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Investigating Self-assembly of Functionalized Nanotubes and Peptides by Tunneling Microscopy

By

Jun Zhang

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APPROVED, THESIS COMMITTEE:

Kevin F. Kelly
Assistant Professor, Department of Electrical and Computer Engineering

Junichiro Kono
Associate Professor, Department of Electrical and Computer Engineering

Peter J. A. Nordlander
Professor, Department of Physics and Astronomy

HOUSTON, TEXAS

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Jun Zhang

Abstract

Self-assembly has proven a powerful technique for patterning and building devices at nanoscale. Scanning tunneling microscopy (STM) is an ideal tool for probing the chemistry and physics of these types of nanostructures. Building upon on our previous carbon nanotube research, we have investigated thiol and thiophene sidewall functionalized single-walled carbon nanotubes (SWNTs). The motivation is to use these functional groups as a means to self-assemble tubes on surfaces by exploiting the well-established Au-S chemistry. Thiol and thiophene substituted nanotubes were self-assembled on bare gold surfaces as well as inserted into hexanethiol self-assembled monolayers and imaged by STM. The thiol and thiophene functional groups work as anchors, strongly binding the SWNTs to the gold. Additionally, we have measured the size and spatial distribution of the functional groups along the nanotube sidewalls. Furthermore, we have extended this self-assembly technique to biological applications where individual fullerene-terminated peptide molecules have been successfully imaged by STM with the help of insertion into close-packed alkanethiol monolayers.
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Chapter 1

Introduction

1.1 Scanning Tunneling Microscopy

The first scanning probe microscope (SPM) was the scanning tunneling microscope (STM), invented in 1981 by Heinrich Rohrer and Gerd Binning of the IBM Zurich Research Center in Switzerland. In 1986 Binnig and Rohrer shared the Nobel Prize in Physics for their design of the STM.¹

The scanning tunneling microscopy is based on the quantum mechanical phenomenon of tunneling. The tunneling current of electrons penetrates the gap between the metal probe tip and the sample surface, which is the classically forbidden energy barrier. Consequently, it allows the STM to investigate the surface nondestructively without contact. The real-space, real-time and sub-angstrom resolution of STM makes it possible to investigate the surface properties of materials on a nanometer scale. Although the understanding of the physics at the STM junction is incomplete even now, the sub-angstrom lateral and vertical resolutions yield some physical and chemical properties related to the behavior of surface electrons. Moreover, STM has also proven an ideal tool in both physical and chemical fields, such as nanometer lithography ² and manipulation³,⁴ and even STM induced chemical reaction.⁵ Working with the high resolution piezoelectric scanner, STM can image the small objects like nanotubes, nanowires and even some specific molecules, which are placed on the conducting or semiconducting surface. The previously demonstrated capabilities of STM promise it a bright future in the nanoscale science field.
1.2 Single-Walled Carbon Nanotubes (SWNTs) and Functionalization

Single-walled carbon nanotubes (SWNTs) are one-dimensional nanometer-diameter cylinders consisting of a single graphene sheet wrapped up to form a seamless tube, typically capped by hemispherical ends composed of pentagons and hexagons. Since their discovery in the early 1990s, there has been intense activity exploring the electrical properties of SWNTs and their potential applications in electronics. Experiments and theory have shown that SWNTs can be either metallic or semiconducting, depending on their diameter and chirality. Their electrical properties can rival, or even exceed, the best metals or semiconductors known. Particularly illuminating have been electrical studies of individual nanotubes and nanotube ropes (small bundles of individual nanotubes). The first studies on metallic tubes were done in 1997 and the first on semiconducting tubes in 1998.

According to various applications of SWNTs, the preparation, processing and manipulation require the dispersion and solubilization of SWNTs, which in their pristine form are not soluble in most common organic solvents and water. To address this problem, functionalization has become a key area of SWNTs chemistry. The solubility of functionalized SWNTs in common organic solvents and/or water allows solution-based techniques to be used in the characterization of the nanotube samples and in the study of fundamental properties of carbon nanotubes. The same solubility also offers unique opportunities in the development of carbon nanotubes-based materials and in the use of the solubilized carbon nanotubes as starting materials for further chemical and biochemical modifications.
Functionalization reactions usually utilize two types of chemistry: open end\textsuperscript{16,17} and sidewall.\textsuperscript{14,18,19} For the sidewall functionalization, successful nondestructive fluorination of SWNT sidewalls, which was demonstrated by Mickelson \textit{et al.} in 1998,\textsuperscript{18} has proven that it can modify the electronic properties of SWNTs. Fluorination might even be the key for tailoring the exceptional electronic properties of SWNTs, providing building blocks of different functionality for molecular electronics.\textsuperscript{20} Furthermore, fluorine atoms on the SWNT wall can be substituted by other groups, such as N-alkylidene amino groups.\textsuperscript{14, 21, 22} Using a sulfur or thiophene containing constituent, the functionalized SWNTs can be bond to Au(111) surface by using well established gold-sulfur chemistry. They can then be scanned by STM as illustrated later in this thesis.\textsuperscript{23}

1.3 Self-Assembled Monolayers (SAMs) and Insertion

The understanding and applications of self-assembly have evolved significantly since the discovery of these structures and their ability to modify the physical and chemical properties of a surface.\textsuperscript{24,25,26} Self-assembly provides a unique link between the science of organic surfaces and technologies that seek to exploit its adaptable character. Self-assembled monolayers (SAMs) are found in applications such as molecular and biomolecular recognition, lithography resists, sensing and electrode modification, corrosion prevention, and other areas where tailoring the physiochemical properties of an interface is required. Patterned SAMs, in which specific self-assembling components have a deliberate spatial distribution on the surface (planar or otherwise), are generated to fabricate sophisticated nanoscale architectures and to provide well-characterized supports for physiochemical and biochemical processes.
SAMs are highly ordered monomolecular layers, spontaneously formed from the exposure of a surface to molecules with chemical groups that possess strong affinities for the substrate or a material patterned on it. Strengthening interactions between molecules and substrates and between molecules themselves include phenomena such as hydrogen bonding, donor–acceptor and/or ion pairing, and the formation of covalent bonds, rendering the assemblies more stable than their physisorbed counterparts.

Much research has been focused on the self-assembly of n-alkanethiols and related molecules on gold substrates. Thiol-based SAMs are attractive structures for several reasons. Well-ordered SAMs can be formed from a variety of sulfur containing species (i.e., thiols, sulfides, disulfides\textsuperscript{24}), yet experiments show that thiol molecules kinetically outcompete the disulfide molecules for available surface sites when the two species are coadsorbed from solution.\textsuperscript{27} The gold surface is relatively chemically inert; it does not readily form a surface oxide nor keep a strong hold of adventitiously adsorbed material, and therefore SAMs can easily be prepared in ambient conditions. SAMs render an ordinarily conductive metal surface to be relatively insulating, yet electrons can be moved controllably through the film through applied potentials when integrated into electrochemical cells. Additionally, the molecules are stable once adsorbed on the surface, yet they can be affixed to the gold such that they can be selectively processed after adsorption.

The surface structures formed by the adsorption of n-alkanethiols on gold surfaces are generally well ordered and crystalline.\textsuperscript{24,28,29} Since the early 1990s, the STM has been used to image SAMs of n-alkanethiolates adsorbed on gold surfaces.\textsuperscript{30,31,32,33} The STM has been able to provide insight into the mechanism of SAM formation as well
as to elucidate important structural features that lend SAMs their integrity as surface-stable entities.

In an effort to understand the intermolecular dynamics of adsorbates on surfaces and to comprehend fully the mechanisms of adsorption and exchange of adsorbates in solution with those on surfaces, molecules can be placed on a surface at low fractional surface coverage within a pre-existing matrix of a SAM that has already formed. Through these studies, it has been shown that incoming "guest" molecules will insert into a "host" SAM at the step edges, domain boundaries and its other defect sites, by exposing the preformed SAM to a solution of guest adsorbates that is of low concentration (typically 0.1-0.5 mM) and for short periods of time (minutes to hours).\textsuperscript{34-38}

Combined with STM, the insertion process is an effective way to exhibit the correct geometrical, chemical and electronic properties for recognition of a specific molecule. In particular, interest in the understanding electronic properties of the nanometer-scale objectives like functionalized SWNTs, has led us to employ this method for creating isolated sites within a non-perfect alkanethiolate SAM film. Additionally, these SAMs chemically and electrically isolate the underlying substrates from their surroundings, due to their crystallinity and insulating nature. As will be demonstrated, functionalized nanotubes can be stably set down on the n-alkanethiolates SAMs by immersing the SAMs to the tube solution for a short period of time, due to the functional group inserting into the SAM and strongly bonding to the gold underneath.
1.4 Outline

Chapter 2 covers the basic theory of STM and SAMs, including tunneling theory, the working principle of STM, characters of alkanethiolates SAMs and insertion theory. Chapter 3 gives basic concepts of SWNTs, thiol and thiophene functionalized SWNTs, describes the details of sample making, and then compares the imaging results with the different substrates (Au(111) and SAMs). The insertion technique also will be discussed in this chapter. Chapter 4 covers some related research work about the insertion of a specific peptide molecule, which is terminated by a fullerene molecule (C_{60}). At last, Chapter 5 summarizes the present research and talks about the future direction and possible applications.
Chapter 2

Background

2.1 Scanning Tunneling Microscopy

The scanning tunneling microscope (STM), the ancestor of all scanning probe microscope, was invented in 1981 by Heinrich Rohrer and Gerd Binning of IBM in Zurich, Switzerland. The invention garnered the two a Nobel Prize in Physics in 1986. The STM allows scientists to visualize regions of high electron density and hence infer the position of individual atoms, where previous arduous study of diffraction patterns from prior methods led to much debate as to the real, spatial lattice structure of the material in question.

The STM is used to obtain images of conductive surfaces at a resolution of 0.2 nm (2 x 10^{-10} m). It can also be used to alter the observed material by manipulating individual atoms, triggering chemical reactions, and creating ions by removing individual electrons from atoms and then reverting them to neutral atoms by replacing the electrons.\textsuperscript{5}

The STM is a non-optical microscope which employs principles of quantum mechanics. An atomically sharp, conducting tip is moved over the surface of the material under study, and a bias voltage is applied between tip and the sample surface. When the tip is brought within about \(~10\ \text{Å}\) of the sample, electrons from the sample start to tunnel through the 10 Å gap into the tip or vice versa, depending on the direction of the bias voltage. The magnitude of the tunneling current is exponentially dependent on the distance between the tip and the sample surface. The tip is mounted on a piezoelectric
tube, which allows tiny movements by applying a voltage at its electrodes. Thereby, the
electronics of the STM system can control the tip position. Either the tunneling current or
the tip movement is recorded and can be used to form an STM image, depending upon
the scanning mode. Obviously, for a tunneling current to occur, both the sample and the
tip must be conductors or semiconductors. Insulators cannot be scanned by the STM.

The tunneling current is an exponential function of distance; if the separation
between the tip and the sample changes by 10% (on the order of 1 Å), the tunneling
current changes by an order of magnitude. This exponential dependence gives STM its
remarkable sensitivity. STM can image the surface of the sample with sub-angstrom
precision vertically, and atomic resolution laterally.

2.1.1 Basic Tunneling theory

Electron tunneling theory, the key of STM principles, is covered in many
introductory quantum mechanics and scanning tunneling microscopy texts.\textsuperscript{30,40} In order
to give a clear and simple presentation of the quantum tunneling, we will begin with a
free particle traversing a one-dimensional (1-D) rectangular potential barrier.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.1.png}
\caption{Schematic of a free particle tunneling through (1-D) rectangular potential barrier.}
\end{figure}
As shown in the Fig 2.1, unlike the classically allowed region, there are still some particles tunneling through the classically forbidden region. To begin with, we try to explain it by using the one-dimensional time independent Schrödinger equation for the free electron,

$$\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + U(x)\psi(x) = E\psi(x)$$

where the state of the same electron is described by a wavefunction \( \psi(x) \), and \( m \) is the electron mass, 0.511 MeV/c\(^2\) (or \( 9.1 \times 10^{-28} \) g). The rectangular potential barrier is at the origin with height \( U \) and width \( a \), and is zero everywhere else. Now for an electron with energy \( E < U \) incident from the left with these initial conditions, the solution of the Schrödinger equation gives us the wavefunction of the electron at both positions, outside and inside the barrier.

Outside the barrier, in the classically allowed region, the wavefunction has the form,

$$\psi(x) \propto \exp(\pm ikx)$$

where

$$k = \frac{\sqrt{2mE}}{\hbar}$$

is the wave vector. This solution shows that the electron has a constant velocity. The \( \pm \) sign indicates that it contains both the incident and reflected wavefunctions.

When inside the barrier, which is a classically forbidden region, the solution will be
\[ \psi(x) \propto \exp(-\kappa x), \]

where

\[ \kappa = \frac{\sqrt{2m(U-E)}}{\hbar} \]

is the decay constant. This means the electron wavefunction will decay exponentially in the \(+x\) direction. In the barrier, the quantum mechanics allows a non-zero probability of finding the electron, which would be totally reflected in a classical theory. The tunneling probability is

\[ p(x) \propto \exp(-2\kappa x) \]

which is proportional to the square of the wavefunction.

Approximately, the one-dimensional potential barrier tunneling model can be used to understand the real metal-insulator-metal tunneling problem which we encounter in STM. Assuming the difference between the barrier potential and the electron’s energy \((U-E)\) is equal to the work function of a typical metal (~4 eV) and assuming a bias voltage much less than the work function, then the value of wave vector \(\kappa\) is around 1 Å\(^{-1}\). It means the tunneling current is very sensitive to changes in barrier width, varying \(e^2 \approx 7.4\), approximately one order of magnitude in current for every 1 Å change in the barrier width. Therefore, the STM has extremely high vertical and lateral resolution.

### 2.1.2 Basic configuration of STM

The basic configuration of STM usually consists of following main elements:
• Scanning head, which includes the piezoelectric scanning elements and tip:

  Sometimes, there are two sets of piezoelectric element working together to control the tip position. One set is used for coarse approaching, and the other controls the fine scanning movement.

• Sample holder for mounting the sample:

  It also offers the bias connection, which is most important for tunneling current occurrence. If there is a variable temperature STM, the heating, cooling units and the temperature measurement unit may be designed inside the sample holder.

• Vibration isolation system:

  Scanning head and sample holder need vibration isolation to reduce the noise that comes from the intrusive mechanical vibration. The ordinary design simply employs a metal frame that suspends the microscope mechanism and uses springs and magnets for damping vibrations.

• Control electronics:

  That includes a feedback loop back to the scanning elements.

• Computer:

  Process the signals and run the accompanying interpretive software to create the STM image.

• Ultra high vacuum (UHV), not necessary:

  Although the STM itself does not need vacuum to operate (it works in air as well as under liquids), sometime UHV is required to avoid contamination of the samples from the surrounding medium.
2.1.3 STM Operation Modes

An STM can be designed to perform in either of two modes: constant-height mode or constant-current mode. In constant-height mode, the tip travels in a horizontal plane above the sample and the tunneling current varies depending on topography and the local surface electronic properties of the sample. The tunneling current measured at each location on the sample surface constitutes the data set and creates the topographic image. The constant-height mode is used mainly to investigate the electronic properties of the sample (spectroscopy).

In constant-current mode, the STM uses the feedback loop circuit to keep the tunneling current constant by adjusting the height of the scanner at each measurement point, if necessary. For example, when the system detects an increase in tunneling current, it adjusts the voltage applied to the piezoelectric scanner to increase the distance between the tip and the sample. The vertical motion of the scanner constitutes the data set. If the system keeps the tunneling current constant to within a few percent, then the tip to sample distance will be constant to within a few hundredths of an angstrom. The constant-current mode is the most common and reproduces the topography of the surface.

Each mode has advantages and disadvantages. Constant-height mode is faster because the system does not have to move the scanner up and down, but it provides useful information only for relatively smooth surface and sometimes tip-crashing occurs. Constant-current mode can measure irregular surface with high precision, but the measurement takes more time.

As a first approximation, an image of the tunneling current maps the topography of the sample. More accurately, the tunneling current corresponds to the electronic density
of the states at the surface. STM actually senses the number of filled or unfilled electron states near the Fermi surface, within an energy range determined by the bias voltage. Rather than measuring physical topography, it measures a surface of constant tunneling probability.

The sensitivity of STM to local electronic structure can cause trouble if you are interested in mapping topography. For example, if an area of the sample has oxidized, the tunneling current will drop precipitously when the tip encounters that area. In constant-current mode, the STM will instruct the tip to move closer to maintain the set tunneling current. The result may be that the tip digs a hole in the surface. However, the sensitivity to electronic structure can be a tremendous advantage. Unlike other techniques for obtaining information about the electronic properties that detect and average the data originating from a relatively large area (a few microns to a few millimeters across), STM can be used as surface analysis tools that probes the electronic properties of the sample surface with atomic resolution. Using STM as a spectroscopy tool, we can obtain the barrier height (work-function) and local density of states (LDOS) profiles, as reflected in the \( I-Z \) and \( I-V \) curves representing chemical and electronic characteristics of a surface.

### 2.1.4 Advantages of STM

Compared to a number of other modern surface analytical instruments and techniques, such as the atomic force microscope (AFM), field ion microscope (FIM), field emission microscope (FEM), low-energy electron diffraction (LEED), scanning electron microscope (SEM), transmission electron microscope (TEM), x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS),
there are several reasons for the diversity of STM and STM-based technological applications.

- STM can perform atomic-level resolution. The lateral and vertical resolutions can reach 0.1 nm and 0.01 nm, respectively, which means individual atoms or molecules can be distinguished. The higher vertical resolution of STM relative to other microscopes also offers advantages with regard to qualitative analysis of surface roughness on a nanometer scale.

- STM can work in different environments, such as air, fluid, vacuum and at high or low temperature. Special techniques for sample preparation are not required in most cases, and samples remain mostly free of damage. With these advantages, STM is suitable especially for in-situ electrochemical and limited biological studies, as well as the evaluation of surfaces in various experimental environments.

- STM measures truly localized interaction on the atomic scale rather than the averaged properties of the bulk phase or of a large surface defects and reconstructions.

- Combined with related techniques, STM can provide information about local surface electronic properties such as charge-density waves, the changes of surface barriers and energy gaps, as well as spectroscopic images.

- Through tip-sample interactions, STM can be employed for the modification of a surface and for the manipulation of atoms and molecules, opening up the prospects of constructing atomic or molecular scale devices.
2.1.5 Tip induced imaging artifact

For atomic resolution STM studies on relatively flat sample surfaces, the STM tip should terminate in a single atom, but the macroscopic shape of the tip is of little importance. Since the tunneling current is exponentially dependent on the tip-surface distance, the tip atom closest to the sample surface always gives the major contribution to the tunneling current. Another tip atom 3 Å more distant from the surface than the front tip atom would make a tiny contribution of only about 0.1% to the total current. However, it can happen that two or more atoms at the front of the tip have nearly the same distance to the sample surface, leading to double or multiple tip imaging artifacts that are easily recognized,\textsuperscript{41, 42} as shown in Fig 2.2.

![Figure 2.2: Illustration of double tip imaging.](image)

![Figure 2.3: Illustration of failure to image of a deep and narrow groove.](image)

For topographic STM studies of larger scale structures on relatively rough surfaces, the macroscopic shape of the tip also becomes important. In Fig 2.3, a tip with a relatively large cone angle fails to penetrate into deep and narrow grooves on the sample surface which leads to a smoothing of topographic surface features in STM images.\textsuperscript{43, 44} The existence of several minitips at the front end of the tip can cause additional imaging artifacts due to switching of the tunneling location from one minitip to another when scanning a rough surface.\textsuperscript{45}
In a general sense, every data point acquired while scanning is a spatial summation of both microscopic and macroscopic shape of the tip and shape of the feature being imaged. Therefore, the real image can be obtained when the tip is much shaper than the surface feature being imaged; otherwise, the scanning actually images the tip itself rather than the surface feature.\textsuperscript{44}

STM tips are typically fabricated from metal wires of tungsten (W), iridium (Ir), platinum-iridium (Pt/Ir), platinum-rhodium (Pt/Rh) or gold (Au), and sharpened by mechanical grinding, cutting with a wire cutter or razor blade, controlled crashing, field emission/evaporation, ion milling, fracture, or electrochemical etching. Tungsten tips, which fulfill the requirement of being stiff, have been used to a great extent to image specimens. However, an oxide layer may exist on the surface of the tip and sometimes makes it difficult to acquire STM images. Platinum, although a soft metal, is a material preferred over W, because it is inert to oxidation. The addition of Ir or Rh to form a Pt/Ir or Pt/Rh alloy adds stiffness while maintaining a chemically inert material. Pt/Ir and Pt/Rh tips are widely employed, particularly in atmospheric and electrochemical environments.

\subsection{C\textsubscript{60}-adsorbed STM tip}

The mechanically cut 250 $\mu$m Pt/Rh (87/13) tips are involved in all ambient experiments that this thesis mentions. During the studies of bare SWNTs and functionalized SWNTs, the STM actually scans relatively rough surfaces when the tip moves across nanotubes, since the ordinary diameters of bare or functionalized SWNTs are around 0.5nm ~ 2nm. Therefore, in order to get the best lateral resolution or even
atomic resolution, we must try to find a way that will reduce the obvious effects of multiple-tips and minitips.

The tunneling current of the STM is sensitive to the local density of states at the Fermi energy ($E_f$) of both the surface and the tip. The adsorption of a molecule such as fullerene ($C_{60}$) onto an STM tip, which can act as a tunneling site, alters the local density of states of the tip in the vicinity of $E_f$, therefore modifying the tunneling current and changing the way the tip samples the electronic states of the surface it is imaging. Resh et al. have reported improved atomic resolution on graphite when $C_{60}$ molecules were adsorbed onto STM tips.\(^{47}\) Kelly et al. have also reported the in situ characterization of $C_{60}$ adsorbed onto the active region of tunneling tips by "inverse image" \(^{48}\) and threefold electron scattering on graphite by using $C_{60}$-adsorbed tips.\(^{49}\)

There are three main reasons for the choice of $C_{60}$ molecules in the functionalization of STM tips:

- The $C_{60}$ can be adsorbed directly on the tip, because the rotational motion of $C_{60}$ is frozen by its charge transfer bonding to metal surface.
- There is no sacrifice of resolution with $C_{60}$-adsorbed STM tips. The spatial extent of the $C_{60}$ allows the tunneling junction between it and the sample to be located far from the bare metal tip. Therefore, contributions from the tunneling states of the metal are negligible due to the exponential dependence of the tunneling current.
- $C_{60}$ molecules can be elastically compressed between the STM tip and sample and still return to their original structure when the pressure is released.\(^{43, 50}\) Structural stability of the molecular tips is necessary due to the "tip crashes" that can occur during scanning,
To create the C₆₀-adsorbed STM tips, we followed the procedure that Kelly et al. mentioned 48,49,51 with a few minor alterations. We used Au (111) on mica as a substitute for highly oriented pyrolytic graphite (HOPG) for depositing the C₆₀ film. The powder form C₆₀ molecules were dissolved into toluene solvent. Then the solution was dispersed onto an Au (111) on mica substrate by drop-casting or spin-coating in ambient condition. The concentration of C₆₀ solution is not critical because the drop-casting or spin-coating usually can not give an even dispersion on the substrate. The monolayer or greater surface coverage is desired, so the ideal color of the solution will be a light-purple. Eventually, by controlling the drop size with a micropipette, the deposition process for each solution was fine-tuned through trial and error to achieve desired coverage.

Once the C₆₀ thin film sample is placed into the STM, the 250 μm Pt/Rh (87/13) tip is then lowered through the film until it reaches the Au (111) surface. The tip is rastered over the film just as in the normal scanning procedure. The Fig 2.4 and 2.5 are typical C₆₀ thin films (almost one monolayer) on the Au on mica substrate.

Figure 2.4: STM image (140nm x 140nm, Vᵢ=-0.8V, Iᵢ= 10.6pA) of a C₆₀ thin film on Au(111) on mica.

Figure 2.5: STM image (60nm x 60nm, Vᵢ=-0.51V, Iᵢ= 10.6pA) of a C₆₀ thin film on Au(111) on mica.
After a few minutes of sweeping the tip through the film (bias: 0.02V–0.03V) in the scale of 50nm by 50nm or a few times of gently "tip crash", the C$_{60}$ molecules adsorb onto the Pt/Rh tip, undergoing charge transfer from the metal to the adsorbate.$^{52}$ This C$_{60}$-metal bonding is strong enough to prevent the C$_{60}$ from diffusing along the metal surface and from rotating in place which is normally observed in bulk films at room temperature.$^{53,54,55}$ This creates a relatively stable tunneling site on the apex of the STM tip. These tips are also very stable with respect to sample transfer. Since the C$_{60}$-adsorbed tip requires no special tunneling parameters, the sample can be scanned in the same manner as with a metal tip.

Although we have already created a fine C$_{60}$-adsorbed tip, the images of nanotubes still look much wider compared to their true diameter. Therefore we measure the heights of nanotubes to represent the diameters instead of the width. But unfortunately, we must be aware that the heights are still combined with the electronic properties of the nanotubes. This also can be an advantage for realizing the characteristics of functionalized nanotubes.

### 2.1.7 Experimental equipment

The ambient STM used for experiments in this whole thesis is a home-built system using RHK electronics and software. The STM is working in constant-current mode. All nanotube images in this thesis were carried out by using C$_{60}$-adsorbed Pt/Rh STM tips.
2.2 Self-assembled monolayers

Self-assembly, one of the most remarkable molecule-substrate interactions is the spontaneous self-organization of atoms and molecules on surfaces into well-ordered arrays or supramolecular assemblies, which often possess short- or long-range order. Self-assembly methods provide an alternative approach to make defined structures with dimensions on the nanoscale.

Self-assembled monolayers (SAMs) are highly ordered monomolecular layers, spontaneously formed from the exposure of a surface to molecules with chemical groups that possess strong affinities for the substrate or a material patterned on it. However, the assemblies' order highly depends on the nature of the chemical interaction between substrate and adsorbate, as well as the type and strengths of intermolecular interactions between the adsorbates that are necessary to hold the assembly together. Normally, there are two types of bindings to hold the molecules on the surface. Physisorption, in which the enthalpies of interactions are rather low (typically from Van der Waals forces), is characterized by bond energy which is lower than 10 kcal/mol. Correspondingly, chemisorption has a bond energy more than 10 kcal/mol. Strengthening interactions between molecules and substrates and between molecules themselves include phenomena such as hydrogen bonding, donor-acceptor and/or ion pairing, and the formation of covalent bonds, rendering the assemblies more stable than their physisorbed counterparts.

Chemisorption renders the modified substrate with properties that differ significantly from the bare substrate. This makes these chemisorbed self-assembled monolayers of prime interest for technological applications. Modification of the exposed groups at the air-monolayer interface leads to a wealth of possibilities to change the
properties of the layer, which can be achieved on the nanometer scale by SPM.\textsuperscript{56, 57, 58, 59} This is critical for determining and designing the interaction strengths of proximal molecules or analytes or for post-assembly modification of the film. The incorporation of functional moieties such as chromophores, electroactive groups or molecules that can bond within the SAM enable capabilities in sensing, electron transfer, molecular recognition and manipulation, and other areas.

2.2.1 STM and SAM

Some nonlocal techniques such as ellipsometry, contact angle measurements, infrared spectroscopy, and x-ray photoelectron spectroscopy have been used to traditionally investigate the dynamics of SAMs. However, STM offers molecular-scale resolution of the surface structure as well as the ability to perform electrical characterization on individual molecules. The STM image will reflect any changes in the electronic features of SAMs, such as functional groups. STM can provide valuable information about binding sites of individual molecules, the orientation of individual molecules with respect to the substrate lattice, the conformation state of individual molecules, the periodicity of ordered molecular surface, as well as defects and domains that are present in ordered molecular surface structures. Meanwhile, the successful STM imaging of SAMs also depends upon the successful monolayer formation, which requires balanced molecule-substrate interaction. A too strong interaction immobilizes the molecules and impedes self-assembly into ordered 2D layers. If too weak, it will lead to a too high mobility, and high-resolution STM imaging become impossible.
Since the early 1990s, the STM has been used to image SAMs of n-alkanethiols adsorbed on gold surfaces.\textsuperscript{30, 31, 32, 33} The STM has been able to provide insight into the mechanism of SAM formation as well as to elucidate important structural features that lend SAMs their integrity as surface-stable entities.

2.2.2 Alkanethiolates SAMs on Au(111)

Much research has been focused on the self-assembly of n-alkanethiols and related molecules on gold substrates. Such organosulfur monolayers now have numerous technological applications, the most recent of which involves their use as positive resists in atomic nanofabrication.\textsuperscript{60, 61, 62} This application has motivated considerable research effort focusing on their structure, assembly mechanism, and experimental parameter dependencies.

It is found that sulfur compounds coordinate very strongly to gold (Au), silver (Ag), copper (Cu), platinum (Pt) and even to gallium arsenide (GaAs).\textsuperscript{63, 64} The most thoroughly studied and best characterized SAMs are those formed by sulfurs adsorbed on Au (111) because of the nonoxidizing character of the gold surface under ambient conditions.

Among the known SAMs of sulfur compounds, alkanethiolates [CH$_3$(CH$_2$)$_n$SH] on Au(111) are one of the most studied systems due mainly to their stability and ease of preparation on atomically flat Au surface. An example can be seen in Fig 2.6, which shows typical hexanethiol SAMs.
From a chemical point of view, the attachment of the sulfur to the Au(111) surface is believed to proceed through a Au-S bonding mechanism, which is well known to be sufficiently strong and stable, with bond energies typically of approximately 44 kcal/mol. The electron transfer from the gold surface to the sulfur atom of the thiol group weakens the S-H bond and results in its dissociation. The presumed adsorption chemistry is,

$$R - SH + Au \rightarrow RS^- - Au^+ + \frac{1}{2} H_2$$

which infers an oxidative addition of S-H bond to the Au surface, followed by a reductive elimination of the hydrogen. On Au(111) the S-H bond is believed to be cleaved at the on-top site, and the sulfur then moves to its final equilibrium position at the threefold hollow site, as shown on the lower right insertion in Fig 2.6. Then the Au-S bond forms.
rapidly, typically within seconds to minutes in solution or gas phase. Recently, it was found that the adsorption kinetics for alkanethiolates is faster for longer alkyl chains, probably due to the increased Van der Waals interactions.\textsuperscript{28} Thus, the formation of the monolayer is probably a two-step process involving chemical bonding of the molecules by diffusion to the surface followed by self-assembly aided by Van der Waals interactions.

Because alkanethiolates have two binding modes at the Au(111) hollow site, one with a bond angle around the sulfur of 180° (\textit{sp}) and other of 104° (\textit{sp}^3), the later being more stable by 0.41 kcal/mol.\textsuperscript{57} Accordingly, at low surface coverage, the alkanethiolate molecules lie flat with their hydrocarbon backbones parallel to the gold surface. It can be called lie-down phase, as shown in the Fig 2.7, which are STM images of butanethiol SAMs. At higher surface coverage, the molecules begin to stand up, with the hydrocarbon tails tilting approximately 30° from the surface normal and close-packed the hydrocarbon tails so as to maximize Van der Waals interactions.\textsuperscript{68} It can be called close-packed phase, in Fig 2.6 and Fig 2.8.
Figure 2.7: STM images of butanethiol SAMs in lie-down phase. The scale of the left image ($V_b = -1.0V$, $I_v = 8.18pA$) is 230nm x 230nm, and the scale of the right image ($V_b = -0.2V$, $I_v = 10.0pA$) is 54nm x 54nm.

Figure 2.8: STM image (40nm x 40nm, $V_b = -0.4V$, $I_v = 9.55pA$) of butanethiol SAMs in close-packed phase.

Several structure features typical of chemisorptions of n-alkanethiolates on Au(111) can be seen using the STM as a local probe.\textsuperscript{33} The basic structure is the hexagonal packing of the alkanethiolates in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer structure. Electron
Diffraction studies of the monolayers show that S-S spacing is 4.97 Å and a calculated area per molecule of 21.4 Å².69, 70, 71 Alkanethiolates SAMs can also form various superlattice structures on the gold surface.72, 73, 74 For example, c(4 × 2) superlattice has a rectangular primitive unit mesh with the dimension of 8.68 Å × 10.02 Å containing four chains. The Fig 2.9 and Fig 2.10 are the typical images of decanethiol SAMs. Fig 2.9 shows the domain and domain boundaries of the SAM monolayer. In the higher resolution image of Fig 2.10, the atomic close-packed structure is visible.

Figure 2.9: STM image (28nm x 28nm, Vb=-0.8V, Ic=6.02pA) of decanethiol SAMs.
Figure 2.10: Atomic resolution in STM image (4.7nm x 4.7nm, \(V_x = -0.6V, I_s = 4.02pA\)) of decanethiol SAMs.

N-alkanethiols SAMs always show a variety of local defects of the molecular lattice including domain boundaries and vacancy islands of SAMs, vacancies within the crystalline lattice of the molecules, and monatomic step edges. Domain boundaries are usually the mismatches in the tilts of the individual alkanethiolate adsorbates or the boundaries of the different packing structure of the lattice. Vacancy islands, where "black holes" as shown in Fig 2.8 and Fig 2.9, are one atomic layer deep of gold have been formed during the adsorption process. Possible mechanisms for the formation of these are from the ejection of individual gold atoms from the surface layer and subsequent rearrangement of the remaining gold atoms, an adsorbate-mediated corrosion whereby S-Au bond formations weaken the surrounding Au-Au bonds, and from the reconstruction of the gold surface (compressed from extra surface atoms) upon adsorbate binding, where about 2 Au atoms per unit cell are released upon lifting the surface reconstruction and the vacancies coalesce into islands.\(^{72,75}\) Monatomic step edges consist
of one atomic layer of gold, which separates the gold terraces from each other with a height difference of \( \sim 2.35 \, \text{Å} \).

### 2.2.3 Insertion

Insertion means that second-component molecules are inserted into the close-packed SAM and adsorbed on the substrate or suspended in the SAM matrix at some defect sites. Substrate vacancy islands, adsorbate vacancies in the molecular lattice, and domain boundaries are critical sites in the monolayer that will enhance and differentiate the effects of post-adsorption processing of the film.\(^{36}\) These defect sites within the "host" SAM are postulated to be the most susceptible to exchange to new "guest" adsorbates exposed to the films.

In an effort to understand the intermolecular dynamics of adsorbates on surfaces and to comprehend fully the mechanisms of adsorption and exchange of adsorbates in solution with those on surfaces, molecules can be placed on a surface at low fractional surface coverage within a pre-existing matrix of a SAM that has already formed. Through these studies, it has been shown that incoming "guest" molecules will insert into a "host" SAM at the step edges, domain boundaries and its other defect sites, by exposing the preformed SAM to a solution of guest adsorbates that is of low concentration (typically 0.1-0.5 mM) and for short periods of time (minutes to hours).\(^{34-38}\)

Alkanethiolate SAMs have been studied in extensive detail by a variety of methods, and with this knowledge we are able to control the types, densities, and distributions of defects of the final monolayer product. The overall quality of the film allows the possibility for further patterning, manipulation and insertion processing, including
thermal annealing and backfilling of defects with guest adsorbates, which will allow for the characterization (and manipulation) of single molecules with the STM. Due to the limited space in the defect sites of the SAM matrix, the guest molecules are forced to stand up from the gold surface, and the conjugated tails of the molecules will then protrude from the host matrix. This arrangement allows us to locate the molecules with the STM, and to probe the molecules end-to-end by using the STM tip and substrate as electrode. This will be very useful to assemble and study nanoscale structures.

The fractional surface coverage of molecules inserted into host SAMs is not only a function of the concentration of guest molecule exposed to the host SAM, nor is it simply a function of the time of exposure. The defect density of the host SAM is of significant importance as well, for guest molecules tend to insert into the host SAMs at defect sites. The higher defect density of SAMs on the surface, the more guest molecules will be inserted. There are some ways to control the insertion fractions. For example, increasing the time for making the SAMs, backfilling with the excess SAM molecules in either solution or vapor phase and thermally annealing the SAM can lower the defect densities.

Combined with STM, the insertion process is an effective way to exhibit the correct geometrical, chemical and electronic properties for recognition of a specific molecule. In particular, interest in understanding the electronic properties of the nanometer-scale objectives like functionalized SWNTs has led us to employ this method for creating isolated sites within a non-perfect alkanethiolate SAM film. Additionally, these SAMs chemically and electrically isolate the underlying substrates from their surroundings, due to their crystallinity and insulating nature.
The butanethiol, hexanethiol, octanethiol and decanethiol SAM molecules dissolved in ethanol are used in our experiments. The concentrations of the SAM solution are usually 1-2 mM.
Chapter 3

Thiol and Thiophene Functionalized SWNTs

3.1 Carbon Nanotubes

Solids of elemental carbon in the \( sp^2 \) bonding state can form a variety of graphitic structures. Carbon can build a variety of amazing structures other than graphite, such as spheres, cones and tubes. In 1985, the first of these structures observed was the \( C_{60} \) molecule by Smalley \textit{et al.} \cite{smalley1985}. During in the study of these soccer ball-like structures, S. Iijima \cite{ijima1991} in 1991 observed the first tubular carbon structures. These nanotubes consisted of a collection of cylindrical concentric shells, later called multi-walled carbon nanotubes (MWNTs). Two years later, single-walled carbon nanotubes (SWNTs) were discovered by S. Iijima \textit{et al.} \cite{ijima1993} and D. S. Bethune \textit{et al.} \cite{bethune1993}. This discovery was of great importance since SWNTs are more fundamental than MWNTs in their nature and have been predicted by theoretical calculations to possess many remarkable properties. One of their properties is that the nanotubes can either be semiconducting or metallic depending on their diameters and orientation of the hexagonal lattice, compared to the tube axis. In 1996, Smalley \textit{et al.} \cite{smalley1996} successfully synthesized bundles of SWNT.

3.2 Single-walled carbon nanotubes (SWNTs)

Single-walled carbon nanotubes (SWNTs) are one-dimensional nanometer-diameter cylinders consisting of a single graphene sheet wrapped up to form a seamless tube, typically capped by hemispherical ends composed of pentagons and hexagons. Since their
discovery in the early 1990s, there has been intense research activity exploring the electrical properties of SWNTs and their potential applications in electronics.

SWNTs typically have a diameter of 1-2 nm and a length of several micrometers. The large aspect ratio makes them nearly ideal one-dimensional objects. As such, the SWNTs are expected to have all the unique properties predicated for these low-dimensional structures. Further more, the C-C covalent bonds in the SWNTs are very strong, resulting in chemical inertness and an extremely high mechanical stability (largest Young's modulus of any known material, about ten times higher than that of steel) which makes them a suitable material for many high tensile strength applications. The strong, covalent bonding also leads to near perfect side-wall structures with very few defects.

SWNTs are the most promising of all nanomaterials, with unique electronic and mechanical properties which lend themselves to a variety of applications, such as field-emission displays, nanostructured composite materials, nanoscale sensors, and elements of new nanoscale logic circuits.

Experiments and theory have shown that SWNTs can be either metallic or semiconducting, depending on the diameter and chirality. Their electrical properties can rival, or even exceed, the best metals or semiconductors known. Particularly illuminating have been electrical studies of individual nanotube and nanotube ropes (small bundles of individual nanotubes). The first studies on metallic tubes were done in 1997 and the first on semiconducting tubes in 1998.
The diameter and chirality of a defect-free SWNT are uniquely characterized by the vector

\[ C_h = na_1 + ma_2 = (n, m) \]

where \( C_h \) connects crystallographically equivalent sites on a two-dimensional graphene sheet, where \( a_1 \) and \( a_2 \) are the graphene lattice vectors and \( n \) and \( m \) are integers, as shown in Fig 3.1. The nanotubes are either armchair \((n = m)\), zigzag \((n = 0 \text{ or } m = 0)\), or chiral (any other \( n \) or \( m \)) type. All armchair SWNTs are metals. Those nanotubes with \( n - m = 3k \), where \( k \) is a non-zero integer, are metallic; and all others are semiconductors with a band gap inversely proportional to the diameter of the nanotube.

![Graphene lattice vectors and roll-up vector](image)

**Figure 3.1:** Schematic showing lattice vectors \( a_1 \) and \( a_2 \) and the roll-up vector \( C_h = na_1 + ma_2 = (n, m) \) on a 2-D graphene sheet.

### 3.3 STM and SWNTs

STM is the ideal tool for probing the chemistry and physics of nanoscale objects like SWNTs, due to its both lateral and vertical atomic resolutions. STM allows us to clearly identify the type of the nanotube and the electronic properties which depend on its chirality. The first atomic resolution STM image of carbon nanotubes was obtained in
1993 by Maohui Ge and Klaus Sattler. They reported the tubes have a helical graphite nature and the tube surfaces are networks of perfect honeycombs. In addition, they observed a superpattern on the tubes due to an incorporated inner tube with different helicity. Later, the same group investigated the SWNTs by using STM and reported the results in 1994. In 1998, two groups, Wildoer et al. and Odom et al. combined the atomic STM images of SWNTs with the scanning tunneling spectroscopy (STS) to confirm the theoretical prediction that the electronic properties depend sensitively on the nanotube diameter and chirality. Along with the calculation of band structures, their studies gave the first clear experimental demonstration of metallic and semiconducting properties of an individual SWNT in real space.

3.4 Functionalization of SWNTs

According to various applications of SWNTs, the preparation, processing and manipulation require the dispersion and solubilization of SWNTs, which in their pristine form are not soluble in most common organic solvents and water. To address this problem, functionalization has become a key area of SWNTs chemistry. The solubility of functionalized SWNTs in common organic solvents and/or water allows solution-based techniques to be used in the characterization of the nanotube samples and in the study of fundamental properties of carbon nanotubes. The same solubility also offers unique opportunities in the development of carbon nanotubes-based materials and in the use of the solubilized carbon nanotubes as starting materials for further chemical and biochemical modifications.
Functionalization reactions usually utilize two types of chemistry: open end\textsuperscript{16, 17} and sidewall.\textsuperscript{14, 18, 19} Both of these two types of chemistry can enhance SWNT solubility and induce some changes of electronic properties. Chemical functionalizations of the nanotube open ends have been most extensively explored through the oxidation of SWNTs and have been shown to form shortened nanotubes with carboxylic acid groups at the end, which have been further derivatized by reactions with thionylchloride and long-chain amines,\textsuperscript{16} or by esterification.\textsuperscript{12} Open end functionalization can change the electronic properties of SWNTs, but they bring only a highly localized transformation of the SWNT electronic structure at the end without changing the bulk properties.

For the sidewall functionalization, successful nondestructive fluorination of SWNT sidewalls, which was demonstrated by Mickelson et al. in 1998,\textsuperscript{18} has proven that it can significantly modify the intrinsic electronic properties of SWNTs, compared to the open end functionalization. Fluorination might even be the key for tailoring the exceptional electronic properties of SWNTs, providing building blocks of different functionality for molecular electronics.\textsuperscript{20} Furthermore, sidewall chemistry make SWNTs more amenable to further chemical reactions. Fluorine atoms on the SWNT wall can be substituted by other organic functional groups, such as alkyls, amines, and carboxylic acids etc. In addition, direct sidewall attachments of hydrogen via Birch reduction,\textsuperscript{90} aryl groups,\textsuperscript{91, 92} nitrenes, carbenes, and radicals\textsuperscript{93} as well as 1,3-dipolar additions\textsuperscript{94} to the SWNTs have been also reported by several research groups.

Initial STM investigation of sidewall functionalized SWNT was performed by Kelly et al.\textsuperscript{95} The nanometer resolution images were obtained with an ambient STM after spin coating the fluorinated nanotubes (fluorotubes) solution on Au(111) substrate. In the later
parts of this chapter, investigation the sidewall chemistry using STM will be shown, and in particular exploiting the well established Au-S chemistry to controllably self-assemble carbon nanotubes on Au(111) substrate. In these experiments, stable STM images were obtained by attaching thiol and thiophene terminated alkane chains on the sidewall for self-assembly of the nanotubes on gold.

3.5 Thiol and Thiophene Functionalized SWNTs

A typical sidewall chemistry of SWNT, which substitutes fluorine atoms by N-alkylidene amino groups\textsuperscript{14, 21, 22} has been explored. For self-assembly of SWNT on Au(111) by using well established gold-sulfur chemistry, we need to induce a thiol or thiophene terminated alkane chains to bond to the nanotube sidewall. HiPCo SWNTs produced by Smalley group at Rice University were purified to remove iron and other impurities,\textsuperscript{96} and subsequently fluorinated, to a C : F ratio of approximately 2.4 : 1, by direct fluorination at 150\textdegree C by a previously reported procedure.\textsuperscript{22} We choose the molecules as shown in Fig 3.2, to functionalize the fluorotubes by reacting with the appropriate amine in the presence of a base catalyst.\textsuperscript{23} The final functionalized SWNTs are shown in the Fig 3.2. The IR spectra of thiol and thiophene functionalized SWNT show bands associated with the substituents.\textsuperscript{23} The thiol and thiophene functionalized SWNTs are synthesized by Lei Zhang in A. R. Barron group at Rice University.\textsuperscript{23}
Figure 3.2: Illustration of functionalized SWNTs, where R represents the thiol or thiophene functional group.

The following experiments will prove that the thiol and thiophene functionalized SWNTs can be strongly bound to the Au(111) surface and inserted in the SAMs. The STM images will reveal the defects along the functionalized tubes due to the electronic properties changes by inducing sidewall functional groups. Also, the defect sites themselves indicate the position of functionalization.

3.6 Experiments and results of Thiophene Functionalized SWNTs

3.6.1 Nanotube solution and deposition

The thiol and thiophene functionalized SWNT can be dissolved in various organic solvents like dimethyl formamide (DMF), isopropanol (IPA) and ethanol. The powder form thiol or thiophene functionalized SWNTs were put into a moderate quantity of DMF solvent, and then sonicated for a while. It is critical that the nanotubes should not be sonicated for a too long time, maximum 20 min usually. Otherwise the tubes will break down to very short pieces that are not good for observing the defects and calculating the defect densities.
Hydrogen flame-annealed Au(111) on mica was used as the substrate in our experiments. SAMs are formed on the Au(111) on mica substrate by immersing into 1 mM or 2 mM hexanethiol solution for 1 hour to form a high-quality SAM, although there were still some defects sites or etch pits (Au vacuum islands) in the SAMs (SAM reference). After removal, the sample went through repeated ethanol rinses and was then dried with nitrogen.

Spin coating is the common deposition method for dispersing nanotubes on surface. However, since our thiol or thiophene functionalized SWNTs have active groups which can bond to Au surface, we can easily deposit tubes by immersing substrates into the thiol or thiophene tube solutions.

3.6.2 Thiophene group works as an anchor to bind nanotubes on Au

Apparently, the thiol functionalized SWNTs can be strongly held on the Au(111) surface by the Au-S bond, since the Au-S chemistry is well known. But to our knowledge, no one has reported that thiophene terminations can be attached to Au(111) surface in the similar manner as Au-S bond. So, first of all, we must prove that the thiophene group can work as an anchor to hold the nanotubes on the Au surface.

As a proof, we performed four similar experiments to deposit nanotubes onto gold substrates. We prepared two solutions: pristine SWNTs in DMF and thiophene functionalized SWNTs in DMF, of the same concentration.

First, we immersed a Au(111) on mica substrate into pristine SWNTs solution for 30 min. After withdrawing the sample and rinsing it out repeatedly with ethanol, it was dried with nitrogen. Scanning was performed with our home-built ambient STM. But we did
not find any pristine SWNTs on the substrate which were presumably removed during the rinsing process.

Second, we used the same procedure, but this time substituted the pristine SWNTs solution by thiophene functionalized SWNTs. The STM images showed many functionalized tubes on the Au surface. See Fig 3.4 and Fig3.5.

Third, we made an 1 hour hexanethiol SAM on the Au(111), then immersed the sample into the pristine SWNTs solution for 30 min. Rinsed out the sample with ethanol for several times and then dried with nitrogen before scanning it by STM. The SAM still looked good, but there were no pristine SWNTs on the surface.

Fourth, following the procedure of the third experiment, but using the thiophene nanotube solution, we observed that the thiophene functionalized SWNTs were held in the preformed hexanethiol SAM on Au(111) surface.

Comparing the first two control experiments, we conclude that thiophene functional groups work well for binding tubes to the gold surface, and there is a reasonably strong Au-thiophene bond. While, the third experiment proved that the pristine tubes cannot be set onto or inserted into the preformed SAMs. The reasonable explanation for the fourth experiment could be the insertion theory, which is illustrated in detail in Chapter 2, and can be simplified as shown in the Fig 3.3. The thiophene functional group is inserted into domain boundaries and defect sites of preformed SAMs, and attaches to the gold surface. In addition, the experiment also indicates that the SAM molecules will not disturb the Au-thiophene bonds.
Figure 3.3: Schematic of functionalized SWNT, which is inserted into hexanethiol SAMs and attaches to the gold surface.

The bump of the STM tip trajectory, seen in the Fig 3.3, represents the electronic property changes induced by the functional group. This will be discussed in detail in the later parts of this chapter along with the corresponding STM images.

3.6.3 STM images of thiophene tubes on Au and inserted into SAMs

The thiophene functionalized SWNTs can be placed directly on the Au(111) surface by following the procedures of the second comparison experiment mentioned above. The Fig 3.4 and Fig 3.5 are two typical STM images of thiophene nanotubes placed on bare gold surface.
Figure 3.4: STM image (660nm x 660nm, \( V_b = -0.9V \), \( I_c = 4.88pA \)) of thiophene functionalized SWNTs, which are placed on bare gold surface.

Figure 3.5: STM image (600nm x 600nm, \( V_b = -0.8V \), \( I_c = 4.73pA \)) of thiophene functionalized SWNTs, which are placed on bare gold surface.
The terrace feature of Au(111) can be seen in both images. There is a significant perturbation of the tubes during the STM imaging. The C_{60}-adsorbed Pt/Rh STM tip was sweeping from left to right or right to left and moving along the latitude of the images. The tubes, which are near perpendicular to the sweeping direction, were likely being moved or cut by the STM tip during the scanning. We were unable to achieve stable functionalized tube images using this method of deposition.

The possible reasons for the perturbation by STM tip are two fold: First, the functional molecule has a certain length, which is about 0.5 nm. When the thiophene head is attached to the Au, the whole molecule will probably lay down on the Au surface. Even though the molecules bind the nanotubes to the Au surface, the tubes still can be moved in a certain space, due to the electrostatic force between the tip and nanotubes. But the moving distance should be limited, due to the small molecular length.

Second, although the well known Au-S bond is very strong in desorption, powerful enough to hold the tubes on the Au surface, but the diffusion energy needed when moving the sulfur atom on Au surface is relatively small. G. E. Poirier et al.\textsuperscript{97} illustrated this principle when they studied alkanethiol liquid phase in low coverage on gold. This means that the mobility of the sulfur terminated molecules is relatively high on the Au surface. Therefore, the movement of sidewall functionalized tubes on Au is reasonable. The movement of thiophene tubes could be a result of combination of these two reasons, though the second reason is probably more significant.

Due to the unstable imaging condition while placing the functionalized SWNTs directly on the bare Au(111) surface, we deposited the tubes on the preformed SAM
instead, in order to insert the sidewall functional groups into the close-packed SAM matrix.

The Fig 3.6 and 3.7 are STM images of thiophene functionalized SWNTs inserted into the hexanethiol SAM. Hexanethiol SAM were preformed by immersing flame annealed Au(111) on mica substrate into 1 mM hexanethiol solution for 1 hour. Then, dip the sample in the solution of thiophene tubes in DMF for another 30 min after rinsing extra hexanethiol molecules out with ethanol. After the final rinse and drying with nitrogen, the sample was ready for scanning by ambient STM. We observed an improvement in the STM image quality.

Figure 3.6: STM image (600nm x 600nm, \( V_b = -0.8V \), \( I_s = 25.4pA \)) of thiophene functionalized SWNTs, which are inserted into hexanethiol SAMs.
The functionalized nanotubes are more stably imaged. The STM can clearly identify the individual nanotubes, as well as show the surprising defect structures along the tubes. Meanwhile, the atomic images of underlying hexanethiol SAM reveal that the SAMs were not affected by the nanotube solution during the insertion.

The insertion, as illustrated in the Fig 3.3 on the early pages, is helpful to isolate and strongly bind the nanotubes to the surface. The sidewall functional groups are forced to stand up by the close-packed SAM molecular matrix. In addition, the close-packed sulfur atoms on Au surface blocked the diffusion of thiophene or thiol terminations. Because of the extinction of the two possible reasons for movement, the tubes will steadily set onto the flexible SAMs without the disturbance of STM tip. The length of the SAM molecules also could play another important role. After comparing hexanethiol, octanethiol and decanethiol SAM molecules in the insertion experiments, hexanethiol SAMs gave the best result, due to their comparable length to the functional groups. We did not try
butanethiol SAM, because it is likely to form liquid phase,\textsuperscript{97} and is therefore not appropriate for our insertion experiments.

In addition, the underlying SAM electronically isolating the nanotubes from the Au surface gives us an opportunity to observe the localized electronic properties induced by the functional groups.

### 3.6.4 Defects of thiophene functionalized tubes and defect distributions

Comparing the STM images of thiophene functionalized SWNTs in Fig 3.8 with the pristine SWNTs images, we observed a number of defects along the thiophene nanotubes. They reflect the changes of localized electronic properties, due to the sidewall functionalization.

![STM image of thiophene functionalized SWNTs](image.png)

**Figure 3.8:** STM image (340nm x 340nm, $V_b = -0.8V$, $I_c = 25.2pA$) of thiophene functionalized SWNTs inserted into hexanethiol SAMs, where the defects along the nanotubes can be seen.
When zooming in on a single thiophene tube as shown in the Fig 3.9, we found that the defects roughly can be divided into two types based on the size. We call them large and small defects. There are three large defects and many small defects in this image.

Figure 3.9: A high resolution STM image ($V_b = -0.8V$, $I_c = 29.7pA$) of a thiophene functionalized SWNT inserted into hexanethiol SAMs, where two types of defect are observed.

The following Fig 3.10 is a high resolution image of the area around one large defect on the thiophene tube above. It is near atomic resolution. Although the individual atoms were not indicated clearly, the helical direction of the tube itself is apparent. Its corresponding 3-D view and the cross-section are shown following the STM image. The defect structures can be identified visibly; there is one large defect and four small defects observed in both the STM image and the cross-section view. As the STM topographic image shows convolution of both physical structure and electronic properties, the true physical diameters of nanotube and defect can not be known from the cross-section measurement. The introduction to the STM tip artifacts in Chapter 2 also mentions that the height cross-section reflects the accurate feature of the object, while the width contains tip shapes. The relative height of the large defect site to the bare area of nanotube is 1.0-1.5 nm.
Figure 3.10: A zoom-in STM image ($V_b=-0.8\text{V}, I_t=30.2\text{pA}$) and the corresponding 3-D view of the area around one large defect on the thiophene nanotube. Lower right is the cross-section.

When taking the cross-section of small defects on the tubes, it is found that the relative heights are only about 0.5 nm, seen in Fig 3.11 and Fig 3.12.
Figure 3.11: STM image ($V_0 = -0.3V$, $I_r = 29.8pA$) and the cross-section of small defects on a thiophene functionalized SWNT.

Figure 3.12: STM image ($V_0 = -1.1V$, $I_r = 6.16pA$) and the cross-section of small defects on a thiophene functionalized SWNT.
Additionally, the defect cross-section in the Fig 3.12 reveals a typical 0.25 nm height of a single Au(111) step. This proves that our cross-section measurement is true and accurate.

The reason for the defects seen in the STM images is probably that the thiophene sidewall functional groups which covalently bond to the Au surface induce a localized change of electronic state densities on the SWNTs. The bumps along the tubes in the STM images mean the tunneling resistance between the tip and substrate is decreased at the functional defect sites. As illustrated in the Fig 3.3, the functional groups provide conducting channels between the tube and Au surface, while, relatively, other parts of the nanotube are electronically isolated from the metal surface by the underlying alkanethiol SAM molecules.

Although the reason should be the same for both large and small defects, the height difference, which is about 1 nm between the large and small defects, is still noticeable. As shown in Fig 3.13. There are three possible reasons for the distinction of the two types of defects.

![Diagram](image)

**Figure 3.13:** Illustration of possible reasons for the difference between small and large defects. The left schematic shows a small defect, and the right shows a large defect.
As the small defects might have only one or very few functional groups attached at the same functional site of the nanotube sidewall, the large defects could indicate more functional groups attached, or the large defects themselves might point out dangling side group not bound to the Au surface. It is also possible that the graphite lattice of the SWNTs, has some chemically induced defects during the chemical process of functionalization, that can causes an electronic property changes resulting in the large defects. Additionally, the difference may be a result from a combination of the above mentioned possibilities.

After analyzing a large quantity of thiophene functionalized SWNTs by taking cross-section in the STM images, the thiophene functionalized SWNTs show pretty even distribution of defects, as shown in Fig 3.14 and 3.15.

Figure 3.14: STM image (\(V_b = -1.1\text{V}, I_t = 6.04\text{pA}\)) of a thiophene functionalized SWNT inserted into hexanethiol SAMs, where the defects are evenly distributed. It should be noted that there a double-tip artifact in this image.

Figure 3.15: STM image (\(V_b = -0.8\text{V}, I_t = 29.7\text{pA}\)) of a thiophene functionalized SWNT inserted into hexanethiol SAMs, where the defects are evenly distributed.
The defect spatial distribution is shown in the Table 3.1. The details of the calculation are affixed at end of the thesis. In total, the average spatial distance between each of the two defects, including both large and small defects, is about 11 nm.

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Table 3.1: Defect spatial distribution of thiophene functionalized SWNTs.

3.6.5 Near atomic resolution of STM images

The STM images with atomic resolution could be a powerful tool to understand the defect phenomenon of the sidewall functionalized SWNTs. If the individual atoms near the defect structures can be identified, the positions of functional groups and the sidewall functional structures may be known exactly.

Unfortunately, we could not get any real atomic level images of thiophene functionalized SWNTs. Due to the scan size and the electronic properties of the functionalized SWNTs as well as the underlying SAMs, the bias voltage for imaging could not be set low enough during scanning by the ambient STM. The most approximate image is shown below in Fig 3.16. The Fig 3.10 shown before is also another near atomic image.
Figure 3.16: A near atomic resolution STM image \( (V_s = -0.5V, I_s = 36.1pA) \) of a thiophene functionalized SWNTs inserted into hexanethiol SAMs.

UHV condition might be helpful to get the atomic resolution of these nanotubes which is planned in future experiments.

3.7 Experiments and results of Thiol Functionalized SWNTs

The thiol functionalized SWNTs were investigated using the similar methods as thiophene. The thiol functionalized SWNTs were initially dissolved in DMF. The insertion of the thiol tubes into hexanethiol SAMs, as shown in the Fig 3.3, was performed in exactly the same four control experiments as discussed for the thiophene nanotubes. The insertion also resulted in more stable STM imaging than attaching thiol tubes directly on Au(111) surface.

However, from the STM images of thiol functionalized SWNTs inserted into SAMs, it is found that the defects, due to the sidewall covalent attachment of sulfur terminated alkane chains, show different features from the thiophene functionalized SWNTs, as can be seen in Fig 3.17, Fig 3.18 and Fig 3.19. We found that the defects along the thiol tubes are much bigger than thiophene tubes, while analyzing the cross-sections. The possible
reason is that the thiol groups have quite dissimilar chemical bond and electronic properties compared to the thiophene groups. It is quite probably related to the tendency of functional group to distribute differently on the sidewall of SWNTs.

Figure 3.17: STM image (460nm x 460nm, $V_b = -0.5V$, $I_t = 3.25pA$) of thiol functionalized SWNTs inserted into hexanethiol SAMs, where the big defects on the thiol nanotubes are observed.

Figure 3.18: A high resolution STM image ($V_b = -0.6V$, $I_t = 3.90pA$) of a thiol functionalized SWNT inserted into hexanethiol SAMs.
Figure 3.19: STM image ($V_b = -0.9V, I_t = 4.38pA$) of a thiol functionalized SWNT inserted into octanethiol SAMs.

The defect density and spatial distribution cannot be calculated easily, because the defect structures are not as regular or as clearly imagable as the ones on the thiophene tubes.

3.8 Difference between the thiophene and thiol functionalized SWNTs

Without atomic level STM images and corresponding scanning tunneling Spectroscopy (STS) data, it is hard to understand the distinction between the thiol and thiophene functionalized SWNTs. But we further confirm our observation with AFM, by reacting the exposed thiol or thiophene terminations with gold nanoparticles (~5 nm) and using them as a chemical marker for the reactive sites. This part of work was done by Lei Zhang in A. R. Barron group at Rice University.23

As shown in the below AFM images in Fig 3.20, the thiol and thiophene functionalized SWNTs were deposited onto a bare mica substrate. On the left image, the Au nanoparticles were complexed, appearing spaced along the length of the thiol tubes. In contrast, the right image of the thiophene tubes shows long bands of continuous Au-functionalized regions.
Figure 3.20: AFM images of Au-nanoparticle attached functionalized SWNTs on a bare mica substrate: (a) a thiol functionalized SWNT, (b) a thiophene functionalized SWNT.

Combined with thermogravimetric analyzer (TGA) and Raman analysis, our conclusion is shown as a schematic in the Fig 3.21. With the similar levels of functionalization, the thiol functional groups are likely to combine together and bind to one Au nanoparticle. While, the thiophene groups appear more evenly distributed and have one Au nanoparticle on each molecule.

Figure 3.21: Illustration of the difference between the thiol and thiophene functionalization, by attaching Au nanoparticles.
This result corresponds very well to the differences we saw in the STM images: thiol functionalized SWNTs have bigger and blurry defects, whereas thiophene functionalized SWNTs have regular, clear and even distributed defects.
Chapter 4

Self-assembly of Fullerene-terminated Helical Peptide

Our self-assembly and insertion techniques of the SWNTs can be extended to biological applications, the field in which nanotechnology promises to have probably its most immediate impact. Recently, increasing attention has been paid to SAMs composed of helical peptides\textsuperscript{99, 100, 101} in an attempt to utilize their unique properties such as the rigid structure, the macrodipole moment, and the ability to place a desired functional group at a predetermined position along the helical axis.

Previously, fullerene-terminated alkanethiolate SAMs have been synthesized and investigated by Kelly \textit{et al.}\textsuperscript{102, 103} By attaching a C\textsubscript{60} molecule onto a dialkyl disulfide, they have combined the favorable characteristics of SAMs with the unique electronic and structural properties of fullerene. Similarly, we attached C\textsubscript{60} to the end of self-assembled peptide to investigate the molecular electronic properties.

4.1 Molecular electronics techniques

An understanding of electron transfer through a single molecule or a group of molecules with a setup of two electrodes for current detection is of primary importance for the realization of molecular electronics.\textsuperscript{104, 105, 106} For the electronic circuit at a molecular level, various techniques such as mechanically controlled break junctions,\textsuperscript{107, 108} electrically controlled break junctions,\textsuperscript{109} nanogap electrodes,\textsuperscript{110, 111} mercury drop-metal junctions,\textsuperscript{112} nanopore junctions,\textsuperscript{113, 114, 115, 116} metal wire crossing,\textsuperscript{117, 118} and scanning probe microscopy,\textsuperscript{34, 37, 119, 120, 121, 122, 123} have been utilized so far.
The molecular-scale resolution of STM makes it a powerful tool to realize the localized molecular electronics measurement of the target molecule, which is precisely located between the tip and a conducting substrate.

4.2 Self-assembly of sulfur-terminated peptide and insertion

Similar to the formation of alkanethiolate SAMs, the sulfur-terminated peptide molecules can be self-assembled onto Au(111) surface, due to the Au-S bonds.\textsuperscript{124, 125, 103} The STM images of the peptide SAMs in previous reports showed large terraces and monatomic steps due to the underlying Au(111) surface.\textsuperscript{125, 126} That is a good evidence for formation of a flat and homogeneous peptide monolayer through Au-S linkage without significant defects.

However, a single helical peptide molecule or a molecular array in the SAMs was not easily observable even by using high-resolution STM. Some groups, which reported the SPM observation of the helical peptide SAM, have not succeeded in the observation of a single peptide molecule either.\textsuperscript{125, 126, 127, 128} In the case of the helical peptide SAMs, it is difficult to observe a single molecule probably due to the occurrence of intermolecular lateral electron hopping,\textsuperscript{129} which makes the molecular imaging ambiguous.

One group succeeded in STM observation of a single helical peptide molecule by incorporating the peptide into alkanethiol SAMs.\textsuperscript{130} It is hard for them to distinguish between individual molecules and a peptide bundle, although it is proved again insertion is an ideal technique even for biological molecules. Additionally, the self-assembled
peptide, protein or DNA can be furthermore patterned by dip-pen lithography on metals or insulators.\textsuperscript{131, 132}

### 4.3 Fullerene termination

Due to their unique structural, electronic, and spectroscopic properties, fullerenes have been widely studied since their discovery in 1985.\textsuperscript{76} Thin films of fullerenes have been prepared using a number of methods including gas-phase deposition,\textsuperscript{133} Langmuir-Blodgett,\textsuperscript{134} and self-assembly techniques.\textsuperscript{135, 136, 137} These films exhibit a wide range of properties such as charge transport,\textsuperscript{138, 139} superconductivity upon doping with alkali metals,\textsuperscript{140, 141} and biological activity.\textsuperscript{142}

Fullerene-terminated alkanethiolate SAMs have been synthesized and investigated by Kelly \textit{et al.}\textsuperscript{102, 103} before. Similarly, we would like to induce C\textsubscript{60} terminations on peptide molecules, in order to better investigate the molecular properties by STM. Here we report an incorporated structure with decanethiol SAMs, as can be seen in the schematic in Fig 4.1. The C\textsubscript{60}-terminated peptide has been inserted into SAMs and bound to the Au surface through Au-S bonds.

![Figure 4.1: Illustration of a fullerene-terminated peptide, which is inserted into decanethiol SAMs, and attaches the gold surface by Au-S bond.](image)

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Wiring a single molecule into an electrical circuit by chemically bonding each end to a metal conductor is a key requirement for molecule-based electronics. Accord to X. D. Cui et al.’s experiment, the chemically bonded contact, such as Au-S bond, which is at the conjunction of target molecule and scanning probe tip, are highly reproducible and lead to the measurement of intrinsic molecular properties. With the help of the insulating alkanethiol SAM matrix, the target molecules are isolated from one another. They measured the electronic properties of 1,8-octanedithiol, one of which ends attached on the Au substrate, while the other end binds to an Au-coated AFM tip. This approach to measuring molecular conductivity avoids the effects of variations in contact force and other problems encountered with nonbonded contacts. In contrast, nonbonded molecular contacts are found to be highly resistive and to have I-V characteristics that are quite different from those of molecules with bonded contacts, showing that the nonbonded contact dominates electrical properties.

Therefore, based on the work done by K. Kitagawa et al., who observed individual helical peptide in the alkanethiol SAM matrix, we would like to attach a C_{60} termination to the end of a peptide for making a bonded contact with a Pt/Rh STM tip, due to the adsorption of C_{60} on the tip, which is mentioned in Chapter 2. C_{60} terminations make the measurement of electronic properties more repeatable and more accurate.

In naturally occurring proteins, helix bundle structures are often found. The packing manner of the helices in the bundles is regulated by several interactions: for example, electrostatic interaction between charged groups, dipolar interaction between macrodipoles of helices, and steric interlocking between side-chains. K. Kitagawa et
al.\textsuperscript{130} reported they found peptide bundle structures at the SAMs domain boundaries, as well as single helical peptide. But their claim for single peptide is not convincing. To truly observe a single peptide structure, C\textsubscript{60} terminations are really helpful as a marker, due to their typical \textasciitilde1 nm diameter in STM images. Even though the peptides are still likely to stay at bundles, the unique properties of fullerenes make peptides themselves counted simply and individually. Furthermore, I-V measurements can be performed on a single molecule.

When using scanning tunneling spectroscopy to investigate this C\textsubscript{60}-terminating structure, the electronic property collected corresponds to a composition of electronic properties from both peptide molecule itself and attached C\textsubscript{60} molecule. As the C\textsubscript{60} has been well-understood, the electronic properties of peptides can achieve relatively, through comparison with other C\textsubscript{60}-included researches, such as C\textsubscript{60} monolayer on Au\textsuperscript{102, 136} and so on.

4.4 STM investigation

The decanethiol SAM matrixes were prepared by immersing the Au(111) on mica substrate for 1 hour in 1 mM ethanol solutions. The samples were then removed and rinsed repeatedly with ethanol before a second, 30 min immersion in a solution of peptide dissolved in ethanol. After removal, the samples went through ethanol rinses and were then dried in a stream of nitrogen gas before scanning in the home-built ambient STM.

The peptide molecules used in this experiment are synthesized by Jianzhong Yang in A. R. Barron group at Rice University, as shown in the below Fig 4.2.
The green atom is the sulfur atom. This is the most compact potential geometry. The sequence in three letter code is:

\textbf{Phe}(C_{60})-\textbf{Glu}-\textbf{Glu}-\textbf{Glu}-\textbf{Glu}-\textbf{Gly}-\textbf{Gly}-\textbf{Gly}-\textbf{Gly}-\textbf{Ser}-\textbf{Cys}-\textbf{COOH}

where, Phe–Phenyalanine; Glu–Glutamic acid; Gly–Glycine; Ser–Serine; Cys–Cystine

Fig 4.3 is an STM image of a decanethiol SAM after immersion in a solution of C_{60}-terminated peptide. The brighter dots at the domain boundary sites are the single C_{60}-terminated peptide molecules, while the black holes are due to etch pits or called Au vacancy islands formed during the self-assembly process of one gold monolayer depth.\textsuperscript{73} In addition, we observed that insertion occurs almost exclusively at the domain boundaries instead of etch pits. This is probably because of the large size of the peptide molecules. It should be noted that the three-time-repeated shape of C_{60}-terminations in the same direction in these images is due to convolution with the multiple STM tip structure. It has been illustrated in detail in Chapter 2.
Figure 4.3: STM image (50nm x 50nm, $V_g = -0.7V$, $I_I = 4.11pA$) of fullerene-terminated peptides inserted into decanethiol SAMs.

Figure 4.4: STM image (18nm x 18nm, $V_g = -0.69V$, $I_I = 4.57pA$) showing atomic resolution of the underlying decanethiol SAMs.
When zoomed in, in Fig 4.4, the atomic lattice of the underlying decanethiol monolayer is clearly observed, demonstrating that the crystalline lattice of SAM is preserved after the insertion process.

To conclude, the single fullerene-terminated peptide molecules have been successfully imaged by insertion into the decanethiol SAM matrixes in our experiments. However, in the present case, due to the thermal drift of our ambient STM and restriction of equipment, the scanning tunneling spectroscopy experiment has not been performed. This is being planned in future UHV STM experiments.
Chapter 5
Future Directions

5.1 Introduction

The experiments done on functionalized SWNTs and fullerene-terminated peptides demonstrate the mechanism of self-assembly and insertion for analysis by STM. In addition, the sizes and the spatial distribution of the functional groups along the nanotube sidewalls have been measured, while the precise positions of peptide molecules have been indicated though imaging the fullerene terminations. However, to understand the molecular electronic properties, spectroscopy must be obtained at the functionalized sites on the nanotube sidewall or directly on the peptide molecules. Therefore, scanning tunneling spectroscopy will play an important role in these types of electronic measurement, due to the ability of simultaneous acquisition with the STM topographic images. Meanwhile, the chemical information is a key point when studying the functionalization of nanotubes. By combining Raman spectra of near-field scanning optical microscopy (NSOM) with scanning probe techniques, we can efficiently identify the chemical information on a single tube or fullerene.

Finally, our goal is to build up truly nanoscale devices with carbon nanotubes by utilizing the self-assembly technique. A possible means for this will be introduced in the following paragraphs.
5.2 Scanning tunneling spectroscopy (STS)

Performed with an STM, scanning tunneling spectroscopy (STS) is a technique which gives information about the local density of electronic states on surfaces at atomic or molecular scale by interrupting the feedback loop and keeping the tunneling gap constant while applying a bias voltage ramp on the tunneling junction. The tunneling current is measured as a function of the bias voltage. As a result, the $I$-$V$ curve is obtained while linearly ramping the bias voltage with the tip positioned over a feature of interest. Because of the inactive feedback loop, the very small tunneling current can be achieved. With this, the bandgap states in semiconductors can be probed without difficulties, which is an important consideration in SWNT research.

The results of STS measurement are usually presented by plotting the current $I$, or $dI/dV$ which is proportional to the density of the electronic states of the sample, as a function of the bias voltage $V$. So there are two curves, $I$-$V$ and $dI/dV$-$V$. The spectroscopic measurements are usually performed in the following manner. First, the region of interest is scanned in constant-current STM mode after which points for STS were selected. On the subsequent scan, the $I$-$V$ curves are acquired simultaneously with the topographic image, assuring the location of the STS over the molecules.

With a lock-in amplifier, the $dI/dV$ can be collected directly. In addition, by recording the lock-in signals during scanning, a $dI/dV$ image can be created simultaneously with the topographic image.

To understand the electronic properties of thiol and thiophene functional groups on the sidewall of SWNTs and the intrinsic electronic characteristic of fullerene terminated peptides, localized STS measurement is necessary.
5.3 Near-field scanning optical microscopy (NSOM) Raman

Near-field scanning optical microscopy (NSOM) is a technique which combines optical and scanning probe microscopes. The basic idea of NSOM is that a higher resolution than the confocal microscopy can be obtained by scanning a tiny aperture in close proximity across the sample. The diffraction limit of confocal microscopy can only be reduced if the wavelength of the excitation light is reduced, but there are strong limitations for the technical realization of this. However, by utilizing a tiny aperture, which is much smaller than the wavelength of light, while the sample is placed within its near field at a distance much less than the wavelength of light, the resolution obtainable is only limited by the diameter of the aperture and no longer by the wavelength.\textsuperscript{144}

There are a few different methods to realize optical near-field imaging, such as optical fibers or a standard AFM cantilever with a hole in the center of the pyramidal tip. Our WiTec instrument uses the second configuration. The AFM cantilever consists of silicon with a hollow silicon dioxide pyramid at the end, where the tiny hole is below 100 nm. These are much more reliable than pulled optical fibers but with a lower light throughput. The cantilever can bend in the vertical direction and distance feedback is easy and uncritical. Nearly all AFM distance feedback modes can be used with these cantilevers. Therefore, when ramping the cantilever on the sample, the NSOM images and the AFM images can be obtained at the same time. Subsequently, by using the same NSOM cantilever, the enhanced Raman spectra can be acquired precisely at the point of interest, according to the former NSOM or AFM images.

Due to the inadequate resolution of AFM compared to STM, if we can find an efficient way to mark the SWNTs on the substrate, such as TEM grids, etc, the chemical
information on a single functionalized nanotube or even precisely at the functional sites can be achieved by combining the enhanced Raman spectra of NSOM with the atomic or molecular resolution of STM.

5.4 Applications of self-assembled functionalized SWNTs

Our final goal is to build up nanoscale devices with carbon nanotubes by utilizing the self-assembly, insertion and other techniques.

Self-assembly has proven a powerful technique for patterning surfaces and building devices at the nanometer level. Some typical techniques, such as micro-contact printing, dip-pen lithography etc, can be achieved by employing self-assembled molecules. Our experiments proved thiol and thiophene functionalized nanotubes can be patterned in a similar manner as the normal self-assembled molecules, by using these techniques. That is a necessary first step toward making mass-produced nanotube devices in the future.

Additionally, by combining the insertion with functionalized alkanethiol SAMs, we can dope the SWNTs at the nanoscale.

As illustrated in the Fig 5.1, the previous group, Hongjie Dai et al. have already done a SWNTs doping experiment. Nanotube PN junction and transistors have been created by combining the bulk lithography with chemical adsorption of amine groups to the SWNTs. But this method limits the resolution at tens to hundreds of nm, due to the limit of bulk lithography.
Figure 5.1: Schematic cited from Hongjie Dai et al., illustrating the nanotube PN junction and transistors.

However, the method we propose below could create truly molecular-based nanotube devices at single nanometer scale, by using nanoscale chemical doping. In Fig 5.2, chemical functionalized alkanethiol SAMs are pattern on the Au surface in advance by micro-contact printing or similar techniques, which have nanometer resolutions. After insertion of the self-assembled nanotubes, there will be a nanoscale PN junction on the nanotube just at the domain boundaries, because NH$_2$ group can donate electrons, and CF$_3$ can donate holes. Even though the intrinsic electronic properties of doped SWNTs might be changed, we still can use double-wall or multiple-wall carbon nanotubes to substitute the SWNTs. The center tubes will be able to keep their metallic or semiconducting properties.

Figure 5.2: Illustration of nanotube PN junction formed by using functionalized alkanethiol SAMs to controllably dope the electrons or holes.
A similar doping technique for fullerene thin films has been demonstrated by the Ishikawa group.\textsuperscript{148, 149} By using this straightforward method, we can controllably dope the SWNTs with the chemical functionality of the SAMs, and furthermore build up the nanoscale devices.

In conclusion, we have performed initial investigations of the thiol and thiophene functionalized SWNTs and fullerene-terminated peptide by STM. The spectroscopic and chemical measurements are already planned for the future works. Furthermore, based on the completed theoretical foundation, only much more hard work might be able to lead us to realize the intelligent ideas, such as building nanoscale devices.
Bibliography

Appendix:

Defect distribution calculation of thiophene functionalized SWNTs.

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Illustration: X means that there are no small or large defects on the thiophene nanotubes.