ABSTRACT

Chemical Vapor Deposition Synthesis of Graphene-Based Materials and Chemical Modulation of Graphene Electronics

by

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Graphene, a two-dimensional sp²-bonded carbon material, has attracted enormous attention due to its excellent electrical, optical and mechanical properties. Recently developed chemical vapor deposition (CVD) methods could produce large-size and uniform polycrystalline graphene films, limited to gas carbon sources, metal catalyst substrates and degraded properties induced by grain boundaries. Meanwhile, pristine monolayer graphene exhibits a standard ambipolar behavior with a zero neutrality point in field-effect transistors (FETs), limiting its future electronic applications.

This thesis starts with the investigation of CVD synthesis of pristine and N-doped graphene with controlled thickness using solid carbon sources on metal catalyst substrates (chapter 1), and then discusses the direct growth of bilayer graphene on insulating substrates, including SiO₂, h-BN, Si₃N₄ and Al₂O₃, without needing further transfer-process (chapter 2). Chapter 3 discusses the synthesis of high-quality graphene single crystals and hexagonal onion-ring-like graphene domains, and also explores the basic growth mechanism of graphene on Cu substrates. To extend graphene’s potential applications, both vertical and planar graphene-carbon nanotube hybrids are fabricated using CVD method and their interesting properties are investigated (chapter 4). Chapter 5 discusses how to use chemical methods to modulate graphene’s electronic behaviors.
Acknowledgments

I give my deepest thanks to Prof. James M. Tour, who is a mentor in research and also a life model for me. He is my prime teacher in this country and I feel so lucky that I got the opportunity to start my graduate study in his lab four years ago. As one world-famous scientist, though Prof. Tour is very busy, he still spent a lot of time with his students. Every week, we could get an opportunity to have a face-to-face talk with Prof. Tour about our research progress. In the last four years, he went through all my 200 weekly reports, 25 co-author papers and 5 disclosures. Without his visionary guidance, insightful advices and genuine support, this thesis would not have been accomplished to its least content.

I also want to thank Dr. Dustin K. James, the lab manager of Tour lab. He is always the first reader of my papers. His suggestions on my writings and research are so valuable to me. I truly appreciate his precious time.

Special thanks to Prof. Pulickel M. Ajayan and Dr. Robert H. Hauge, who not only are generous to serve as my committee members but also for providing insightful suggestions and valuable instructions in our collaborated research projects.

Great thanks to my parents, Ruzhou Yan and Xiuyun Chen, who have always put enormous support and trust in me. I am deeply grateful to my wife Di Bian. Her love and care have always been the flourishing power behind.
I also would like to express my gratitude to the people who have been very influential in my research and life during the last four years. Among them are: Dr. Zhengzong Sun, Dr. Jun Yao, Dr. Jian Lin, Dr. Yu Zhu, Zhiwei Peng, Yuanyue Liu, Changsheng Xiang, Lulu Ma, Lei Li, Bo Chen, Carter Kittrell, Abdul-Rahman O. Raji, E Loïc Samuel, Xiewen Wen, Jiebo Li, Kewei Huang, Jiakui Wang and Heng Ji among many others. It has been a very fruitful four years for me because of your support, influence and friendship.
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<td>1D</td>
<td>One Dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two Dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three Dimensional</td>
</tr>
<tr>
<td>ABS</td>
<td>Poly(acrylonitrile-\textit{co}-butadiene-\textit{co}-styrene)</td>
</tr>
<tr>
<td>ADF-STEM</td>
<td>Annular Dark Field STEM</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
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<tr>
<td>AR-STEM</td>
<td>Atomic-Resolution STEM</td>
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<tr>
<td>BF-STEM</td>
<td>Bright-Field STEM</td>
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<td>CP-CVD</td>
<td>Controlled Pressure CVD</td>
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<td>CNTs</td>
<td>Carbon Nanotubes</td>
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<td>Chemical Vapor Deposition</td>
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<td>Density Functional Theory</td>
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<tr>
<td>DP</td>
<td>Dirac Point</td>
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<tr>
<td>EDLC</td>
<td>Electrochemical Double-Layer Capacitor</td>
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<tr>
<td>FETs</td>
<td>Field-Effect Transistors</td>
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<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transformed Infrared Spectroscopy</td>
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<tr>
<td>FWHM</td>
<td>Full Width at Half-Maximum</td>
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<tr>
<td>h-BN</td>
<td>Hexagonal Boron Nitride</td>
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<td>Abbreviation</td>
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<tr>
<td>HGoRs</td>
<td>Hexagonal Graphene Onion Rings</td>
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<tr>
<td>HIPS</td>
<td>High Impact Polystyrene</td>
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<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
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<tr>
<td>HR-TEM</td>
<td>High Resolution TEM</td>
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<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
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<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
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<td>MoS₂</td>
<td>Molybdenum Disulphide</td>
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<td>MWCNTs</td>
<td>Multi-Walled Carbon Nanotubes</td>
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<td>PDMS</td>
<td>Polydimethylsiloxane</td>
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<tr>
<td>PEG</td>
<td>Poly(ethylene glycol)</td>
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<td>PEI</td>
<td>Poly(ethylene imine)</td>
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<td>PMMA-derived Graphene</td>
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<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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<td>PPMS</td>
<td>Poly(2-phenylpropyl)methysiloxane</td>
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<td>Polystyrene</td>
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<tr>
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<td>Transmission Electron Microscope</td>
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Chapter 1

Growth of Graphene from Solid Carbon Sources

This chapter was entirely copied from reference 1.

1.1. Introduction

After being first obtained as a transferable one-atomic-thick material in 2004, graphene and its growth quickly caught the attention of physicists, chemists and material scientists\textsuperscript{2-5}. Much of the research has focused on obtaining large sheets of monolayered or bilayered graphene. This has been recently achieved by CVD method of CH\textsubscript{4} or C\textsubscript{2}H\textsubscript{2} gases on Cu or Ni substrates\textsuperscript{6-8}. However, CVD is limited to the use of gaseous raw materials, making it difficult to apply the technology to a wider variety of feedstock.

With its extraordinary electronic and mechanical properties, graphene is showing promise in a plethora of applications\textsuperscript{8-14}. Graphene can now be obtained by several
different approaches. The original mechanical peeling method from highly oriented pyrolytic graphite (HOPG) yields small amounts of high quality graphene\textsuperscript{2}. Liquid exfoliation and reduction of graphene oxide have been used to produce chemically converted graphene in large quantities\textsuperscript{15, 16}. Annealing SiC, growth from amorphous carbon and CVD methods have been used to synthesize large-size graphene on wafers\textsuperscript{6-8, 17, 18}. By introducing Ni and Cu as the substrates for CVD growth, the size, thickness and quality of the produced graphene is approaching industrially useful specifications\textsuperscript{6-8}. However, intrinsic graphene is a zero band gap material which shows a weak ambipolar behavior. These graphene based transistors show small ON/OFF ratios, therefore they are too metallic for many designed electronics applications\textsuperscript{19}. In order to modify the Fermi level of graphene and manipulate its electronic and optical properties, doping the graphene matrix with heteroatoms is a straightforward way to make an n-type, p-type or hybrid doped graphene\textsuperscript{20-23}.

1.2. Pristine Graphene Derived from Solid Carbon Sources

In the present work, the growth of monolayered pristine graphene from solid carbon sources atop metal catalysts is demonstrated as shown in Figure 1.1a. The first solid carbon source used was a spin-coated PMMA thin film (~100 nm) and the metal catalyst substrate was a Cu film. At a range as low as 800 °C or as high as 1000 °C (tested limit) for 10 min, with a reductive gas flow (H\textsubscript{2}/Ar) and under low pressure conditions, a single uniform layer of graphene was formed on the substrate. The graphene material thus produced was successfully transferred to different substrates for further characterization.
Figure 1.1 Synthetic protocol, spectroscopic analysis and electrical properties of PG. (a) Monolayered PG is derived from the solid PMMA films on Cu substrates at 800 °C or higher, up to 1000 °C. (b) Raman spectrum (514 nm excitation) of a monolayered PG obtained at 1000 °C. (c) Room temperature $I_{ds}$-$V_{G}$ curve on a PG-based back-gate FET device. The upper inset shows the $I_{ds}$-$V_{ds}$ characteristics as a function of $V_{G}$. $V_{G}$ changes from 0 V (bottom) to -40 V (top). The lower inset in (c) is the SEM (JEOL-6500 microscope) image of this device where the PG is perpendicular to the Pt leads. (d)
SAED pattern of PG. (e, f and g) HRTEM images of PG films. Black arrows in (g) indicate the Cu atoms.

The Raman spectrum of this monolayered PMMA-derived graphene (PG) is shown in Figure 1.1b and the spectrum is characteristic of >10 locations recorded over 1 cm$^2$ of the sample. The two most pronounced peaks in this spectrum are the G peak at 1580 cm$^{-1}$ and the 2D peak at 2690 cm$^{-1}$. The $I_{2D}/I_G$ intensity ratio is about 4 and the full width at half maximum (FWHM) of the 2D peak is about 30 cm$^{-1}$, indicating that the graphene is monolayered. The D peak ($\sim$ 1350 cm$^{-1}$) is in the noise level for PG, indicating the presence of few sp$^3$ carbon atoms or defects$^{24}$.

**Figure 1.2** Additional FETs after prolonged evacuation. Two representative pristine graphene FETs atop 200 nm SiO$_2$ with highly doped p$^{++}$ Si back gate measured after storage at 10$^{-6}$ Torr for 7 days. Under vacuum, the Dirac point recovers from positive gate voltages and stabilizes at zero as surface adsorbents are removed. Mobilities of $\sim$400 cm$^2$ V$^{-1}$s$^{-1}$ at room temperature were achieved.
The electrical properties of the PG were evaluated with back-gated graphene-based field-effect transistor (FET) devices atop a 200 nm thick SiO₂ dielectric. Typical data for the FET devices is shown in Figure 1.1c. For this particular device, the estimated carrier (hole) mobility is ~410 cm²V⁻¹s⁻¹ at room temperature and the ON/OFF ratio is ~2, which is expected in graphene-based FET devices of this size. Although the graphene was pristine without any doping atoms, it still shows a weak p-type behavior with the Dirac point (DP) moved to positive gate voltage, probably arising from the physisorption of small molecules such as H₂O. Placing these graphene FETs under high vacuum (10⁻⁵ Torr) for several days moves the DP to zero (Figure 1.2), confirming that the weak p-type behavior was due to physisorption of volatile molecules.

**Figure 1.3** AFM characterization of PG. AFM image (left) and the height profile (right) of a monolayer PG on a SiO₂/Si substrate. Step 1 (red) is the SiO₂/Si substrate; step 2
(green) is the graphene edge. Step height is ~ 0.7 nm, suggesting the thickness of PG. Scale bar in AFM is 1 μm.

Transmission electron microscopy (TEM) images of the pristine PG and its diffraction pattern are shown in Figure 1.1d-g. The selected area electron diffraction (SAED) pattern in Figure 1.1d displays the typical hexagonal crystalline structure of graphene. The layer count on the edges of the images indicates the thickness of the PG. The PG edges in Figure 1.1e-g were randomly imaged under TEM and most were monolayered or bilayered PG, which corroborates with the Raman data. Although most of the PG surface was continuous and crystalline according to its diffraction pattern, there is adsorbed PMMA resulting from the transfer step. Metal atoms or ions were also found to be trapped on the PG surface (see black arrows in Figure 1.1g) and became charge impurities, which should increase the charge density but decrease the mobility of the PG. Similar phenomena have been observed with CVD-generated graphene. AFM was used to characterize the surface profile of PG on a SiO₂/Si substrate. In Figure 1.3, the thickness of the PG is about 0.7 nm, which confirms the monolayer nature of this material. However, limited by the wet-transfer technique, graphene’s intrinsic corrugation is still obvious in the AFM image.

Graphene’s electronic properties are strongly associated with its thickness. Therefore, it would be useful to be able to control the thickness when producing the graphene by tuning the growth parameters. We have found that PG’s thickness can be controlled from monolayer, to bilayer to a few layers by changing the Ar and H₂ gas flow.
rate. Typical thicknesses were evaluated by Raman spectroscopy (Figure 1.4a) and UV transmittance (Figure 1.4b) of the graphene. At 1000 °C, a bilayered PG was obtained when the Ar flow rate was 500 sccm and the H₂ flow rate was 10 sccm. When the Ar flow rate was 500 sccm and the H₂ flow rate was 3-5 sccm, few-layered PG formed. When the H₂ flow rate increased to 50 sccm or higher, only monolayered graphene was formed on the Cu substrate. Monolayered graphene showed a transmittance of 97.1% (Figure 1.4b). It had a sheet resistance (Rₛ) of 1200 Ω/sq by the 4-probe method, which makes it a transparent electrode material of interest. The bilayered graphene’s transmittance is 94.3%, which shows linear enhancement in the UV absorption. The few-layered PG sheet in Figure 1.4a has a transmittance of 83% at 550 nm, which can be estimated as a 6-layered PG. Both the shape and the positions of the 2D peak are significantly different from monolayered graphene to bilayered graphene and few-layered graphene (Figure 1.5). For monolayered graphene, the 2D peak can be fitted with single sharp Lorentz peak. The observed 2D splitting in bilayered and few-layered graphene can be assigned to the electronic band splitting caused by the interaction of the PG planes²⁴. The Raman mapping of the G to 2D peak ratio illustrates the uniformity of the graphene films over 70-75 μm² areas investigated (Figure 1.6). For monolayered graphene, more than 95% of the film has this signature with I₆/I₂D< 0.4. The bilayered graphene has more than 85% coverage, with an I₆/I₂D ~ 0.8. H₂ acts as both the reducing reagent and the carrier gas to remove C atoms that are extruded from the decomposing PMMA during growth. A slower H₂ flow leaves more C sources for the growth of multilayered graphene. Due to the low concentration and solubility of the carbon source in Cu, traditional CVD-grown graphene on Cu usually terminates as a monolayer. In this experiment, highly
concentrated and uniformly dispersed carbon sources favor multilayered graphene when the H₂ flow is low. The higher order layers might form through graphitization directly atop the first layer, which blocks the contact of the carbon sources with the metal catalyst. Some metal catalysts, such as Ni, are known to reverse graphene growth by converting graphene to hydrocarbon products, therefore cutting graphene along specific directions. This reverse reaction does not appear to occur on the PG which is atop the Cu.

Figure 1.4 Controllable growth for pristine graphene films. (a) Difference in Raman spectra from PG samples with controllable thicknesses derived from different flow rates of H₂. (b) The ultraviolet-visible (UV) absorption spectra of monolayered graphene and bilayered graphene. The UV transmittance (T %) of the corresponding PG is measured at
550 nm. (c) Raman spectra of graphene derived from sucrose, fluorene and PMMA. (d) HRTEM picture of PG grown on a Ni film. The PG was 3-5 layers at the edges.

**Figure 1.5** Fitted Raman spectra. Raman 2D peak fittings of different layered PGs; monolayered PG’s 2D band was fitted with a single Lorentz peak. Bilayered and few-layered graphene 2D bands were split into 4 components: 2D1B, 2D1A, 2D2A, 2D2B (green peaks, from left to right) \(^{24}\). Solid lines are the original data. Square points are the fitting curves.
Figure 1.6 Raman spectral mapping. Two-dimensional Raman (514 nm) mapping of (a) monolayered graphene film (70 × 75 μm²) and (b) bilayered graphene film (75 × 75 μm²). The color gradient bar to the right of each map represents the G/2D peak ratio. The green and black areas in (a) are monolayer graphene with an I_G/I_{2D} < 0.4, suggesting at least 95% monolayer coverage. The blue area in (b) represents bilayered graphene with an I_G/I_{2D} ~0.8. More than 85% in (b) is bilayered PG. The lateral scale bars are 20 μm.

High quality monolayered PG was obtained at 800 °C by this method, lower than the original report for CVD growth temperature on Cu⁷ (Figure 1.7). For the semiconductor industry, the lower processing temperature used is favorable because temperatures as high as 1000 °C would be problematic in the fabrication of the multilayered stacks of heterogeneous materials. Therefore, in addition to changing the Ar/H₂ flow rate, the graphene growth process was conducted using different temperatures. The quality of the graphene films was monitored by the D/G peak ratio from Raman spectroscopic analysis. The D/G ratio for graphene sheets obtained at 800 °C is less than 0.1. At 750 °C, the D/G peak ratio was ~0.35; hence 800 °C is the lower limit for high
quality graphene from PMMA. We used other solid carbon sources including fluorene (C_{13}H_{10}) and sucrose (C_{12}H_{22}O_{11}) to grow monolayered graphene on Cu catalyst under the same growth conditions as was used for the PG. Because these precursors are powders not films, 10 mg of each as a finely grinded powder was placed directly on a 1 cm$^2$ Cu foil. After subjecting the powder-coated Cu films to the same reaction conditions as used for PG, Raman spectra indicated that all of the solid carbon sources have been transformed into monolayered graphene with no D peak observed (Figure 1.4c). Although these solid carbon precursors contain potential topological defect generators (the five-member ring in fluorene) or high concentration of heteroatoms (oxygen), they produce high quality pristine graphene. It is possible that at elevated temperatures under vacuum, C has a higher affinity for the metal catalyst surface than the heteroatoms; atom rearrangement occurs and most of the topological defects are self-healed as the graphene is formed.

Other substrates such as Ni, Si<100> with native oxide and 200-nm thick SiO$_2$ thermally grown were also tested to determine if they would grow graphene when coated with PMMA. Figure 1.4d is the HR-TEM image of PG grown on a Ni catalyst, which clearly illustrates the few-layered structure around the edges of PG. The Raman spectra in Figure 1.8 confirm that Ni is an efficient catalytic substrate to convert PMMA into highly crystalline graphene materials with no D peak around 1350 cm$^{-1}$. Under the same growth conditions, neither graphene nor amorphous carbon were obtained on Si or SiO$_2$ substrates according to the Raman spectroscopic analysis of the surface after the reaction. This demonstrates the potential to grow patterned graphene from a thin film of shaped Ni
or Cu deposited directly on SiO₂/Si wafers without post lithographic treatment since PG will not grow on the Si or SiO₂ surfaces.

Figure 1.7 Raman spectra of PG at lower growth temperatures. Raman spectra of PG grown at 800 °C (top) and 750 °C (bottom). PG (800 °C) has a D/G ratio less than 0.1.
For PG grown at 750 °C, the D/G ratio is greater than 0.35. Therefore, 800 °C is the low temperature limit for high quality PG growth.

![Raman spectra of PMMA films](image)

**Figure 1.8** PG growth or attempted growth on other surfaces. Raman spectra of PMMA films that were heated on Ni, Si with native oxide or thermally grown SiO$_2$.

### 1.3. N-doped Graphene Made from Solid Carbon Sources

A doping reagent melamine (C$_3$N$_6$H$_6$) was mixed with PMMA and spin-coated onto the Cu surface. In order to keep the nitrogen-atom concentration in the systems, we use conditions similar to the PG growth except that the growth was done under atmospheric pressure. The prepared polymer films were successfully converted into N-doped graphene, with an N content of 2-3.5%. The XPS data (Figure 1.9a) shows the difference of the C1s peaks between PG and N-doped PG. The shoulder around 287 eV
can be assigned to the C-N bonding. The N1s peak of N-doped PG indicates that only one type of N is present, at 399.8 eV, corresponding to graphitic N in graphene. The N1s signal does not come from the melamine but that the N atoms are uniformly bound into the graphene structure. The D peak of this material is always present in the Raman spectra because the heteroatoms break the graphene symmetry and thereby introduce defects that are detected by Raman analysis (Figure 1.9c). The D’ peak is also found in doped graphene materials obtained by the other doping methods\textsuperscript{22, 28}. The 2D peak position and $I_{2D}/I_G$ intensity ratio reveals that this N-doped PG is monolayered graphene. Compared to PG, the $I_{2D}/I_G$ decreased from 4 to 2, implying a successful doping according to the electrostatically gated Raman results\textsuperscript{30}.

Doping effects were also demonstrated by N-doped PG-based FETs. The n-type behavior shown in Figure 1.9d, with the DP shifted to negative gate voltage, is consistently observed for devices on the same piece of N-doped PG. After keeping the N-doped PG-based FET devices under vacuum ($10^{-6}$ Torr) for 24 h, their DP did not move to zero, indicative of the covalent bonding between carbon and nitrogen rather than just physisorption; the dopant N atoms donate free electrons to graphene. Meanwhile, the N-doped graphene’s mobility calculated from the N-doped FETs was about 1 order of magnitude lower than in PG\textsuperscript{21}. Due to the broken symmetry of the N-doped graphene’s lattice structure, the N atoms act as scattering centers that suppress its mobility\textsuperscript{26}. Patterned hydrogenation on graphene already shows its band gap opening\textsuperscript{31}. Similarly, if the doping atoms are periodically dispersed in graphene’s matrix, they can not only tune the Fermi level of graphene, but tailor its band gap. However, in the present N-doped graphene, the ON/OFF ratio does not increase, which suggests that the N atoms are
randomly incorporated into the graphene matrix. In order to manipulate both the Fermi level and the band gap of graphene, patterned doping has to be achieved\textsuperscript{31}.

**Figure 1.9** Spectroscopic analysis and electrical properties of PG and N-doped PG. (a) XPS analysis from the C1s peak of PG (black) and N-doped PG (red); the shoulder can be assigned to the C-N bond. (b) XPS analysis of the N1s peak (black line) and its peak fitting (square points) of N-doped PG. The atomic concentration of N for this sample is about 2\% (C is 98\%). No N1s peak was observed for PG. (c) Raman spectra for PG and
N-doped PG. (d) Room temperature, $I_{ds}$-$V_G$ curves with n-type behavior obtained from three different N-doped graphene-based back-gate FET devices.

### 1.4. References


### 1.5. Experimental Contributions

Zhengzong Sun designed the experiments, discovered the procedures for graphene growth from solid carbon sources, and performed the spectroscopic characterizations and analyses. Zheng Yan optimized the growth conditions of PMMA-derived graphene, like
finding that high-quality monolayer graphene could grow on Cu foils under the reduced chamber pressure. Zheng Yan proposed to use other solid carbon sources, including sucrose, fluorene and melamine, for graphene growth and performed the related-growth experiments. Zheng Yan also contributed to Raman characterizations of as-made graphene samples. Jun Yao and Elvira Beitler performed the electrical measurements and analyses. Yu Zhu carried out the sheet resistances and transmittance measurements.
Chapter 2

Synthesis of Bilayer Graphene on Insulating Substrates

This chapter was entirely copied from references 1 and 2.

2.1. Introduction

Since its first isolation in 2004, graphene has garnered enormous interest because of its promising electronic applications\(^3\)-\(^6\). Unlike monolayer graphene, AB-stacked (Bernal) bilayer graphene has a tunable bandgap and twisted bilayer graphene has angle-dependent electronic properties, thereby being more attractive for many electronic and optical device embodiments\(^7\)-\(^8\). For such applications, uniform-thickness and large-size bilayer graphene films on insulating substrates are desirable. However, the present growth methods either need an additional lift-off step to transfer graphene from the metal catalyst surfaces to the insulating substrates, such as in CVD and solid carbon source
synthesis methods\textsuperscript{9-15}, or they have difficulty yielding uniform bilayer graphene films directly on insulating substrates, as in epitaxial growth methods from SiC\textsuperscript{16-21}. Pristine monolayer graphene is a semimetal and demonstrates zero bandgap electronic structure, limiting its electronic and optical applications. Progress has been made in opening the bandgap of graphene, including using special substrates or defining nanoscale graphene ribbons\textsuperscript{22-24}. Another method to modify the bandgap structure of graphene is to periodically replace the carbon atoms in the graphene matrix with heteroatoms such as nitrogen and boron\textsuperscript{12}. Recent discoveries demonstrate that a widely tunable bandgap can be realized in bilayer graphene\textsuperscript{7} and bilayer graphene-BN heterostructures\textsuperscript{25}, which opens a new door for applications of graphene in electronic and optical devices.

\textbf{2.2. Direct Growth of Bilayer Graphene on SiO\textsubscript{2}, h-BN, Si\textsubscript{3}N\textsubscript{4} and Al\textsubscript{2}O\textsubscript{3}\textsuperscript{1}}

In this section, we demonstrate a general transfer-free method to directly grow large areas of uniform bilayer graphene on insulating substrates (SiO\textsubscript{2}, h-BN, Si\textsubscript{3}N\textsubscript{4} and Al\textsubscript{2}O\textsubscript{3}) from solid carbon sources such as films of poly(2-phenylpropyl)methylosiloxane (PPMS), poly(methyl methacrylate) (PMMA), polystyrene (PS), and poly(acrylonitrile-\textit{co}-butadiene-\textit{co}-styrene) (ABS), the latter leading to N-doped bilayer graphene due to its inherent nitrogen content. Or, the carbon feeds can be prepared from a self-assembled monolayer (SAM) of butyltriethoxysilane atop a SiO\textsubscript{2} layer. The carbon feedstocks were deposited on the insulating substrates and then capped with a layer of nickel. At 1000 °C, under low pressure and a reducing atmosphere, the carbon source was transformed into a bilayer graphene film on the insulating substrates. The Ni layer was removed by
dissolution affording the bilayer graphene directly on the insulator with no traces of polymer left from a transfer step.

Figure 2.1. Synthetic protocol and spectroscopic analysis of bilayer graphene. (a) Bilayer graphene is derived from polymers or SAMs on SiO₂/Si substrates by annealing the sample in an H₂/Ar atmosphere at 1,000 °C for 15 min. (b) Raman spectrum (514 nm excitation) of bilayer graphene derived from PPMS. (c) Bilayered 2D peaks were split into four components: 2D₁₁, 2D₁₈, 2D₂₁, 2D₂₈ (yellow peaks, from left to right)²⁶⁻²⁷. (d-e)
Two-dimensional Raman (514 nm) mapping of the bilayer graphene film (112 × 112 μm²). The color gradient bar to the right of each map represents the D/G peak ratio (d) or G/2D peak ratio (e) showing ~90% bilayer coverage. The scale bars in d and e are 20 μm.

The scheme of direct growth of bilayer graphene on insulating substrates is shown in Figure 2.1a. Here, SiO₂ (500 nm)/Si⁺⁺ and PPMS were used as the insulating substrate and the carbon source, respectively. The SiO₂/Si⁺⁺ wafer was cleaned with oxygen-plasma and piranha solution (4:1 sulfuric acid: hydrogen peroxide). Then, a PPMS film (~ 4 nm thick) was deposited on the SiO₂ by spin-coating 200 μL of PPMS solution in toluene (0.1 wt %) at 8000 rpm for 2 min. A 500-nm Ni film was deposited on top of the PPMS film using a thermal evaporator (Edwards Auto 306); the Ni was used as the metal catalyst for graphene formation. At a temperature of 1,000 °C for 7 to 20 min, with a reductive gas flow (H₂ /Ar) and under low pressure conditions (~ 7 Torr), a 1-cm² homogeneous bilayer of graphene was synthesized between the insulating substrate and the Ni film. Marble’s reagent was used to dissolve the Ni layer. The end result was that bilayer graphene was directly synthesized on the insulating surface, eliminating the transfer process. Instead of using a polymer film, a SAM of butyltriethoxysilane was made on the SiO₂. Using the same Ni deposition and growth conditions, a bilayer of graphene was formed.

Raman spectroscopy and transmission electron microscopy (TEM) were used to characterize the as-grown graphene. As a simple tool, Raman spectroscopy was generally used to evaluate the quality and identify the number of layers of graphene made by both
CVD and solid carbon source methods\textsuperscript{12-15}. Here, Raman spectroscopy was first used to characterize graphene derived from PPMS on a SiO$_2$/Si\textsuperscript{++} substrate. Figure 2.1b shows the Raman spectrum of the PPMS-derived graphene, which is characteristic of 10 locations recorded over 0.5 cm$^2$ of the sample. The two most pronounced peaks in the spectrum are the G peak at ~1,580 cm$^{-1}$ and the 2D peak at ~2,700 cm$^{-1}$. The full-width-at-half maximum (FWHM) of 2D peak and the I$_G$/I$_{2D}$ peak intensity ratio for bilayer graphene are significantly different from monolayer graphene and few-layer graphene\textsuperscript{13-15, 26-27}. Figure 2.1b shows that the FWHM of the 2D peak is about 50 cm$^{-1}$ and the intensities of the G peak and 2D peak are comparable. Furthermore, the 2D peak in Figure 2.1b displays an asymmetric lineshape and can be well-fitted by four components: 2D$_{1B}$, 2D$_{1A}$, 2D$_{2A}$, 2D$_{2B}$ (Figure 2.1c, yellow peaks, from left to right), individually with FWHM of 30 to 35 cm$^{-1}$. This data indicates that the PPMS-derived graphene is indeed bilayered\textsuperscript{12-15, 26-27}.

The D peak (1,350 cm$^{-1}$) corresponds to defects in the graphene film. Figure 2.1b shows that the D peak is very low (I$_D$/I$_G$ < 0.1), indicating few defects in the PPMS-derived graphene. The quality of PPMS-derived graphene over the large area was demonstrated by Raman mappings of the D to G peak ratio (Figure 2.1d). Areas of 112 $\times$ 112 $\mu$m$^2$ were investigated. In the green and black regions (Figure 2.1d), the D/G peak ratio is below 0.1, suggesting that high-quality graphene covers ~ 95% of the surface.\textsuperscript{12} The quality of PPMS-derived graphene was further confirmed by the low sheet resistance of the graphene film, which is ~ 2,000 $\Omega$ sq$^{-1}$ by the four-probe method\textsuperscript{12}. The uniformity and the coverage of PPMS-derived bilayer graphene were first illustrated by the Raman mappings of the G to 2D peak ratio (Figure 2.1e). An area of 112 $\times$ 112 $\mu$m$^2$ was
investigated and the bilayer region was identified by areas $I_G/I_{2D}$ valued between 0.7 (ref. 10) and 1.3 (ref. 14). The blue region in Figure 2.1e is bilayer graphene, suggesting bilayer coverage of ~ 90%.

**Figure 2.2.** TEM analysis of PPMS-derived bilayer graphene. (a-b) Low-resolution TEM images showing bilayer graphene films suspended on a TEM grid. (c) Hexagonal SAED pattern of the bilayer graphene with a rotation in stacking of 5° between the two layers. (d) HR-TEM picture of PPMS-derived graphene edges. The PPMS-derived graphene was 2 layers thick at random exposed edges.
TEM was further used to confirm the bilayer nature of the obtained graphene samples. Although, the PPMS-derived graphene does not need to be transferred to another substrate in order to be used in most applications, the graphene film was peeled from the SiO₂/Si⁺⁺ substrates using buffered oxide etch (BOE) for TEM measurements. TEM images of the pristine PPMS-derived graphene and its diffraction pattern are shown in Figure 2.2. The suspended graphene films on the TEM grids are continuous over a large area as seen under low-resolution TEM (Figure 2.2a and 2.2b). The SAED pattern in Figure 2.2c displays the typical hexagonal crystalline structure of graphene. A 5° rotation is found between the two layers, suggesting non-AA or AB-stacked bilayer graphene films. The diffraction analysis over a large area shows ~ 90% bilayer coverage in the analyzed region with twisted angles having values between 0° and 30°, correlating with that of the I_G/I_2D Raman mapping and the statistics of the FWHM of Raman 2D peak. In the bilayer region, only a small portion (3-5%) appears to be Bernal stacked. The layer count on the edges indicates the thickness of this PMMA-derived graphene. The edge in Figure 2.2d is randomly imaged under TEM and most is bilayer graphene, which corroborates the Raman data and diffraction data, and provides direct evidence that the as-grown graphene is bilayered.

The electrical properties of the obtained graphene were evaluated with back-gated graphene-based field-effect transistor (FET) devices on a 500-nm-thick SiO₂ dielectric. The drain-source current was modulated by applying a back gate voltage. Standard electron-beam lithography and lift-off processes were used to define the source and drain electrodes (30-nm-thick Au) in the graphene devices. Graphene stripes (10 µm wide) were further defined by oxygen-plasma etching. Typical data for the FET devices are
shown in Figure 2.3a. The PPMS-derived graphene FET shows an ambipolar behavior, which is similar to that of CVD-grown graphene.\textsuperscript{8-13} For this particular device, the carrier (hole) mobility estimated from the slope of the conductivity variation with respect to the gate voltage is \( \sim 220 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) at the room temperature. In the experiments, more than five devices were made, with the mobilities of approximately 220, 180, 150, 130 and 120 cm\(^2\) V\(^{-1}\) s\(^{-1}\) at room temperature.

**Figure 2.3.** Electrical properties of PPMS-derived graphene and spectroscopic analysis of graphene from different carbon sources and substrates. (a) Room temperature \( I_{DS} - V_G \) curve from a PPMS-derived bilayer graphene-based back-gated FET device. \( I_{DS} \), drain-source current; \( V_G \), gate voltage; \( V_{DS} \), drain-source voltage. (b) Difference in Raman
spectra from PMMS-derived bilayer graphene samples prepared from different thicknesses of the starting PPMS film. (c) Raman spectra of graphene derived from PS, PMMA, ABS and the SAM made from butyltriethoxysilane. (d) Raman spectra of graphene derived from PPMS on h-BN, Si$_3$N$_4$ and Al$_2$O$_3$ (sapphire).

![Diagram](image)

**Figure 2.4** The scheme for the proposed growth mechanism of PPMS-derived bilayer graphene. The PPMS film decomposed and dissolved into the Ni film during the annealing process (1000 °C). When the sample was removed from the hot-zone of the furnace and cooled to room temperature, the part of that carbon that dissolved in the bulk metal precipitated from the both sides of the Ni to form graphene on both the top and the bottom of the Ni layer.

The top Ni surface was analyzed after the reaction and it indeed had its own graphene layer, and it often appeared by Raman analysis to be a bilayer, though the signal is more difficult to analyze when on metal. Hence, some carbon below the Ni had diffused through the 500-nm-thick Ni film and formed a top graphene bilayer (Figure 2.4). In one case, we treated the top bilayer graphene film with UV-ozone (directed at the top-
surface of the Ni), thereby destroying the top-bilayer graphene as verified by Raman analysis (Figure 2.5). After Ni dissolution, the bottom graphene bilayer was pristine. Hence, this excludes the possibility that the graphene on top of the Ni drops to the bottom surface after the Ni dissolution.

**Figure 2.5** Raman spectra analysis (514 nm) of PPMS-derived graphene. (a) After annealing Ni/PPMS/SiO$_2$/Si$^{++}$ at 1000 °C with H$_2$/Ar for 15 min, the top surface of Ni was characterized by Raman spectra (b) suggesting that graphene was also grown on the top surface of Ni. After placing the sample in UV-ozone for 15 min, the graphene on the top surface of Ni was badly damaged as observed by Raman analysis (c). Then the Ni was removed by etchant, and high-quality bilayer graphene was still obtained on SiO$_2$/Si$^{++}$ (d). Thus, the following conclusions can be made from the above experiments: (1) graphene was grown on both sides of the Ni-film due to the diffusion of C at the high temperature; (2) the graphene that formed on the SiO$_2$/Si$^{++}$ was from the bottom side of the Ni-film. All of the three Raman spectra are characteristic of 10 locations recorded over 0.5 cm$^2$ of the samples.
We propose a limited carbon source precipitation process for the growth mechanism of the polymer and SAM-derived bilayer graphene. In the CVD method, the thickness of graphene is difficult to control when using Ni as the substrate due to the continuous supply of carbon and the high solubility of carbon in Ni.\textsuperscript{9,11} In our present method, the amount of feed carbon is limited and fixed between the insulating substrate and the Ni film at the start of the experiment. The amount of carbon in the 4-nm-thick PPMS film corresponds to \( \leq 20\% \) of the saturated carbon concentration in a 500-nm-thick Ni-film at 1000 \( ^\circ \text{C} \).\textsuperscript{30} As illustrated in Figure 2.4, the 4-nm-thick PPMS film decomposed and dissolved into the Ni film during the annealing process. When the sample was removed from the hot-zone of the furnace and rapidly cooled, graphene films precipitated from the Ni. The sub-saturated carbon concentration in the Ni film facilitates the growth of bilayer graphene rather than few-layer graphene.\textsuperscript{31}

According to the above proposed mechanism, the amount of carbon in PPMS films will affect the graphene growth. Indeed, we controlled the thicknesses of PPMS films by adjusting the concentrations of PPMS-film-forming solutions; the thicknesses of PPMS films were determined by ellipsometry. A 200 µL sample with a concentration of 0.025, 0.1, 0.5 and 1 wt% of PPMS in toluene yielded thicknesses of approximately 1.5, 4, 10 and 20-nm-PPMS films, respectively, at spin-coat rates of 8,000 rpm. Figure 2.3b shows that 4-nm-thick PPMS film was the optimal thickness for the growth of high-quality bilayer graphene (the red curve in Figure 2.3b). When the thickness of PPMS film was 1.5 nm, the amount of carbon in the related PPMS-film is apparently not enough for the formation of graphene (Figure 2.3b). Too much carbon caused the growth of multilayer graphene with increased defects. Interestingly, the amount of carbon in \( \sim 4\)-
nm-thick film of PPMS is very similar to the amount of carbon in four layers of graphene where there is a bilayer below the Ni and an approximate bilayer above the Ni. When this amount of carbon is exceeded, multilayers and amorphous carbons are formed instead of precisely controlled growth tri- or four-layer graphene. When the amount of carbon is insufficient, discontinuous graphene films are formed (Figure 2.3b).

Figure 2.6 Raman spectral analysis of graphene synthesized using copper as the catalyst. (a) A 4-nm PPMS film was deposited on SiO$_2$/Si and the PPMS film was capped with a layer of copper (500 nm thick). Otherwise the experimental conditions were the same as those for using Ni as the catalyst. The spectrum shows that amorphous carbon was produced rather than graphene. (b) When the SAM-derived from butyltriethoxysilane was used as the carbon source, and the SAM was capped with copper and subjected to the same reaction conditions as in a, but few-layer graphene was obtained.

For the SAM, we used butyltriethoxysilane as the precursor to make a carbon layer on SiO$_2$. Figure 2.3c shows that the SAM was successfully transformed into bilayer graphene. The sheet resistance was similar to that of PPMS-derived graphene at $\sim$ 2,000 $\Omega$ sq$^{-1}$. Copper was also used as the catalyst for the direct growth of graphene on
insulating substrates. Figure 2.6 shows that copper transformed a 4-nm-thick PPMS film into amorphous carbon while the SAM was transformed into multilayer graphene with a large D peak. The growth of graphene on Cu is due to surface catalysis rather than precipitation of carbon from the bulk metal as occurs in Ni\textsuperscript{10}.

Other polymers, PS, PMMA and ABS, were used as carbon feed sources for the direct growth of graphene on insulating substrates. We selected SiO\textsubscript{2}/Si\textsuperscript{++} (500 nm SiO\textsubscript{2}) as the substrate and the reaction conditions were the same as those used for the PPMS-derived graphene. The Raman spectra in Figure 2.3c indicated that all these carbon sources were transformed into bilayer graphene when their thicknesses were fixed at \(~ 4\) nm. For PMMA and ABS, the Raman spectrum of the obtained graphene showed slightly larger D peaks (Figure 2.3c). In ABS, where N-doped bilayer graphene is obtained, a larger D peak is expected due to the broken lattice symmetry.\textsuperscript{12} The sheet resistance for PMMA-derived graphene was \(~ 3,000 \ \Omega \ \text{sq}^{-1}\) and the sheet resistance for ABS-derived graphene was \(~ 5,000 \ \Omega \ \text{sq}^{-1}\), larger than that of PPMS-derived graphene. For PS-derived graphene, the low-D peak demonstrates the high quality of the obtained graphene film. Its sheet resistance is \(~ 2,000 \ \Omega \ \text{sq}^{-1}\), similar to that of the PPMS-derived graphene. This can be understood in that PS only contains carbon and hydrogen.

Using similar conditions, bilayer graphene was also synthesized on several other insulating substrates, thereby underscorign the universality of this direct bilayer graphene growth. The conditions were kept the same as those used for graphene growth on SiO\textsubscript{2} substrates except for replacing the insulating substrates with hexagonal boron nitride (h-BN), Si\textsubscript{3}N\textsubscript{4} or Al\textsubscript{2}O\textsubscript{3} (sapphire). Large area h-BN was synthesized by CVD of ammonia borane on copper\textsuperscript{32} and then transferred onto the SiO\textsubscript{2}/Si. After annealing Ni/PPMS/h-
BN/SiO$_2$/Si at 1000 °C for 15 min and dissolving Ni, Raman spectra of the film had G peak and 2D peak signals with comparable intensities, demonstrating the successful synthesis of bilayer graphene on h-BN (Figure 2.3d). While pure h-BN is non-conductive, the sheet resistance of the obtained graphene/h-BN hybrid film was ~ 2,000 Ω sq$^{-1}$, measured by the four-probe method. Graphene films were also synthesized on Si$_3$N$_4$ or Al$_2$O$_3$ as shown in Figure 2.3d. The sheet resistances of the graphene films on these substrates were both ~2,000 Ω sq$^{-1}$.

2.3. Growth of Bilayer Graphene on SiO$_2$ by Carbon Diffusion through Nickel$^2$

In this section, we demonstrate a facile synthesis of bilayer graphene directly on SiO$_2$ substrates by the diffusion and precipitation of carbon in nickel layers. The carbon sources come from either solid polymer films of poly (methyl methacrylate) (PMMA), high impact polystyrene (HIPS), or acrylonitrile-butadiene-styrene (ABS) or gas flow of methane on the top side of nickel layers. When the samples were annealed under Ar/H$_2$ flow and at 1000 °C, the carbon sources decomposed and the carbon dissolved and diffused into the nickel layer and deposited on both sides of the nickel to form graphene upon cooling. After etching away the nickel, bilayer graphene was obtained directly on the SiO$_2$ substrates.

Figure 2.7 illustrates the procedure for the growth of bilayer graphene directly on the SiO$_2$ substrate. The SiO$_2$ substrate was cleaned with oxygen-plasma and Piranha solution (4:1 sulfuric acid: hydrogen peroxide), and then a 400-nm-thick nickel film was
thermally evaporated onto the top of the SiO$_2$ substrate used as the metal catalyst. Either solid polymers (PMMA, HIPS or ABS) or gas phase methane were used as carbon sources for the transfer-free growth of bilayer graphene. For the solid carbon source, the polymers were spin-coated onto the top of the nickel film, followed by annealing samples at 1000 ºC for ~ 10 min with a reductive gas flow (H$_2$/Ar) under low pressure conditions (~7 Torr). For the gas carbon source, methane was used during the annealing process under ambient pressure. Detailed growth procedures are summarized in the experimental section. During the annealing process, the carbon sources decomposed, and dissolved and diffused in the nickel film. Upon fast cooling, carbon precipitated from the nickel film and formed graphene on the both sides of the nickel film. After dissolving away the nickel film together with graphene on its top using Marble’s reagent, bilayer graphene was obtained directly on the SiO$_2$ substrate, eliminating any transfer process.

**Figure 2.7** Schematics of the growth of bilayer graphene from a solid carbon source. A 400-nm nickel film was thermally evaporated onto SiO$_2$ substrate, followed by the spin-coating of polymers on the nickel. After annealing samples at 1000 ºC under a reductive Ar/H$_2$ pressure for ~ 10 min, and then etching away the nickel, bilayer graphene is
obtained directly on SiO₂. The polymer film formation can be replaced by exposure to methane during the annealing step.

**Figure 2.8** Raman spectra of PMMA-derived bilayer graphene. (a) Typical Raman spectrum of PMMA-derived bilayer graphene. The inset shows that 2D peak can be deconvoluted into four components: 2D1B, 2D1A, 2D2A and 2D2B from the left to the right. (b) D/G peak ratio mapping of the PMMA-derived bilayer graphene film over a 100 × 100 µm² area. (c) G/2D peak ratio mapping of the PMMA-derived bilayer graphene film over a 100 × 100 µm² area. (d) FWHM Raman mapping of the PMMA-derived bilayer graphene film over 100×100 µm² area. The scale bar in (b), (c) and (d) is 20 µm.
With PMMA used as the solid carbon source for the transfer-free growth of bilayer graphene on SiO$_2$, Raman spectroscopy was used to analyze the number of layers and the quality of the graphene. Figure 2.8a is the typical Raman spectrum of the PMMA-derived bilayer graphene on SiO$_2$, showing that the G peak at ~1580 cm$^{-1}$ and the 2D peak at ~2700 cm$^{-1}$ are comparable in intensity, and the FWHM of the 2D peak is about 50 cm$^{-1}$. Furthermore, the 2D peak (the inset in Figure 2.8a) is asymmetric, and can be deconvoluted into four small peaks: 2D1B, 2D1A, 2D2A and 2D2B, which correspond to four permissible photon transitions in graphene$^{26-27}$. The 2D peak position, FWHM and shape, together with G to 2D peak ratio, all indicate that PMMA-derived graphene on SiO$_2$ is bilayered$^{26-27}$. The small D peak at ~1350 cm$^{-1}$ in Figure 2.8a suggests that PMMA-derived bilayer graphene has few defects or symmetry broken sites. The high quality of PMMA-derived bilayer graphene over large areas was demonstrated by the Raman mapping of the D to G peak intensity ratio. Figure 2.8b shows that D to G peak ratio over around ~ 99% area is below 0.1, suggesting the high quality of the obtained graphene film. A four-probe measurement of the graphene film shows a sheet resistance of ~2000 Ω/sq, which further confirms the high-quality of the PMMA-derived graphene film. The uniformity and the coverage of PMMA-derived bilayer graphene were determined by Raman mapping of the G to 2D peak intensity ratio (Figure 2.8c) and FWHM (Figure 2.8d) over a 100 × 100 μm$^2$ area. Considering that many factors could affect the Raman spectra of graphene, we set a range of the G to 2D peak ratio from 0.7 to 1.3 and the FWHM of the 2D peak from 45 cm$^{-1}$ to 60 cm$^{-1}$ to estimate the bilayer coverage$^{10,12,15}$. Those that have a G to 2D peak ratio lower than 0.7 and FWHM of 2D peak lower than 45 cm$^{-1}$ are considered to be monolayer graphene, and the samples that
have a G to 2D peak ratio higher than 1.3 and FWHM of 2D peak higher than 60 cm\(^{-1}\) are considered few-layer graphene. According to this criterion, the bilayer graphene coverage was \(\sim70\%\). Monolayer and few-layer graphene can also be found in \(\sim20\%\) and \(\sim10\%\) of the area respectively.

**Figure 2.9** TEM analysis of PMMA-derived bilayer graphene. (a) Low-resolution TEM image showing bilayer graphene films over large area on a TEM grid. (b) and (c) HR-TEM images of bilayer graphene edges that show two carbon layers. (d) Hexagonal SAED pattern of the bilayer graphene that shows a rotation angle of \(\sim12^\circ\) between the two layers.
PMMA-derived bilayer graphene was further characterized by TEM. The graphene film was removed from the SiO$_2$ substrate using BOE and then transferred onto TEM grids for further characterization. The suspended graphene films on the TEM grids are continuous over a large area as shown in low-resolution TEM (Figure 2.9a). Randomly imaged graphene edges (Figure 2.9b and 2.9c) show two carbon layers, verifying the bilayer nature of the graphene film$^{33}$. The randomly SAED pattern clearly shows two typical hexagonal crystalline structures of graphene with a small angle $\theta$. In Figure 2.9d specifically, $\theta$ is about 12$^\circ$, but in other areas $\theta$ could be from 0$^\circ$ to 30$^\circ$. If we reduced the spot size of the SAED analysis, two sets of hexagonal diffraction patterns were still found. We also did FFT calculation in an area as small as 20 $\times$ 20 nm$^2$. Two sets of hexagonal diffraction patterns remained, indicating that the obtained graphene layers are non-Bernal (non-AB) stacked. Although some areas appear to be Bernal (AB) stacked by only one 6-fold symmetric pattern, most of the bilayer graphene (~95%) are non-Bernal. We cannot determine whether the angle results from transfer to the TEM grid or during the growth process. There is a possibility that the SAED patterns in Figure 2.9d could come from two very small single domains (<20 $\times$ 20 nm$^2$) of Bernal bilayer graphene. This highly polycrystalline graphene film should have a larger D peak in Raman, which has not been observed in our case.

A carbon diffusion mechanism is proposed for the growth mechanism of bilayer graphene on SiO$_2$ substrates. During the annealing process at 1000 $^\circ$C, the PMMA decomposed, dissolved and diffused into the whole nickel film due to high solubility of carbon in nickel. When the sample is removed from the hot zone of the furnace and
rapidly cools, carbon precipitates from both sides of the nickel layer to form graphene films. In most cases, few-layer graphene was obtained on the top of nickel (see the black curve in Figure 2.10a). However, after etching nickel films, bilayer graphene was obtained directly on SiO$_2$, as the constrained environment between the nickel film and the SiO$_2$ substrate apparently benefited the growth of bilayer graphene.

![Graphene Raman Spectra](image)

**Figure 2.10** Raman spectroscopic analysis of graphene from different growth conditions. (a) Raman spectra of graphene on the top of nickel layer before and after UV-ozone exposure, and graphene on the substrate after UV-ozone exposure and nickel removal. (b) Raman spectra of PMMA-derived graphene by different metal catalyst.

A control experiment was conducted and shown in Figure 2.10a to demonstrate that the graphene layer on the SiO$_2$ is not from the top side of the nickel. The black curve in Figure 2.10a shows that the graphene on the top side of the nickel has a small D peak with $I_D/I_G < 0.1$. After being treated by UV-ozone for 15 min, the D peak increases, with $I_D/I_G \approx 0.8$, indicating the graphene film on the top of nickel was badly damaged. After etching nickel film using Marble’s reagent, bilayer graphene with a small D peak was
still obtained on SiO$_2$. From this control experiment, it is evident that the bilayer graphene on the SiO$_2$ is indeed formed underneath the nickel layer and is not from the top of the nickel layer. As a comparison, copper was also used as the catalyst for the transfer-free growth of graphene. Here a 400-nm copper film was deposited on the SiO$_2$ substrate, PMMA was used as the carbon source, and other conditions are similar with that of nickel. However, after etching the copper film using Marble’s reagent, almost no carbon was obtained on the SiO$_2$ substrate (the black curve in Figure 2.10b). From this result, it is apparent that carbon has too low of a solubility in copper and it is difficult for carbon to diffuse below the copper film.

![Raman Spectra](image)

**Figure 2.11** Raman spectra of bilayer graphene from different carbon sources and UV-Ozone experiments. (a) Raman spectra from of bilayer graphene films from different PMMA thicknesses by adjusting spin-coating speeds. (b) Raman spectra of PMMA-
derived graphene with different thicknesses of nickel layers. (c) Raman spectra of PMMA-derived graphene grown at different temperatures. (d) Raman spectra of HIPS-, ABS- and CVD-derived bilayer graphene.

The above proposed growth mechanism of bilayer graphene was further supported by the following experiments. The amount of PMMA on the top of the nickel was adjusted by changing the spin-coating speed and its effect on the graphene growth was determined. Figure 2.11a demonstrates that all four spin-coating speeds led to the growth of bilayer graphene on SiO₂ substrates, suggesting that the constrained environments between nickel films and SiO₂ substrates plays a major role in the growth of bilayer graphene. However, if none of carbon source was put on top of the nickel, nothing was obtained on the SiO₂ under similar growth conditions. Meanwhile, the effects of nickel film thickness on bilayer graphene growth were also investigated. Figure 2.11b shows that nickel film thickness has a limited effect on the bilayer graphene growth since all three nickel film thicknesses, 400 nm, 250 nm and 170 nm, led to the formation of bilayer graphene on SiO₂. However, when the thickness of the nickel film was decreased below 170 nm, most of nickel evaporated during the annealing process at 1000 °C and results in the growth of discontinuous graphene with a large D peak.

Different annealing temperatures were also used for the growth of PMMA-derived bilayer graphene. Figure 2.11c demonstrates that the lower limit of annealing temperature for high-quality graphene growth is ~900 °C; when the annealing temperature was lowered to 800 °C, the obtained bilayer graphene had a large D peak in the Raman spectrum, with I_D/I_G ~ 0.7. This was also consistent with previous experiments,
where a lower growth temperature would cause a larger D peak. Other polymers including HIPS and ABS were also deposited on the top of nickel film and used as solid carbon sources for the transfer-free growth of graphene. The Raman spectra in Figure 2.11d indicate that both HIPS and ABS lead to the formation of bilayer graphene on SiO$_2$ substrates. The Raman mapping of G/2D peak ratio, D/G peak ratio and FWHM of HIPS-derived graphene indicate that the quality of HIPS-derived bilayer graphene is almost as high as PMMA-derived graphene. For ABS-derived graphene, a larger D peak is observed with $I_D/I_G ~ 0.2$. This is because ABS contains nitrogen elements in its chemical structure and results in the formation of nitrogen-doped graphene. A gas phase carbon source, methane, was also used for the transfer-free growth of graphene on SiO$_2$ substrates. The blue curve in Figure 2.11d indicates that methane-derived graphene is also bilayered.

2.4. References


2.5. Experimental Contributions

Zheng Yan discovered the procedures, conducted the graphene growth experiments, and performed the spectroscopic characterizations and analyses. Zhiwei Peng optimized the growth conditions, and contributed to graphene growth experiments. Zhengzong Sun performed TEM characterizations and analyses. Jun Yao performed the electrical measurements and analyses. Yu Zhu carried out the sheet resistances and transmittance measurements. Zheng Liu synthesized h-BN.
Chapter 3

Growth of Graphene Single Crystals

This chapter was entirely copied from references 1, 2 and 3.

3.1. Introduction

To date, the best-quality graphene is mechanically exfoliated from graphite though limited to small flakes and low yields, whereas large-area graphene grown on transition metals by CVD method\textsuperscript{4-7} has produced polycrystalline structures with reduced electrical and mechanical properties\textsuperscript{8-9}. Meanwhile, graphene’s electronic and optical properties are strongly linked to its thickness. For example, monolayer graphene has zero band gap\textsuperscript{10}. Bi- and tri-layer graphene demonstrate rich electronic and optical properties that are dependent on their interlayer stacking orders\textsuperscript{11-12}. Therefore, CVD synthesis of large mono-, bi- and trilayer graphene single crystals that can be isolated from their
growing substrates would provide a material with both fundamental interests and practical applications. In addition, it is unclear how the few-layer graphene single crystals are grown, and what determines the interlayer stacking. A combination of experimental and theoretical studies would offer useful guidance towards controlled synthesis of nanocarbon materials.

Meanwhile, precise spatial control of materials is the key capability of engineering their optical, electronic and mechanical properties. However, growth of graphene on Cu was revealed to be seed-induced 2D growth, limiting the synthesis of complex graphene spatial structures. Thus, the in situ fabrication of complex spatial graphene structures during the growth process could extend graphene’s potential optical and mechanical applications.

3.2. Growth of Millimeter-Sized Monolayer Graphene Single Crystals

In this section, we constructed a CP-CVD system by adding a metering valve, as shown in Figure 3.1a, which can be used to precisely manipulate the chamber pressure, ranging from 1 mT to 1500 Torr. This modification allows us to adjust the chamber pressure during the annealing or growth process to control the shapes and sizes of graphene domains.

Using this system, the synthesis of large-size (~ 4.5 mm²) single-crystal monolayer graphene on Cu was achieved as follows. Cu surfaces were first cleaned using the electrochemical-polishing method and then annealed at 1500 Torr and 1077 °C for 7 h with a H₂ flow rate of 500 sccm. After annealing, the flow rate of H₂ was decreased to 70 sccm and the chamber pressure was adjusted to ~ 108 Torr by the metering valve. The
graphene growth was started by introducing 0.15 sccm CH₄ into the chamber, with the H₂ held at 70 sccm, for 125 min. After the reaction, the Cu foils were quickly removed from the hot zone of the CVD furnace and permitted to cool to room temperature.

**Figure 3.1** Synthesis of large-size single-crystal graphene monolayer domains using the CP-CVD system. (a) A drawing of the CP-CVD system, where a metering valve was added to precisely manipulate the chamber pressure ranging from 1 mT to 1500 Torr. (b) The typical optical and SEM images of as-produced graphene domains on Cu. (c) The SAED mapping protocol of the graphene transferred onto a TEM grid. The diameter of TEM grid was ~ 3 mm and the distance between the 9 adjacent selected points was ~ 0.5
mm. (d) The overlaid 9 SAED patterns. (e) A HR-TEM image randomly taken from the graphene domain edge, verifying that it is monolayered.

After the graphene growth, the Cu foils were heated in air for 1 min at 215 °C and the oxidation of Cu foils makes the graphene domains optically visible. Figure 3.1b is a typical optical image of a Cu surface after the graphene growth, showing four graphene domains in this ~ 7 mm × 7 mm area. Three of them are ~ 2.3 mm and the middle domain is ~ 1 mm, suggesting the graphene nucleus related to these four graphene domains did not form simultaneously. The SEM images in Figure 3.1b shows that the obtained graphene domain is hexagonally shaped, has straight edges and well-identifiable 120° corners. Its edge-to-edge distance is ~ 2.3 mm and the surface area is ~ 4.5 mm².

![Figure 3.1b](image)

**Figure 3.1b** Typical optical image of a Cu surface after the graphene growth, showing four graphene domains in this ~ 7 mm × 7 mm area. Three of them are ~ 2.3 mm and the middle domain is ~ 1 mm, suggesting the graphene nucleus related to these four graphene domains did not form simultaneously. The SEM images in Figure 3.1b shows that the obtained graphene domain is hexagonally shaped, has straight edges and well-identifiable 120° corners. Its edge-to-edge distance is ~ 2.3 mm and the surface area is ~ 4.5 mm².

![Figure 3.2](image)

**Figure 3.2** SEM images of graphene domains grown at different times. SEM images of
graphene domains grown in (a), 10 min, (b), 30 min, (c), 60 min or (d), 125 min, in four different experiments. In the SEM images, only one graphene domain was found in (a) ~ 3 mm × 3 mm area. The scale bar is 100 μm in all figures. In (d), there are two rough edges to the graphene domain that arise from the mixtures of zigzag and armchair terminations. (e) Plot of variations of the edge-to-edge distances of graphene domains as a function of the growth time. (f) The surface area of the graphene domains as a function of the growth time.

In four different experiments, we halted the reactions after 10, 30, 60 or 125 min, respectively, as shown in Figure 3.2. In all of these cases, only one graphene domain was found in the ~ 3 mm × 3 mm region (Figure 3.2a-d). The growth rates were estimated from the SEM images and demonstrated in Figure S1e and f. The growth rate of edge-to-edge distance is relatively uniform, ~ 18 μm/min under these experimental conditions (Figure 3.2e). However, Figure 3.2f indicates that the surface areas of graphene domains had an accelerated growth rate. This can be understood by the fact that, with the increase in the perimeters of the graphene domains, greater graphene edge-lengths are exposed to the Cu foil, consequently leading to an increase in the amount of active carbon species captured by graphene edges per unit time.

In order to analyze these large-size graphene domains, a SAED mapping pattern was performed across the entire graphene and 9 different points were selected, as shown in Figure 3.1c. The distance between adjacent points is ~ 0.5 mm. All of the SAED patterns of these 9 points had the same orientations and were overlaid to produce a combined pattern (Figure 3.1d), indicating a single-crystalline lattice structure. The slight
offset in the SAED patterns is occasionally observed because of the intrinsic corrugation in the graphene flake or accidental folding introduced during the transfer.\textsuperscript{9} The HR-TEM image in Figure 3.1e was randomly taken from numerous graphene domain edges. The layer count on the edge of the HR-TEM image indicates as-grown graphene is monolayered.

Figure 3.3 Spectroscopic characterizations of graphene domains transferred to SiO\textsubscript{2}/Si wafers. (a) A typical SEM image of one graphene domain transferred onto SiO\textsubscript{2}/Si. (b) The enlarged SEM image of the yellow squared region in (a). (c) The optical image taken from the corner of one graphene domain. (d) 3D Raman maps of D peak, G peak and 2D peak. The Raman mapping is performed on the graphene corner shown in e and the data
is extracted from D (1,350 cm$^{-1}$), G (1,580 cm$^{-1}$) and 2D (2,690 cm$^{-1}$) locations. The scale bar is 5 μm.

As-produced graphene was transferred onto SiO$_2$/Si wafers for further characterization. Figure 3.3a is a typical SEM image of the graphene domain on the SiO$_2$/Si wafer. Figure 3.3b and c are the SEM and optical images taken from corners of different graphene samples. The clean surfaces shown in Figure 3.3a-c demonstrate that PMMA have been removed during the transfer process. All of these SEM and optical images demonstrate uniform color contrast, suggesting uniform monolayer graphene was obtained. The straight edges and 120° corners indicate that the original shapes of the transferred graphene samples are preserved.

Raman spectroscopy was done on the transferred graphene samples to evaluate their quality and thickness. Figure 3.3d shows the Raman spectra recorded at 12 different spots from the graphene in Figure 3.3a, 6 within the graphene and 6 over the graphene edge. The Raman spectra indicate that the D peaks within the graphene are in the noise level, signifying the presence of few defects and that it has high quality, comparable to that of the exfoliated graphene$^{13}$. The D peaks recorded from the graphene edges are slightly higher than those within the graphene, and are thought to arise from the lower symmetry of the edges$^{14-15}$. In all these 12 Raman spectra, the intensities of 2D peaks are more than twice those of G peaks and the FWHM of the 2D peaks are ~ 30 cm$^{-1}$, suggesting the as-produced samples are monolayer graphene$^{13}$.

Raman mapping provides a direct, statistically sound method to confirm the quality, thickness and uniformity of graphene samples. Therefore, Raman mapping was
performed on the graphene corner shown in Figure 3.3c; the step size was 0.5 μm and the investigated region was ~25 μm × 25 μm. 3D Raman maps of D (1,350 cm⁻¹), G (1,580 cm⁻¹) and 2D (2,690 cm⁻¹) peaks were extracted and plotted in Figure 3.3e, where different colors indicate different intensities (Iₓ, where x = D, G or 2D). Figure 3.3e shows that I_D is negligibly small over the area of the graphene, with the exception of the edges, revealing that the as-grown graphene sample was almost defect-free. The graphene edges have relatively large D peaks in the spectra and the ratio of the I_D to I_G peak is ~0.1, consistent with previous studies of graphene edges, suggesting the edges are dominated by zigzag terminations. Figure 3.3e shows that I_G and I_2D are relatively uniform and the I_2D is more than twice as large as I_G over the graphene corner, indicating complete monolayer graphene coverage in the investigated region.

Figure 3.4 Graphene Hall bar device with resistivity, conductivity and mobility from a FET measured at 300 K. (a) SEM image of a graphene Hall bar FET on a SiO₂/Si
substrate. (b) Resistivity of graphene *versus* the back gate voltage. (c) Conductivity of graphene as a function of carrier density. The collected data is plotted as a black line while the data fitted by a Boltzmann model is indicated by the red filled circles. (d) Plot of the density-dependent field effect mobility of graphene as a function of carrier density.

To evaluate the quality of single-crystal graphene domains, Hall bar FETs with a highly doped p-type silicon back gate were fabricated. Figure 3.4a shows the SEM image of a fabricated Hall bar FET device. The plot of resistivity *versus* back gate voltage, $V_{gs}$, is shown in Figure 3.4b, indicating the ON/OFF ratio is ~ 10. The device exhibits low resistivity (270 $\Omega$/$\square$) at high carrier density and a sharp resistivity peak of 2.5 k$\Omega$/$\square$ at the Dirac point ($V_{Dirac} = 2.4$ V). The conductivity $\sigma$ *versus* carrier density $n$ (given by $n = C_g(V_{gs} - V_{Dirac})/e$, $C_g = 11.5$ nF/cm$^2$) is shown in Figure 3.4c, which exhibits almost linear $\sigma$ for both positive and negative carriers. To further characterize the transport characteristic of the single-crystal graphene device, a commonly used self-consistent Boltzmann theory$^{16-17}$ was used that includes long- and short-range scattering sources to fit the conductivity: $\sigma^{-1} = (\mu_c n e + \sigma_0)^{-1} + \rho_s$. In this model, $\mu_c$ denotes the density-independent charge mobility corresponding to the long-range scattering; $\rho_s$ is the resistivity contributed from short-range scattering; and $\sigma_0$ is the residual conductivity at the Dirac point. From the data, fitted as shown in Figure 3.4c, the density-independent charge mobility can be extracted, to give $\mu_c = 10400$ cm$^2$V$^{-1}$s$^{-1}$ for positive charge carriers. The extracted density-independent mobilities for positive charge carriers, from a total of 10 tested devices, ranged from 7900 to 11000 cm$^2$V$^{-1}$s$^{-1}$. These high mobilities within a relatively narrow range indicate an electrical performance comparable to that of
exfoliated graphene on a SiO$_2$ substrate. Figure 3.4d is the density-dependent field effect mobility $\mu_{FE} = \sigma / ne$, using a simple Drude model.\textsuperscript{18} For positive charge carriers $\mu_{FE}$ spans from 8600 cm$^2$V$^{-1}$s$^{-1}$ at a carrier density of 2 $\times$ 10$^{12}$ cm$^{-2}$ to greater than 12500 cm$^2$V$^{-1}$s$^{-1}$ at a density less than 5 $\times$ 10$^{11}$ cm$^{-2}$. Overall, the high electrical performance of the graphene devices indicates the high quality of the as-grown single-crystal graphene. The carrier mobility of the as-produced graphene can likely be further improved by using boron nitride substrates\textsuperscript{17} or by fabricating suspended devices\textsuperscript{19}.

**Figure 3.5** Illustration of the Cu-based graphene growth mechanism and the influence of different parameters on the graphene domain sizes and shapes. (a) The scheme for the Cu-based graphene growth mechanism. Here, red hexagons are used to symbolize the
active sites of the Cu surface and blue spots signify active carbon species (CH_{x<4})_S. From the proposed mechanism, the active carbon species from the dissociated CH_4 are apt to agglomerate into thermodynamically stable (C_nH_y)_S species on the active sites of the Cu surface to initialize the graphene growth. (b-g) show the typical SEM images of graphene synthesized under different growth conditions: b (E1), c (E2), d (E3), e (E4), f (E5) and g (E6).

Table 3.1. Growth conditions of E1-E11 in the CP-CVD system

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</table>

The growth of graphene is restricted to the catalyst surface due to the low solubility of carbon in Cu (<0.001 atomic %)\textsuperscript{20}; the process demonstrated here might be feasible for the production of wafer-sized single-crystal graphene. To reach this goal, the most challenging tasks are the development of a deep understanding of the mechanism of graphene growth and the probable requirement for a single seed of graphene to start the growth. Based on the data presented here, we propose a growth mechanism for Cu-based graphene (Figure 3.5a) and demonstrate reaction conditions that reduce the graphene nucleation density and allow the growth of larger-size graphene domains using an extended growth period (Figure 3.5 b-g and Table 3.1).
The overall growth processes for Cu-based graphene are described in Figure 3.5a; to illustrate the process, it is divided into three main steps. Red hexagons are used to symbolize the active sites of the Cu surface, such as impurities, sharp wrinkles and defects, which are known to act as active heteronuclei in the early stages of graphene growth. (1) CH$_4$ dissociates and is chemically adsorbed on the Cu surface to form the active carbon species (CH$_{x<4}$)$_s$,\textsuperscript{21-23} where “s” signifies “surface-adsorbed” to distinguish it from a gaseous molecule. The exact nature of the active carbon species has not been well-defined\textsuperscript{23} and we used carbon monomers (C) to represent all types of active carbon species in Figure 3.5a. (2) From recent research, the carbon-Cu interaction is weak and the desorption rate of active carbon species is comparable to its mobility on Cu surface above 870 °C.\textsuperscript{24} Under the growth conditions described in this paper, the temperature is > 1000 °C, suggesting that the movement of active carbon species on the Cu surface is dominated by diffusion and desorption. (3) Theoretical calculations show that active carbon species are thermodynamically unstable and tend to agglomerate into thermodynamically stable (C$_n$H$_y$)$_s$ species on the active sites of the Cu surface, ultimately leading to the formation of graphene nuclei. Once the graphene nuclei are formed, most of the active carbon species will be captured and consumed in growth of graphene, reducing the probability that new graphene nuclei will be formed in the nearby areas of the Cu catalyst.

From the data that has been presented, reducing the concentrations of both active sites and active carbon species on the Cu surface is the key factor in reducing graphene nuclei density, enabling the growth of larger-size graphene domains during the extended growth time. Based on this mechanism, we explored the influences of several parameters
on the graphene domain sizes. 11 growth experiments (E1-E11) were performed; they are listed in Table 3.1. For every experiment, the same temperatures were used in the annealing and growth processes.

![Figure 3.6](image)

**Figure 3.6** Cu-surface cleaning through the electrochemical-polishing method. (a) A scheme for Cu-surface electrochemical-polishing. (b-c) SEM images of fresh Cu and polished Cu, respectively, indicating electrochemical-polishing does not have obvious influences on Cu surface morphology. The scale bars in (b) and (c) are 50 μm. (d) The variation of the electrochemical-polishing current as a function of the polishing time. The electrochemical-polishing voltage was 4.8 V. According to the equation, \( d = \frac{(I \times t \times M)}{(4 \times e \times N_A \times \rho \times s)} \), the electrochemical-polishing process removed ~ 15 nm Cu. Here, \( d \) is the thickness of the Cu, \( I \) is the electrochemical-polishing current, \( t \) is the
electrochemical-polishing time, M is the mole mass of Cu, e is the electric charge, \( N_A \) is Avogadro's constant, \( \rho \) is the density of Cu, and \( s \) is the surface area of the Cu. (e) After heating the samples at 215 °C in air for 1 min, fresh Cu was still shiny and polished Cu was completely oxidized, suggesting an oxide layer was removed during the electrochemical-polishing process.

Figure 3.7 High-pressure annealing of Cu. (a) A scheme for high-pressure annealing of Cu. (b-e) SEM images of high-pressure annealed Cu under different magnifications, suggesting the Cu surface became flat and the sharp wrinkles and defects were removed as compared to fresh Cu (Figure 3.6b) and polished Cu (Figure 3.6c). The scale bars in (b-e) are 1 mm, 300 \( \mu \)m, 30 \( \mu \)m and 1 \( \mu \)m, respectively. Here, the annealing pressure was
1500 Torr, the annealing time was 7 h, the annealing temperature was 1077 °C and the H$_2$ flow rate was 500 sccm.

In the following experiments, we stopped the graphene growth before a continuous film formed in order to directly demonstrate the shapes and sizes of as-grown graphene domains under different growth conditions. We began the experimental series with E1, which is the CVD-based graphene growth condition that was generally used in our laboratory. Under the conditions of E1, the obtained graphene domains were square and the domain sizes were ~ 15 μm (Figure 3.5b). In E2, the CH$_4$ flow rate was lowered to 0.15 sccm and the flow rate ratio of H$_2$ to CH$_4$ was increased to ~ 460; both contributed to diluting the concentration of active carbon species on the Cu surface. In this case, the graphene domain sizes increase to ~ 30 μm after extended periods of time (Figure 3.5c). From E3 to E10, electrochemical polishing and the high pressure annealing were used to improve the quality of the Cu. Electrochemical polishing cleans the Cu surface and removes the impurity layer (Figure 3.6); high-pressure annealing can eliminate sharp wrinkles, steps and defects to improve the quality of the Cu (Figure 3.7). Both apparently reduced the Cu surface active sites and consequently decreased the graphene nucleus density. Figure 3.5d shows that the graphene domains size increased to ~ 0.3 mm on the electrochemical-polished and high-pressure annealed Cu substrates (E3) when other conditions are similar with E2. In this case, the graphene domain shapes are still square.

The graphene domain shapes become hexagonal when adjusting the chamber pressure to ~ 108 Torr during the growth process (E4-E11 and Figure 3.5e-g). The shape
evolution is attributed to the fact that H$_2$ has different etching abilities on zigzag and armchair terminations in different H$_2$ partial pressures and temperatures.

**Figure 3.8** One graphene seed produced in ~ 1 cm × 1 cm Cu (E8). (a) The SEM images of the graphene seed, suggesting that the shape is hexagonal and the size is ~ 100 μm. The scale bars in (a) and the inset of (a) are 1 mm and 10 μm, respectively. (b-e) show the SEM images of the left, right, bottom and top sides of the same graphene seed in (a), respectively, indicating that only one graphene seed was found in ~ 1 cm × 1 cm Cu. The yellow squared regions in (b-e) are the same graphene seed as shown in (a). The scale
bars in (b-e) are 1 mm. The black circled spots in (a), (c) and (e) are the same one, and not graphene or growing carbon.

Interestingly, the graphene domain sizes further increased when raising annealing and growth temperatures (E5-E7). Figure 3.5e-g show that the sizes of the graphene domains increased from ~ 0.4 mm to ~ 1 mm and ~ 1.8 mm as the temperature increased from 1060 °C (E4, Figure 3.5e) to 1070 °C (E5, Figure 3.5f) and 1075 °C (E6, Figure 3.5g). The higher growth temperature reduces the concentration of active carbon species on the Cu surface by speeding desorption and the higher annealing temperature improves the quality of Cu substrates. Both of these contributed to the reduction of the graphene nucleation density and consequently the increase of the graphene domain sizes in the extended growth time. A temperature of 1077 °C (E7, Figure 3.1b) is the limit of our CP-CVD system and in this case the graphene domain sizes increased to ~ 2.3 mm. Moreover, graphene synthesized using the conditions of E7 has a cleaner and flatter surface than those of graphene obtained using E1, suggesting its improved quality.

Figure 3.9 SEM images of graphene domains over Cu grain boundaries. The growth condition is E5. The scale bar in the two SEM images is 100 µm.
Interestingly, when the flow rate of H\textsubscript{2} was increased to 150 sccm from 70 sccm to dilute CH\textsubscript{4} (E8), only one graphene nucleus was found on ~ 1 cm × 1 cm Cu after 90 min growth (Figure 3.8). Moreover, no graphene nucleus was found on ~ 1 cm × 1 cm Cu after 125 min growth when further increasing the flow rate of H\textsubscript{2} to 200 sccm (E9). Limited by our simple 1-inch quartz-tube furnace, additional optimizations were not performed. Meanwhile, the slow edge-to-edge growth speed of the graphene domain (~ 1 μm / min) under E8 also placed an obstacle for the final synthesis of centimeter-size single-crystal graphene. However, these two experiments (E8-E9) indicate the possibility of one-seed requirement on the wafer-scale Cu through the further optimizations of growth conditions. In addition, the control experiments (E10-E11) demonstrate that the combination of Cu-surface electrochemical-polishing and high-pressure annealing is necessary for the synthesis of high-quality and large-size single-crystal graphene. Figure 3.9 demonstrates that graphene domains can grow across Cu grain boundaries, suggesting the weak influence of Cu grain size on graphene growth.

3.3. Bi- and Tri-layer Graphene Single Crystals with Varied Interlayer Rotations\textsuperscript{2}

In this section, we demonstrate the synthesis of ~ 100 μm bi- and trilayer single-crystal graphene domains with hexagonal shapes on pretreated Cu foils. The as-made graphene domains can be isolated from the Cu surfaces and transferred onto silica wafers or trench-patterned silica wafers to suspend them without introducing damages or folds. This process has great potential for studying the stacking-dependent electronics and optics in these graphene domains. Moreover, we found that the as-produced graphene
domains show almost exclusively either 0° or 30° interlayer rotations. Raman spectroscopy, TEM and FT-IR with synchrotron radiation were used to demonstrate that bilayer graphene domains with 0° interlayer stacking angles were Bernal stacked. Since the 0° Bernal stacking is known to dominate in graphite\textsuperscript{25}, the 30° interlayer rotation is anomalous because it has a high stacking energy\textsuperscript{26}. We propose a theory on the growth mechanism of few-layer graphene that is supported by first-principle calculations, and that explains the origin of the interlayer rotations and agrees well with the experimental observations.

**Figure 3.10** Bi- and tri-layer graphene domains on SiO\textsubscript{2}/Si. (a) The scheme of bi- and trilayer graphene domains synthesized on pretreated Cu, which were fabricated via a double-annealing procedure\textsuperscript{2}. (b-g) Representative optical images of as-made bi- and trilayer graphene domains transferred onto SiO\textsubscript{2} (100 nm)/Si substrates, indicating that monolayer, bilayer and trilayer are all hexagons and have well-defined 0° or 30°
interlayer stacking orientations. The scale bars in (b-g) are 30 μm. Assuming orientation angles of monolayer hexagons in all few-layer graphene domains are 0° and depending on different bi- and trilayer stacking orders, there are two types of bilayer domains, b (0-0) and c (0-30), and four types of trilayer domains, d (0-0-0), e (0-0-30), f (0-30-0) and g (0-30-30).

The fabrication of single-crystal hexagonal bi- and trilayer graphene domains was achieved in one batch on electrochemically polished and high-pressure annealed Cu foils via a double-annealing process (Figure 3.10a). After growth, graphene domains were transferred onto SiO$_2$ (100 nm)/Si substrates via a PMMA-assisted transfer method$^1$ for optical characterizations, which permit the direct visualization of shapes and thicknesses of the as-produced graphene domains. Figure 3.10b-g provide representative optical images of as-produced graphene domains transferred onto SiO$_2$/Si wafers. From these optical images, we can see that individual single-crystal graphene domains could be completely isolated from growing substrates and transferred onto silica wafers without inducing any damages or folds, indicating great potential for studying their stacking-order dependent electronic and optical properties. It is also apparent that, in the same graphene domains, mono-, bi- or trilayer regions show hexagonal shapes and could be differentiated under optical microscopy, with lateral distances of monolayer hexagons at ~ 100 μm. Interestingly, though, in the same graphene domain, mono-, bi- or trilayer hexagons show decreased lateral sizes and share almost the same hexagonal center, meaning they nucleated from the same active sites at different times or at different growth rates.
Additionally, according to recent research, the secondary graphene layer should nucleate and grow underneath the first graphene layer\textsuperscript{27}.

More interestingly, in contrast to graphite where Bernal stacking dominates\textsuperscript{25}, the as-produced few-layer graphene single crystals on the pretreated Cu demonstrated both 0° and 30° rotation preference. In this research, 90 few-layer graphene domains were investigated, with ~ 48% of 0° interlayer stacking, ~ 46% of 30° interlayer stacking and only ~ 6% of randomly twisted stacking. Two types of bilayer graphene domains and four types of trilayer graphene domains were synthesized in this research, according to their different interlayer stacking orders. Assuming orientation angles of monolayer hexagons in all graphene domains are 0° and, depending on different interlayer stacking orders, the as-made bi- and trilayer graphene domains are named as follows: 0-0 bilayer, 0-30 bilayer, 0-0-0 trilayer, 0-0-30, 0-30-0 and 0-30-30 (Figure 3.10b-g, respectively). Figure 3.10b-g also demonstrate that all six types of well-defined graphene domains could be isolated from the growing substrates and transferred onto silica wafers, indicating the ability to study their stacking-order-dependent electronic and optical properties. In the same growth batch, through the investigation of 115 graphene domains, ~ 50% are bilayer domains, ~ 30% are trilayer domains and ~ 20% are monolayer and tetralayer domains, with domain sizes of monolayer hexagons ranging from ~ 70 μm to ~ 130 μm. All of the different graphene domains can be transferred onto the same target substrate, such as a silica wafer, for further optical and electronic investigations.

To investigate stacking-order dependent ballistic transport behaviors or thermal conduction of graphene domains, they need to be suspended over holes or trenches\textsuperscript{19}. In this research, we made well-aligned trench patterns on SiO\textsubscript{2} (300 nm)/Si wafers, with the
width at ~ 3 μm or ~ 5 μm, the length at ~ 20 μm and the depth at ~ 250 nm, and then transferred the as-produced graphene domains onto these trench-patterned silica wafers using a PMMA-assisted transfer method\(^1\). Figure 3.11 demonstrates that both bi- and trilayer graphene hexagons could be free-standing over trenches, indicating the potential of studying their stacking-order dependent ballistic transport behaviors and thermal conduction in the future.

![Figure 3.11](image)

**Figure 3.11** Suspended bi-and tri-layer graphene domains. (a-c) Typical SEM images of bi- and trilayer graphene domains transferred onto trench-patterned SiO\(_2\) (300 nm)/Si wafers, showing both bilayer and trilayer graphene could be free-standing over trenches, indicating great potential for studying ballistic transport behaviors and thermal conductions of such materials.
As a demonstration, in this research, we investigated two types of bilayer graphene domains, 0-0 bilayer and 0-30 bilayer, using Raman spectroscopy, TEM and FT-IR with synchrotron radiation (Figure 3.12). Figure 3.12a is a typical optical image of 0-0 bilayer graphene domains, showing concentric mono- and bilayer hexagons with 0º interlayer stacking orientation. Raman spectroscopy, a powerful tool to determine thickness and quality of graphene\textsuperscript{13}, was first used to investigate this graphene domain. More than ten points were characterized by Raman spectroscopy on this 0-0 bilayer graphene domain, and the typical data of the monolayer region (point A) and the bilayer region (point B) are shown in Figure 3.12b. Figure 3.12b demonstrates that point A has the typical Raman spectrum of monolayer graphene, with an intensity ratio of G to 2D less than 0.5 and the FWHM of the 2D peak at ~ 30 cm\textsuperscript{-1}. In contrast, the Raman spectrum of point B has an intensity ratio of G to 2D of ~ 1 and the FWHM of the 2D peak of ~ 50 cm\textsuperscript{-1}. Furthermore, the 2D peak displays an asymmetric line shape and can be well-fitted by four components, each with fwhm of ~ 30 cm\textsuperscript{-1}. These data indicate that the 0-0 bilayer graphene domain is Bernal-stacked\textsuperscript{13}. Meanwhile, no obvious D peaks were detected in either the mono- or bilayer regions of 0-0 bilayer graphene domains, indicating the presence of few sp\textsuperscript{3} carbon atoms or defects\textsuperscript{13}. SAED patterns corroborate the stacking order in 0-0 bilayer graphene domains. Figure 3.12c shows only one set of SAED patterns in the bilayer region of 0-0 bilayer graphene domains. The (1-210) intensity was ~ 3 times stronger than the (1-100), further demonstrating the Bernal stacked order of 0-0 bilayer graphene domains\textsuperscript{28-29}. 
Figure 3.12d is a typical optical image of 0-30 bilayer graphene domains, showing concentric mono- and bilayer hexagons with 30° stacking orientation. The Raman spectra in Figure 3.12e show that both the monolayer region (point C) and the bilayer region (point D) demonstrate typical Raman spectrum of monolayer graphene, meaning that the top layer and the bottom layer are fully decoupled in the 0-30 bilayer graphene domains. Additionally, no D peaks were observed in Figure 2e, demonstrating the high-quality of as-produced 0-30 bilayer graphene domains. Two sets of SAED patterns (Figure 3.12f) were observed in the bilayer region of 0-30 bilayer graphene domains, with the twist angle at 30°, matching well with the optical observation in Figure 3.12d.
optical image of 0-0 bilayer graphene domains. (b) Raman spectra recorded from point A and B in (a). (c) A typical SAED pattern taken from the bilayer region of 0-0 bilayer graphene domains, showing only one set of diffraction patterns. (d) One typical optical image of 0-30 bilayer graphene domains. (e) Raman spectra recorded from points C and D in (d). (f) A typical SAED pattern taken from the bilayer region of 0-30 bilayer graphene domains, showing a 30° rotation between the two stacking layers. (g) A representative reflection spectrum by FT-IR with synchrotron radiation recorded from the bilayer region of 0-0 bilayer graphene domains, showing a dip around 350 meV. (h) A representative reflection spectrum by FT-IR with synchrotron radiation recorded from the bilayer region of 0-30 bilayer graphene domains. The FT-IR spectra were normalized to the reflection spectrum of the substrate, SiO₂ (300 nm)/Si.

The stacking order can be further confirmed by FT-IR with synchrotron radiation. As shown in Figure 3.12g, 0-0 bilayer graphene shows a dip at ~ 350 meV in the reflection spectrum. This can be ascribed to the Van Hove singularity of optical transition between two parallel bands in A-B stacked bilayer graphene. In contrast, 0-30 bilayer graphene’s reflection spectrum has no dip feature in the mid infrared range (Figure 3.12h), which reflects the decoupled nature of the two layers at low energy. 15 0-0 bilayer graphene domains and 15 0-30 bilayer graphene domains were investigated by FT-IR with synchrotron radiation in this research and the results were consistent with those shown in Figure 3.12 g-h.

An important question is, Why are the interlayer rotations in the as-made graphene domains almost exclusively either 0° or 30°? The 0° Bernal stacking is not a
surprise, since it also dominates in graphite as well\textsuperscript{25}. This is due to the Van der Waals interlayer interaction, which has an energy minimum at 0°, the Bernal stacking configuration. In contrast, the 30° orientation is incommensurate, with high stacking energy\textsuperscript{26}, and thus barely appears in graphite. However, as demonstrated in this research, the 30° graphene domain is one of the two preferred orientations. This surprising fact suggests that the interlayer interaction is no longer the guiding force of graphene orientation. In fact, as shown in Figure 3.13, it is the interaction between the Cu step and graphene during the nucleation stage that determines its orientation.

**Figure 3.13** First-principle calculations. (a) Schematic of graphene nucleation on a Cu step. The C atoms are represented by black spheres, and the Cu are shown in red, where the topmost Cu
layer is highlighted in bold color. (b) The orientation angle between graphene and Cu(111) surface. (c) The relaxed atomic structure of graphene|Cu step interfaces for different orientation angles. (d) The graphene|Cu step interface energy (defined in eq. 3.1) as a function of orientation angle. The two data points at the same orientation angle represent the computational accuracy, due to different strain levels of periodic cell size$^2$.

**Figure 3.14** Electron-density-enhancement isosurfaces (in blue, defined in eq 3.2) of the graphene|Cu step interface. The C atoms are represented by black spheres, and the Cu are shown in red. For clarity, only two Cu layers are displayed. The numbers are the orientation angles of graphene with respect to the Cu (111) surface.

The CVD growth of graphene starts from a nucleation site, and then extends via sequential addition of C atoms to the graphene edge$^{15}$. For electrochemically polished and annealed Cu, impurities and sharp wrinkles have been removed$^1$, leaving the Cu steps (Figure 3.13a) as major nucleation sites since they provide low-energy sites for C atoms.
In addition, the fact that the few-layer graphene are almost concentric suggests that they share the same nucleation site. During the nucleation, a graphene|Cu interface is formed, and defines the orientation between graphene and Cu surface, as shown in Figure 3.13b. After the nucleation, the edges of the graphene domain are bound by the Cu, which fixes the orientation during the growth. The energy-preferred graphene|Cu interface will lead to preferred orientation between graphene and Cu, and eventually result in preferred orientation between graphene layers. The pretreated Cu foil used here is mainly composed of (111) surfaces\(^2\), on which the Cu steps are microscopically straight with closest-packed atoms (Figure 3.13b), as the most stable configuration. The graphene edge atoms tend to be close to the step atoms, in order to efficiently saturate their dangling bonds and minimize the energy. Among all the orientations, the 0° and 30° render straight ZZ and AC graphene edges, respectively, and thus could be expected to contact the Cu steps more efficiently. Other orientations have non-straight graphene edges with kinks\(^32\), which leads to high energy interfaces.

The above mechanism was quantified by first-principle calculations. DFT calculations were performed with Perdew–Burke–Ernzerhof parametrization (PBE) of generalized gradient approximation (GGA) and projector-augmented wave (PAW)\(^33\) potentials, as implemented in the Vienna \textit{ab Initio} Simulation Package (VASP)\(^34\). Graphene ribbons and Cu steps were placed in contact and then relaxed to model the graphene|Cu interface. The periodic cell was chosen to reduce the lattice mismatch below 4%. Further details of the computations can be found in the supporting information. Figure 3.13c shows the atomic structure of graphene|Cu interfaces, for four orientations: 0°, 19.1°, 25.3° and 30°. Clearly, for 0° and 30° interface, both the graphene edges and
Cu steps remain almost straight, similar to their isolated structures. However, for 19.1° and 25.3°, the Cu steps are distorted, and the graphene edges are highly buckled in the surface normal direction (middle panel of Figure 3.14), suggesting unstable interfaces. Figure 3.13d shows the interface energy as a function of the orientation angle. The interface energy is defined in eq 3.1:

$$\gamma = \gamma_{\text{graphene}} + \frac{[E (g+Cu) - E (Cu) - E (g)]}{L}$$

where \(\gamma_{\text{graphene}}\) is the edge energy of graphene, taken from ref. 32. \(E (g+Cu)\) is the total energy of the system, \(E (Cu)\) is the energy of the Cu steps, and \(E (g)\) is the energy of graphene, and \(L\) is the length of the interface. So \([E (g+Cu) - E (Cu) - E (g)]/L\) gives the binding energy (per length) of the interface. The vertical spread of data points for the same orientation reflects the computation uncertainty due to the difficulty of matching the graphene and Cu lattices in the periodic cell so as to minimize the mismatch strain in the system. The interface energies have two clear local minima at 0° and 30°, in agreement with their undistorted atomic structures. Therefore, the graphene|Cu interface has two preferred orientations: 0° and 30°.

Interestingly, though the edge energy of graphene decreases monotonically as a function of orientation angle\(^{32}\), its interface energy with Cu step has a concave shape. This is because ZZ graphene edge is bound more strongly to Cu step, which reduces the interface energy more significantly. It can be better seen from the electron-density-difference \(\Delta \rho\) (eq 3.2), as shown in Figure 3.14:

$$\Delta \rho = \rho (g+Cu) - \rho (g) - \rho (Cu)$$

where \(\rho (g+Cu)\) is the electron density of the graphene|Cu interface. \(\rho (g)\) and \(\rho (Cu)\) are the electron densities for graphene and Cu, with same atomic coordinates as in the
interface. We observe electron density accumulation at the interface, suggesting the graphene|Cu interface has covalent bonding features. The electron depletions are mainly located on the Cu atoms, while not plotted in Figure 3.14 for clarity. At the 0° interface, the ZZ edges are bound with both Cu step atoms and those under the step. In contrast, at the 30° interface, the AC edges are only bound with Cu step atoms. The extra coordination of the ZZ edge enhances its binding with Cu (0.76-0.79 eV/Å, compared to the AC edge binding energy 0.61 eV/Å), and thus reduces its interface energy. For other angles, the graphene edges are combinations of ZZ and AC segments. The ZZ segment tends to be docked between the Cu step and the layer underneath, similar to the pure ZZ edge, while the AC segment favors only the Cu steps. As a result, the edge becomes corrugated (Figure 3.14), leading to high interface energy.

During the CVD growth, the graphene sheet could grow across the Cu step where it originally nucleated by addition of C atoms to the interface. Those C atoms come from the decomposed hydrocarbons on the surface (or terrace), and transport through surface or subsurface diffusion. Therefore the Cu steps can be re-exposed and serve as the nucleation sites for a second graphene layer. The new layer again has preference for 0° and 30°. Eventually, few-layer graphene grows on clean Cu, with either 0° or 30° orientation with respect to each other.

3.4. Hexagonal Onion-Ring-like Graphene Domains

Existing graphene growth methods on Cu have fundamental limitations that are based on a seed-induced 2D growth mechanism and do not allow one to fabricate in situ complex spatial graphene structures during the growth process. In this section, it has been
demonstrated that 3D growth of new graphene layers on the edges of the original 
graphene layer could be induced by controlling H\textsubscript{2} partial pressure during the growth 
process. This stands as a complementary method to CVD growth while permitting growth 
of complex graphene-based spatial structures. By this method, onion ring-like 3D 
hexagonal graphene structures (hexagonal graphene onion rings, HGoRs) were fabricated 
via the \textit{in situ} growth of graphene ribbon rings on the edge and under hexagonal 
monolayer graphene domains. The structure models of HGoRs are demonstrated in 
Figure 3.15a, showing that the topside monolayer graphene domain (gray color) and the 
bottomside few-layer graphene ribbons (blue color) combine together to form a onion 
ring-like pesudo-3D graphene structure.

\textbf{Figure 3.15} Synthesis and spectroscopic analysis of HGoRs. (a) Top view and side view 
of the structure models of HGoR, which was a combination of the topside monolayer 
graphene domain (gray color) and the bottomside few-layer graphene ribbons (blue color). 
HGoRs are synthesized on Cu foils by heating in a H\textsubscript{2}/CH\textsubscript{4} atmosphere at 1074 °C with
the chamber pressure held at 500 Torr. (b–c) Typical optical images of as-produced HGoRs transferred onto SiO₂/Si wafers, showing blue graphene ribbon rings somewhat concentrically grow on or under lighter monolayer graphene domains. The scale bars in b and c are 50 µm and 20 µm, respectively. (d) Raman spectra of point A and point B in c. (e) SAED patterns and the TEM image of one HGoR transferred onto a TEM grid. The scale bar is 100 nm.

Growth of HGoRs on Cu foils was achieved as follows. Cu foils were first cleaned using electrochemical-polishing and high-pressure annealing. The pretreated Cu was loaded into the CVD chamber and annealed for 30 min at 1074 °C with the flow rate of H₂ at 500 sccm and the chamber pressure at 500 Torr. The growth of HGoRs was started by introducing 7 sccm CH₄ into the chamber, with the H₂ held at 500 sccm, for 35 min. After the reaction, the Cu foils were quickly removed from the hot zone of the CVD furnace using a magnetic rod and permitted to cool to room temperature.

![Raman spectra](image)

**Fig. 3.16** Raman spectra recorded from graphene 1 and 2 in Figure 3.15b. The spectra are
characteristic of >12 locations recorded over the two graphene domains. The $I_{2D}/I_G$ intensity ratio is about 3 and the FWHM of the 2D peak is about 30 cm$^{-1}$, indicating that graphene 1 and 2 are monolayer. The D peak is in the noise level, indicating the high quality of graphene 1 and 2.

After the growth of HGoRs, the samples were transferred onto SiO$_2$ (100 nm)/Si wafers for further characterizations. Optical microscopy is a useful tool for graphene characterization because graphene areas with different thicknesses can be distinguished by their contrast difference. Figure 3.15b-c provide several typical optical images of as-produced HGoRs transferred onto SiO$_2$/Si wafers. In these optical images, one can see that blue graphene ribbon rings concentrically grow upon or under the lighter hexagonal graphene domains to form onion-like 3D graphene structures. Figure 3.15b exhibits 7 domains, with graphene domains 1 and 2 and onion domains 1 through 5, suggesting that the yield of HGoRs is $\sim$ 70 %. This approximate value is consistently observed under the described growth conditions. Graphene domains 1 and 2 are monolayer based on the Raman spectra in Figure 3.16. In addition, they show a uniform optical contrast, indicating 100 % monolayer graphene coverage. Graphene domain 1 was a well-defined hexagon while graphene domain 2 was partially damaged during the transfer process. From Figure 3.15b, it is seen that most of the HGoRs (1-4) have the edge-to-edge distances ranging from 70 to 90 µm, suggesting that monolayer graphene domains in HGoRs 1-4 nucleate at similar intervals during the growth process. Through the investigation of 54 HGoRs, $\sim$85 % of them have the edge-to-edge distances ranging from 70 to 90 µm, indicating a narrow size distribution. Meanwhile, a much smaller HGoR 5,
with the edge-to-edge distance at \( \sim 30 \mu m \), was also observed in Figure 3.15b, indicating that the monolayer graphene domain in HGoR 5 started growing later than those in HGoRs 1-4. Interestingly, HGoR 5 merged with the adjacent HGoR 1 to form a polycrystalline onion. HGoRs 1-5 have distinct innermost graphene ribbon ring sizes, an indication that growth initiation of the innermost graphene ribbon ring was random and different for each HGoR. The ribbons appear more concentric than spiraling. Raman spectroscopy was used to characterize the HGoR shown in Figure 3.15c. Two points were selected from this HGoR, point A and point B. Figure 3.15d demonstrates that the middle region (point A) of this HGoR is monolayer and the blue graphene ribbon rings (point B) of this HGoR are multilayer\(^\text{13} \), indicating that the formation of HGoRs is based on the growth of few-layer graphene ribbons on or under monolayer graphene domains.

**Figure 3.17** TEM characterizations of the sample in Fig. 3.15e. (a) The high resolution TEM image of the graphene ribbon in Figure 3.15e, indicating the ribbon is tetralayer. (b) The overlaid image of two SAED patterns in Fig. 3.15e. The slight rotation of SAED patterns was due to the regional waviness of the graphene film, which was partially induced by the graphene ribbon.
As-produced HGoRs were also transferred onto TEM grids for further characterizations. Figure 3.15e represents a typical TEM image of a graphene ribbon grown under a suspended graphene film on the TEM grid. From Figure 3.15e, one can see the graphene ribbon has smooth edges and its width is \( \sim 200 \) nm. Counting the layers at the graphene ribbon’s edge indicates that it is tetralayer (Figure 3.17). The selected area electron diffraction (SAED) patterns of areas e1 and e2 display typical hexagonal crystalline structures of graphene, confirming graphene films exist at the both sides of the graphene ribbon. Interestingly, a slight rotation was observed when overlaying the SAED patterns of areas e1 and e2 (Figure 3.17b). This slight rotation of SAED patterns was sometimes observed in single-crystal graphene and is suggested to arise from the waviness of the graphene films. In this particular case, the regional waviness of the graphene film in Figure 3.15e could be exacerbated by the graphene ribbon as described below for the wrinkling.
Figure 3.18 Electrical properties of HGoRs. (a) Resistivity of HGoR as function of carrier density measured at room temperature. Inset is the optical image of the fabricated graphene onion Hall bar field effect transistor on SiO$_2$/Si substrate and the scale bar is 20 µm. (b) Plot of density-dependent field effect mobility of graphene onion versus carrier density from the device indicated in a. Calculated from the Drude model$^{18}$, at carrier density of $5\times10^{12}$ cm$^{-2}$, the mobility shows $\sim 4000$ cm$^2$V$^{-1}$s$^{-1}$ for the holes, which is indicative of the high quality of the HGoR. (c) A representative optical image of a fabricated six-terminal device on SiO$_2$/Si substrate. The numbers label the electrodes of the device, which is also indicated in I-V curves for d. The scale bar in c is 20 µm. (d) Two-terminal I-V characteristics of the indicated devices in (c) measured at room temperature. The two-terminal I-V curves are measured from two groups, group I and II. Group I is from diagonal sides (1-4, 2-5, 3-6), and group II is from neighboring sides (1-6, 2-3, 4-5). The observed overlapped I-V characteristics from both of the groups indicate that the electrical transport through each side of the HGoR is homogenous. This demonstrates the overall uniformity of the HGoRs. The conductance difference between the two groups is likely due to the difference in device structure.

The electrical transport properties were evaluated by fabricating multi-terminal devices on HGoRs transferred onto SiO$_2$/Si wafers. The measurements were performed at room temperature under a pressure of less than $10^{-5}$ Torr. A gating effect was observed on a Hall bar device and is shown in Figure 3.18a with a mobility of $\sim 4000$ cm$^2$V$^{-1}$s$^{-1}$ at a carrier density of $5\times10^{12}$ cm$^{-2}$ based on the Drude model$^{18}$ (Figure 3.18b), indicating the high quality of the HGoR. Additionally, 6 electrodes were patterned on the 6 edges of a
HGoR (Figure 3.18c), which demonstrate the overall uniformity of HGoRs (Figure 3.18d).

**Figure 3.19** H$_2$SO$_4$ intercalations on HGoRs. According to recent research$^{36}$, H$_2$SO$_4$ could intercalate into graphite to form stage 1 graphite intercalation compounds (G1) with the help of (NH$_4$)$_2$S$_2$O$_8$. When G1 forms, the Raman 2D peak will disappear and G peak will shift to ~1634 cm$^{-1}$ from ~1585 cm$^{-1}$. In this research, we use this technique to determine the location of the graphene ribbons. If graphene ribbons are on the top side of single-layer graphene domains (a), after intercalation, G1 will form. In this case, the 2D peak will disappear and the G peak will shift to ~1635 cm$^{-1}$. If graphene ribbons are on the bottom side of single-layer graphene domains (b), intercalation will not happen because graphene is impermeable$^{12}$. In this case, the top layer graphene would be doped by H$_2$SO$_4$. (c) The H$_2$SO$_4$ intercalation experiments on HGoRs demonstrates that the 2D peak did not disappear and the G peak did not shift after intercalation. A small G’ peak arose at ~1605 cm$^{-1}$, which was induced by the doping of the top layer graphene$^{36}$. Through the intercalation experiments, we could confirm that graphene ribbons reside on the bottom sides of single-layer graphene domains.
Whether the graphene ribbons reside on the top or the bottom of the hexagonal monolayer graphene domain is critical for understanding the growth mechanism. According to recent research, for bilayer graphene formation on Cu, the secondary layer grows from the Cu side\textsuperscript{27}. In this research, we use H\textsubscript{2}SO\textsubscript{4} intercalation experiments\textsuperscript{36} to further demonstrate that graphene ribbons also reside on the bottom of the hexagonal monolayer graphene domains in this special case (Figure 3.19). H\textsubscript{2}SO\textsubscript{4} treatment only doped the top layer hexagonal graphene, but did not intercalate between the nanoribbons on the underside.

\textbf{Figure 3.20} SEM and AFM characterizations of HGoRs transferred onto SiO\textsubscript{2} /Si wafers. (a) A typical SEM image of HGoRs, showing sharp wrinkles and hexagonal ribbons. (b) A typical SEM image of single-crystal hexagonal monolayer graphene domains,\textsuperscript{1} demonstrating a flat surface. (c) A typical AFM image of the HGoR, with the height scale
bar (right), demonstrating that the root square surface roughness is ~ 5 nm. The small particle in the middle is the seed that initialized the growth of this particular HGoR. (d) A typical AFM image of monolayer graphene. The root square surface roughness is ~ 1 nm.

Figure 3.20a is a typical SEM image of HGoRs transferred onto a SiO$_2$/Si wafer, showing that graphene ribbon rings have smooth edges and ~ 120° corners. Sharp graphene wrinkles were observed on the surface of the HGoRs. In contrast, a characteristic SEM image of single-crystal hexagonal monolayer graphene\textsuperscript{1} transferred onto a SiO$_2$/Si wafer is shown in Figure 3.20b, showing a much smoother surface than that of the HGoR in Figure 3.20a. This suggests that the graphene ribbons grow on the bottom face of the hexagonal monolayer graphene and makes the bottom sides wavy. Thus, many sharp wrinkles were produced during the transfer process.

Figure 3.21 AFM characterizations of HGoRs. The same AFM image (left) of the HGoR shown in Figure 3.20c and its height profile (right), demonstrating that the graphene ribbon is hexagonal and its thickness is ~ 3 nm. Due to the high flexibility of graphene,
the height profile could not be used to determine upon which side of the HGoR the graphene ribbons were located.

AFM was used to characterize the topology of the HGoRs transferred onto SiO₂/Si wafers (Figure 3.20c and Figure 3.21). Figure 3.20c provides one typical AFM image of the center of a HGoR, showing a graphene ribbon ring overlaid with several sharp graphene wrinkles. A 120°-angle indicates the hexagonal shape of the graphene ribbon ring. A section analysis for the same HGoR in Figure 3.21 demonstrates that the height of the graphene ribbon was ~ 3 nm, corresponding to the approximate thickness of tetralayer graphene. From Figure 3.21, we can see heights of graphene wrinkles in HGoRs as high as ~ 20 nm. Moreover, several graphene wrinkles crossed the edge of the graphene ribbons without showing sharp discontinuity, which suggests that graphene ribbons were on the bottom of the HGoRs. Figure 3.20c also shows that the root square surface roughness of this HGoR is ~ 5 nm. As a comparison, an AFM image of single-crystal monolayer graphene is shown in Figure 3.20d, indicating a relatively flat surface with its root square surface roughness at ~ 1 nm. In addition, a small particle was observed in the middle of the HGoR (Figure 3.20c and Figure 3.21), with its width ~ 150 nm and its height ~ 20 nm, which could be the seed that initialized the growth of this HGoR. Graphene ribbon segments with ~ 90° corners were also observed and might originate from the small perturbation of growth environments, such as in the temperature and the flow rate of CH₄, during the growth process. Beyond that suggestion, we do not presently have a rationale for the observation.
Figure 3.22 The proposed growth-mechanism of HGoRs. (a) A monolayer graphene domain forms on the surface of the Cu foil. (b) New graphene layers nucleate and grow on the edge of the monolayer graphene domain. (c) A 1D hexagonal graphene ribbon ring forms along the edge of the monolayer graphene domain. (d) A new edge was exposed because the monolayer graphene domain has faster growth than that of the underlayers. (e) Repeated growth leads to the final formation of one HGoR. (f) The scheme for the 3D layer-by-layer growth process. The new layer (2nd) is nucleated on the edge of the topmost (1st) layer. The blue dots represent the nucleation site, and the growth direction is indicated by arrows. TEM images of graphene ribbons in HGoRs, with different widths of (g) ~ 10 nm, (h) ~ 200 nm and (i) ~ 450 nm. i demonstrates that ribbon 2 nucleates and
grows on the edge of ribbon 1, providing direct evidence of the edge-nucleated 3D growth mechanism.

The growth of graphene on Cu has been shown to be the direct result of nucleation, growth and coalescence of graphene seeds, resulting in the formation of polycrystalline graphene films. However, the formation mechanism of HGoRs is distinct from the seed-induced 2D growth. Here we propose an edge-nucleated 3D growth mechanism to explain the formation of HGoRs, as described in Figure 3.22a-f. In the initial growth stage, a monolayer graphene domain nucleates on the Cu surface and gradually grows larger via continuously adding adjacent carbon adatoms (Figure 3.22a). However, at hydrogen rich growth environment, a new graphene layer could nucleate from the edge of a growing top layer, namely, edge nucleation (Figure 3.22b). The edge-nucleated graphene would evolve to a hexagonal ribbon (Figure 3.22c), as a result of kinetic factors, which will be discussed later as well. After edge nucleation, new graphene layers start layer-by-layer growth from the bottom side of the previous layer to form few-layer graphene ribbons (Figure 3.22f). The sizes of the innermost graphene ribbon rings vary (see Figures 3.15b-c), indicating that the time of activation of the edge of each monolayer graphene domain is random for each HGoR. Meanwhile, monolayer graphene top-layer domains keep growing when new graphene layers nucleate on their edges. Due to the more efficient contact with the adatom sources, monolayer graphene domains have higher growth rates than those of edge-nucleated new graphene layers, leading to the exposure of new graphene edges (Figure 3.22d). As the reaction time progresses, new graphene layers nucleate and grow again on the newly exposed edges to
form additional hexagonal graphene ribbon rings. After repeated exposure of new monolayer graphene domain edges, more graphene ribbons grow concentrically on the new edges to form HGoRs (Figure 3.22e-f).

**Figure 3.23** HGoRs on pretreated Cu. (a) Pretreatments of Cu surface through electrochemical polishing and high-pressure annealing. Through these two pretreatments, the Cu surface was flattened and there is a decrease in the graphene seed densities. (b) A typical SEM image of HGoRs on Cu, indicating the weak relation between Cu morphology and graphene ribbon nucleation, further demonstrating the hydrogenation-induced edge-nucleation growth mechanism.

The proposed edge-nucleated 3D growth mechanism was further confirmed by TEM characterizations. Figure 3.22g-i show TEM images of three graphene ribbons on suspended graphene films, which were randomly found in the HGoR samples with their widths ranging from 10 nm to 450 nm. Figure 3.22g shows that the width of the graphene ribbon is ~ 10 nm and it is monolayer, suggesting that this graphene ribbon has just nucleated and it is in the initial growth stage. The graphene ribbon shown in Figure
3.22 h has already grown to ~ 200 nm and it is tetralayer via counting its edge, meaning that more graphene layers would grow on the graphene ribbon via edge nucleation during the extended growth time. Interestingly, two stacked graphene ribbons, ribbon 1 and ribbon 2, were observed in Figure 3.22i, showing that ribbon 2 grows from the edge of ribbon 1 and providing direct evidence for the proposed edge-nucleated 3D growth mechanism. Meanwhile, Figure 3.23 shows a typical SEM image of HGoRs on the growth substrate, Cu, indicating a weak relation between graphene ribbons and the Cu surface, which excludes the possibility that graphene ribbons nucleate at the sites of the Cu surface features and further confirm the hydrogenation-induced edge-nucleation growth mechanism.

**Figure 3.24** Control experiments and nanoreactor model\(^{23}\) for the graphene nucleation. (a) A continuous monolayer graphene film was obtained after 120 min growth when the H\(_2\)
partial pressure was 8.4 Torr (E1 in Table 3.2). (b) A continuous HGoR film was made after 120 min growth when the H₂ partial pressure was 500 Torr (E2 in Table 3.2). (c) Energies (shown by bars) and atomic structures of C adatom adsorbed at the intact edge (I), near the intact edge (II), in the interior of graphene (III), near the hydrogenated sp² edge (IV), near the hydrogenated sp³ edge (V). The energies refer to that of a C atom in graphene on Cu (VI), which is set to zero. The graphene is represented by orange sticks, the Cu substrate by white spheres, the H in green, and the C adatoms in blue.

Why might HGoRs form using these particular conditions? To answer this question, nine experiments (E1-9) to investigate the effects of different growth parameters on the formation of HGoRs were performed and are summarized in Table 3.2. From Table 3.2, it can be seen that the growth time, temperature and the CH₄ flow rate have weak influences on the formation of HGoRs. The crucial parameter that determines the formation of HGoRs is the partial pressure of H₂. For example, Figure 3.24a shows that when the partial pressure of H₂ is ~ 8.4 Torr (E1), a uniform monolayer graphene film was obtained after 120 min growth. In contrast, a continuous HGoRs film was obtained while keeping other conditions the same and increasing the partial pressure of H₂ to ~ 500 Torr (E2, Figure 3.24b).

The role of H₂ in the formation of HGoRs can be explained by the nanoreactor model²³ shown in Figure 3.24c I-V, which represents the energies of a C adatom at different states, computed from first-principles. The energy of a C atom in graphene on Cu is set to zero (Figure 3.24c VI). The nucleation of a new graphene layer should start from a single C adatom. It can be adsorbed at the growth front, on the zigzag edge²³, near
the edge, or in the interior of the growing graphene sheet. At low H₂ pressure, the edge exposes pure sp² C with one dangling bond for each edge atom. During the growth, the majority of C atoms migrating to graphene will be adsorbed by the free edge (Figure 3.24c I), leaving very few C adatoms entering underneath graphene (Figure 3.24c II and III) as a result of their large energy difference of ~1.4 eV. In this case, the growth of graphene still remains 2D rather than forming a new graphene layer on the original layer. However, at high H₂ pressure, some of the edge C atoms can be hydrogenated. The hydrogenation of the growing edge could increase the probability of new graphene layer nucleation near the edge by increasing its affinity to C adatom. For example, Figure 3.24c II and V show that hydrogenation would decrease the energy of a C adatom near the edge by ~ 0.7 eV, which corresponds to an increase of absorption probability by a factor of $e^{\Delta E/kT} \sim 10^2$ (given a synthesis temperature ~1347 K). In this case, the enhanced absorption arises from the hydrogenation-induced sp³ state of an edge C atom, which forces the neighboring C into the same four coordination state, thereby facilitating the adsorption of the C adatom. Overall, it is shown that the hydrogenation of the graphene edge at high H₂ pressure could facilitate the nucleation of the new graphene layer near the growing edge of the previous layer. As the C accumulates around the edge, C clusters would be formed at the edge and a new graphene layer starts to grow. The growth rate is faster along the edge direction (i.e. growth front) of the upper layer than the normal direction. This behavior originates from kinetic factors: growth along the edge is fed with the accumulated C near the edge, while growth normal to the edge requires the C transport across the edges, where most C would be adsorbed by the outer edges before they arrive at the inner growth front. Therefore, the different C concentrations lead to
highly anisotropic growth rates and result in a ribbon-like shape. The spacing of the ribbons is thus determined by the relative rate of nucleation and growth normal to the edge. As more ribbons are formed during the growth, less C is available for inner ribbon growth due to the adsorption of the outer ribbon edges, thus impeding the inner ribbon growth, avoiding the formation of continuous few-layer graphene films.

**Figure 3.25** Making graphene nanoribbons from HGoRs. As described in a, graphene nanoribbons could be made from HGoRs by using Ar plasma\(^ {37} \) to remove the top layer graphene. (b) A typical TEM image of graphene nanoribbons made from HGoRs, with width at around 30 nm and displaying typical hexagonal crystalline structures of graphene. (c) A typical Raman spectrum of graphene nanoribbons after the removal of top-layer graphene. The intensity ratio of D to G is ~ 0.2, indicating the high-crystallinity of graphene nanoribbons and the D peak is likely from the ribbon edges.\(^ {37} \) The detailed conditions of Ar plasma etching are as follows: RIE power is 10 W; the chamber pressure is 40 mTorr; the flow rate of Ar is 2 sccm; the etching time is 10 s. The RIE model is an Oxford Plasma Lab 80 Plus RIE.
Table 3.2 Control experiments for exploring the key parameter which affect the formation of HGoRs.

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Different from general 2D graphene structures, HGoRs have demonstrated two special features due to their 3D structures with modulated thickness. The first feature is that HGoRs could be used to make graphene nanoribbons by using Ar plasma to remove
the top-layer single-crystal graphene domains (Figure 3.25). Furthermore, according to recent research\textsuperscript{9, 23}, single-crystal graphene domains made on Cu by CVD method show clean zigzag edges. Thus, through further optimizations, this edge-nucleated technique could allow the direct bottom-up growth of graphene nanoribbons with clean edges on Cu substrates, without needing lithography patterns of metal nanowires or organic synthesis procedures. Secondly, according to recent theoretical research\textsuperscript{38-39}, single-layer graphene is not suitable for Li storage because of the weak Li binding energy on single-layer graphene surface. As shown in Figure 3.26, according to first-principles calculations, HGoRs could be suitable for Li storage because Li binding energy in-between ribbon layers is 1.8 eV and Li binding energy at ribbon edges is 3.3 eV, higher than Li cohesive energy (1.6 eV). This feature, though interesting, would only be made practical with suitable scaling.

![Figure 3.26: HGoRs for lithium storage. According to recent theoretical research\textsuperscript{10}, single-layer graphene is not suitable for Li storage because of the weak Li binding energy on single-layer graphene. According to our first-principles calculations, graphene nano-onions will be a suitable material for Li storage because the Li binding energy in-between](image-url)
ribbon layer is 1.8 eV and Li binding energy at ribbon edges is 3.3 eV, higher than Li cohesive energy (1.6 eV). The cartoon shows the lithium storage in-between ribbon layers and at ribbon edges.

3.5. References


3.6. Experimental Contributions

Zheng Yan designed and conducted the experiments, discovered the procedures and performed the spectroscopic characterizations and analysis. Jian Lin performed FET device fabrications and measurements. Zhiwei Peng contributed to sample preparations, and TEM characterizations and analyses. Yuanyue Liu performed first-principle calculations. Long Ju conducted FT-IR measurements of bilayer graphene single crystals. Lei Li contributed to the electrochemical polishing of Cu foils. Yu Zhu and Elvira Pembroke contributed to AFM characterizations.
Chapter 4

Graphene and Carbon Nanotube Hybrid Materials

*This chapter was entirely copied from references 1 and 2.*

4.1. Introduction

Following the pioneering research by Geim and his colleagues\(^3\), graphene has been intensively studied over the last decade\(^4\)-\(^10\). Since many of the rapidly realizable targets have been reached \(^11\), researchers have now started to concentrate on graphene-like 2D atomic crystals\(^12\)-\(^16\) and graphene-based heterostructures\(^17\)-\(^26\). For example, two typical graphene analogues, h-BN and MoS\(_2\), have been successfully synthesized by CVD methods\(^12\)-\(^13\) and their unique optical and electronic properties were revealed \(^14\)-\(^16\). Recent technology advancements have enabled the successful synthesis of several
graphene-based heterostructures, such as graphene/h-BN\textsuperscript{17-20}, graphene/MoS\textsubscript{2}\textsuperscript{21}, graphene/graphane\textsuperscript{22} and graphene ribbons/CNTs\textsuperscript{23-24}.

1D CNTs\textsuperscript{25} and 2D graphene\textsuperscript{6-7} are among the most studied carbon allotropes in the last decade due to their excellent electronic, mechanical and optical properties. Accordingly, if CNTs and graphene can be in-situ grown together, in plane or vertically, new carbon materials with interesting properties would be afforded.

4.2. Rebar Graphene\textsuperscript{1}

In this section, we describe the successful fabrication of planar graphene/CNT hybrid sheets. Just as macroscopic reinforcing bar (rebar) can toughen materials, the planar graphene/CNT is a toughened form of 2D material, and it is termed here as “rebar graphene”. Using functionalized CNTs as raw materials on Cu foils Figure 4.1a schematically shows the process. Dodecyl-functionalized single wall carbon nanotubes (DF-SWCNTs) were used to demonstrate the synthesis of rebar graphene. The SWCNTs were HiPco-produced and purified\textsuperscript{26}, with diameters ranging from 0.8 nm to 1.2 nm, only slightly thicker than monolayer graphene. DF-SWCNT chloroform solutions were prepared using the method reported in ref. 27 (Figure 4.1b). The synthesis of rebar graphene was achieved as follows. The DF-SWCNT solutions were dispersed on the pretreated Cu foils\textsuperscript{28} using a spin-coater. Then, the Cu foils were loaded into the CVD furnace and annealed for 15 min at 1080 °C with the flow rate of H\textsubscript{2} at 50 sccm, the flow rate of Ar at 500 sccm, and the chamber pressure at 7 Torr. No exogenous carbon growth source was added. After annealing, the Cu foils were quickly removed from the hot region of the CVD chamber using a magnetic rod and then cooled to room temperature.
Figure 4.1 Synthesis and spectroscopic analysis of rebar graphene hybrid sheets. (a) The synthesis of rebar graphene sheets was achieved on Cu foils by heating functionalized CNTs in a H₂/Ar atmosphere at 1080 °C for 15 min. In this case, the as-grown graphene was polycrystalline. (b) A typical optical image of the DF-SWCNT chloroform solution and the related structural models. (c) Raman spectra showing that high-quality rebar graphene sheets were successfully synthesized by annealing DF-SWCNT-covered Cu foils. The blue curve is a typical Raman spectrum of monolayer graphene on Cu. The strong backgrounds of the Raman spectra are from the photoluminescence of Cu. (d-e) TEM and BF-STEM images indicating the formation of interconnected SWCNT networks in rebar graphene sheets. (f) An AR-STEM image showing the defect-free hexagonal lattice of monolayer graphene, indicating the high-quality monolayer nature of
Raman spectroscopy was used to investigate the formation of rebar graphene on Cu foils. The black curve in Figure 4.1c is a typical Raman spectrum of DF-SWCNTs deposited on Cu before annealing. The intensity ratio of the D band at ~1340 cm\(^{-1}\) to the G band at ~1590 cm\(^{-1}\) was ~ 0.5 and no obvious RBMs could be detected at ~ 250 cm\(^{-1}\), indicating that sp\(^2\) structures of SWCNTs were distorted due to the covalent bonds of the dodecyl groups\(^{27}\). The red curve in Figure 4.1c is a representative Raman spectrum of rebar graphene grown on Cu foils. RBMs appear at ~ 250 cm\(^{-1}\). During the annealing process, SWCNTs could self-heal as the dodecyl groups decomposed and became graphene on Cu, enabling the formation of rebar graphene heterostructures. The appearance of the RBMs in the annealed rebar graphene supports the suggestion of self-healing of SWCNTs. Moreover, in the 2D band, there is a shoulder at ~ 2698 cm\(^{-1}\), related to the position of the 2D band of monolayer graphene on Cu (the blue curve in Figure 4.1c), indicating the dominant monolayer nature of the graphene in the as-made rebar graphene sheets. This was further confirmed by TEM characterizations (\textit{vide infra}). In addition, the intensity ratio of the D to G bands decreased to less than 0.1, indicating the presence of few sp\(^3\) carbon atoms or defects\(^{28-29}\). The X-ray photoelectron spectroscopy (XPS) analysis is shown in Figure 4.2. After annealing, the position of the C 1s peak moves from 284.9 eV to 284.5 eV, with an asymmetric tailing toward high bonding energy; the FWHM decreased to ~ 0.8 eV from ~ 1.2 eV, indicating that the sp\(^3\)-carbon structures in DF-SWCNTs were transformed into sp\(^2\)-carbon-based graphitic structures\(^{30-31}\).
Figure 4.2 XPS spectra of C 1s peaks recorded from DF-SWCNTs on Cu foils before (black curve) and after (red curve) annealing. After annealing, the C 1s peak position moves from 284.9 eV to 284.5 eV with an asymmetric tailing toward high bonding energy and the FWHM contracted to ~0.8 eV from ~1.2 eV, indicating that sp³-related carbon structures in DF-SWCNTs were transformed into sp²-related graphitic carbon structures after annealing³⁰-³¹.

As-produced rebar graphene was transferred onto c-flat TEM grids (Protochips) for further characterization. Figure 4.1d and e are typical TEM and BF-STEM images, respectively, of suspended rebar graphene on TEM grids, indicating that individually dispersed SWCNTs formed interconnected networks on continuous graphene sheets to form a quasi-2D carbon material. More than 10 graphene locations in rebar graphene were investigated using STEM. Typical AR-STEM images are shown in Figure 4.1f, indicating defect-free hexagonal lattices of monolayer graphene. These AR-STEM
images, corroborating the above Raman analysis, further confirm the high-quality monolayer nature of the graphene in the rebar graphene. Second-layer graphene islands could be occasionally found and a typical TEM image is shown in Figure 4.3. Due to the different chemical reactivity of graphene and SWCNTs, the rebar graphene should have potential applications in sensors, electronics and biotechnology by the selective modification of graphene and SWCNTs.

Figure 4.3 A typical TEM image of rebar graphene sheets dotted with second-layer graphene islands. From recent research, the secondary graphene layer should nucleate and grow underneath the top layer of the graphene.

In recent research, the use of polymers such as PMMA and PDMS as support layers has become unavoidable for isolating CVD-based graphene, graphene-like 2D layered materials or in-plane graphene-based heterostructures from the catalyst metal substrates. Surface contaminations from polymer residues have long-been a
troublesome issue, limiting the analyses of the intrinsic properties of the carbon materials and retarding their applications in surface chemistry, ultrahigh-speed electronics and bio-devices. In this research, we found that the SWCNTs reinforced the rebar graphene, thus enabling polymer-free transfers onto target substrates such as TEM grids and SiO$_2$/Si wafers. Figure 4.4a is a representative photograph of one rebar graphene sheet, floating on water containing 1% butanol by volume. This free-standing rebar graphene was ~ 1 cm × 1 cm, not pre-coated with any polymer and was ready to be transferred onto other substrates for further research. The grown catalyst substrate, Cu foil, was already etched away using ammonium persulfate-based etchant solution$^1$. Here, butanol was used to lower the surface tension of the water. The butanol residue could be readily removed by vacuum treatment after transferring the rebar graphene sheets onto target substrates. In a control experiment, we found that without the polymer pre-coating, both conventional CVD polycrystalline graphene films and millimeter-sized single-crystal graphene broke into small pieces using the same etchant containing butanol when the substrates were etched away. This underscores that only the rebar graphene hybrid structure can endure on water without destruction. Additionally, TEM images in Figure 4.4b demonstrate that the non-polymer transferred rebar graphene sheet had a cleaner surface than that of the PMMA-assisted transferred rebar graphene. Polymer-free transfers could facilitate the uses of rebar graphene in transparent electrode technologies, chemical modification, sensors and bio-devices where trace impurities cause use limitations.

We used STEM to explore the reinforcement effects of SWCNTs in rebar graphene transferred onto TEM grids using the polymer-free transfer method$^1$. 
Nanometer-sized cracks could occasionally be found in the suspended rebar graphene sheets when butanol was not used to lower the water surface tension. Figure 4.4c and d show typical ADF-STEM images of the cracks. From the ADF-STEM images, it is apparent that several individually dispersed SWCNTs straddle the crack, restraining its further extension. Figure 4.4e shows an AR-STEM image of the region of the suspended SWCNT in Figure 4.4d indicated by the yellow section, showing a clear moiré pattern with a periodicity at ~ 0.8 nm. This indicates that the SWCNT is chiral and can be represented by a pair of indices (n, m)\(^{34}\). By simulating TEM images of SWCNTs with different (n, m) indices (Figure 4.4f-g), we concluded that a SWCNT with indices n = 10 and m = 4 (Figure 4.4f) best matched the experimental image. The diameter could be calculated\(^{34}\), which was ~ 0.978 nm. However, the measured diameter of this SWCNT by STEM was ~ 0.864 nm. This diameter shrinkage is evidence that the SWCNT is under tensile stress, demonstrating how SWCNTs could reinforce and strengthen rebar graphene sheets and enable their polymer-free transfers.

An interesting question is: How are graphene and SWCNTs connected in the rebar graphene sheets? The graphene-SWCNT interfaces were investigated using STEM; two types of graphene-SWCNT connections, π-π stacking and covalent bonds, were revealed (Figure 4.5 and Figure 4.6). Figure 4.5a is a typical BF-STEM image of π-π stacked graphene-SWCNT interfaces; the structural model is shown in Figure 4.6a. From Figure 4.5a, it is apparent that there is no buckling or distortion around the graphene-SWCNT interface, indicating that, in this case, the graphene sheet and the SWCNT are intimately combined together via π-π stacking rather than sp\(^2\) or sp\(^3\) bonds. The FFT patterns of a1 and a2 show the typical hexagonal crystalline structures of monolayer
graphene and demonstrate the same rotation angles, meaning the graphene lying on both sides (a1 and a2) of this SWCNT belong to the same monolayer graphene grain. This can be understood if we assume that the SWCNT in this area has a sp$^2$-carbon bonded graphitic structure without dangling bonds or sp$^3$-carbon related defects, thus the graphene grew beneath it to form the $\pi$-$\pi$ stacked interface with the SWCNT during the annealing process. Additionally, Figure 4.6 b and c indicate a 6000 count increment in the intensity profile from the graphene region to the SWCNT region, equivalent to the intensity of two graphene layers (Figure 4.7), which further demonstrates that the graphene and the SWCNT are overlapped via $\pi$-$\pi$ stacking rather than covalent welding. Both images were acquired under the same conditions to ensure the number of counts is the same for both.
Figure 4.4 CNT reinforcement in rebar graphene sheets. (a) A free-standing rebar graphene sheet, highlighted in yellow at the corners, floating on water with 1% butanol by volume. (b) TEM images indicating that a conventional PMMA-assisted transferred rebar graphene sheet is dotted with polymer residues (left) and the polymer-free transferred rebar graphene sheet that has a clean surface (right). (c-d) ADF-STEM images of rebar graphene suspended on TEM grids, demonstrating that SWCNTs straddle cracks and work to strengthen the rebar graphene sheet. This sample came from a water float that did not contain 1% butanol. The bright contrast in the graphene region originates from hydrocarbon contamination absorbed from the air. (e) An AR-STEM image of the region of the SWCNT indicated by the yellow region in (d), showing a clear moiré pattern with a periodicity at ~0.8 nm. (f-g) Structural models and simulated TEM images of the chiral SWCNT (10, 4) and the chiral SWCNT (10, 3).

Figure 4.5 Graphene-SWCNT interfaces in rebar graphene sheets. (a) FFT patterns (a1 and a2) and the BF-STEM image of one π-π stacked graphene-SWCNT interface. The
STEM-derived intensity profile of similar structures (Figure 4.6 and 4.7) further demonstrates the graphene-SWCNT overlapping structures. (b) The BF-STEM image of a covalently bonded graphene-SWCNT interface. (c) The high-resolution image after applying a filter of the FFT in the raw BF-STEM image of the yellow selected area in (b). (d) The scheme for graphene growth from the edges of a partially unzipped SWCNT. This would likely reside on the bottom face of the SWCNT that is contact with the Cu.

Figure 4.6 The intensity analysis on the π-π stacked graphene-SWCNT interface. (a) The structural model of the π-π stacked graphene-SWCNT interface. (b) The ADF-STEM image of one π-π stacked graphene-SWCNT interface. (c) The STEM-derived intensity profile of the indicated area in (b). There is a 6000 count increment in the intensity profile.
from the graphene region to the SWCNT region, equivalent to the intensity of two graphene layers (Figure 4.7), demonstrating the graphene-SWCNT overlapping structure.

Figure 4.7 The intensity analysis of suspended monolayer graphene. (a) The ADF-STEM image of one suspended monolayer graphene area. (b) The STEM-derived intensity profile of the indicated suspended monolayer graphene in (a), showing the intensity of monolayer graphene is around 3000 counts.

Figure 4.5b-c are typical BF-STEM images of covalent bonding in the rebar graphene. From Figure 4.5b, as indicated by the area in the yellow square, one SWCNT
wall disappeared where the graphene and SWCNT were bonded together in-plane. Figure 4.5c is a high resolution STEM image of the region indicated by the yellow square in Figure 4.5b, evidence that graphene and SWCNT covalently bonded via aromatic rings. The proposed formation mechanism of the covalent bonded interface is as follows: (1) SWCNTs could be partially unzipped due to the etching by the Cu foil at high temperature (Figure 4.5b and c); (2) the exposed SWCNT edges could capture active carbons for graphene growth (Figure 4.5d); (3) graphene and SWCNTs are covalently welded together by aromatic rings in the partially unzipped SWCNT regions (Figure 4.5b and c). In addition, based on the Raman spectrum in Figure 4.1c, RBMs were detected in the rebar graphene sheets; the intensity ratio of the D to G bands dropped to < 0.1, demonstrating the weak etching effects of Cu on SWCNTs because of the low solubility of carbon in Cu (<0.001 atom % at 1000 °C)\(^{35}\). Thus, π-π stacked graphene-SWCNT interfaces dominated in rebar graphene sheets synthesized on Cu foils, but there are sufficient amounts of covalent regions to render a noticeable toughening of the rebar graphene over typical graphene films.

The electrical transport properties of rebar graphene sheets were evaluated by fabricating Hall bar field effect transistors on SiO\(_2\) (100 nm)/Si substrates. The measurements were performed at room temperature at a pressure of less than 10\(^{-5}\) Torr. The inset of Figure 4.8a provides a typical optical image of the as-made Hall bar device based on rebar graphene sheets; its related electrical behaviors are shown in Figure 4.8a-b. From Figure 4.8a, a gating effect was observed on this Hall bar device, with the on/off ratio of ~ 11. Moreover, Figure 4.8a indicates that the as-made device shows typical ambipolar behavior, meaning that graphene dominated the electronic properties in rebar
graphene sheets. The calculated carrier (hole) mobility for the device in the inset of Figure 4.8a was $\sim 2200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at a carrier density of $5 \times 10^{12} \text{ cm}^{-2}$ based on the Drude model$^{36}$ (Figure 4.8b). More than five rebar graphene based Hall bar devices were fabricated on SiO$_2$/Si substrates. All of them had typical ambipolar behavior, with the carrier (hole) mobilities ranging from $\sim 1500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $\sim 2200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at a carrier density of $5 \times 10^{12} \text{ cm}^{-2}$. The mobilities are comparable to those of CVD polycrystalline graphene$^{8-9}$, indicating the high quality of the rebar graphene sheets.

![Graphene electrical properties](image)

**Figure 4.8** Electrical properties and control growth experiments of rebar graphene on Cu- and Ni-foils. (a) Resistivity as function of carrier density measured at room temperature. The inset is an optical image of the fabricated rebar graphene Hall bar field effect transistor on a SiO$_2$/Si substrate; the scale bar is 20 $\mu$m. (b) Plot of density-dependent field effect mobility of rebar graphene vs. carrier density from the device indicated in the
inset of (a). (c) Raman spectra indicating the weak etching ability of Cu on SWCNTs at 1080 °C for 15 min and 3 h. (d) Raman spectra demonstrating the high etching ability of Ni on SWCNTs. Here, DF-SWCNTs were used as raw materials and deposited on surfaces of Cu- and Ni- foils using a spin-coater.

Cu and Ni are the most widely used catalyst metals for the growth of graphene and graphene-based heterostructures. The influence of these two catalyst substrates on the rebar graphene growth was investigated. From Figure 4.8c, it is apparent that extending the annealing time has little effect on the synthesis of rebar graphene sheets on Cu foils. Even after annealing DF-SWCNTs on Cu for 3 h at 1080 °C, RBMs were still clearly detected from the as-made hybrid material. In contrast, Figure 4.8d indicates that after annealing DF-SWCNTs on Ni foils for 3 min at 1080 °C and then cooling the sample to room temperature, no carbon-related structures could be detected by Raman spectroscopy. This is because: (1) Ni has a high etching ability on SWCNTs because of its high carbon solubility (~1.3 atom % at 1000 °C). During the annealing process, the DF-SWCNTs were completely dissolved by the Ni. Thus, no SWCNTs could be detected by Raman spectroscopy after annealing. (2) The carbon supplied by DF-SWCNTs was not enough for the precipitation growth of graphene on the Ni foil during the cooling process. Thus, graphene signals were absent after annealing. Considering the low etching ability of Cu and the high etching ability of Ni on SWCNTs, the graphene-CNT interface composition might be controlled in the future using properly designed Ni-Cu alloys as the growth substrates.
Figure 4.9 Rebar graphene based transparent conductive electrodes. UV-vis spectra and sheet resistances of rebar graphene sheets derived from (a) DF-SWCNTs, (b) arylsulfonated-SWCNTs and (c) Pluronic 127 wrapped MWCNTs on glass slides. The CNTs used in (c) were M-grade MWCNTs (NanoTechLabs, Inc.). On the right bottom of (a-c) are photos of rebar graphene films of $\sim 2\, \text{cm} \times 2\, \text{cm}$ in sizes on 1 mm thick glass slides; the rebar graphene sheets are labeled at the corners with highlights. On the left bottoms of (a) and (b) are the structural models of DF-SWCNTs and arylsulfonated-
SWCNTs. For arylsulfonated-SWCNTs, the functional groups are 2-tert-butylbenzene sulfonic acid. (d) Typical TEM images of MWCNTs, indicating that they are ~ 11-walled and the diameters are ~ 12 nm. (e) Photographs of bent rebar graphene sheets transferred onto polyethylene terephthalate (PET) substrates. In e, rebar graphene sheets were derived from Pluronic 127 wrapped MWCNTs. The sheet resistance was ~ 600 Ω/□. In this section, polymer-assisted transfer method\(^{27}\) was still used to transfer large-sized rebar graphene sheets (≈ 2 cm × 2 cm) onto the target substrates.

One potential application of graphene and CNTs is as a flexible transparent conductive electrodes because of their high optical transmittance, conductivity and flexibility\(^{8, 38-39}\). DF-SWCNTs, arylsulfonated-SWCNTs and Pluronic 127 wrapped multi-walled CNTs (M-grade from NanoTechLabs, Inc.) were used as raw materials to make rebar graphene sheets as all-carbon flexible transparent conductive electrodes (see Figure 4.9 for details). The optimal growth conditions were used to fabricate the electrodes. The growth conditions are described as follows: the CNTs-coated Cu foil was loaded into the CVD system and the reaction chamber was evacuated to ~ 1 mT by completely opening the vacuum valve. The temperature was increased to 1080 °C, and then 500 sccm of H\(_2\) were introduced into the system for 10 min. After this, the Cu foil was moved into the hot region of the furnace by a magnetic rod and annealed for 90 s. After annealing, 0.7 sccm of CH\(_4\) was introduced into the reaction chamber for 15 min. After the growth, the CH\(_4\) flow was turned off and the Cu foil was quickly removed from the hot region using a magnetic rod and permitted to cool to the room temperature.
The rebar graphene sheets derived from Pluronic 127 wrapped multi-walled CNTs had ~ 95.8% transmittance at 550 nm wavelength with a sheet resistance of ~ 600 Ω/□, indicating better performance than that of stacked CVD bilayer graphene \(^{39}\) (a sheet resistance of ~ 900 Ω/□ with a transmittance of ~ 95.2% at 550 nm wavelength). Improvements could be expected using predominantly metallic or long SWCNTs as raw materials or applying chemical doping \(^{38}\). In addition, if additives could be further introduced into the rebar graphene sheet matrix during the annealing process, such as nitrogen and borane doping, the doped hybrid material could have potential applications in fuel cells and lithium batteries \(^{40-41}\).

4.3. Metal-Graphene-Carbon Nanotube Multifunctional Hybrids\(^{2}\)

In recent research, the seamless growth of CNTs from planar graphene sheets was demonstrated \(^{42}\). In this section, graphene was grown directly on porous nickel films, followed by the growth of controlled lengths of vertical CNT forests that seamlessly emanate from the graphene surface. The metal-graphene-CNT structure is used to directly fabricate field-emitter devices and double-layer capacitors. The three dimensional nanostructured hybrid materials, with better interfacial contacts and volume utilization, can stimulate the development of several energy-efficient technologies.

Figure 4.10 shows the procedures for the growth of CNT-graphene hybrids on porous nickel substrates. The porous nickel substrate used in this research is a foam-like 1.2-mm-thick nickel film, a widely used commercial battery material (Figure 4.11). Although the entire procedure can be done using a single layer of graphene, in the optimal procedure here for devices, few-layer graphene was grown on the porous nickel
films using the CVD method. The obtained graphene were characterized by Raman spectroscopy and TEM (Figure 4.12), demonstrating the few-layered structure and the high crystallinity of the graphene. A 1.5 nm-thick layer of catalytic Fe was deposited on the surface of the graphene using e-beam evaporation, followed by the deposition of a 10 nm-thick Al₂O₃ as the buffer layer to ensure the catalytic activity of the Fe. Ethylene was used as the carbon source to grow CNTs at 750 °C. Water was also introduced during the CNT-growth process to remove amorphous carbon. However, using this protocol, the CNT forests raise the Fe/Al₂O₃ catalyst layer during the growth process while the vertically grown CNTs connect to the graphene layer through covalent bonds, leading to seamless high-quality CNT-graphene-metal interfaces. The Fe/Al₂O₃ catalyst layer was deposited on both sides of the porous nickel films to increase the amount of CNTs attached to the substrates.

**Figure 4.10** Scheme for the synthesis of CNT forests on graphene-porous nickel. (a) The porous nickel substrate. (b) Few-layer graphene is formed on the porous nickel by a CVD
method. (c) Fe and Al₂O₃ are sequentially deposited on the graphene using ebeam evaporation. (d) A CNT forest is directly grown from the graphene surface while lifting the Fe/Al₂O₃ catalyst layer.

**Figure 4.11** Images of the porous nickel films. (a) The SEM image of the porous nickel. (b) Photograph of the starting porous nickel sheet.
**Figure 4.12** Raman and TEM characterizations of graphene grown on porous nickel. (a) Raman spectra of the graphene (excitation wavelength 633 nm). No D peak was observed, indicating the high quality of obtained graphene\(^{29}\). The intensity ratio of G to 2D peak is \(\sim 1.6\), suggesting the graphene is few-layered\(^{29}\). (b) Hexagonal SAED pattern of the graphene, suggesting the high crystallinity of obtained graphene. (c-d) HR-TEM images of graphene edges. The obtained graphene was 3 or 4 layers thick by counting randomly exposed edges, in concert with Raman spectroscopy shown in (a).

Figure 4.13a shows optical images of porous nickel, graphene-porous nickel and CNT-graphene-porous nickel, respectively. SEM images of CNTs grown on graphene-porous nickel are shown in Figure 4.13b-e. Figure 4.13b and c are the overviews of the as-grown three-dimensional material, demonstrating an interconnected network structure. The surface region of Figure 4.13d is the Fe/Al\(_2\)O\(_3\) catalyst layer that was lifted off during the growth of CNTs. Figure 4.13e shows the CNT-graphene interface, which is also an enlarged view of the CNT forests. The HR-TEM image in Figure 4.13f indicates that most of the as-grown CNTs are single-walled, double-walled or triple-walled, and the diameters are between 3 nm and 7 nm. The high degree of crystallinity of the CNTs was verified by Raman spectroscopy in Figure 4.13g, showing a strong G peak at \(\sim 1580\ \text{cm}^{-1}\) and a 2D peak at \(\sim 2620\ \text{cm}^{-1}\). The G/D ratio of the CNTs is \(\sim 3:1\), suggesting the presence of few defects. The defects in CNTs are mainly sp\(^3\) carbon atoms, which were introduced during the growth process and can be evaluated by the D peak\(^{28}\). The G peak arises from sp\(^2\) carbon atoms in CNTs. Thus, comparing the ratio of intensities between the graphitic G peak and the defect-induced D peak is an efficient way to evaluate the
quality of carbon nanotubes. The strong RBM signals in the inset of Figure 4.13g suggest that the diameters of the CNTs are small, corresponding to the HR-TEM observation.

Figure 4.13 Characterization of CNT-graphene hybrids synthesized on porous nickel films. (a) Photographs of porous nickel, graphene-porous nickel and CNT-graphene-porous nickel (from left to right). (b-e) SEM images of the same samples. The samples
were synthesized using 1.5 nm Fe/10 nm Al₂O₃ as the catalyst and the growth time was 10 min. (d) The side view of the CNT-catalyst interface, showing that the catalyst layer was raised up during the growth of CNTs. (e) The side view of CNT-graphene interface. (f) TEM images of the CNTs indicating the number of tube layers. (g) Raman spectra of the obtained CNTs under 633 nm excitation wavelengths. Inset: the spectra of the RBMs. (h-j) The SEM images of obtained CNTs at different growth times. The samples were grown using 1.5 nm Fe/10 nm Al₂O₃ as the catalyst. The length of CNTs can be adjusted from ~3 μm to ~250 μm by changing growth time.

**Figure 4.14** Images of CNT-graphene hybrids after etching porous nickel films. (a) A photograph of self-supporting CNT-graphene after etching the porous nickel. (b-d) The SEM images of CNT-graphene after etching the porous nickel. The SEM images show
that CNTs bundle together after etching the nickel due to a solvent-induced bundling effect. The growth time of the sample shown in (a-d) was 10 min using 1.5 nm Fe /10 nm Al₂O₃ as the catalyst.

**Figure 4.15** Electronic properties of CNT-graphene hybrids after etching porous nickel. (a) Two experiments performed to measure the I-V responses of CNT-graphene hybrids. (b) The I-V curves of CNT-graphene in the horizontal direction and the vertical direction. The size of the device used for I is 20 × 20 × 0.8 mm and the size of device used for II is 1.5 × 1.5 × 0.8 mm. The two devices are made by 60-min-growth CNTs on graphene-porous nickel.

The 3D hybrid material is hydrophobic; the measured water contact angle was ~135°. After etching and removal of the porous nickel films using a mixture of HCl and FeCl₃, free-standing 3D CNT-graphene networks were obtained (Figure 4.14). The thickness of the sample decreased to ~0.8 mm from ~1.2 mm after the etching step. The
CNTs bundled together due to the solvent-induced bundling effect (Figure 4.14b-d) \(^4\). Throughout the etching process, CNTs were not washed away. This further confirmed that the CNTs were chemically attached to graphene. Ohmic contact at the junction of the CNTs and graphene was observed\(^4\), suggesting a high-quality CNT-graphene interface. Figure 4.15 shows that CNT-graphene hybrids exhibit isotropic electrical properties. This identical electrical response from CNTs or graphene to the metal electrode indicates isotropic electrical properties.

![Figure 4.15](image)

**Figure 4.15** Effects of the thickness of catalysts and graphene on the CNT growth. In (a-c), the effects of the thickness of catalysts were studied. In these experiments, graphene was grown on porous nickel in advance. (a) The SEM image of the obtained sample using 0.5 nm Fe/3 nm Al\(_2\)O\(_3\) as the catalyst for 5 min growth at 750 °C. In this case, CNTs
grew poorly due to the rapid deactivation of the catalyst. (b) The SEM image of the sample using 1 nm Fe/3 nm Al₂O₃ as the catalyst for 5 min growth at 750 °C. In this case, CNTs covered almost all the graphene surface. However, CNTs were easily bent due to the cracking of the catalyst layer. (c) CNTs were aligned well even after 10 min growth at 750 °C when a thicker catalyst layer, 1.5 nm Fe/10 nm Al₂O₃, was used. (d) CNTs did not grow well when directly on the porous nickel without the previous coverage of graphene layer. In this experiment, 1 nm Fe/10 nm Al₂O₃ was used as the catalyst and the growth time was 10 min.

The effects of the catalyst thickness and graphene on CNTs growth were studied. For a convenient comparison, similar growth conditions were used to prepare the four samples shown in Figure 4.16a-d. Figure 4.16a-c are the SEM images of the samples grown on graphene-porous nickel films, separately using 0.5 nm Fe/3 nm Al₂O₃, 1 nm Fe/3 nm Al₂O₃ and 1.5 nm Fe/10 nm Al₂O₃ as the catalysts. Few CNTs were observed when the 0.5-nm-thick Fe layer was used as the catalyst (Figure 4.16a). This is due to the rapid deactivation of the catalyst layer. The problem was solved by increasing the thickness of the Fe layer from 0.5 nm to 1 nm (Figure 4.16b). However, when using 1 nm-thick Fe as the catalyst, CNTs became bent during the growth process due to the instability of the Al₂O₃ catalyst layer. For well-aligned growth of CNTs on graphene-porous nickel, the optimized catalyst thickness was 1.5- nm-thick Fe with 10-nm-thick Al₂O₃ (Figure 4.16c). Figure S5d shows that it was difficult to grow the CNTs directly on the porous nickel without the graphene layer. Without graphene as the buffer layer on the nickel, the thin catalyst layer would likely deactivate due to alloying with nickel.
Figure 4.17 Images of obtained CNTs at different growth time. (a) The SEM image of CNTs obtained at 1 min growth. (b) The enlarged SEM image of the blue circled region in (a). (c-d) The SEM images of samples grown for 30 min growth. (e-f) The SEM images of samples obtained at 60 min growth and 120 min growth, respectively.

For some applications, the properties of the devices are closely related to the length of the CNTs. In this research, the CNT length can be controllably adjusted from 3 μm to 250 μm by changing the growth time (Figure 4.13h-j and Figure 4.17).
4.13h-j show the SEM images of the obtained samples after separately growing for 1 min, 5 min or 10 min using 1.5 nm Fe/10 nm Al₂O₃ as the catalysts. Figure 4.13h and Figure 4.17a-b show that the CNTs rapidly grow to ~3 μm in 1 min. After 5 min and 10 min growth, the lengths of the CNTs were ~15 μm and ~35 μm, respectively (Figure 4.13i and j). If the growth time was further extended to 30 min, ~120 μm-length CNTs were obtained (Figure 4.17c-d). However, during a 30 min growth, the catalyst layer broke and CNTs were bent due to losing support from the Al₂O₃ layer. After 60 min growth, the catalyst was still active and the length of obtained CNTs was ~250 μm (Figure 4.17e). If the growth time was extended to 120 min, no obvious change in CNTs length was observed and much amorphous carbon was produced (Figure 4.17f). Apparently after 60 min of growth, the catalyst layer lost activity and the carbon sources were mainly transformed into amorphous carbon.

CNTs are known for their applications in field-emission devices⁴⁵-⁴⁶. In this research, we used the CNT-graphene-porous nickel to fabricate field-emission devices without needing any etching or post-transfer processing. As shown in Figure 4.18a, porous nickel serves as the cathode, graphene serves as the linking surface, CNTs are the field-emission emitters and ITO-coated glass is used as the anode. Figure 4.18b shows the test setup and the inset in Figure 4.18b is an optical image of a field-emission device. Figure 4.18c presents the emission current density as a function of applied voltage in three different devices, S1 (CNT, 60 min), S2 (CNT, 5 min) and S3 (CNT, 2 min), which are, respectively, made using CNTs obtained after 60 min, 5 min and 2 min of growth. The related lengths of CNTs are ~250 μm, ~15 μm and ~7 μm. From Figure 4.18c, both the emission current density and the turn-on field are strongly affected by CNT lengths.
The device fabricated using 60 min of CNT growth had the best field emission properties, the lowest turn-on field and the highest emission current. The turn-on field for S1 (CNT, 60 min), measured at a current density of 0.01 mA/cm², is 0.26 V/μm, one of the lowest values reported⁴⁵-⁴⁶. For the same device, the current density at a field of 0.87 V/μm is 12.67 mA/cm², one of the highest reported values, to date⁴⁵-⁴⁶.

Figure 4.18 Field-emission characteristics of the CNT-graphene-porous nickel electrodes. (a) Schematic illustration of the field-emission setup. (b) The test setup for the field-
emission devices. The inset in the upper right is the photograph of an emitting device. (c) Variation of the emission current density as a function of the applied field for S1 (CNT, 60 min), S2 (CNT, 5 min) and S3 (CNT, 2 min). The inset is the enlarged data, from which the turn-on fields are determined at the current density of 0.01 mA/cm$^2$. (d) Fowler-Nordheim plots obtained for S1 (CNT, 60 min), S2 (CNT, 5 min) and S3 (CNT, 2 min).

Fowler-Nordheim plots are shown in Figure 4.18d. At least two distinct slopes are observed in the plots, often seen in carbon nanotubes and attributed to a non-metal-like emission process from discrete energy states. The corresponding field-enhancement factors ($\beta$) were estimated for high operation conditions from Fowler-Nordheim plots (Figure 4.18d), ranging from 2700 to 7200.

**Figure 4.19** Field-emission characteristics of the CNT-graphene-porous nickel, graphene-porous nickel and porous nickel electrodes. (a) Variation of the emission current density as a function of the applied field for porous nickel (blank curve), graphene-porous nickel (red curve) and CNT-graphene-porous nickel (blue curve)
electrodes. (b) The enlarged figure of (a). From (b), the turn-on voltages of porous nickel, graphene-porous nickel and CNT-graphene-porous nickel were determined, which are, respectively, 3.26 V/μm, 1.91 V/μm and 1.14 V/μm at the current density of 0.01 mA/cm².

The emission properties are also related to the number of CNTs attached to the porous nickel through the graphene. When CNTs were grown on only one side of the porous nickel instead of both sides, the as-made device demonstrated poorer field-emission properties (sample CNT-graphene-porous nickel, blue curves in Figure 4.19) as compared to those of the device made by growing CNTs on both sides of the porous nickel (sample S2, CNT, 5 min, red curves in Figure 4.18c). The growth conditions for these two samples were the same. Surprisingly, pristine porous nickel also showed some field-emission responses (black curves in Figure 4.19). Nickel nanowires are known for their field-emission properties⁴⁷; hence, porous nickel surface protrusions may be the source of the field emission. After coating the porous nickel with graphene, better field-emission properties were observed (red curves in Figure 4.19). However, the contributions of the porous nickel and the graphene to the field-emission response of CNT-graphene-porous nickel samples are almost negligible in the applied field regime of the field-emission test here. Hence the CNT-graphene-metal hybrid is indeed unique in its functionality.

To demonstrate the high-quality of the CNT-graphene-porous nickel contact interface, the capacitive properties were measured (Figure 4.20). Porous nickel was used
as the current collector to fabricate an EDLC without the need of any post-transfer or post-etching processes. Aqueous KOH (6 M) was used as the electrolyte in the measurements. Figure 4.20 demonstrates that the EDLC made by this CNT-graphene-porous nickel structure exhibited excellent double-layer electrochemical performance and high-rate performance. Figure 4.20a shows the CVs of EDLC at different scan rates. With an increase in scan rate, the current response increased accordingly, without any significant changes in the shape of the CV curve, indicating a good rate performance. The rectangular and symmetric shape of the CVs was also observed at high scan rates of 500 mV/s, supporting the suggestion of low contact resistance for the CNT-graphene-porous nickel interface.
Figure 4.20 Double-layer capacitor performances of the devices fabricated using CNT-graphene-porous nickel. (a) CV curves for different scan rates. The rectangular shapes indicate the capacitive behavior. (b) Nyquist plot, showing the imaginary part versus the real part of impedance. Inset shows the data at high frequency ranges. (c) Galvanostatic charge/discharge curves of CNT-graphene-porous nickel based double-layer capacitor measured in the 6 M KOH electrolyte under different constant currents. (d) Various specific capacitance versus discharging current density. The device was made by 2 min-growth CNTs on graphene-porous nickel.

Figure 4.20b is the Nyquist plot based on a frequency response analysis of the frequency range from 1 MHz to 10 mHz. The Nyquist plot is almost a vertical line, indicating a nearly ideal capacitive behavior of the EDLC. The inset in Figure 4.20b is the magnified data in the high-frequency range and the obvious transition between the RC semicircle and the migration of electrolyte corresponds to a resistance of 1.25 Ω. Figure 4c shows the Galvanostatic charge-discharge curves at four different current densities. The specific capacitance was calculated from the discharge curves with values of 104, 99, 101, and 100 F/g obtained at current densities of 0.2, 0.33, 0.67 and 1.00 A/g, respectively (Figure 4.20d). The almost constant specific capacitance as the scan rate increased up to 1.00 A/g indicates the high diffusion conductivity of the active material and the electrolyte. Meanwhile, the calculated value is about five times higher than that of the EDLC fabricated by directly growing CNTs on Inconel without graphene as the linking surface and is also comparable with the best recently reported values of the EDLC made with graphene oxide\textsuperscript{48-50}. 
4.4. References


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### 4.5. Experimental Contributions

Zheng Yan designed and conducted the experiments, discovered the procedures and performed the spectroscopic characterizations and analyses. Zhiwei Peng contributed to sample preparations and performed TEM characterizations and analyses. Jian Lin performed FET device fabrications and measurements. Gilberto Casillas performed STEM characterizations and analysis. Lulu Ma and Shubin Yang conducted fabrications and measurements of supercapacitors. Indranil Lahiri contributed to the fabrications and measurements of field emission emitters. Changsheng Xiang prepared carbon nanotube solutions, and performed spectroscopic characterizations and analyses. Abdul-Rahman O. Raji performed TEM characterizations of MWCNTs.
Chapter 5

Chemical Modulation of Graphene Electronics

*This chapter was entirely copied from references 1 and 2.*

5.1. Introduction

Since its first isolation in 2004, graphene, one atomic layer of graphite, has attracted enormous attention for its excellent electronic properties\(^3\)-\(^6\). In particular, its extremely high mobility and potential for use in top-down fabrication of electronic devices has made it a promising candidate for high frequency transistors\(^7\)-\(^8\). Pristine graphene exhibits a standard ambipolar behavior with a zero neutrality point in FETs on standard SiO\(_2\) substrates, and the ambipolar properties limit its electronics applications. In this regard, many efforts have been made to modify the electronic structure of graphene to make n- and p-type FETs\(^9\)-\(^19\). Present doping methods either suppress
graphene’s mobility or are not stable long-term\textsuperscript{11-19}. Thereafter, for both pristine graphene and doped graphene, different methods to produce high quality, monolayer graphene films have been disclosed\textsuperscript{19-21}.

Similar to the use of silicon in the semiconductor industry, doping and controlling the electrical structure of graphene has become important if it is to be used in place of or in addition to silicon. Direct substitution with boron and nitrogen in the graphene lattice can lead to p- and n-type doping, respectively\textsuperscript{16-19}. However heteroatom substitutions break the symmetrical structure of the graphene lattice and lead to a 10-100-fold decrease in graphene’s carrier motilities\textsuperscript{16-19}. Other methods include physically doping graphene with small molecules\textsuperscript{12-15}. Physically adsorbed molecules are not stable and are easily desorbed under vacuum or heat. Thus, stable chemical modulation in graphene electronic properties are desirable for the future graphene-based electronics.

5.2. Modulating Graphene Electronic Properties by Self-Assembled Monolayers\textsuperscript{1}

The use of SAMs is a technique well-known for modification of surfaces including SiO\textsubscript{2}\textsuperscript{22-26}. The use of SAMs has made a significant impact on the electrical properties of organic thin film transistors and single-walled carbon nanotube FETs\textsuperscript{22-26}. However, limited research has been done to provide controllable doping, both n-type and p-type, in graphene FET devices by functionalizing the SiO\textsubscript{2} substrates with SAMs.

In this section, the electrical transport behavior of graphene transistors was investigated after the modification of the SiO\textsubscript{2} substrates with alkyltriethoxysilane-based SAMs. The threshold voltage shift (V\textsubscript{th}), which directly corresponds to the neutrality
point in graphene FET devices, can be systematically controlled. Both n-type and p-type FET behaviors have been demonstrated through this technique. Additionally, the SAM-induced doping has a limited impact on graphene’s mobility and the SAMs remain stable even in vacuum.

Figure 5.1 Characteristics of pristine graphene. (a) Raman spectrum (laser 514 nm) of a monolayer graphene film transferred on a SiO₂/Si substrate. (b) HR-TEM images of a suspended graphene film onto a TEM grid. Inset is the hexagonal FFT pattern of the image, which indicates the single-crystalline structure of the graphene. (c) SEM image of a graphene-based FET device (4 μm × 5 μm (L × W)) atop a 100 nm SiO₂/Si wafer with 30 nm Pt as the source and drain electrodes. (d) The FET I-V curve of pristine graphene on untreated SiO₂/Si substrate (I_{ds} = 100 mV).
The graphene film was grown using a solid carbon source: PMMA.\textsuperscript{19} The obtained graphene was monolayer, which was confirmed by both Raman spectroscopy and high resolution transmission electron microscopy (HR-TEM) (Figure 5.1a and b). The sharp 2D peak in the Raman spectrum at 2690 cm\(^{-1}\) has a FWHM of ~ 30 cm\(^{-1}\) and the \(I_{2D}/I_G\) ratio is about 3, hence indicative of a typical monolayer graphene. The hexagonal FFT pattern for the HRTEM image suggests the graphene film is highly crystalline with few defects, a finding which correlates with the presence of the small D peak (1350 cm\(^{-1}\)) in the Raman spectrum. A highly doped Si substrate (\(\rho = 0.005\) Ohm-cm) capped with a 100 nm thick SiO\(_2\) layer was used for the back gated graphene FETs and a SEM of the as-made device is shown in Fig. 1c. The source and drain electrodes (30 nm thick Pt) were defined by conventional electron-beam lithography and lift-off processes on the graphene devices. Graphene stripes (5 \(\mu\)m wide) were further defined by oxygen-plasma etching. Figure 5.1d shows the \(I_{ds}/V_g\) curve of the control sample, which exhibits a weak p-type behavior due to the unintentional doping induced by water, oxygen or other species adsorbed from the atmosphere.

Three alkyltriethoxysilane compounds were used to prepare SAMs on the SiO\(_2\) and four different SAM films were ultimately prepared. The alkyltriethoxysilanes used to prepare the SAMs were: \(1H,1H,2H,2H\)-perfluoroctyltriethoxysilane, (F-SAMs); butyltriethoxysilane, (CH\(_3\)-SAMs); 3-aminopropyltriethoxysilane (H\(_2\)N-SAMs); and the protonated form produced from the H\(_2\)N-SAMs, H\(_3\)N\(^+\)-SAMs. In Figure 5.2, both XPS and water contact angle measurements support the conclusion that the SAMs were successfully prepared on SiO\(_2\). Figure 5.2a and 2b demonstrates the F1s and C1s high-resolution spectra of the F- and CH\(_3\)-SAMs, respectively, which agree well with the
reported values. Figure 5.2c displays the N1s high-resolution spectra for the H$_2$N-SAMs. The N1s peak in Figure 5.2c can be fitted with two components centered at 399.1 (90%) and 401.5 eV (10%), which can be assigned to the free amine (H$_2$N-) and the ammonia cation (H$_3$N$^+$), respectively. The H$_3$N$^+$-SAMs were obtained through protonation of the H$_2$N-SAMs with 1.0 M sulfuric acid for 24 h. The H$_3$N$^+$-SAMs XPS spectrum (Figure 5.2d) displays a large contribution of the ammonia cation (90%) and only a small portion of the free amine (10%). The thicknesses of the SAM films were determined by ellipsometry and the values are listed in Table 5.1. All four SAM films showed an average thickness ~ 1 nm, implying a monolayer level coverage. After forming the SAMs, graphene films were transferred to the SAMs/SiO$_2$/Si substrates and made into FET devices. Figure 5.3 shows a schematic structure of the completed devices, where the SAM layers are in-between the graphene and SiO$_2$ and directly bonded to the SiO$_2$ substrates.

To determine the doping effects of the SAMs, the transport properties of the graphene FETs on different SAMs were measured in vacuum (Figure 5.4). For the graphene FET device made atop F-SAMs, the most positive $V_{th}$ shift was observed (~ +30 V, Figure 5.4a), while only ~ -8 V $V_{th}$ shift (Figure 5.4b) was observed for the device made on CH$_3$-SAMs, indicating butyl groups lead to a weak n-doping effect in the graphene FET devices. For the device fabricated on H$_2$N-SAMs, the $V_{th}$ is downshifted to ~ -18 V (Figure 5.4c), suggesting that aminopropyl SAMs have a relative strong n-doping in the graphene FET device. Compared to H$_2$N-SAMs, the opposite doping effect is shown in Figure 5.4d on H$_3$N$^+$-SAMs supported devices, with a $V_{th}$ upshifted to ~ +20 V. With the four different SAMs, a wide range of $V_{th}$ values have been obtained, from -18 V
(H$_2$N-SAMs, n-doping) to +30 V (F-SAMs, p-doping). For each SAM films, more than five devices were fabricated and similar results were observed for each set (standard deviation < 3).

**Table 5.1. Summary of characterization data on SAMs.**

<table>
<thead>
<tr>
<th>End group</th>
<th>CF$_3$</th>
<th>CH$_3$</th>
<th>H$_2$N</th>
<th>H$_3$N$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM thickness</td>
<td>Present results</td>
<td>11.1 Å</td>
<td>6.2 Å</td>
<td>10 Å</td>
</tr>
<tr>
<td></td>
<td>Calculated results</td>
<td>10.6 Å$^{27}$</td>
<td>5.3 Å$^{23}$</td>
<td>5.5 Å$^{22}$</td>
</tr>
<tr>
<td>Water contact angle</td>
<td>Present results</td>
<td>102°</td>
<td>78°</td>
<td>58°</td>
</tr>
<tr>
<td></td>
<td>Calculated results</td>
<td>105°$^{27}$</td>
<td>75°$^{23}$</td>
<td>60°$^{29}$</td>
</tr>
</tbody>
</table>

**Figure 5.2** Characteristics of SAM films. (a) XPS analysis from the F1s peak (688 eV) and the water contact angle of F-SAMs film (102°). (b) XPS analysis of the C1s peak
(284.5 eV) and the water contact angle of CH$_3$-SAMs film ($78^\circ$). (c) XPS analysis from the N1s peak (398.8 eV) and the water contact angle of H$_2$N-SAMs film ($58^\circ$). (d) XPS analysis of the N1s peak (401.8 eV) and the water contact angle of H$_3$N$^+$-SAMs film ($17^\circ$). No F1s, C1s or N1s peaks were observed for the untreated substrate.

Figure 5.3 Schematic diagram of the graphene FET devices fabricated in this study.
Figure 5.4 $I_d/V_g$ characteristics of graphene based FET devices on different SAMs. Room temperature $I_{ds}$-$V_g$ curves of the FET devices fabricated on (a) F-SAMs, (b) CH$_3$-SAMs, (c) H$_2$N-SAMs and (d) H$_3$N$^+$-SAMs at $V_{ds} = 100$ mV.

The observed systematic doping can be explained by built-in electric dipoles and the charge transfer between SAMs and the graphene channels. The dipole alignment of the SAM molecules is thought to produce a built-in electric field and modify the carrier density of organic field-effect transistors$^{22}$. The theoretical model works well in explaining CH$_3$- and F-SAMs induced doping in graphene transistors. The dipoles of molecules similar to F-SAMs and CH$_3$-SAMs have been calculated by Kobayashi et al. using DFT$^{22}$. The dipole moments along the molecular axes were computed as -2.202 and 0.831 Debye for F-SAM and CH$_3$-SAM, respectively. The built-in electric field inside the SAMs can be estimated by $E = N \left( \mu / \epsilon \epsilon_0 \right)$, where $N$ is the molecular density, $d$ is the length of the SAM molecule, $\epsilon$ is the effective dielectric constant inside the SAM molecules and $\epsilon_0$ is the permittivity of free space. For the SAMs in this study, $N$ is about $1-2 \times 10^{14}$ cm$^{-2}$, $d_{F\text{-SAMs}}$ is 1.1 nm, $d_{CH_3\text{-SAMs}}$ is 0.6 nm and $\epsilon$ is between 2 and 3.$^{22}$ According to the above formula, the calculated electric fields inside the SAMs are $E_{F\text{-SAMs}} = \left( 2.5 \text{ to } 7.4 \right)$ MV/cm and $E_{CH_3\text{-SAMs}} = 0.94$ to 2.8 MV/cm. To produce the same electric field by applying a voltage across the 100-nm-thick SiO$_2$ gate insulator, a gate voltage of 25-74 V for F-SAMs and - (9.4 to 28) V for CH$_3$-SAMs is necessary, which agrees well with the shifts in electrical transport characteristics observed in our devices.
However, since the amine group bears a lone pair of electrons and the ammonium group is positive charged, H$_2$N-SAMs and H$_3$N$^+$-SAMs induced doping in graphene transistors cannot be understood simply by using the built-in electric field model. Dai et al. have discussed the possible charge transfer mechanism between carbon nanotubes and aminopropyltriethoxysilane or polyethylene imine molecules, suggesting that the electron-donating ability of the amine groups led to the efficient n-doping in carbon nanotubes$^{30-31}$. A charge transfer mechanism, arising from the position of the HOMO and LUMO of the molecule with respect to the Dirac-point of graphene and orbital hybridization, was also proposed to explain small molecule-induced doping. The amine group in H$_2$N-SAMs can donate its lone pair to graphene’s channel, increasing electron carrier density and inducing n-doping. In H$_3$N$^+$-SAMs, the lone pairs are occupied by H$^+$. The ammonium cations in H$_3$N$^+$-SAMs are positively charged, which is anticipated to withdraw electrons from graphene channel, decreasing electron carrier density and inducing hole doping.

![Figure 5.5](image_url)

**Figure 5.5** $I_{ds}$-$V_g$ curves of the devices fabricated on NH$_2$-SAMs (a) and F-SAMs (b) after kept under vacuum (10$^{-6}$ Torr) for three days (black lines) and seven days (red lines) at $V_{ds}$=0.1V.
Table 5.2. Threshold voltage $V_{th}$ and field-effect mobility $\mu$.

<table>
<thead>
<tr>
<th>End group</th>
<th>$H_2N$</th>
<th>$CH_3$</th>
<th>untreated</th>
<th>$H_3N^+$</th>
<th>$CF_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{th}$ (V)</td>
<td>-18</td>
<td>-8</td>
<td>4</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>$\mu$ (cm$^2$V$^{-1}$s$^{-1}$)</td>
<td>661</td>
<td>460</td>
<td>449</td>
<td>363</td>
<td>450</td>
</tr>
</tbody>
</table>

In order to define the impact of the SAMs on graphene’s mobility, field-effect mobilities were extracted from the $I_{ds}/V_g$ curves using the following formula: $\mu = [(\Delta I_{ds}/V_{ds})(L/W)/C_{ox}\Delta V_g]$.$^{32}$ Here, L and W are the length and the width of the graphene channel, respectively. And $C_{ox}$ is calculated by $\varepsilon_0\varepsilon_rA/d$, where d is the thickness of SiO$_2$, A is unit area, $\varepsilon_0$ is the permittivity of free space and $\varepsilon_r$ is 3.0 for PVD SiO$_2$ without annealing.$^{32}$ The calculated data are summarized in Table 5.2. Of particular interest, the carrier mobilities of transistors on SAMs are of the same order of magnitude as transistors fabricated on untreated SiO$_2$ substrates. The small variances in the mobilities of these five transistors come from both the different quality of graphene due to the domain size and the different SAMs. SAM doping arises from electric dipoles and charge transfer which do not introduce more scattering centers into the graphene lattice than into the bare SiO$_2$ substrates, therefore having limited effects on the mobilities. In addition, unlike small molecule doping that is caused by physisorption on the graphene plane, SAMs are covalently attached to the SiO$_2$ surface and cannot be cleaved even in vacuum. Two SAM doping cases, $H_2N$-SAMs and $F$-SAMs were tested under vacuum (Figure 5.5). After keeping the samples under vacuum ($10^{-6}$ Torr) for 7 d, only a small positive threshold voltage shift was observed in comparison with that obtained after keeping the
samples under vacuum ($10^{-6}$ Torr) for 3 d, which was attributed to the desorption of species adsorbed from the atmosphere, including O$_2$ and H$_2$O.

5.3. Ambipolar-to-Unipolar Conversion in Graphene Field-Effect Transistors Induced by Surface Coating of Poly(ethylene imine)/Poly(ethylene glycol) Films

Much research has been done in the ambipolar-to-unipolar conversion of carbon nanotube-based FETs$^{33-35}$. Amine groups in PEI are effective electron donors since they each bear a lone pair of electrons, hence PEI has been generally used to make n-type carbon nanotube transistors$^{35-39}$. Avouris et al. also have used PEI to make ambipolar n-type graphene transistors$^{11}$. However, limited research has been conducted to produce unipolar n-type graphene transistors$^{40}$.

In this section, we disclose an ambipolar-to-unipolar (n-type) conversion in graphene FETs along with an apparent increase in the electron mobility. By coating the graphene layer with a film of PEI in PEG, we observe a suppression in the hole conduction and an increase in the electron conduction with an increase in the transconductance, demonstrating an unipolar n-type (electron-doping) behavior. The recorded unipolar n-type behavior is similar to that observed in unipolar carbon nanotube-based devices$^{35,39}$. Moreover, the electron mobility in the PEI-coated graphene FETs also increased by several times. These traits are desirable improvements in making graphene FETs of high quality. We propose that the amine groups in the PEI film provide doping/dedoping to the electron/hole carriers in the graphene layer modulated by an
external gate bias voltage. If PEI alone is used, delamination of the polyamine from the graphene occurs upon drying. However, with the addition of PEG, the dried film remains physisorbed to the graphene. This type of enhanced physisorption using PEG could also prove to be useful in other film-forming formulations with graphene.

![Figure 5.6](image)

**Figure 5.6** Raman spectra and electronic properties of PMMA-derived pristine graphene. (a) Raman spectrum (514 nm excitation) of a monolayer graphene film transferred on a SiO$_2$/Si substrate. (b) The FET $I$-$V$ curve of pristine graphene on a SiO$_2$/Si substrate ($V_{ds} = 1$ V). The inset is the SEM image of a graphene-based FET device (5 $\mu$m $\times$ 5 $\mu$m (L $\times$ W)) atop a 100 nm SiO$_2$/Si wafer with 30 nm Pt as the source and drain electrodes.

The graphene film was grown using a solid carbon source, PMMA, as described previously$^{19}$. Devices were made from monolayer graphene, as determined by Raman spectroscopy (Figure 5.6a). The two most pronounced peaks in this spectrum are the G peak at 1580 cm$^{-1}$ and the 2D peak at 2690 cm$^{-1}$. The 2D/G intensity ratio is about 4 and the full width at FWHMH of the 2D peak is about 30 cm$^{-1}$, indicating that the graphene is monolayer$^{19}$. The graphene was transferred to a doped Si substrate ($\rho = 0.005$ Ohm-cm)
capped with a 100-nm-thick SiO$_2$ layer. Standard electron-beam lithography and lift-off processes were used to define the source and drain electrodes (30-nm-thick Pt) in the graphene devices, with the doped Si substrate serving as the back-gate electrode. Graphene stripes (5 µm wide) were further defined by oxygen-plasma etching. The SEM image of the as-made device is shown in the inset of Figure 5.6b. Electrical characterizations were performed in a probe station (Desert Cryogenic TT-probe 6 system) under vacuum ($10^{-6}$ Torr). The I–V data were collected using an Agilent 4155C semiconductor parameter analyzer at room temperature. Figure 5.6b shows the transport properties of the as-made graphene FET in vacuum ($10^{-6}$ Torr) after pumping for ~3 d to exclude effects from air adsorption. It shows a typical ambipolar transport behavior with the neutrality point near 0 V.

**Figure 5.7** Ambipolar-to-unipolar conversion induced by surface coating of PEI/PEG layer. (a) Schematic diagram of the graphene FET coated with a PEI/PEG layer. (b) Electrical transport curves from a typical graphene FET before and after coating with the PEI/PEG (1:2 w/w) layer with thickness of ~5 µm ($V_{ds} = 1$ V). The red arrows show the
increase in the electron conduction and the suppression in the hole conduction. $I_{ds}$, $V_g$ and $V_{ds}$ represents the drain-source current, back-gate voltage and drain-source voltage.

The thin layer of PEI film in PEG, with a thickness of ~5 μm, was formed atop the graphene channel by a spin-coating the mixture solution of PEI (average molecular weight 800) and PEG (average molecular weight 400) in methanol. Figure 5.7a shows a schematic of the PEI-coated device. After coating the device with a layer of PEI/in PEG, several altered electrical characteristics were observed in the graphene FET (the measurement was made under vacuum, see the red curve in Figure 5.7b). First, the hole conduction was suppressed with respect to the gate voltage in the negative bias region, whereas the electron conductance in the positive biased region was increased. These two changes result in a transition from ambipolar behavior to unipolar n-type behavior. Note that the conduction from the PEI film is negligible and the effect of PEG along on the transport behavior of graphene FET is limited. Hence the observed ambipolar-to-unipolar conversion come from modification of the graphene channel induced by PEI in the film as amines (pK$_b$ = 3.3) are far more electron donating that are ethers (pK$_b$ = 17.5). Meanwhile, we also observed an apparent change in the graphene field-effect mobilities. The field-effect mobilities were extracted from the $I_{ds}/V_g$ curves using the following formula: $\mu = [(\Delta I_{ds}/V_{ds})(L/W)]/C_{ox}\Delta V_g$. Here, L and W are the length and the width of the graphene channel, respectively. And $C_{ox}$ is calculated by $\varepsilon_0\varepsilon_r A/d$, where d is the thickness of SiO$_2$, A is unit area, $\varepsilon_0$ is permittivity of free space and $\varepsilon_r$ is 3.0. The calculated electron mobility for the PEI-coated graphene FET (~4100 cm$^2$V$^{-1}$s$^{-1}$) is ~4 times that of the pristine FET before PEI/PEG coating (~900 cm$^2$V$^{-1}$s$^{-1}$). In contrast, the
hole mobility decreases to ~60 cm²V⁻¹s⁻¹ from ~1100 cm²V⁻¹s⁻¹ after coating with the PEI/PEG film. Both the ambipolar-to-unipolar transition and the changed mobilities are highly reproducible in more than five FETs that were independently prepared.

**Figure 5.8** Schematic of carrier (electrons, represented as red circles, and holes represented as blue circles) migration at the PEI/graphene interface when a (a) positive or (b) negative $V_g$ is applied.

We propose that the observed phenomena result from the effective carrier density modulation in the graphene layer by the PEI/PEG thin film. As a strict 2-D electronic system, a capacitor model has been effective and frequently adopted to describe transport in graphene FETs\textsuperscript{41-42}. For the weak dependence of carrier mobility on carrier density in graphene\textsuperscript{43}, the conductance change is approximately proportional to the change in carrier density that is linearly modulated by an external gate voltage. This results in the typical linear ambipolar behaviors in our as-made pristine graphene FETs (black curve in Figure 5.7b). The coating of the PEI/PEG layer on the graphene surface breaks the linear relationship between the increase of carrier-density and the gate voltage as described in a simple capacitor model by introducing an additional carrier injecting/withdrawing source. As the amine groups in PEI are effective electron donors since they bear lone pair
electrons, electron carriers from these sites are pulled into the graphene layer by the downward electric field induced by a positive back-gate voltage (see illustration in Figure 5.8a), resulting in a sudden increase in electron density and hence conductance increases (red curve in Figure 5.7b). Meanwhile, the amine groups are electronegative (via the sigma-bond framework) and can serve as effective hole traps. This type of lone-pair electron donation with concomitant electronegativity through the C-N bonds is commonly see in the reactivity of organic compounds. The increased hole carriers generated by a negative back-gate voltage are pulled into the PEI layer and trapped by the amine groups (see illustration in Figure 5.8b), resulting in an almost flat $I_{ds}-V_g$ curve in the negative gate voltage region (red curve in Figure 5.7b). Since there are a finite number of amine groups near the graphene, the carrier modulation is also expected to be finite. This is seen in the red curve in Figure 5.7b; above +10 V the $I_{ds}-V_g$ curve goes back to the original trend (paralleling the black curve of the pristine graphene FET in Figure 5.7b).

**Figure 5.9** (a) Transport curves ($I_{ds}-V_g$) of a graphene FET after spin-coating the PEI/PEG films at different spin-coating rates ($V_{ds}= 1$ V). (b) Transport curves ($I_{ds}-V_g$) of
a graphene FET before (gray curve) and after (yellow curve) coating with an extremely thin PEI/PEG layer having a thickness of ~ 2 nm ($V_{ds} = 1$ V).

We also find that the spin-coating speed has a limited effect on the transport behavior of graphene FETs. As shown in Figure 5.9a, similar ambipolar-to-unipolar conversions were observed when using spin-coating rates of 2,000, 4,000 or 8,000 rpm. Under these three different coating speeds, the thickness of the PEI film was measured by SEM and was between 3 µm and 6 µm, suggesting that the doping comes from the local amine groups near the PEI/graphene interface. When the graphene device coated with the PEI film was put into methanol for 1 h to remove most of the PEI/PEG, the thickness of the PEI/PEG film decreased to ~ 2 nm, as measured by ellipsometry. In this case, the ambipolar-to-unipolar conversion disappeared. Ambipolar n-type behavior is observed in the graphene FET and the $I_{ds}$-$V_g$ curve is dominated by the shift of the neutrality point to negative gate voltages (see yellow curve in Figure 5.9b). This shift is due to a doping from the PEI at the PEI/graphene interface and has been observed in graphene FETs with very thin layer PEI films atop the graphene channel.

Methanol and chloroform were also used as solvents for PEI (no PEG) to make films. After coating with a fresh film using either of these solvents, similar ambipolar-to-unipolar transitions were observed. However, if the PEI film is permitted to dry in vacuum ($10^{-6}$ Torr), becoming nearly methanol or chloroform-free, a simple shift in the neutrality point was observed, which could be due to poor interfacial contact between the PEI and graphene. The use of PEI/PEG mixtures can address this deficiency. After being
placed in vacuum (10^{-6} Torr) for 24 h, five out of six devices were successfully prepared and demonstrated an obvious ambipolar-to-unipolar conversion, indicating around 80 % reproducibility. In the sixth device, the PEI film delaminated and only one simple shift in the neutrality point was observed in this device.

5.4. References


39. M. Shim, A. Javey, A. Wong, S. Kam, H. Dai, Polymer functionalization for air-


\subsection*{5.5. Experimental Contributions}

Zheng Yan designed the experiments, performed the fabrications and measurements of graphene FET devices, and conducted the spectroscopic characterizations and analyses. Jun Yao contributed to FET device fabrications. Zhengzong Sun and Yu Zhu performed TEM characterizations. Wei Lu performed the measurement of water contact angles.