Covalent Graphene Functionalization for the Modification of Its Physical Properties

HU LI
Graphene, a two dimensional monolayer carbon sheet with the atoms tightly packed in a hexagonal lattice, has exhibited so many excellent properties, which enable graphene to break several material records with regard to carrier mobility, strength yield and thermal conductivity to name a few. Therefore, graphene has been placed as a potential candidate to allow truly next-generation material. Graphene is a zero band gap material, implying that an energy band gap around the Dirac point is supposed to be open to make graphene applicable as a semiconductor. Covalent bond graphene functionalization becomes an essential enabler to open the energy gap in graphene and extend graphene applications in electronics, while the densely packed hexagonal carbon atoms as well as the strong sp2 hybridization carbon-carbon bonds jointly result in a changeling topic of allowing graphene to be decorated with functional groups.

Here in this thesis, different routes to realize graphene functionalizations are implemented by using physical and chemical ways. The physical functionalization methods are the ion/electron beam induced graphene fluorination as well as local defect insertion and the chemical ways correspond to the photochemistry techniques to approach hydrogenation and hydroxypropylation of graphene. Furthermore, to incorporate graphene into devices, the tuning of mechanical properties of graphene is desired. Towards this aim, the structure modification of graphene is employed to investigate the nanometer size-effect of crystalline size of graphene on the mechanical properties, namely Young’s modulus and surface energy. In the process of the graphene hydrogenation project, we discovered a high yield way to synthesis high quality graphene nanoscroll (GNS). Interestingly, the GNS shows superadhesion property through our atomic force microscopy measurements. This superadhesion is around 6-order stronger than van der Waals interaction and even higher than the hydrogen bonding enhanced and solid/liquid interfaces.

Keywords: graphene; functionalization; nanomechanical property, graphene nanoscroll
To my family and friends
List of Papers

This thesis is based on the following papers, which are done in the PhD period and referred to in the text by their Roman numerals.


* Equal Contribution

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Paper Contributions

**Paper I**
Conducted the FIB cutting experiments and the calculation, contributed to the electrical measurements and a major part of manuscript writing.

**Paper II**
Conducted the AFM experiment, corresponding calculations and Raman measurements. Contributed to a part of the manuscript writing.

**Paper III**
Conducted the site-selected fluorination, the XPS and Raman characterizations. Designed the control experiments and performed the related experiments and characterizations. A major part of the manuscript writing.

**Paper IV**
Conducted the E-beam fluorination, XPS elemental analysis and valence band spectra experiments. A major part of the manuscript writing.

**Paper V**
Contributed to experiment design. Conducted the graphene hydrogenation experiments, Raman and XPS measurement. A part of the manuscript writing.

**Paper VI**
Contributed to the experiment design. Conducted the graphene hydroxypopylation synthesis, Raman, XPS and AFM measurements. A part of the manuscript writing.

**Paper VII**
Conducted the ion beam irradiation and followed Raman and AFM characterizations. Established the graphene models with various sizes and performed the surface energy calculation. A major part of the manuscript writing.

**Paper VIII**
Conducted the GNS synthesis, XPS, Raman and AFM measurements. Performed the strain related calculations to understand the adhesion mechanism. A major part of the manuscript writing.
These papers are not listed in the thesis


XVI  Anna Lundstedt*, Raffaello Papadakis*, **Hu Li***, Joakim Bergman, Klaus Leifer, Helena Grennberg, Henrik Ottosson. Metal-Free Photohydrogenations of graphene. *-In Manuscript.*

XVII  Fengzhen Sun, **Hu Li**, Klaus Leifer, and Kristofer Gamstedt. Effects of sectioning velocities on thermoplastic instabilities during sectioning amorphous polymers at nanoscale. *-In Review.*


Nan Wang, Hu Li, Klaus Leifer, Li-lei Ye and Johan Li. Large-scale graphene based film with ultra-high thermal conductivity. *In Manuscript.*

* Equal Contribution
Contents

1. Introduction ........................................................................................................... 15
   1.1 Motivation ....................................................................................................... 16
   1.2 Aim and Objective ...................................................................................... 17
   1.3 Thesis Outline ............................................................................................ 18

2. Graphene Synthesis and Modifications .......................................................... 19
   2.1 Graphene Synthesis .................................................................................... 19
       2.1.1 Mechanical exfoliated graphene ...................................................... 19
       2.1.2 Chemical vapor deposited graphene .............................................. 20
       2.1.3 Epitaxial graphene ......................................................................... 21
   2.2 Graphene Functionalization ....................................................................... 22

3. Basic Properties of Graphene ........................................................................... 24
   3.1 Electronic Properties of Graphene ............................................................. 24
   3.2 Mechanical Properties of Graphene ............................................................ 25
       3.2.1 Tensile strength and Young’s modulus ......................................... 25
       3.2.2 Adhesion property ........................................................................ 26

   4.1 Focused Ion Beam (Paper I) ....................................................................... 27
   4.2 Atomic Force Microscopy (Paper II) ......................................................... 28
   4.3 X-ray Photoelectron Spectroscopy ............................................................. 30
   4.4 Raman Spectroscopy ................................................................................ 32
   4.5 Transmission Electron Microscopy ............................................................ 32

5. Graphene Functionalizations and Nanometer Size-Dependent
   Mechanical Property ....................................................................................... 34
   5.1 Introduction .................................................................................................. 34
   5.2 Graphene Fluorinations ............................................................................. 35
       5.2.1 Site-selective fluorination of graphene induced by ion beam
               irradiation (Paper III) ................................................................. 35
       5.2.2 Reversible fluorination of graphene induced by electron beam
               irradiation: towards the band gap manipulation (Paper IV) ......... 36
   5.3 Photofunctionalization of Graphene: Hydrogenation and
       Hydroxypropylation .................................................................................... 39
       5.3.1 Photohydrogenation (Paper V) ....................................................... 39
       5.3.2 Photohydroxypropylation (Paper VI) ............................................. 40
5.4 Nanometer Size Dependent Mechanical Properties of Graphene
(Paper VII)........................................................................................................42
5.5 Conclusion.............................................................................................43

6. Graphene Nanoscrolls (Paper VIII) .....................................................44
   6.1 Introduction .......................................................................................44
   6.2 A New Allotrope of Carbon with Superadhesion.............................45
   6.3 Conclusion.......................................................................................47

Conclusions and Outlook.............................................................................48

Sammanfatting På Svenska.........................................................................50

Acknowledgements....................................................................................52

References.................................................................................................54
# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>Two-Dimensional</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Function Theory</td>
</tr>
<tr>
<td>$E_{\text{binding}}$</td>
<td>Binding Energy</td>
</tr>
<tr>
<td>$E_k$</td>
<td>Kinetic Energy</td>
</tr>
<tr>
<td>$E_p$</td>
<td>Photon energy</td>
</tr>
<tr>
<td>ESEM</td>
<td>Environmental Scanning Electron Microscope</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>GaAs</td>
<td>Gallium arsenide</td>
</tr>
<tr>
<td>GNS</td>
<td>Graphene Nanoscroll</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly Oriented Pyrolytic Graphite</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscope</td>
</tr>
<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
</tr>
<tr>
<td>LOM</td>
<td>Light Optical Microscope</td>
</tr>
<tr>
<td>PF-QNM</td>
<td>Peak Force Quantitative Nanomechanical Mapping</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Silicon Dioxide</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>VBM</td>
<td>Valence Band Maximum</td>
</tr>
<tr>
<td>XeF$_2$</td>
<td>Xenon Difluoride</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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1. Introduction

In the year 2004, a milestone discovery in the material community is the isolation of graphene\textsuperscript{1-5}, a single layer of carbon atoms packed in a hexagonal lattice, by using scotch tape from graphite. In a long period, it is believed that strictly two-dimensional (2D) packed atoms were not stable enough to exist, because the thermal fluctuations of the atoms will be stronger than the binding forces that holding them together\textsuperscript{6}. However, the successful exfoliation of graphene completely overturned such assumptions on 2D materials, and further theoretical and experimental research indicates that graphene is actually very stable can be seen as one of the most chemically inert materials ever found. Due to several outstanding properties found latter, graphene has been seen as a promising candidate to replace silicon as a next generation of materials\textsuperscript{2,7-9}. Ever since the isolation of the graphene, an enormous amount of research has been directed to the isolating other two materials, and consequently, a series of new 2D materials were reported such as graphane\textsuperscript{10-13}, borophene\textsuperscript{14}, phosphorene\textsuperscript{15}, hexagonal boron nitride\textsuperscript{16-19}, etc. The rapidly growing research on 2D materials with their unique characteristics has considerably boosted the application.

The producing of high quality graphene is rather convenient and like a small game. Put a small amount of graphite, the central core of a pencil, on a scotch tape and pull the graphite several time until the flake looks small enough, then transfer to a silicon dioxide (SiO\textsubscript{2}) substrate. Under a light optical microscope, the graphene flakes can be observed. However, graphene synthesized by this simple method has broken several material records in view of electronic, mechanical and thermal properties.

Graphene has shown an experimental electron mobility of 200000 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} at room temperature\textsuperscript{6,8,20,21}, which has so far the highest carrier mobility in the whole materials world. Moreover, the observation of the room temperature quantum Hall effect has placed graphene in the material class that can show quantum Hall effect after silicon and gallium arsenide\textsuperscript{22}. All of these unique electronic properties of graphene are mainly attributed to the unique electronic structure. Graphene is a zero band gap material and the conduction band and the valence band meet at the Dirac point. The band structure near the Dirac point (Brillouin zone) shows a linear behaviour and results in the massless Dirac electrons\textsuperscript{23}, which directly caused the unique electronic properties of graphene. However, in order to obtain graphene or a graphene derivative useful for electronics applications, a band gap needs to
be opened. This is possible, but to date, opening a bandgap of the order of 1eV in graphene, still leads to a strong reduction of the mobility\(^6\).

Graphene shows also interesting mechanical properties being the strongest material ever reported\(^{24-26}\), and the experimental result shows a tensile strength of 130 GPa and a Young's modulus of 1 TPa. These anomalous properties are mainly attributed to the strong and densely packed in-plane carbon-carbon bonds\(^{27-29}\).

Another outrageous property of graphene has shown is its ultrahigh sensitivity and it is mainly owed to its large and inert surface area\(^ {2,3,30}\). However, to apply graphene in the electronic devices, graphene still need a long way to go. The absence of the intrinsic band gap means that graphene cannot be used as a semiconductor in electronics and the lack of selectivity in the sensing process implies that graphene cannot distinguish different gases. Graphene functionalization is an efficient way to solve all of the problems. Due to the high chemical stability of graphene, the chemical functionalization method by covalent bonds which is a preferred method used to obtain sensitivity and selectivity in sensors becomes difficult. Yet, since other functionalization methods, relying on π-π stacking or van der Waals bonds, are in general less stable than covalent bonds, the fabrication of covalently functionalized graphene is an important goal for the development of graphene devices. Therefore, the transformation of graphene from a semi-metal to a semi-conductor and from pristine graphene to covalently functionalised graphene has become a challenging barrier that must be overcome, and the functionalization of graphene by means of mild and cheap synthetic methodologies is currently highly desired.

### 1.1 Motivation

In year of 2012, I started my PhD in the field of materials analysis with the emphasis on graphene and corresponding carbon materials. My research starts with the instrument license trainings (SEM, ESEM, FIB, AFM, XPS, Maskalingen, Evaporator, Plasma stripper, Wire bonder, Wet benches, etc.). This period is quite essential to me since, as for a researcher in materials analysis, the instrument is similar to our hands. Since then, my interests were increasing to not only know how to use the machine, but to explore and improve the potential applications of the instruments. My first attempt to use my instrument knowledge on two key devices of my thesis, the focused ion beam (FIB) and the atomic force microscope (AFM) in scientific research is demonstrated in the first two papers (Paper I and II), even if the research topics deviate a little bit from my main topic of graphene.

Graphene functionalization towards the final electronic application is a common challenging topic in graphene community. Even though hundreds of functionalization methods have been reported on graphene synthesised by
chemical reduction of graphene oxide, the monolayer graphene has been found to be challenging to be functionalized, while the outstanding properties are mainly reported on this monolayer graphene such as exfoliated and chemical vapour deposited graphene. Therefore, towards this aim, to overcome this barrier in the real application of graphene becomes an essential motivation to me. When graphene is functionalized, the carrier mobility normally will drop due to the localization of the $\pi$ electrons. How to achieve an optimized way that not only maintains the functionalization, but still keeps the intrinsic high mobility of the graphene becomes another challenging topic and motivation to me. Then the site-selective functionalization method is a potential way to solve the problem.

Another motivation of my work comes from the research itself, and surprising bonus result from research can always bring fun. For instance, when I worked on a graphene hydrogenation project, a control experiment inexpertly led to a surprising morphology change from a graphene sheet to a graphene nanoscroll. Interestingly, the resulted graphene nanoscroll still maintains the graphene signature in Raman scattering and exhibits a superadhesion property, which is stronger than the adhesion property of graphene and even higher than the hydrogen bonding enhanced interfaces.

1.2 Aim and Objective

The main aim of this thesis is to develop different physical and chemical routes to realize graphene functionalization in view of a modification of its mechanical properties and electronic structure. The main topics of this thesis are shown in the Figure 1.1 and summarized as below:

(a) Physical means: the particle (ions and electrons) induced fluorination of graphene and its characterizations of its electronic structure. Chemical means: the photochemical ways to approach hydrogenation and hydroxypropylation of graphene.

(b) Structural modification: by changing the grain sizes, nanometer size dependent mechanical properties of graphene can be tuned.

(c) Graphene nanoscroll: The graphene nanoscroll is synthesized and the adhesion property is characterized.
1.3 Thesis Outline

In this doctoral thesis, different routes to approach graphene functionalization will be discussed and the corresponding property modifications are characterized by means of techniques. As a new carbon material, the synthesis method as well as the superadhesion measurement of the GNS will also be introduced.

Chapter 1 presents a brief introduction of the thesis, the motivation and the final scientific goal of the work. Chapter 2 provides a detailed description of the graphene synthetic methods, and the recent development of the graphene functionalization will also be introduced in this chapter. Chapter 3 presents the basic properties of graphene in terms of electronic and mechanical properties. Chapter 4 mainly focuses on the characterization techniques of graphene and its derivative. In this chapter, different instruments, e.g. FIB (Paper I), AFM (Paper II), XPS, TEM and Raman, will be introduced. In Chapter 5, graphene functionalization approaches by physical and chemical routes are described. The physical routes (Paper III and IV) include the particle (ions and electrons) induced fluorination of graphene, whereas the chemical routes (Paper V and VI) are concentrated on the photochemical ways to hydrogenation and hydroxypropylation. In the last part of this chapter, the nanometer size dependent mechanical properties of graphene (Paper VII) will be discussed. Chapter 6 presents the study of the GNS (Paper VIII) including synthesis and properties measurements.
2. Graphene Synthesis and Modifications

Graphene\textsuperscript{1,6,31,32} is a single atomic layer of carbon atoms bonded in a hexagonal lattice, in which each carbon atom forms three $\sigma$ bonds with its neighbor atoms and one $\pi$ bond oriented out of the lattice plane. After the initial successfully mechanical exfoliation of graphene from graphite in 2004, various graphene synthesis methods have been developed rapidly. This chapter focuses on the different graphene synthesis methods and the research progress in the graphene modifications regarding properties.

2.1 Graphene Synthesis

Monolayer graphene can be obtained by three main routes namely, mechanical exfoliation, chemical vapor deposition (CVD) and epitaxial growth.

2.1.1 Mechanical exfoliated graphene

The mechanical exfoliation of monolayer graphene was initially reported by Geim and Novoselov\textsuperscript{6,33}. In their experiment, they initially pull of highly oriented pyrolytic graphite (HOPG) by using normal scotch tape. After multiple exfoliation steps, the flakes become thinner and are finally deposited on a SiO2/Si substrate. The monolayer of graphene is visible under light optical microscope (LOM), as shown in the Figure 2.1 (a) and (b). This mechanical exfoliation method normally results in single crystals graphene which has lowest defect density and highest carrier motilities and the monolayer graphene flakes can be distinguished from multilayer graphene and from the SiO2 substrate. Combing the photo/electron beam lithography technique, the metal contacts can be fabricated on graphene, as shown in Figure 2.1(b), and the device then can be used to characterize the electrical and electronic properties of graphene.
The mechanically exfoliated graphene shows excellent performance, e.g. an experimental carrier mobility\textsuperscript{21} of $200000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, for research dedicated to basic scientific research. However, the intrinsic 1µm to 20µm flake size considerably limits its application in devices. Electronic applications require large surface area graphene in order to fabricate and build complicated devices or integrate into other semiconductor device fabrication flows. Obviously, the size of a few micrometers of exfoliated graphene flakes does not meet the scaling requirement.

### 2.1.2 Chemical vapor deposited graphene

Chemical vapor deposited graphene\textsuperscript{19,34–37} is considered as a milestone in the graphene roadmap of graphene synthesis. By employing using metal foils as a substrate material and employing chemical vapor deposition growth, graphene films are directly synthesized on the metal surface with the monolayer coverage of more than 95%. This technique produces relatively high quality graphene and, more importantly, on a large scale. However, it is still quite challenging to synthesize completely uniform CVD graphene film. The reason is mainly owing to the dynamics of the CVD process, where the mixed gases are affected by the dynamic diffusion and the exhaustion of the reactants occurs at the further ends of the metal foils. Figure 2.2 shows the scanning electron microscopy (SEM) image of a CVD graphene sample, where the graphene grains are visible and the darker islands inside the sample are the double layer graphene. In this thesis, the CVD graphene is mainly used as in the experiments, because the CVD graphene is big and suitable for the characterizations, and also has the good quality.
2.1.3 Epitaxial graphene

Epitaxial graphene\textsuperscript{38–43}, which is graphene on a silicon carbide surface, is believed as the platform on which the first electronic measurements of monolayer graphene were carried out, even earlier than on the mechanically exfoliated graphene. By heating the hexagonal silicon carbide to 1000°C under high vacuum of $10^{-6}$ Torr, monolayer graphene will appear on the Si-face side. The outstanding surface condition of uniformity and flatness as well as the large surface area allows epitaxial graphene perfect candidate for atomic scale observation and quantum Hall measurements. Figure 2.3 shows the STM observation of the epitaxial graphene, in which the carbon hexagonal lattices are clear.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2_3.png}
\caption{Scanning tunneling microscope image of the epitaxial graphene on silicon carbide substrate.}
\end{figure}
However, due to the semiconductor behavior of silicon carbide, there will be a considerable charge transfer from the graphene layer to the substrate. Moreover, the hybridization of the $\pi$ graphene electrons and the SiC d-orbital electrons can significantly modify the electronic structure\textsuperscript{44,45}, leading to a distinct electronic behavior as compared to graphene on SiO$_2$.

2.2 Graphene Functionalization

Compared with semiconductors, graphene does not have an energy gap, implying that graphene cannot be directly utilized in electronics, in which the transistor turn on and off behaviors are necessary\textsuperscript{8,46–49}. Underlying all of these challenges is the intrinsic chemical inertness of the graphene. The reason of the low chemical reactivity of graphene is mainly attributed to the strong and densely packed carbon-carbon $sp^2$ hybridization bonds. Normally, a reaction would prefer the locations where the weak or dangling bonds and localized charges are presented, but none of them are easily found in graphene, thus covalent functionalization is highly hindered in graphene. By using strong reactants, e.g. acids or radicals, the graphene functionalization can be approached\textsuperscript{10,12,13,18,32,50–55}.

Graphene hydrogenation is one of the most thoroughly researched topics in terms of theoretical and partial experiment studies. Graphane\textsuperscript{56,57}, fully hydrogenated graphene, is expected to be direct gap material with the band gap of 3.5 eV. The main experimental approach on the hydrogenated graphene is realized by using hydrogen gas under high temperature and high pressure condition with the catalysis of transition metals. Another approach to hydrogenated graphene is to use hydrogen plasmas\textsuperscript{58,59}. The specific conditions that used for graphene hydrogenation will decide the final status of the irreversible defects in graphene, especially in the extreme process conditions such as high energy plasmas and high temperatures.

Due to the high electronegativity, fluorine has been seen as a good candidate to induce an energy gap in graphene. Moreover, in theory, by tuning the concentration of the covalent bonded fluorine atoms, the band gap can be tuned. The experimental approach of the graphene fluorination is firstly performed by pure XeF$_2$ gas flush\textsuperscript{60–62}. XeF$_2$ is a stable gas in room temperature, but when it is exposed to graphene, the fluorine will chemically attached to graphene carbon, leading to the fluorination of graphene. Covalent bonded fluorine atoms significantly change the optical and electronic properties of graphene. According to the study of Robinson\textsuperscript{60}, fluorinated graphene will lose the optical contrast with SiO$_2$ substrate, in other words, become transparent to visible light. This observation indicates an insulating property of the fluorinated graphene. However, this method has a quite slow yield in the fluorination and, for one side fluorination, there is an atomic ratio of F to C limit of 25% (C$_4$F).
The covalent oxidation of graphene\textsuperscript{10,63–67} is a more complicated process than fluorination and hydrogenation, because oxygen atom is supposed to form two bonds with graphene carbon atoms rather than one bond case. The common used graphene oxide compound is mainly synthesized by using Hummers method\textsuperscript{68}, which is a typical wet chemistry method with the starting material of graphite. Even though this method is the most common way to oxide graphene, the resulted graphene oxide is extremely inhomogeneous.
3. Basic Properties of Graphene

Due to the unique atomic structure, graphene exhibits special electronic and mechanical properties. In this chapter, these properties will be introduced and discussed.

3.1 Electronic Properties of Graphene

![Electronic structure of graphene. (adopted from the Ref[16], and reproduced with the permission of NPG)](image)

The remarkable electronic properties of graphene origin from the special band structure of graphene shown in the Figure 3.1. Fundamentally, graphene is a zero band gap semi-metal, where the conduction bands and valence bands intersect at the Dirac points (k points). At low energy region of the energy-k space diagram, the graphene band structure shows linear behavior when close to the Dirac points, implying that the effective mass for electrons and holes are both zero. This unique band structure and the presence of massless fermions give graphene extreme high carrier mobility, which are further confirmed experimentally. Novoselov et al.\(^5\) has reported the electron mobility of graphene of 15000 cm\(^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}\), independent of temperature between 10 K and 100 K, while Bolotin et al.\(^21\) reported the experimental observation of the electron mobility of 200000 cm\(^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}\) in suspended graphene. Due to the massless property of the charge carriers, graphene electrons perform similar as photons that can move more than 2 \(\mu\text{m}\) without scattering (ballistic transport)\(^8,69\).
Room-temperature quantum Hall effect is another milestone that has been reached on graphene. Quantum Hall effect relies on the quantized electronic structure of a material, resulting in the Hall conductance to be quantized, and was only reported in Si and GaAs at low temperature and high magnetic field before the discovery of graphene. Graphene exhibiting the room-temperature Hall effect is mainly attributed to the presence of massless Dirac electrons. When graphene is placed perpendicular in a strong magnetic field (above 10 Tesla), the energy spectra of the Dirac electrons will show Landau levels exactly at the Dirac point. These Landau levels will result in the quantization of the Hall conductivity.

3.2 Mechanical Properties of Graphene

3.2.1 Tensile strength and Young’s modulus

The mechanical properties of graphene are found to be outstanding. Due to the short and strong carbon-carbon bonds, in the experiment, graphene shows an tensile strength of 130 GPa and Young’s modulus of 1 TPa, which makes graphene the strongest and stiffest material ever discovered. There is a figurative analogy to describe the strongest material of graphene by saying that one meter square graphene film can hold a four kilograms cat, but the weight of the graphene is only 0.77 milligrams, which is only one whisker of the cat.

![Schematic representation of the nanoindentation process by using atomic force microscopy on graphene membrane, and the recorded force displacement curve. (Adopted from the Ref[11], and reproduced with the permission of NPG)](image)

Due to the atomically thick property, conventional nanoindentation method cannot be applied to graphene. Thus, atomic force microscope (AFM) was used to characterize the mechanical properties of graphene, as shown in Figure 3.2. By the indentation of an AFM tip, the force-displacement curves can be recorded and the intrinsic tensile strength and the Young’s modulus of the graphene can be extracted.
3.2.2 Adhesion property

Another exciting mechanical property of graphene is its ultrastrong adhesion\textsuperscript{70}. Adhesion plays an essential role in a large variety of fields ranging from biology to industry applications. The adhesion energy, also called interfacial energy, is used to describe the adhesion strength of the interface. When two objects are contacting physically, the van der Waals force makes them adhesive to each other. But the van der Waals force is not considered as a strong adhesion force. The strongest adhesion forces are normally observed at liquid-solid and hydrogen-bonding enhanced interfaces when only considering physisorption mechanisms\textsuperscript{71,72}. Interestingly, comparably strong adhesion was observed on monolayer graphene\textsuperscript{70,73,74}, which has generated considerable interest in the material for adhesion applications.

Figure 3.3 shows the adhesion energies comparison of graphene with graphite. Graphene exhibits average adhesion energy of 0.45 J/m\textsuperscript{2}, which is 5-order higher than the van der Waals interactions and comparable to liquid/solid interaction in typical micromechanical devices. This anomalously high interface adhesion of graphene is mainly attributed to the smaller atomic coordination numbers of the carbon atoms as compared to bulk graphite, resulting in an intrinsic strain formed inside graphene lattices\textsuperscript{73}. It is commonly known that surface atoms usually have a smaller atomic coordination numbers in contrast to bulk atoms and will exhibit special properties\textsuperscript{75–77}, e.g. stronger and shorter bond lengths. Compared with graphite, graphene is a surface material with an atomic coordination number of three\textsuperscript{78} (the effective atomic coordination number for bulk graphite is 5.335). This small coordination number constrains the relaxation of graphene and finally leads to a stored lattice strain. When graphene is physically contacted with other object, this strain energy will contribute to the interfacial adhesion energy\textsuperscript{73,79}.

![Figure 3.3 graphene/SiO\textsubscript{2} adhesion energies compared with graphite adhesion energies. One layer of graphene (black circles), two layers (red squares), three layers (green triangles), four layers (blue triangles) and five layers (cyan diamonds). (This figure is adopted from the Ref\textsuperscript{[25]}, and reproduced with the permission of NPG)](image-url)
4. Characterization Techniques of Graphene and Its Derivate

4.1 Focused Ion Beam (Paper I)

Focused ion beam (FIB/SEM, FEI Strata DB235) is a commonly used instrument in nanofabrication, which is a maskless technique and has been widely used to fabricate reproducible structures down to nanometer precision\textsuperscript{80–88}. The setup of FIB is similar to a scanning electron microscope (SEM). By using electrostatic lens, the ion beam can be focused and scanned on the target sample, then used to image or fabricate structures.

To realize the electrical characterization of single or few molecules\textsuperscript{89}, FIB is used to mill sub-5 nm gaps on a gold wire. In FIB, the minimum ion beam probe size is \( \sim 7 \) nm at 30 kV accelerating voltage and 1 pA beam current. The applied ion dosage is tuned to realize a differential sputtering of gold matrix and gain boundaries. In the process, this differential sputtering can result in the grain boundaries to be sputtered more compared to the gold main body, and the sub-5 nm nanogap will appear when the boundaries are cut, while the gold matrix is not yet milled shown. Figure 4.1 shows the evolution of the nanogap under focused ion beam milling. With an increase in the applied ion dosage, the nanogap becomes more and more clear and the critical ion dosage to achieve the gap is found to be \( 5 \times 10^{10} \) ions/cm. Combining the SEM observation and electrical characterization, the minimum nanogap was found to be \( \sim 2 \) nm.

Therefore, through the precise focus of the ion beam and control of the ion dosage, sub-5 nm gaps are achieved in FIB milling. In our graphene functionalization projects, we have also explored further this instrument to approach graphene fluorination and more details will be presented in the next chapter.
Figure 4.1 SEM images of (a) raw 250 nm wide gold wire, (b) after FIB milling of $4.6 \times 10^{10}$ ions/cm ion dosages, (c) $5 \times 10^{10}$ ions/cm, (d) $6.7 \times 10^{10}$ ions/cm, (e) $8.3 \times 10^{10}$ ions/cm. The sample under $5 \times 10^{10}$ ions/cm is tilted at 55° in shown in (f).

4.2 Atomic Force Microscopy (Paper II)

Atomic force microscope (AFM) is one family member of the scanning probe microscopes and, by measuring the interaction force between the AFM tip and the target sample, different information of the sample could be obtained, e.g. the surface topography, surface phases, etc. The AFM that is used in this thesis is a Multimode 8 AFM, Bruker90–95.
Peak force quantitative nanomechanical mapping (PF-QNM) is a technique in AFM that is used to quantitatively investigate the surface physical properties. This technique is mainly based on the force-displacement feedback loop, namely force volume curve, which the interaction force between the tip and the sample as a function of the displacement of the piezo scanner can be recorded in real time shown in the Figure 4.2. Therefore, several intrinsic properties of the sample, e.g. elastic modulus, adhesion force and energy dissipation can be extracted.

Figure 4.3 presents the single rutile surface topography images as well the adhesion mapping by employing the PF-QNM technique. The main purpose of this project is to understand the mechanism of protein catalyzed biomineralization on single crystalline rutile. From the AFM morphologic images, both protein treated and untreated single rutile show a rather flat surface with the roughness 1-2 nm, even though the scratches from fine polish are visible. But from the adhesion mapping, it is found that after protein treatment, single rutile shows a considerably higher adhesion forces in contrast to untreated samples. The result agrees well with the corresponding SEM observation of the biomineralization on single rutile, and also gives an experimental support to the thermal dynamics explanation of the mechanism (more information can be found in Paper II).
Figure 4.3 AFM morphologic images of single rutile on (001), (100) and (110) faces (a)-(c) and after 2 hours protein treatment (d)-(f). AFM adhesion mapping of single rutile on (001), (100) and (110) faces (g)-(i) and after 2 hours protein treatment (j)-(l).

This novel technique gives us a tool to investigate nanomechanical properties of nano-objects and has been intensively used in the graphene projects. For example, the observation of superadhesion property of graphene nanoscrolls is performed under this set up and more applications of this technique on graphene will be introduced in the next chapter.

4.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS)\(^{10,47,64,96,97}\) is a surface sensitive characterization technique to identify which elements are present in the surface and the bonding types that exist between these elements. The principle of XPS is interpreted in Figure 4.4. Under the irradiation of X-ray, the core electrons of the sample can be excited and escape from the orbitals, which are then called photoelectrons. When the photoelectrons are captured by a detector, the binding energy \(E_b\) between the core level and the Fermi level can be calculated as:

\[
E_{\text{binding}} = E_p - E_k
\]

where \(E_p\) and \(E_{\text{kinetic}}\) are the incoming X-ray energy and kinetic energy of the photoelectrons. The calculated binding energy of the core shell electrons can provide fingerprint information of the element.
XPS is also used to analyze the bonding types by measuring the binding energy shift. For example, carbon atom in a methyl group will have slightly different binding energy compared with the carbon atom in carboxyl group. Therefore, XPS is an efficient tool in the characterization of the functionalized graphene. Figure 4.5 illustrates the XPS C 1s peak of the pristine graphene, where the peak can be deconvoluted into Sp² carbon, Sp³ carbon, C-O and C=O sub-peaks based on different binding energies. The Sp² carbon signal origins from the graphene lattice and the rest peaks are supposed to be from the residual contaminations from the transfer process.

Figure 4.5 XPS C 1s peak of CVD pristine graphene.
4.4 Raman Spectroscopy

Raman spectroscopy is a widely used spectroscopic technique in material analysis. It is mainly used to observe the vibrations, rotations and low-frequency modes in a material system, in which the fingerprint of molecules can be identified\textsuperscript{33,63,98–101}. The mechanism of the Raman spectroscopy is based on Raman scattering by using a monochromatic laser light. The incoming laser light can interest with the molecules in terms of vibrations and leads to an energy shift in the photons. This energy shift can be measured and used to calculate the information of the vibration modes of the molecules.

In graphene research, Raman spectroscopy is commonly used. Figure 4.6 gives the fingerprint Raman spectrum of graphene under the laser light of 532 nm.

![Figure 4.6 Raman spectrum of the graphene under the laser light of 532 nm](image)

In the Raman measurement of graphene, the energy shift of the photon can show two main bands: the biggest 2D band (at \( \sim 2700 \text{ cm}^{-1} \)) and G band (at 1580 cm\(^{-1}\)). The 2D band is the second order overtone of the D band (at 1350 cm\(^{-1}\)) and the G band is generated from the activation of the E\(_{2g}\) mode at the \( \Gamma \) points (in-plane carbon-carbon vibration mode)\textsuperscript{63,102,103}. Compared with graphite, the lacking of Bernal stacking in graphene layer results in a non-splitting of the 2D band and finally leads to a sharp and high intensity 2D band in Raman scattering.

4.5 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a microscopy technique in which electrons, typically accelerated to energies of 50-300keV, interact with the sample and a signal resulting from this interaction process is acquired\textsuperscript{104}. The resolution of the TEM is ultimately limited by the electron wavelength which is in the order of picometer and typical resolutions of a
modern TEM in materials science range from 0.5 to 2Å. A wealth of signals can be obtained from the electron-sample interaction process using different detectors such as energy filters, energy dispersive X-ray detectors, CCD cameras and detectors analyzing electrons at some scatter angles $^{105-109}$. In this work, phase contrast images were acquired, which are obtained by bringing beams that were scattered in different directions to interfere in the image plain. For a crystalline sample oriented on a zone axis, such high resolution TEM (HRTEM) images contain networks of bright and dark dots that can be interpreted as representing the positions of atomic columns.

Figure 4.7 HRTEM image of multilayer graphene taken at 300keV with FFT (insert). Courtesy to Max Karlsson.

Figure 4.7 shows the HRTEM image of multilayer graphene, in which the lines on the sample represent the lattice of the multilayer graphene, indicating the atomic resolution in the image. The fast Fourier transform (FFT) shows several hexagonal patterns, whereas for monolayer graphene, only a single hexagonal pattern would be expected. This can be interpreted as at least three layers being present with a slight difference in the orientation.
5. Graphene Functionalizations and Nanometer Size-Dependent Mechanical Property

5.1 Introduction

Due to the massless Dirac fermions of graphene, the development of graphene applications in semi-conductor devices has aroused substantial attention. Graphene exhibits properties as semi-metal, having an energy band gap around the Dirac point. A band gap is supposed to be open to make graphene applicable as a semiconductor. Therefore, covalent bond graphene functionalization becomes an essential enabler to open the energy gap in graphene and extend graphene applications in electronics. However, the densely packed hexagonal carbon atoms as well as the stable sp² hybridization carbon-carbon bonds jointly result in a challenge to decorate graphene with the functional groups.

In this chapter, different routes of covalent graphene functionalizations are introduced. Size-selective graphene fluorination is realized by focused ion beam irradiation and this technique not only allows for a local functionalization of graphene independent of photo/electron-lithography technique, but also has the potential to enable a wide range of graphene functionalizations using various gases. The electron beam induced graphene fluorination has overcome the F concentration limit of 20% in one-side graphene fluorination and resulted in a fully one side fluorination of graphene. More important, by tuning the processing time of the fluorination and combing de-fluorination, the fluorination degree of graphene can be controlled at any desirable value, which means that the energy band gap of graphene is not only open, but can be easily and precisely manipulated from 0 eV to maximum of 6 eV.

When we consider the chemical routes to reach graphene functionalizations, we are excited to find that graphene performs much more reactive with the presence of light, this interesting property open a door and allows us to approach various graphene functionalizations like hydrogenation and hydroxypropylation.

Taking advantage of ion irradiation to alter the effective grain sizes of graphene is another route to modify the physical properties of graphene. By using this method combing the AFM technique, graphene with various grain
sizes are obtained and the nanomechanical properties are measured through PF-QNM technique and the result shows that structural modification of graphene has significant influence on the mechanical properties of graphene, especially when the grain sizes are smaller than the transition point of 7 nm as observed from Raman spectroscopy.

5.2 Graphene Fluorinations
5.2.1 Site-selective fluorination of graphene induced by ion beam irradiation (*Paper III*)

![Figure 5.1 Schematic of the size-selective fluorination of graphene](image)

In this project, the site-selective fluorination of graphene is performed under focused ion beam irradiation in XeF₂ gas atmosphere of high vacuum condition (5.5×10⁻⁵ mbar). The main idea of this method shown in Figure 5.1 is to employ high energy ion irradiation (Ga⁺ ions) to radicalize the graphene surface, namely creating carbon dangling bonds. At the same, a fluorine precursor gas of XeF₂ is provided and subsequently reacted when with the carbon atoms are in the radicalized state. The purpose is to create a local, stable and covalent bond between F and C.
By a systematic series of experiments utilizing this technique, it is found that the ion-sample-precursor interaction strongly increases the local fluorine concentration where the overall fluorine concentration on graphene is 6-fold higher than the conventional fluorinations. We find that the fluorine atoms are predominately localized within the nanometer regime around the defect-ed sites, which is further confirmed by the STM observation (Figure 5.2). The F-C bond remains stable up to temperatures of about 250°C. This novel technique is mainly based on the site-selective radicalization of graphene surface that reacts with injected molecules. Therefore, it has the potential to be used as a general graphene functionalization route to realize different functionalizations by using a wide range of the gases.

5.2.2 Reversible fluorination of graphene induced by electron beam irradiation: towards the band gap manipulation (Paper IV)

Owing to the strong electronegativity, fluorine can induced a significantly band gap opening in graphene electronic structures\textsuperscript{61}, thus graphene fluorination has attracted significant interest in the scientific community. As reported in litterature\textsuperscript{60}, the saturated degree of one side graphene fluorination is the coverage of 25\% (C\textsubscript{4}F) under XeF\textsubscript{2} gas exposure and fully fluorination (CF) can be only achieved in graphene membrane after long time fluorine gas exposure\textsuperscript{62}. However, the drawbacks by using the method of pure gas exposure hinder the real application of fluorographene in electronics. First of all, the processing time is quite and it usually takes hours or days to reach the fluorographene. Moreover, the fluorine concentration, especially the one side fluorination case, has the limit of 20\% (C\textsubscript{4}F). Finally, the process is not re-
versible, which means the band gap of the fluorinated graphene cannot be manipulated according to specific applications. Based on the work of the ion beam induced fluorination, we have developed a novel technique to realize a reversible electron beam induced fluorination of graphene, in which a precise fluorine concentration can be obtained by the electron beam induced fluorination and defluorination.

In this approach, high energy electrons are used to decompose the XeF$_2$ molecules to create a fluorine radical gas under high vacuum condition ($5 \times 10^{-6}$ mba). Simultaneously, graphene will be emerged in the fluorine radical gases and be fluorinated. Through the optimization of the electron energy, an electron beam of 5 kV acceleration voltage and 650 pA is chosen as the experiment setup. Figure 5.3(a) shows the fluorination as a function of processing time. By using this method, one-side fluorination of graphene can easily overcome the concentration limit of 20% in the one side gas exposure and achieve the fully one-side fluorination with the F concentration over 33% (C$_2$F). Because the ionization cross section of the fluorine-carbon bonds are at a maximum energy of 80 eV$^{110}$, it provides another graphene defluorination thought by using 5 kV electron beam irradiation as shown in Figure 5.3 (b).

![Figure 5.3 (a) Electron induced fluorination concentration as a function of time. (b) Electron induced defluorination as a function of time.](image-url)
Figure 5.4 Valence band spectra of fluorographene, where the Fermi level locates at the binding energy of 0 eV. From top to bottom, the F concentrations are 0, 22%, 28% and 35%, respectively.

Theoretical calculations have predicted possibility of bandgap engineering in fluorographene by tuning the fluorination degree\textsuperscript{62,111}, however, to the best of our knowledge, there is still no experimental approach to demonstrate the real band gap opening in fluorographene and also the modification of the band gap. XPS valence band spectra can be seen as the projected density of states, which can reflect the electronic structure of the measured materials. By using this technique, Figure 5.4 displays the measured XPS valence band spectra of fluorographene with various fluorine concentrations. In pristine graphene, two features are observed: (1) the valence band maximum (VBM) of ~0 eV (the Fermi level) and (2) a strong $\pi$ states signal, which corresponds well with the electronic structure of graphene shown in chapter 2. Here, the VBM is defined as the energy where the linear least square fitted straight line intersects the baseline of zero intensity. With the increase in the fluorine concentration, fluorographene exhibits an increased VBM, which indicates the band gap opening and widening effect. Moreover, the intensity of the $\pi$ state electrons decreases with increased F-concentration, implying that the free mobile $\pi$ states electrons are localized by the fluorine atoms by covalent bondings.
5.3 Photofunctionalization of Graphene: Hydrogenation and Hydroxypropylation

5.3.1 Photohydrogenation (*Paper V*)

Graphane, fully hydrogenated graphene, has been claimed to be a potential and promising candidate in the electronic applications. The synthetic method to fabricate graphane hitherto are mainly high temperature and reactions between pressurized pressure hydrogen gas with graphite oxide \(^{112}\) or graphene supported by the transition metals \(^{12,50}\), where the metal performs as catalysis. However, the hydrogenation of monolayer graphene at metal free and ambient conditions has not yet been reported.

![Figure 5.5](image)

*Figure 5.5 (A) XPS C 1s of pristine graphene and graphane. The inserted image shows the zoomed in peaks of C1s, in which the shift of the binding energy is clear. (B) The XPS C 1s peaks of pristine graphene and graphane after deconvolution. (C) Raman spectra of pristine graphene and graphane.*

The photohydrogenation of graphene is conducted by immersing the chemical vapor deposited graphene in aqueous HCOOH/H\(_2\)O under the white LED illumination for at least 24 hours. The characterization of the graphane is shown in the Figure above. The significant D band and the transformation from the Sp\(^2\) in pristine graphene to Sp\(^3\) after reaction show that graphene has been reacted and transferred to graphane.
5.3.2 Photohydroxypropylation *(Paper VI)*

In this photohydroxypropylation project, we reported a novel and facile metal-free photochemical method that leads to covalent functionalization of graphene by usage of isopropanol. Chemical vapor deposited (CVD) graphene on SiO₂ substrate immersed in isopropanol was irradiated by white light-emitting diode (LED) at ambient conditions, and finally a high degree of functionalization, hydroxyl and ether groups, was achieved.

![Diagram](image)

*Figure 5.6 Different ways that isopropanol can covalently bond to graphene from A) the top B) the side.*

Figure 5.6 shows the schematic of the reaction between the graphene and isopropanol. The result from the XPS, Raman and AFM adhesion force measurements (Figure 5.7) reveal that a considerable modification in both characteristics and properties of the hydroxypropylated graphene in contrast to pristine graphene. From the comparison of the XPS spectra, a significant increase in the sp³ carbon and the C-O signals were observed in the reacted graphene, which confirms the covalent functionalization. Raman scattering reveals the presence of an intense D peak and an obvious reduction of the 2D peak, which indicates the breaking of the in-plane Sp² carbon-carbon bonds and corresponds well with the result from XPS. Furthermore, in the AFM adhesion force measurements at setpoint force of 600 nN, pristine graphene an adhesion of 40 nN while a much stronger adhesion of 180 nN is observed for the hydroxypropylated graphene. This enhanced adhesion force can be explained by the hydrogen bonding between the hydroxyl and ether groups on the hydroxypropylated graphene and the oxidized silicon of the AFM tip. Due to high reactivity of the functional groups, this new hydroxyisopropyl/isopropyloxy graphene could be used as platform materials for creating many different novel graphene derivatives.
Figure 5.7 XPS C 1s peak obtained before (A) and after (B) the reaction with isopropanol. Raman spectra obtained before (C) and after (D) the reaction with isopropanol. Force volume curves of pristine graphene sample (E) and photohydroxypropylated graphene (F), where both curves were recorded at the setpoint force of 600 nN.
5.4 Nanometer Size Dependent Mechanical Properties of Graphene (Paper VII)

![Graph of effective grain sizes vs. ion dosages](image1)

*Figure 5.8 Plot of the effective grain sizes as a function of ion dosages.*

![Graphs of Young's moduli and surface energies vs. grain sizes](image2)

*Figure 5.9 (a) the Young's moduli and (b) surface energies of graphene as a function of effective grain sizes.*

Owing to the outstanding mechanical properties, graphene has become an encouraging candidate for the fabrication of super strong and lightweight nanomechanical devices. However, sometimes the mechanical properties of graphene need to be modified in order to incorporate into the devices according to different applications. For example, graphene shows ultrastrong adhesion properties, which will be greatly desirable for devices that need highly stability, but most cases in micromechanical devices, comparably low adhesion is needed, which requires graphene to modify the adhesion.

Size effect on the physical properties of nano-object has been observed since decades. Theoretical physicist have predicted changes of Young’s modulus when graphene becomes nanometer sized from DFT calculations, which in turn is proposed as a way to tune the mechanical properties of graphene by varying the grain sizes. However, the experimental prove of the nanometer size effect of the mechanical properties of graphene has not been
reported since the transition grain size is normally within the range of few nanometers, which is still challenging to all of the nanofabrication techniques to achieve. In our work, by utilizing ion beam irradiation, various effective grain sizes of graphene are approached, which built the basis for us to use PF-QNM technique in the AFM to investigate the mechanical properties, such as Young’s modulus and surface energies (adhesion properties) of graphene.

In Raman scattering of graphene, the intensity ratio of D band and G band can be transformed into the effective grain sizes of graphene. By tuning the applied ion dosage of the focused ion beam irradiation, different grain sizes can be achieved, shown in the Figure 5.8. Since in pristine graphene, the D band intensity is negligible, thus the grain size of graphene can be equally treated as infinite. We then obtain that the polycrystalline graphene has the grain sizes ranging from 4 nm to infinite. As introduced in the chapter 3, PF-QNM technique gives us an efficient tool to investigate the Young’s modulus and surface adhesion properties.

Fig. 5.9 exhibits the plot of Young’s modulus and surface energies as a function of effective grain sizes. It clearly shows that when the grain size of the graphene is smaller than 7 nm, both the Young’s modulus and surface energies drop considerably, indicating that the transition to size effect in mechanical properties in graphene happened at the effective grain size of 7 nm.

5.5 Conclusion
In this chapter, different physical and chemical methods were utilized to approach graphene functionalizations, and the characterization results indicate that functionalized graphene samples displayed XPS and Raman spectra showing the presence of the functionalizing groups. More essentially, the XPS valence band spectra show that the energy band gap of graphene is open after functionalization by optimizing the beam chemistry approach. The modification of the structure of graphene is another route to change the properties of graphene, and our study shows that, by tuning the grain size, the Young’s modulus and surface energy of graphene can be modified, and a transition grain size of 7 nm was observed.
6. Graphene Nanoscrolls (Paper VIII)

6.1 Introduction

Carbon nanoscrolls, consisting of a continuous carbon sheet with an open-ended and spirally rolled-up geometry, are firstly reported by Viculis through sonication of graphite under an intercalation of alkali metals. This chemical route allows a scrolling of graphite into carbon nanoscrolls and the production yield is supposed to be ~80%. Even though the Raman scattering indicates that the scrolled carbon nanosheet is not monolayer of graphene, but this approach opened a door towards the fabrication of a totally new carbon allotrope. After that, several synthesis methods of the carbon nanoscrolls were published mainly based on graphite and sonication. However, the quality of the carbon nanoscrolls is not easily controlled and, more importantly, no superior properties were observed in this new material, which is probably one reason why makes carbon nanoscrolls where ignored by the academic community in a long period.

In 2009, a milestone discovery in carbon nanoscrolls was reported by Xie and, by using mechanically exfoliated graphene and isopropanol, graphene nanoscroll (GNS) is successfully synthesized. Interestingly, Raman scattering of the graphene nanoscroll shows a strong and non-splited 2D peak, indicating that the Bernal stacking does not exist in the new material. Similar to graphene, the lack of interlayer interactions in the GNS will result in the low coordinate number of the carbon atoms, which means that the GNS will maintain the outstanding properties of graphene in contrast to graphite. However, this reported approach is based on mechanical exfoliated graphene and it is too small to carry out synthetic research on the materials, which hinders the progress of the GNS in both fundamental research and applications.

In this chapter, we describe a synthetic process that can be used to produce high quantity and quality GNS with the yield over 95%. Importantly, the adhesion measurements using atomic force microscopy reveal that the synthesized GNS has a 2.5-fold stronger adhesion than pristine graphene. This adhesion is even higher than the liquid-solid and hydrogen-bonding enhanced interfaces involved in typical micromechanical systems and thus this method has the potential to produce macroscopic quantities of the GNS with superadhesion property, opening the way for novel material design.
6.2 A New Allotrope of Carbon with Superadhesion

The synthesis of large quantities of GNS is achieved through applying mild synthesis conditions to chemical vapor deposited (CVD) graphene. A CVD-grown graphene sample on SiO₂ (0.5 cm × 0.5 cm) was placed in a glass vial containing a freshly prepared 1/1 (v/v) HCOOH/H₂O mixture, in a way that the graphene sample was fully immersed in the aqueous HCOOH mixture. The vial was sealed with a rubber septum and degassed with Ar gas, then placed in an oil bath with a regulated temperature of 45°C for 24 h. After this period, the graphene sample was repeatedly washed with water (to remove HCOOH) and finally dried using a light stream of Ar gas.

Figure 6.1 Light optical image (a) and atomic force image (b) of the graphene nanoscroll.

Figure 6.1 shows the LOM and AFM images of the GNS. It can be seen that the synthesis process results in more than 100 μm long GNS and the typical height of the AFM is ~120 nm. When counting the proportion of the scrolled area over the whole area through the optical microscopy image, a yield of over 95% is obtained. Through the comparing of the Raman spectra of monolayer graphene and the GNS, it is found that the GNS has clearly maintained the graphene signature with the sharp 2D band and the intensity ratio of 2D band and G band more than three. The sharp 2D band in GNS together with the absence of 2D band splitting reveals that the graphene layers in the GNS lack π-stacking between each other, and overall, they show a Raman spectroscopy signature that is very similar to monolayer graphene. Thus, the GNS in this work are significantly different from conventionally fabricated carbon nanoscrolls (CNS). The reason of the 2D band non-splitting phenomenon is mainly due to the deviation in the orientation from Bernal stacking, which has been observed during the deformation of multilayer graphene. The increased c-plane spacing as measured from high resolution TEM is increased as compared to graphite and this could contribute to the observation of the graphene signature in the Raman spectra. The D band at 1350 cm⁻¹, normally indicating the presence of defects, is nearly
negligible in pristine graphene and has a slight increase in GNS. The G band, generated from the activation of the E$_{2g}$ mode at the Γ points, shows a $\sim 10$ cm$^{-1}$ left-shift in GNS compared to pristine graphene (inserted graph in Figure 2a), indicating a $\sim 0.7\%$ in-plane strain in the GNS layers. X-ray photoelectron spectroscopy (XPS) was performed to investigate the chemical modification of the pristine graphene immerged in HCOOH/H$_2$O. The result clearly indicates that, before and after scrolling up, all peak areas, corresponding to different bonds, of pristine graphene and GNS remain nearly the same, indicating that the synthesis mechanism is mainly a physical intercalation process instead of a chemical reaction.

![Figure 6.2 Raman and XPS characterization of the GNS. (a) Raman spectra comparison of monolayer graphene and GNS. (Inserted plot shows the left-shift of G band after scrolling up). (b) XPS of the C 1s peaks shows no chemical reaction observed during the fabrication, meaning that physical intercalation and rolling up should be the main synthesis mechanism.](image)

More importantly, the adhesion energy measurement of the GNS, shown in the Figure 6.3 by using atomic force microscope technique reveals that the GNS has a 2.5-fold increase in adhesion compared with monolayer graphene. This adhesion is so high that it is even higher than the liquid/solid and hydrogen bonding enhanced interfacial adhesion energies, thus it is named as “superadhesion”.

The mechanism of this superadhesion is mainly attributed by to the stored strain energy in the GNS layers. Due to the intrinsic property of the GNS that inner layer are not π-π stacking with each other, which is totally different with to graphite and the multiwall carbon nanotubes, the stored strain energy in each layer can be accumulated, finally results in the strong a dramatically increased adhesion energy when the GNS is contacting with other object physically.
6.3 Conclusion

This chapter mainly concentrates on a new carbon material, the graphene nanoscrolls. By using a simple physically scrolling method, large quantity GNS were synthesized with the yield more than 95%. The Raman study showed that inner layer of the GNS lacks Bernal stacking, which leads to sharp and non-spilited 2D band, implying the lack of Bernal stacking. The feature of the GNS allows the straining stored inside graphene lattice to be accumulated when the GNS is contacted with other object physically, resulting in a superadhesion property. This superadhesion is more than 6-order higher than the van der Waals interaction and even higher than the liquid/solid and hydrogen bonding enhanced interfaces.
Conclusions and Outlook

The work presented in this PhD thesis shows the routes to modify the structure and properties of graphene by physical and chemical ways and the main results can be summarized as:

Graphene functionalizations
Functionalization is normally seen as an efficient enabler for the band gap opening in graphene electronics. In this thesis, beam chemistry based graphene fluorinations are developed by using ion/electron beam interacting with XeF$_2$ precursor gas in the vicinity of the graphene surface. During the ion irradiation with simultaneous XeF$_2$ injection, the graphene surface is radicalized and reacted with the fluorine molecules, leading to a site-selective fluorination. By using this method, the fluorine atoms are localized only at the defected sites, which imply the possibility of atomic localization of fluorine atoms. The electron beam induced fluorination is realized by the electron irradiation of the XeF$_2$ molecules to create fluorine radicals. The characterization of the fluorinated graphene shows that the atomic F to C ratio can reach more than 0.5, which implies that it has overcome the limit ratio of 0.25 in the one-side fluorination. More importantly, the XPS valence band spectra confirm the opening of the band gap and the transformation of graphene from a semi-metal to an isolator. The chemical routes of the graphene functionalizations are realized by means of photochemical ways. In these approaches, formic acid is used as the reagent for graphene hydrogenation and isopropanol is chosen as the reagent for graphene hydroxypropylation.

Size-dependent nanomechanical properties of graphene
By changing the effective grain size, it is found that graphene will show the size-dependent behavior in the nanomechanical properties, e.g., Young’s modulus and surface energy. When the grain size of graphene is smaller than 7 nm, graphene will show significant drops in the Young’s modulus and surface energy. This result provides a way to tune the mechanical properties of graphene and also important fundamental knowledge of graphene in real applications.
**Graphene nanoscroll**

The graphene nanoscroll (GNS) is a new member in the carbon family and only little research in both fundamental and applied studies, as compared to other carbon materials is published. In this thesis, we presented a way to synthesize high quality and quantity GNS by using CVD graphene. More importantly, the adhesion measurement by using AFM technique indicates that the synthesized GNS shows superadhesion property. This superadhesion is even higher than the hydrogen bonding and solid/liquid enhanced interfaces, which are normally considered as the strongest adhesions in physisorption. Therefore, the GNS has the potential to be used as superglue in the electronic devices and the GNS synthetic technique can also allow for making new molecular intercalated materials.

**Outlook**

The modifications in the electronic structure of graphene by covalent functionalization methods will make graphene a great candidate in the application of flexible and transparent electronics. But when the band gap becomes larger, a significant carrier mobility loss will be obtained, thus the next crucial step is to balance these factors to meet the requirements of different applications. Moreover, the band gap of the functionalized graphene is directly determined by the coverage of the covalent bonded groups, thus the precisely controlled of the functionalization level, e.g. in the photochemical routes, is still a technical problem that need to be solved.

In this thesis, a synthetic method with high yield to fabricate the GNS is reported and the synthesized GNS has shown interesting adhesion properties. But more properties of the GNS need to be investigated systematically in future. Fabrication of molecular intercalated GNS or related materials has be done. Such material can be interesting for using as drug carrier and delivery, and gas storage.
Arbeten som presenteras i denna avhandling handlar om olika fysikaliska och kemiska metoder för modifiering av struktur och egenskaper hos grafen. De viktigaste resultaten kan sammanfattas som följande:

**Grafen funktionalisering**


**Storleksberoende nanomechaniska egenskaper av grafen**

Genom att ändra kornstorlek av grafen har det visat sig att de nanomekaniska egenskaperna, så som elasticitetsmodul och ytenergi, är storleksberoende. När kornstorleken av grafen är mindre än 7 nm kommer dess elasticitetsmodul och ytenergi att minska betydligt. Resultat från de här undersökningarna är viktig, eftersom de bidrar till förståelse av grafens grundläggande mekaniska egenskaper och de visar att man kan finjustera dessa egenskaper för praktiska tillämpningar.
Grafen nanoscroll


Framtidsutsikt


GNS som rapporteras i denna avhandling visar intressanta vidhäftningsegenskaper, men ännu flera egenskaper hos GNS måste undersökas systematiskt i framtiden. Tillverkning av molekylinskjutna GNS och liknande material bör också göras. Sådana material kan vara intressanta för att vända som bärare för läkemedelsfrisättning och som material för gaslagring.
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58
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