that was originally fluorinated. The distance between these is such that with AFM it appears that multiple Au nanoparticles may be complexed per region. These results are summarized in Scheme 2.

From these results we conclude that while AFM and the complexation of a “chemical marker” nanoparticle is an excellent method for determining the presence of functionalization on SWNT side walls, it can lead to confusing results with regard to the distribution of the functional groups. Conversely, STM provides excellent information as to substituent location. Finally, we note that while the presence of a D mode in the Raman spectra of SWNTs indicates disorder (*i.e.*, side wall substitution) it cannot differentiate between the number of substituents and their distribution.

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- Ethanol solutions of the functionalized SWNTs were spin coated on a mica surface. The nanotubes-coated mica substrate was submersed in HPLC grade water (10 mL) containing 5 nm gold colloids (0.1 mL, 5×10^{13} particles mL^{-1} , Ted Pella) for 1 h. The surface was then washed with HPLC grade water (10 mL) and dried at 4000 rpm on the spin coater.
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