Studies on graphitization of graphene oxide

Xu, Yanping

2011

Xu, Y. (2011). Studies on graphitization of graphene oxide. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/46293>

<https://doi.org/10.32657/10356/46293>

NANYANG
TECHNOLOGICAL
UNIVERSITY

STUDIES ON GRAPHITIZATION OF GRAPHENE OXIDE

XU YANPING

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2011

STUDIES ON GRAPHITIZATION OF GRAPHENE OXIDE

XU YANPING

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University

in fulfillment of the requirement for the degree of
Doctor of Philosophy

2011

Abstract

Graphene has become a hot research topic in fundamental physics, nanoelectronics, photonics, chemistry and materials science since 2004. Besides being a precursor for chemical production to produce graphene with large scale and low cost, graphene oxide (GO) holds unique structural, chemical, physical, electrical and optical properties, which make it another important nanomaterial for both fundamental study and industrial applications. This thesis focuses on how to improve the production method and graphitization of GO, and how to explore the large size and high crystalline quality graphene. A series of researches were performed on preparation of ultra-large GO, graphitization of GO by different routes, and evaluation of graphitized samples by Raman spectroscopy, electrical measurements of field-effect transistors (FET).

In Chapter 4, the first part of our researches was described. We improved the Hummers' method to get ultra-large single-layer GO sheets (up to 3mm in lateral size). In our method, the first aggressive oxidation process was replaced and a sonication treatment was added. We also confirmed that the size of the GO sheets was closely related to the sonication times, and large GO sheets can be produced with short sonication time.

Different kinds of graphitization processes, as the second part of our researches, were performed in Chapter 5 & 6. In Chapter 5, conventional methods was used to treat GO, including hydrazine reduction and thermal annealing. The thin-film electrodes made of ultra-large rGO sheets have lower sheet resistance than those of small-sized rGO sheets. Moreover, after thermal reduction at 800 °C, effective hole mobility ranging from 4~12 cm²/Vs can be generated in the FET devices which were fabricated from these single-layer rGO sheets. Raman spectroscopic data revealed that rGO sheets with better graphitization can only be obtained after high temperature annealing. The I(2D)/I(G) ratio of 2D peak to

G peak correlates to the effective hole mobility values in rGO sheets.

In Chapter 6, the alcohol-Chemical Vapor Deposition (CVD) treated rGO sheets exhibited highly graphitic structures and excellent electrical conductivity. The sheet resistances of transparent thin films could be reduced to ~ 15 kohm/sq ($>96\%$ transparency). FETs made from these single-layer rGO sheets had very high field-effect hole mobility up to $210 \text{ cm}^2/\text{Vs}$. Raman spectroscopic studies revealed that the removal of oxygen functional groups and the formation of six-fold carbon rings were responsible for the increasing of electrical conductivity in the low mobility regime. In the high mobility regime, the growth of the graphitic domain size dominated the enhancement of electrical conductivity. Thus, we improved the method to produce rGO sheets with excellent electrical properties for potential electronic applications.

In Chapter 7, the third part of our researches was focused on studying the heavily *p*-doping behavior in alcohol-CVD treated rGO sheets, with the purpose of getting comprehensive understanding of their crystalline structure and electrical properties. After high temperature CVD treatment, strong interactions between rGO sheets and silicon dioxide substrates were generated, which activated rGO to be easily *p*-doped from surrounding oxygen molecular or moisture. Through studying the Raman data of dimethylformamide (DMF) doped or transferred rGO, the widely used Tuinstra-Koenig (TK) relation was found sensitive to doping, which was rarely studied in graphene related system. Herein it was involved in our study. Comparing with other CVD graphitization methods, the alcohol-CVD method was proved to be the one with better efficiency. It can produce rGO sheets with better Dirac curves, higher field-effect hole motilities up to $210 \text{ cm}^2/\text{Vs}$ and higher $I(2D)/I(G)$ ratio up to 2.85.

In the last part of our researches (Chapter 8), we summarized our research works and recommended some future works.

Acknowledgements

I want to gratefully thank my supervisor Associate Prof. Zhang Hua for his greatly help on my thesis revision and instruction on final defense presentations. I also deeply appreciate Assistant Prof. Li Lain-Jong who inspired my work since the very beginning, and for his great support, vision, and instruction without which I would never have acquired so many progresses during my four years of PhD study.

Furthermore, I would like to thank Dr. Su Ching-yuan (Dept. of engineering and system Science, National Tsing Hua University), for his kind collaboration and help on my experiments and valuable discussion during my research.

I thank Assistant Prof. Zhao Yang for his kind instruction on spectral physics and leading me into the study of quantum physics.

I also thank Mr. Ye Jun, Dr. Li Bing, Dr. Zhou Xiaozhu for their valuable discussion and also thank Dr. Qi Xiaoying for her help on my thesis revision.

I also need thank Mr. Shawn Lee, the engineer of Witec Raman system for his persistent support on the Raman instrument.

I also want to thank my group members (Zhao Jianwen, Zhang Wening, Dong Xiaochen, Chen Fuming, Fu Dongliang, Shi Yumeng, Han Xuanding, Hosea Tantang et al.) for their inspiration, sharing of knowledge, and encouragement. My thanks will go to the technicians in Material Science & Engineering for their technical assistance.

In the end I'd like to thank my wife Jessie for her everlasting encouragement and patient love of me. I also thank my wife's family and my family for their financial support as well as spiritual encouragement.

Table of Contents

Abstract.....	I
Acknowledgements.....	III
Table of Contents	IV
List of Figures	VI
List of Tables.....	X
Chapter 1 Introduction	1
1.1 Background	1
1.2 Briefly Review of Graphene and GO	2
1.3 Applications of GO.....	4
1.3.1 Graphene Production	4
1.3.2 Optical and Electrical Applications	5
1.3.3 Graphene Paper and Composites	5
1.4 Graphitization of GO	6
1.4.1 Necessity of GO Graphitization	6
1.4.2 Graphitization Methods	7
1.4.3 Chemicals Graphitization	8
1.4.4 Thermal Graphitization.....	9
1.5 Structure Evolution during Graphitization	10
1.6 Device Fabrication	12
1.6.1 Thin Film Feposition	12
1.6.2 FET Device Fabrication.....	14
1.7 Characterization of Graphene-based Materials	18
1.7.1 Optical Microscopy	18
1.7.2 Scanning Electron Microscopy (SEM).....	18
1.7.3 Scanning Probing Microscope (SPM)	20
1.7.4 Transmission Electron Microscopy (TEM)	21
1.7.5 X-ray Photoelectron Spectroscopy (XPS)	21
1.7.6 X-ray Diffraction (XRD).....	23
1.7.7 UV-Vis Absorption Spectroscopy	23
1.7.8 Raman Spectroscopy	24
1.7.9 FET Electrical Characterization	26
Chapter 2 Aims and Motivations	29
2.1 Objectives and Scopes	29
2.2 Hypothesis	30
Chapter 3 Experimental Details	32
3.1 Materials.....	32
3.2 GO Deposition, Reduction and Devices Fabrication.....	32
3.3 Graphene by mechanically exfoliation	34
3.4 Optical microscopy.....	34
3.5 AFM	35
3.6 Raman Spectroscopy	37
3.7 Electrical Measurement	37
3.8 UV-Vis Absorption Spectroscopy	38
3.9 Sheet Resistance Measurement	38
3.10 XPS.....	38
3.11 SEM.....	38
Chapter 4 Preparation of Ultra-Large GO.....	39

4.1 Introduction	39
4.2 Procedures of Large GO Preparation.....	40
4.3 Results and Discussions	41
4.4 Influence of Sonication Time on Sheet Size.....	43
4.5 Conclusions	45
Chapter 5 Graphitization by Hydrazine Reduction and Thermal Annealing.....	46
5.1 Introduction	46
5.2 Influence of Sheet Size on Sheet Resistance	47
5.3 Electrical Study of rGO FETs.....	48
5.4 Correlation between Electrical Properties and Raman Characteristics.....	53
5.5 Conclusions	56
Chapter 6 Graphitization by Alcohol-CVD Method.....	57
6.1 Introduction	57
6.2 Graphitization of GO Using Alcohol Vapors.....	58
6.3 Electrical Properties of alcohol-CVD Treated GO	61
6.3.1 Sheet Resistance Measurement of TCFs	61
6.3.2 Electrical Measurement of FET devices.....	62
6.4 Correlation between Spectroscopic Data and Electrical Properties.....	64
6.5 Conclusions	69
Chapter 7 Influence of Doping on Alcohol-CVD Graphitized rGO	70
7.1 Introduction	70
7.2 Evolution of Raman Spectra of rGO by Different Graphitization Progresses.....	71
7.3 Raman Spectroscopic Study of Doped and Transferred Graphene.....	73
7.4 Electrical Properties of Transferred rGO.....	77
7.5 Comparing Alcohol-CVD with Other CVD Methods	78
7.6 Conclusions	80
Chapter 8 Conclusions and Future Recommendations	81
8.1 Conclusions	81
8.2 Future Recommendations.....	82
8.2.1 Increasing the Quality and Size of rGO.....	82
8.2.2 Study the Mechanism of alcohol-CVD Graphitization.....	83
8.2.3 Fabrication of Suspended rGO FET Devices	84
Reference	85
List of Publications	98

List of Figures

Figure 1-1 Optical image of mechanically exfoliated graphene with different layer numbers. Reproduced with permission from Peter Blake.	3
Figure 1-2 Comparison of GO paper and graphene paper. (a) GO paper is a strong, bendable and transparent insulator. (b) graphene paper is metallic, porous, fragile, opaque [73].	6
Figure 1-3 Mechanism of epoxide reduction by hydrazine. Reprinted from [46], Copyright (2007), with permission from Elsevier.	9
Figure 1-4 Chemical structure of GO. Reprinted from [123], Copyright (1998), with permission from Elsevier.	11
Figure 1-5 Structure evolution of GO during a multi-step reduction process: NaBH_4 , H_2SO_4 and thermal annealing treatment. Reprinted by permission from Macmillan Publishers Ltd: Nature chemistry [93], Copyright 2009.	12
Figure 1-6 (a) Experimental set up for vacuum filtration. (b) GO thin film on membrane obtained by vacuum filtration. Reprinted by permission from Macmillan Publishers Ltd: Nature chemistry, [15], Copyright 2009.	13
Figure 1-7 (a) Schematic diagram of GO thin film deposition by spin-coating. (b) AFM morphology. Reprinted with permission from [71]. Copyright 2008, American Chemical Society.	14
Figure 1-8 PMMA residue influence on AFM data and electrical data. Reprinted with permission from [147]. Copyright 2009, American Chemical Society.	16
Figure 1-9 Examples of field-effect transistors made by conventional photolithography with a channel length of $7\mu\text{m}$. Reprinted by permission from Macmillan Publishers Ltd: Nature chemistry [58], Copyright 2009.	17
Figure 1-10 FET devices fabricated by shadow mask (a) copper grid, (b) gold electrode pattern, (c) graphene between two electrodes (100X).	17
Figure 1-11 SEM and optical images of rGO on top of SiO_2/Si substrate. Reprinted with permission from [49]. Copyright 2009, American Chemical Society.	19
Figure 1-12 STM topographic images of (a) single-layer and (b) multilayer graphene. The underlying atomic structure is shown by red ball hexagonal ring model. A honeycomb structure is observed in (a). The characteristic three-for-six STM image of the surface of bulk graphite is observed in (b). Reprinted from [152]. Copyright 2007, National Academy of Sciences, U.S.A.	21
Figure 1-13 High-resolution XPS data on: (a) GO film before reduction. (b) rGO film by hydrazine vapor. Following thermal annealing in vacuum at (c) 400°C and (d) 1100°C . C–N signal in (b) and (c) was from hydrazine. C–F ($\sim 292\text{ eV}$) in (c) was contaminated by the vacuum system. Reprinted from [50], Copyright 2008,	

American Chemical Society.....	22
Figure 1-14 UV-Vis absorption spectra shift as a function of hydrazine reduction time. Reprinted by permission from Macmillan Publishers Ltd: Nature chemistry [51], Copyright 2009.	24
Figure 1-15 A typical Raman spectrum of rGO with Lorentzian fittings.	26
Figure 3-1 Lindberg furnace used for GO graphitization.	34
Figure 3-2 (a) and (b) Optical images of rGO sheets on SiO ₂ with different filters.	35
Figure 3-3 (a) and (b) Optical images of micro-mechanically exfoliated graphene sheets on SiO ₂ using different optical filters.	35
Figure 3-4 AFM image of rGO, Height ~1.157nm.	36
Figure 3-5 AFM image of mechanically exfoliated graphene, Height ~0.497nm.	36
Figure 4-1 (a) As-prepared GO solution. (b) Optical image for a single-layer GO sheet (on 300 nm SiO ₂) produced by the modified method (with 2 hr sonication). (c) The corresponding AFM image and (d) AFM height profile for a GO sheet. AFM measurement along the dotted line in the optical image showed that the sheet was ~1 nm thick. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.....	42
Figure 4-2 Optical microscopy images of ultra-large GO on 300nm SiO ₂ substrate. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.....	42
Figure 4-3 (a) SEM and AFM images of the ultra-large GO sheets (on quartz) produced from the modified method (with 1 hr sonication). (b) SEM photo for the single sheet after the 800°C reduction process. (c) The optical micrograph for the GO sheets produced from the modified method with 2hr sonication. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.....	44
Figure 4-4 AFM images of dip-coated (a) small GO sheets and (b) ultra-large GO sheets on 300 nm SiO ₂ substrates. The domains in image (b) were tightly linked with each other. However, the small GO sheets in (a) were sparsely distributed on the substrate. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.	44
Figure 4-5 (a-b) SEM and (c) optical images of the ultra-large GO sheets (produced with 1hr sonication as detailed in the text) on 300nm SiO ₂ substrates. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.....	45
Figure 5-1 Sheet resistance as function of transparency (T% at 550nm) for the electrodes prepared from ultra-large, large and small size rGO sheets after 800 oC thermal annealing (20% H ₂ in Ar). Reprinted with permission from [184]. Copyright 2009, American Chemical Society.	48
Figure 5-2 (a) Optical image and transfer curve (I_d - V_g), (b) drain current vs. drain voltage for the transistor device made from a single-layer rGO sheet under different applied gate voltages. Reprinted with permission from [184]. Copyright 2009,	

American Chemical Society.....	50
Figure 5-3 The statistical mobility values extracted from the transistor devices made from single-layer GO sheets treated by three processes: (1) hydrazine only, (2) hydrazine+ 400 °C annealing (20% H ₂ /Ar) and (3) hydrazine+800 °C annealing (20% H ₂ /Ar). The number in the parenthesis indicates the number of devices tested. Reprinted with permission from [184]. Copyright 2009, American Chemical Society.	50
Figure 5-4 Transfer curves for several devices made from rGO sheets.....	51
Figure 5-5 The XPS spectra and identified binding energies for (a) unreduced GO sheets, and the GO sheets after (b) hydrazine, (c) hydrazine + 400 °C annealing (20% H ₂ /Ar) and (d) hydrazine + 800 °C annealing (20% H ₂ /Ar). Reprinted with permission from [184]. Copyright 2009, American Chemical Society.....	52
Figure 5-6 (a) Raman spectra for 5 selected transistor devices with various values of effective mobility. The labels M0.4, M1.0, M4.6, M6.9, and M12 represent the devices with mobility 0.4, 1.0, 4.6, 6.9 and 12 cm ² /Vs respectively. (b) Various ratios for the integrated peak area for D, G, 2D and D+G bands. Reprinted with permission from [184]. Copyright 2009, American Chemical Society.....	55
Figure 6-1 (a) Raman spectra for single-layer GO sheets before and after various reduction procedures including hydrazine vapor soaking (Hy), H ₂ -annealing (900 °C; 20% H ₂ in Ar), alcohol reduction (at 900 °C; Ar as a carrier gas) and alcohol/H ₂ reduction (900 °C; 20% H ₂ /Ar as a carrier gas). (b) Raman spectra for the GO sheets after alcohol reduction at 600, 700, 800, 900 and 1000 °C. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.....	59
Figure 6-2 Raman spectra taken at the sites with and without GO on SiO ₂ substrates. (a) Sample was treated by alcohol (with 20%H ₂ /Ar) at 900 °C. (b) Sample was treated with alcohol but no H ₂ gas at 900 °C. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.....	60
Figure 6-3 Raman spectrum taken on HOPG after it was exposed to alcohol (20% H ₂ /Ar) at 900 °C. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.	60
Figure 6-4 (a) Typical output characteristics (drain current I _d vs. drain voltage V _d) and (b) transfer curves for a single-layer GO sheet after 1000°C alcohol-CVD with or without DMF treatment. (c) The statistical mobility data for the devices made from single-layer GO sheets treated at various temperatures. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.....	63
Figure 6-5 Transfer characteristics for two other devices made from alcohol treated GO sheets (1000°C). These devices were treated with DMF soaking before measurements. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.....	64
Figure 6-6 The correlations of (a) G peak position, (b) 2D peak width, (c) integrated peak ratio of I(D)/I(G) and (d) integrated peak ratio of I(2D)/I(G) and, (e) 2D peak frequency with the field-effect hole mobility. Reprinted with permission from	

[192]. Copyright 2009, American Chemical Society.	65
Figure 6-7 Raman (a) D, G and D' , and (b) TO+LA, 2D, D+G, 2D' peaks fitted with Lorentzian peaks. The Raman spectrum was taken from a rGO sheet (alcohol-CVD at 900°C). Reprinted with permission from [192]. Copyright 2009, American Chemical Society.	68
Figure 6-8 (a) XPS data for the rGO sheets treated at indicated various temperatures. (b) The estimated graphene nano-graphitic size (L_a) increased with the mobility. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.	68
Figure 7-1 Raman spectra evolution of rGO under different reduction methods: hydrazine vapor (Hy), hydrazine following thermal annealing in H_2 (Hy+ H_2), annealing in Argon (Ar), alcohol-CVD graphitization (A-CVD). Mechanically exfoliated graphene (M-graphene) with different defect levels and Transferred A-CVD (the same A-CVD sample after PMMA transfer) Raman spectra were also listed for comparison. The numbers in parentheses denotes the reduction temperature (°C).	72
Figure 7-2 2D peak position Pos(2D) as a function of G peak position Pos(G) before and after PMMA transfer.	75
Figure 7-3 I(2D)/I(G) ratio as a function of G peak position Pos(G).	75
Figure 7-4 G peak width FWHM(G) as a function of G peak position Pos(G).	75
Figure 7-5 (a) D, (b) 2D peak width as a function of graphitization temperatures after DMF doping and PMMA transfer.	76
Figure 7-6 (a) I(D)/I(G), (b) I(2D)/I(G) as a function of graphitization temperatures.	77
Figure 7-7 Resistance as a function of gate voltage V_g for (a) different alcohol-CVD graphitized graphene samples, (b) mechanically exfoliated graphene (M-graphene) and alcohol-CVD graphitized graphene.	78
Figure 7-8 Comparing FET mobility values between alcohol-CVD and other CVD methods.	79

List of Tables

Table 5-1 Comparison of ultra-thin electrodes prepared from various rGO sheets. Reprinted with permission from [184]. Copyright 2009, American Chemical Society.....	48
Table 5-2 Raman characteristics for five selected transistors made from rGO. Reprinted with permission from [184]. Copyright 2009, American Chemical Society.....	55
Table 6-1 Comparison of ultrathin GO electrodes treated under different conditions. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.....	61
Table 7-1 Summarizing of different CVD graphitization methods.....	79

Chapter 1 Introduction

1.1 Background

In the science fiction “*This Immortal*” an extremely light tent called a “Gauzy” was described: “a one-molecule-layer tent, opaque, feather-light, and very tough”. This is exactly what atomically thin graphene sheet likes. Since single-layer graphene (SLG) was discovered in 2004 [1-3], extensive interest has been triggered due to its unique physical properties such as high carrier mobility ($\sim 200,000 \text{ cm}^2/\text{Vs}$) [4], quantum electronic transport [5, 6], tunable band gap [7, 8], high mechanical strength and elasticity [9] and superior thermal conductivity [10]. These outstanding properties make graphene to be a promising material for high speed transistor applications [11-15], photonics [16], transparent conductive films (TCF) [15, 17, 18], micro- or nano-mechanical systems [19], reinforced composites [20, 21] and energy storage [22].

With a bright future in fundamental study and industrial applications, a large scale and controllable production method of graphene would be the key premise. Mechanical exfoliation of graphite is able to provide high quality graphene for fundamental research, but its yield is very low [1-3]. CVD method, (such as the decomposition of ethylene on nickel [23, 24] and ruthenium surfaces [25], or decomposition of methane on copper foils [26, 27]), and epitaxial growth method from SiC [28-30], still have challenges to grow single-layer graphene uniformly. Chemical methods (like chemically exfoliation from graphite) hold the feasibility to produce uniform single-layer graphene in large quantity. Under mechanical stirring or ultrasound sonication, graphite oxide can be easily exfoliated into single-layer form: GO. Upon different treatment, conducting graphene with a lot of defects can be obtained, referred to reduced GO (rGO) or reduced graphene.

It is a method with quite a lot advantageous to fabricate large TCFs with high conductivity, controllability, and reproducibility [20, 31-34].

1.2 Briefly Review of Graphene and GO

Previously it was thought that two-dimensional (2D) structures could not exist in the free state based on both theory and experiments studies [35, 36]. Atomic thin crystals have been presumed to exist only on top of three-dimensional (3D) structures. For example thin films epitaxially grew on the surfaces of single crystals with matchable crystal lattices [37, 38]. Until 2004, the above ideas were subverted by the accidental discovery of graphene [1]. The discovery of single-layer of graphite was quite lucky as only a simple technique called “Scotch-tape method” was used [1, 3]. Other materials (like single-layer boron nitride and half-layer BSCCO) could also be obtained using the same method [3]. Figure 1-1 shows a mechanically exfoliated graphene sample with different layer numbers on top of silicon dioxide. Although it is atomic thin, graphene is visible under optical microscope [1, 39]. As shown in Figure 1-1 the optical contrast of graphene varies with its layer numbers. These atomic thin crystals could exist on any type of substrates [2, 3, 6], in colloidal form [1, 20] and even suspended over trenches [40]. The existence of intrinsic ripples on the scale of 1 nm are believed to be responsible for the stability of graphene-like 2D crystals [40].

Graphene and GO are two different things. GO is a kind of chemically modified graphene (CMG) and exfoliated from graphite via oxidation in liquid phase. During oxidation, many oxygen functional groups are covalently attached to the flat aromatic network of graphene, leading to the structure transformation of graphene to GO. Owing to the structure variation, GO sheets exhibit quite different electrical, optical, mechanical, chemical properties to graphene [41, 42].

Figure 1-1 Optical image of mechanically exfoliated graphene with different layer numbers. Reproduced with permission from Peter Blake¹.

Actually, GO has a longer history than graphene. Before we discuss GO, graphite oxide must be mentioned. Graphite oxide is first formed after oxidation of graphite in solution. Then GO (one layer of graphite oxide) is exfoliated from it by mechanical force or ultrasound sonication. Graphite oxide was first fabricated in 1859. Benjamin C. Brodie mixed graphite, several oxidants like potassium chlorate (KClO_3) and fuming nitric acid (HNO_3) together, in the end brown colored graphite oxide solution can be obtained [43]. Followed in 1898, sulfuric acid (H_2SO_4) was used as the new oxidizing agent by Staudenmaier [44]. The most commonly used method was developed in 1957 by Hummers and Offeman, which was much safer, faster, and with more efficiency. A mixture of H_2SO_4 , sodium nitrate (NaNO_3), and potassium permanganate (KMnO_4) was used in this method [45]. The produced material remained a layered structure, and its color was lighter because the electronic conjugation of graphite was destroyed during oxidation process [46]. The bulk material obtained after oxidation could be dispersed in water or organic solvents to

¹ Graphene Industries Ltd. Email: peter@grapheneindustries.com

produce entirely monolayer sheets with the aid of ultrasound sonication [31, 46] or mechanical stirring [32, 41, 47]. The uniform single-layer sheets are ~ 1 nm in height and considered to be entirely exfoliated GO [20, 31, 46].

1.3 Applications of GO

1.3.1 Graphene Production

Producing graphene from GO is a solution-based, low cost and low temperature process, and so far it is the best way to produce large scale graphene sheets [15, 32, 46, 48, 49]. The current industrial solution-processing techniques could be used to deposit GO for large-area, scalable and flexible electronics applications [15, 17, 18, 50-55]. This approach can produce graphene in tons' scale [32]. However, comparing with other synthesis methods of graphene, many chemical and structural defects exist in the basal plane of GO, which restricts its application in electronics.

It was found by Kovtyukhova [56] that, prior to the GO preparation, pre-oxidization of graphite was necessary. Otherwise, incompletely oxidized graphite-core/GO-shell particles would exist in the final product. This modified Hummers' method is mostly adopted in publications on preparation of graphite oxide or GO [32, 51, 56, 57]. The size of produced GO depends on several parameters: starting materials size and oxidation degree. Typical lateral dimensions of obtained GO sheets were $\sim 20 \mu\text{m} \times 40 \mu\text{m}$ [58]. Other method like thermal pyrolysis of graphite oxide [59, 60] was seldom used. "Improved method" [49, 53, 61] was also developed to increase the size and yield. Luo et al.[49] utilized a microwave-assisted pre-expansion step before oxidation to produce GO with large size (up to $2000 \mu\text{m}^2$) and high yield (90%). Their results confirmed that the graphitic structure of graphene could be preserved and fewer defects were introduced during oxidation process with the aid of microwave. Aforementioned methods provided ways to produce large size

GO with fewer defects for the application of graphene in TCFs.

1.3.2 Optical and Electrical Applications

Large area graphene sheets are ideal for the applications of TCFs because due to their unique properties, such as high electrical conductivity and optical transparency (380-1300nm). GO can be easily incorporated into current thin film deposition technologies due to its excellent solubility in different solvents [32, 41, 53, 62]. The sheet resistance of ideal graphene is $6\text{k}\Omega/\square$ at 98% transmittance, while the sheet resistance of Indium Tin Oxide (ITO) is below $100\Omega/\square$ at 90% transmittance. To approach to these values, a lot of work have been carried out to improve the sheet resistance of rGO thin films [53, 55, 63, 64].

In the electrical applications, GO has been used in radio frequency (RF) devices [65] and FET transistors [15]. The vacancies and functional groups inside the plane of GO make it a sensitive material for electrical sensors [66-69].

1.3.3 Graphene Paper and Composites

As reported GO could be easily modified by adding other functional groups or nanoparticles to fabricate hybrid materials [70]. Thanks to the rich functional groups, paper-like GO provides more excellent mechanical properties than pure graphene paper [33, 71]. Its contrast is shown in Figure 1-2. GO paper is strong, smooth, bendable, while graphene paper made from solution-phase graphene without covalent functionalization is porous and extremely fragile [72]. The oxygen-containing functional groups on the basal plane of GO bind those individual sheets together to form a microscopic structure with the highest Young's modulus (185GPa) [71]. Radio frequency resonators made from GO is also better than those made from pure graphene [71].

Figure 1-2 Comparison of GO paper and graphene paper. (a) GO paper is a strong, bendable and transparent insulator. (b) graphene paper is metallic, porous, fragile, opaque [73].

rGO can be incorporated into not only insulating materials like polymer [20, 74-79] or ceramic matrices [80], but also conducting polymers [81] to fabricate bulk heterojunction (BHJ) photovoltaic devices [81], field emission devices [82-84]. Detailed information could refer to review [55]. In a recent study [85] rGO served as nanofillers to improve the tensile strength of epoxy nanocomposites up to 40%, overbeating multi-wall carbon nanotubes with only 14% in tensile strength.

1.4 Graphitization of GO

1.4.1 Necessity of GO Graphitization

Exfoliation of graphite oxide in solution provides an easy way to produce graphene on a large scale, however GO is electrically insulating as the delocalized π system is disrupted by oxygen-containing functional groups and could not be used directly for electrical purposes [86]. So the graphitic structure of GO must be restored before use. rGO has a tunable band gap through adjusting the reduction degree [42, 47, 87], which could be reflected from the observation of fluorescence from near infrared, visible to ultraviolet

wavelength [42, 88-92]. Although the term “reduction” has been widely used in publications, strictly speaking typically two steps are involved: reduction (de-oxygenation of functional groups) and graphitization (increase of aromatic domain size).

So far most efforts are focused on reduction of GO, namely to find an efficient reducing protocol to remove oxygen functional groups thoroughly. For example almost all the oxygen functional groups of GO could be removed by a two-step reduction process [93]. Thermal annealing at high temperature could graphitize GO to a certain degree [50, 64, 93]. However the electrical properties of obtained rGO sheets were quite poor and the issues of carbon loss existed. The development of novel graphitization method to restore the crystalline structure of rGO is necessary.

1.4.2 Graphitization Methods

In the oxidation process, different kinds of oxygen-containing functional groups (phenols, carboxyl, epoxides, carbonyls) are attached to the graphene basal plane, and some of these groups will be negative charged after deprotonated in water [94], offering electrostatic repulsion to uniformly disperse GO sheets in water or polar organic solvents [32, 41, 51, 62]. GO can be reduced either in solution phase or on different substrates.

To remove oxygen functional groups and restore the disrupted π system, conventional chemical methods could be utilized such as exposing GO to reductants like: hydrazine [15, 32, 46, 48, 49, 51, 95], NaBH_4 [96-98], NaBH_4 and H_2SiO_4 [93], hydroquinone [99], dimethylhydrazine [20], hydrogen sulphide [100] or thermal annealing in inert or reducing gases [15, 18, 31, 49, 50, 93, 101-104]. New routes like UV-assisted photocatalytic reduction [105], flash reduction[106], electrochemical reduction[107-109], hydriodic acid [53, 64, 110] are environmental friendly and can be operated at low temperature. Moreover, they can be used to reduce GO films on flexible plastic substrates. Among these methods,

thermal annealing has been demonstrated to be the most effective method to remove oxygen functional groups and restore the conductivity of GO [50].

1.4.3 Chemicals Graphitization

Normally rGO sheets agglomerate in solution due to their hydrophobic character [31, 46, 49, 51, 58, 111], unless they are stabilized by adding surfactants [20], stabilizers [57] or mixture of solvents [48]. One concern of using solution phase reduction is that the surfactants or stabilizers may influence the electrical properties of produced rGO thin film device. There are many types of rGO suspensions according to the review paper [32]. For solid phase reduction, GO is deposited onto a substrate first and then reduced by hydrazine [15, 18, 31, 46, 49-51, 112-115], NaBH_4 [93, 96, 97] and then thermal annealing [15].

Hydrazine is widely used to reduce GO because 1) it can remove epoxy and hydroxyl groups effectively and 2) hydrazine monohydrate does not react with water [41], and 3) it could act as dispersing solvent for rGO [58]. Initially, Tung et al. added GO film paper into 98% anhydrous hydrazine with a ratio of 15mg to 10ml under stirring [58]. After one week, a stable suspension of hydrazinium graphene solution was obtained and could be spin-coated onto various substrates to form thin films. Here anhydrous hydrazine plays two roles: reduction agent and dispersion solvent (positive N_2H_4^+ counter-ions). Stankovich et al. proposed a mechanism for hydrazine reduction of epoxy groups as shown in Figure 1-3 [46]. The oxygen can be removed through ring-opening of epoxide and nitrogen can be covalently incorporated to carbon network in the presence of hydrazine, after that thermal elimination will restore the conjugated graphene network in GO.

Figure 1-3 Mechanism of epoxide reduction by hydrazine. Reprinted from [46], Copyright (2007), with permission from Elsevier.

The carboxyl and carbonyl acid groups at the edge are difficult to be reduced by hydrazine [46, 51, 93]. Hydrazine-based reduction method is toxic and will incorporate nitrogen impurities into graphene basal plane which will increase sheet resistance [96]. In view of these disadvantages Shin et al. [96] found that as a reducing agent NaBH_4 was better than hydrazine. With similar C:O ratio ($\text{NaBH}_4 \sim 5.3 : \text{N}_2\text{H}_2 \sim 5$), sheet resistances (R_{sh}) of the rGO reduced by NaBH_4 is $59 \text{ k}\Omega/\square$ far below $3460 \text{ k}\Omega/\square$ by hydrazine. Gao et al. also proves that $\text{C}=\text{O}$ is easy to be reduced by NaBH_4 rather than epoxides and carboxylic acids [93]. The problem for using NaBH_4 is that it slowly hydrolyzes in water and high concentration is needed [41]. This problem would hinder the scalability of its application to reduce GO.

1.4.4 Thermal Graphitization

Chemicals graphitization is suitable for flexible substrates with low glass transition temperature. But the oxygen groups can not be fully removed as the highest C/O ratio obtained is ~ 8.6 (NaBH_4) [96], ~ 12 (HI) [53, 110], ~ 11 (hydrazine) [48] and ~ 15.27 (HI-AcOH) [64], respectively. Thermal annealing can be used to further reduce oxygen functionalities, and the high C/O ratio >246 was reported by Gao et al. [93]. Initially, NaBH_4 was used to deoxygenate GO (C/O ~ 4.78), and then H_2SiO_4 was used to further dehydrated the material (C/O ~ 8.57). Finally it was annealed at 1100°C under Ar/H_2 for 15mins and the C/O ratio was >246 which is close to graphite power with C/O ratio >256 .

The density functional theory (DFT) simulation results reveal that when C/O ratios are above 16:1, reduction of GO becomes difficult [55, 116]. Inhwa Jung et al. also showed that thermal annealing plus hydrazine reduction gave the best conductivity of rGO [69]. Wang X. et al. has reported effective restoration of electrical properties of GO using a similar high-temperature graphitization method at 1100 °C [18].

Thermal annealing is proved to be more efficient under higher temperatures [15, 18, 50]. However, in previous reports [46, 59, 117] GO is not thermally stable, and poor Raman spectra and low FET mobility values were obtained due to carbon loss (vacancies) after thermal annealing.

1.5 Structure Evolution during Graphitization

The structure of GO is under debating for a long time [32, 118-120]. It is because that the detailed structure is closely dependent on starting material, specific fabrication methods, and degree of oxidation[118, 121]. It has been extensively studied by theoretical calculation or experimental studies [32, 56]. The widely adopted structural model is put forward by Lerf and Klinowski [122, 123], and listed in Figure 1-4. Epoxide (C-O-C, bridging oxygen atoms) and hydroxyl (-OH) hold large portion of oxygen functionalities and lie inside the graphene basal plane. Other small portion functional groups like carbonyl (=CO), carboxyl (-COOH) groups attach to edges [59, 122, 123]. These functional groups are responsible for the buckling (deviation from planarity) and hydrophilicity of GO sheets [59, 124, 125]. The Lerf-Klinowski model coincides closely with the experimental observations, and has been used to explain the most properties of GO. However, the model is still not perfect, and revision is made by adding functional group like lactol, phenols, ketones [93, 126] on to the plane, and some new models are also discussed [41, 127].

Figure 1-4 Chemical structure of GO. Reprinted from [123], Copyright (1998), with permission from Elsevier.

In the oxidation process oxygen functional groups destroy the sp^2 hybridization of carbon network, therefore sp^3 hybridization is formed. The sp^3 C-O bonds make GO predominantly amorphous, and could be identified by the broad D and G peaks in Raman spectroscopy [128]. Reduction is not only to remove these sp^3 sites but also to restore the sp^2 hybridization, referred to graphitization. Based on calculation the blue shift of G peak in GO corresponds to the existence of isolated double bonds inside GO structure [128]. Hence even graphene plane is heavily oxidized, C=C double bonds still exist inside these sp^3 sites. The arrangement and quantity are of importance for the better understanding of GO's structures. Another interesting thing is that GO sheets still possess the honeycomb lattice [129, 130].

Figure 1-5 shows a typical evolution of GO structure during a multi-step reduction. The epoxide groups were removed by $NaBH_4$ and sulfuric acid dehydrates hydroxyl groups. And after high temperature annealing almost no functional groups left [93]. The great enhancement in electrical conductivity reflects that the graphitic structure of rGO is restored partly.

Figure 1-5 Structure evolution of GO during a multi-step reduction process: NaBH_4 , H_2SO_4 and thermal annealing treatment. Reprinted by permission from Macmillan Publishers Ltd: Nature chemistry [93], Copyright 2009.

1.6 Device Fabrication

1.6.1 Thin Film Deposition

GO thin films can be easily formed on any desired substrates by established methods such as dip coating [18], spin coating [50, 67, 71, 80, 131, 132], spraying coating [52, 112] Langmuir-Blodgett (LB) [95, 133], Langmuir-Schaefer (LS) [98], vacuum filtration [15, 134, 135], self assembly [53, 136, 137], electrophoretic [109]. Among these methods, only spin coating, vacuum filtration, LB and LS methods are able to be used as controllable method to control the thickness and continuous of the films, while dip coating can just be used to get individual GO sheets for fundamental study

LB and LS methods can be used to fabricate highly uniform monolayer film on substrates [95, 98, 133]. But they are time consuming and not suitable for large-scale production of thin films. Vacuum filtration method could also provide uniform graphene thin films rapidly [15, 138]. The film thickness could be controlled by adjusting concentration and volume of graphene solution. In Figure 1-6(a) GO solution was poured onto one cellulose

ester membrane with nanometer sized pores, and GO sheets were blogged by the pores therefore the thickness could be self-adjusted by the permeation rate of the solvent [15]. Film thickness can be tuned from single-layer to few layers with low concentration of GO solution ($\sim 0.5\text{mgL}^{-1}$) [15]. The film in Figure 1-6(b) was very uniform and its size was only limited by the membrane size. Finally, it could be easily transferred to other substrates by dissolving the membrane with acetone [15, 138].

Figure 1-6 (a) Experimental set up for vacuum filtration. (b) GO thin film on membrane obtained by vacuum filtration. Reprinted by permission from Macmillan Publishers Ltd: Nature chemistry, [15], Copyright 2009.

Spin-coating is another rapid method for rapid and large scale thin film deposition, as shown in Figure 1-7. GO solution was dropped onto a high speed rotating substrate. To improve adhesion of GO sheets to substrates, it is crucial to evaporate the solvent in a very short time during spin-coating by using solvent like methanol and blowing with nitrogen gas (Figure 1-7(a)). GO sheets after spin-coating are less wrinkled because of the centrifugal force, as shown in Figure 1-7(b). Hydrophilic substrates with piranha washing or oxygen plasma treatment, or (aminopropyl)triethoxysilane (APTES) coating are also necessary for successful film deposition. The sheets inside the films attach to each other by Van der Waals forces and hydrogen bonding. The obtained thin films are strong enough to withstand vigorous processing steps like transferring, rinsing, nitrogen blowing and

lithography process [131].

Figure 1-7 (a) Schematic diagram of GO thin film deposition by spin-coating. (b) AFM morphology. Reprinted with permission from [71]. Copyright 2008, American Chemical Society.

1.6.2 FET Device Fabrication

Electrical measurement of FET transistors is a useful technique to study the electrical properties of graphene and rGO. Usually three methods can be used to fabricate graphene or rGO transistor devices: electron beam lithography (EBL) [4, 49, 86, 112, 139-141], conventional photolithography [47, 58, 67] and hard mask [50, 142-145]. Electron-beam lithography was the only feasible way to fabricate electrical devices using GO sheets with small size, as the channel length of FETs ranging from 10nm to several hundred nms. Importantly, the lateral size of rGO sheets was increased over 20μm recently [58], enabling the usage of conventional photolithography or hard mask method to fabricate metal electrodes.

(1) Electron Beam Lithography (EBL)

EBL has been used to fabricate FET devices with high resolution in most of published papers. However, this method is expensive, low yield, and only useful for fabricating devices on nano-size samples. Polymethyl methacrylate (PMMA) resist was first

spin-coated on top of single-layer graphene sheets and selectively exposed by electron beam. After developing the resist, metal electrodes were then evaporated on to the surface and followed by lift-off process to remove the undeveloped resist. Linear metal markers, which are used to mark the position of graphene samples for EBL, were fabricated by photolithography prior to the deposition of graphene.

The residue of resist after lithography process is a common problem which will degrade the performance of graphene devices [4, 58, 139-141, 146, 147]. For example Jeremy et al. [67] showed that the atomic resolution images could not be observed under STM because graphene surface was contaminated by a continuous film after EBL procedure. Ishigami M. et al. [146] confirmed that the residue came from resists rather than from substrates. PMMA residue could cause unknown and uncontrollable contamination or doping effect on graphene, therefore, to remove the residue is quite necessary for studying the intrinsic structural and electrical properties of graphene.

Usually two approaches are adopted to remove the PMMA residue: 1) Thermal annealing under Ar/H₂ flow at 400 °C for 1hr [146]. 2) Electrical current annealing to remove the resist residues as well as chemical doping and carrier scattering [4, 140, 141].

Figure 1-8 illustrates the necessity of cleaning step. After lift-off process, the thickness of graphene was increased to 1.8nm, and it could be reduced to 0.8nm by thermal annealing under Ar/H₂. Doping concentration also decreased two-third and carrier mobility increased four-times [147].

Figure 1-8 PMMA residue influence on AFM data and electrical data. Reprinted with permission from [147]. Copyright 2009, American Chemical Society.

(2) Conventional photolithography

Photolithography is a well established process for semiconductor fabrication, as it is cheaper than EBL and easily scaled up. When graphene or GO is uniformly grown or deposited on substrates, the advantage of conventional photolithography will be revealed. An example of fabricate rGO FET devices by using photolithography is shown in Figure 1-9. Lots of electrodes with 7 μm channel lengths were fabricated at one time [58]. Unlike EBL, it is difficult to selectively fabricate electrodes on desired graphene or GO sheets by conventional photolithography method. Same as EBL, the photoresist residue is also a common issue and need to be avoided.

(3) Hard mask method

As graphene is visible under optical microscope, the position of desired samples could be located easily. Then shadow mask like TEM copper grids could be put on top of desired graphene sheets, as shown in Figure 1-10(a). After coating metal films, the shadow mask

can be removed and electrodes are left on substrates (Figure 1-10(b)). Figure 1-10(c) shows that a rGO sheet is covered by two electrodes. This method requires operator's good crafts to put copper grid on desired angle and position. Another disadvantage is that during thin film deposition gold particle will be easily diffuse onto graphene surface if the samples and substrates are not closely covered by the grids. This will induce *p*-type doping into graphene and also make it more defective. Thus, it is quick, cheap timesaving, no photoresist residue and comparable the former two kinds of methods.

Figure 1-9 Examples of field-effect transistors made by conventional photolithography with a channel length of $7\mu\text{m}$. Reprinted by permission from Macmillan Publishers Ltd: Nature chemistry [58], Copyright 2009.

Figure 1-10 FET devices fabricated by shadow mask (a) copper grid, (b) gold electrode pattern, (c) graphene between two electrodes (100X).

1.7 Characterization of Graphene-based Materials

To fully explore the properties of graphene it is critical to find proper characterization methods. Optical microscopy and Atomic force microscopy (AFM) played the most important roles in the discovery of graphene [1]. In following studies on graphene, other methods like Raman spectroscopy, Scanning tunneling microscopy (STM), FET measurement, Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), etc. have greatly helped researchers to dig out lots of interesting and useful properties of graphene.

1.7.1 Optical Microscopy

Due to the visibility of graphene and rGO on top of SiO₂ [39, 58, 148], optical microscopy has become a suitable tool to quickly locate and characterize graphene samples. Usually graphene samples are deposited onto SiO₂/silicon substrates and desired graphene sheets are selected under an optical microscope to fabricate FET devices. Although this method requires the experiences of operators, it is faster, easier and nondestructive in locating and observing samples compared to other methods like AFM, SEM and Raman microscopy. To get more information from graphene, following methods are needed.

1.7.2 Scanning Electron Microscopy (SEM)

Unlike that the observation of graphene using optical microscope is limited by the image contrast and field size (~ hundreds micrometers under 20X objective), SEM can be used to view graphene samples with large size at one shot. Sometimes graphene is invisible under optical microscope if it is deposited on some special substrates. In such cases SEM could also be used and the image contrast between single-layer and multilayer graphene sheets is clear. However, the irradiation of electron beam may cause damages on graphene

basal plane [139] and sometimes can cause deposition of amorphous carbon on the surface of graphene sample [148].

In Figure 1-11 the SEM and optical images of rGO sheets on 300nm SiO₂ substrates are given. Under SEM the opacity contrast between single, double and multilayer rGO sheets are quite higher than that in the optical images. It is clearly seen that rGO sheets aggregate and randomly overlap with each other with a lot of wrinkles. SEM could be used to check the quality of deposited GO thin films. Although the distribution and size of GO sheets can be easily indentified under SEM, it is noted that the SEM images provide us the information of electronic structure instead of the information of topography structure. Thus another method AFM is needed to measure the thickness and surface roughness of graphene sheets [58].

Figure 1-11 SEM and optical images of rGO on top of SiO₂/Si substrate. Reprinted with permission from [49]. Copyright 2009, American Chemical Society.

1.7.3 Scanning Probing Microscope (SPM)

SPM such as AFM and STM can probe lots of useful information from atomic thin graphene. AFM can identify the presence of graphene sheets and give their height with high resolution at low throughput. The thickness of single-layer graphene is 0.4 nm~1 nm [1, 149], which is larger than the theoretical thickness 0.34nm due to existed water layer between graphene and substrates. The measurement instrument could also introduce variation to the actual height of graphene layers [150]. Because oxygen functional groups are attached on both sides of GO basal plane, the thickness of GO sheet is increased to $\sim 1.1 \pm 0.2$ nm [31, 59, 86, 114, 151].

The use of AFM to characterize graphene is time consuming and its scanning area is limited. So it could not give the lateral size of large graphene sheets like SEM. AFM images of GO on mica and highly orientated pyrolytic graphite (HOPG) showed the roughness and wrinkles of GO sheets [86]. It was said that sp^3 sites and point defects were responsible for those phenomena [86]. To deeply study these structural deformations, STM measurement could be adopted.

STM could be used to probe the electronic structure of graphene in atomic level. In Figure 1-12, the hexagonally symmetric honeycomb structure was observed on graphene (Figure 1-12(a)) while a three-fold symmetry pattern was observed on multilayer graphene (Figure 1-12(b)), which is the same as graphite. The AB stacking structure of graphite makes its electronic structure differ from that of graphene [152].

Figure 1-12 STM topographic images of (a) single-layer and (b) multilayer graphene. The underlying atomic structure is shown by red ball hexagonal ring model. A honeycomb structure is observed in (a). The characteristic three-for-six STM image of the surface of bulk graphite is observed in (b). Reprinted from [152]. Copyright 2007, National Academy of Sciences, U.S.A.

1.7.4 Transmission Electron Microscopy (TEM)

Although STM could image the atomic-scale features like graphene on a solid-state surface under ambient, it requires that the measured sample must be conductive and clean. TEM is usually used to observe heavy atoms, not light atoms. Surprisingly lighter atoms like hydrogen could be observed on top of graphene by standard TEM [153]. Graphene and GO have been used as ideal supports for observation of exbiomolecules and nanoparticles under TEM [153, 154]. Atomic resolution imaging of graphene [124], GO and rGO [120, 124, 155] could be done by high resolution TEM or STEM (scanning TEM). Through TEM measurements intrinsic corrugations were found to exist in suspended graphene sheets, which may explain why two-dimensional atomic thin film could exist in nature [40].

1.7.5 X-ray Photoelectron Spectroscopy (XPS)

XPS can be used to analyze the chemical compositions of surface because of its low

penetration depth. X-ray beam with low energy is irradiated on the sample surface and the number of escaped electrons is recorded together with their kinetic energy at the same time. It has been widely used to probe the electronic structure and structural evolution of carbon materials during different treatment [156]. For example it can tell the ratio of sp^2 to sp^3 during amorphization [156-158]. The structure evolution during GO reduction can also be monitored by XPS [50, 159]. High resolution XPS data of GO and rGO are shown in Figure 1-13. GO films were reduced by hydrazine vapor and thermal annealing at 400 °C to 1100 °C. The increasing percentage of C-C peak (~ 284.8 eV) after above reduction indicated the effective removal of oxygen functional groups C-O (286.2 eV), C=O (~ 287.8 eV) and C-N (~ 285.7 eV) which represents nitrogen impurities from hydrazine reduction [31, 46, 50]. By calculation the area of C1s and O1s, the C/O ratio could be calculated to show the efficiency of used reductants.

Figure 1-13 High-resolution XPS data on: (a) GO film before reduction. (b) rGO film by hydrazine vapor. Following thermal annealing in vacuum at (c) 400 °C and (d) 1100 °C. C-N signal in (b) and (c) was from hydrazine. C-F (~ 292 eV) in (c) was contaminated by the vacuum system. Reprinted from [50], Copyright 2008, American Chemical Society.

1.7.6 X-ray Diffraction (XRD)

XRD has been used to study graphite and turbostratic carbon [160]. It could monitor the intercalation of graphite and reduction of GO thin films. The interlayer distance (d-spacing) of graphite is 3.38 Å, which could be calculated by XRD measurement: $2\theta = 26.4^\circ$ from the (002) peak [96]. After oxidation, the peak shifts to smaller degrees depending on water content. For example the peak is 10.27° (d-spacing 8.60 Å) in GO thin films, after reduction the peak becomes 24.57° (d-spacing 3.62 Å) [64]. However, the XRD diffraction peak disappears as the sheets of graphite oxide are exfoliated into single GO sheets [59, 161].

1.7.7 UV-Vis Absorption Spectroscopy

UV-Vis absorption spectra of GO in different solvents could be used to monitor the structural change of GO during reduction [62]. In Figure 1-14 the absorption peak shifted from 230 nm to 270 nm with the increasing of reduction time [51]. The maximum peak at ~230 nm is due to the $\pi \rightarrow \pi^*$ transition of aromatic C-C bonds. And one peak shoulder at ~300 nm, which can be attributed to $n \rightarrow \pi^*$ transitions of C=O bonds [62]. The shift of absorption peak and increase of spectra intensity indicate the restoration of π conjugation [51]. As the degree of reduction increases, rGO evolves from insulative to semiconductive with a finite band gap, and in the end rGO becomes semimetal with zero band gap [42, 162]. The band gap of rGO could be calculated from UV-Vis diffuse reflectance spectra [163]. Band gap engineering is also reflected by on/off ration of rGO FET devices. All these studies show the potential of GO in photonic applications [87, 164, 165].

Figure 1-14 UV-Vis absorption spectra shift as a function of hydrazine reduction time. Reprinted by permission from Macmillan Publishers Ltd: Nature chemistry [51], Copyright 2009.

1.7.8 Raman Spectroscopy

As a non-destructive characterization technique, Raman spectroscopy is especially useful for characterizing the crystalline structure and electronic structure of carbon materials [166]. From the Raman spectra of defected graphene or rGO sheets, several typical Raman peaks can be observed: D peak($\sim 1350\text{ cm}^{-1}$), G peak($\sim 1580\text{ cm}^{-1}$), D' peak($\sim 1620\text{ cm}^{-1}$), overtones and combination of D, D' and G peaks: 2D($\sim 2700\text{ cm}^{-1}$), D+G peak(2930 cm^{-1}), 2D'($\sim 2940\text{ cm}^{-1}$), as shown in Figure 1-15. The D and D' features are disorder induced bands, and edges like both armchair and zigzag types, could also induce the occurrence of D and D' peaks. They arise from the Double Resonant (DR) process, and “intervalley” and “intravalley” DR processes are responsible for the D and D' peaks respectively [167, 168]. The D peak is also corresponding to a breathing mode with A_{1g} symmetry near K zone boundary and is not active in perfect graphite. It only comes out when disorder is induced [169].

G peak lies at 1580 cm^{-1} , which is related to the in-plane bond-stretching motion of $\text{sp}^2\text{ C}$ atoms pairs (the first order of the E_{2g} phonons scattering), and it does not indicate the

existence of aromatic rings. While D peak indicates the presence of aromatic rings [169, 170]. The intensity ratio of D to G peak $I(D)/I(G)$, which is known as Tuinstra-Koenig (TK) relation, is found to change inversely with graphitic domain size [171] and widely used to study the crystalline quality of graphite or graphene after different kinds of treatment [169, 170]. During the oxidation and reduction processes of GO, the perfect aromatic structure of graphene basal plane is destroyed with functional groups (C-OH, C=O, O=C-OH) or vacancies defects. It is reflected in the variation of D, G and D' peaks and their overtones or combination peaks in position, width and intensities. The increase of $I(D)/I(G)$ after the reduction of GO was observed in published papers [46, 57, 68, 86, 125, 172] which indicates that the average size of the sp^2 domains decreases quite a lot. This is contrary to the idea that the aromaticity of graphene lattice might be restored after chemical reduction [125], according to the fact that the conductivity of rGO increased about 5 orders of magnitude than before reduction [46]. Stankovich et al. [46, 159] attributed this phenomena to the formation of smaller size graphitic domains yet with increasing numbers during reduction. But Paredes J. I. et al. [125] disagreed with this explanation due to the fact that $I(2D)/I(G)$ ratio usually increased after reduction. Thus TK relation could not be used to evaluate the structure change from amorphous to graphitic stage [169]. Oxygen functional groups destroyed the sp^2 hybridized aromatic rings and also distorted the carbon basal plane which accounted for the extremely amorphous structure of GO. But after removal of functional groups, distortion of carbon plane was disappeared, hereby the increase of $I(D)/I(G)$ was observed [125].

Figure 1-15 A typical Raman spectrum of rGO with Lorentzian fittings.

1.7.9 FET Electrical Characterization

Extremely high mobility and ambipolar behavior of graphene FETs are due to the special delocalized π electronic system of graphene. For rGO the higher graphitization degree is, the better delocalized π electronic system is restored. Therefore, mobility could be an important parameter to assess the graphitization degree of GO reduction. Inter-sheet junction effects could be avoided if FETs are fabricated from individual sheet. Measurements of this kind of devices could provide useful information on the electrical transport mechanism of rGO [49, 69, 86, 98]. Mobility is influenced by many factors like electrode materials, gating method, channel length. Back-gated device structure with metal contacts like Au or Au/Cr is widely adopted in published works. Although carbon electrodes or liquid gating have been used to improve the mobility value [104, 173], the crystalline quality of rGO was not actually improved.

There are two kinds of methods to calculate the field effect mobility: using the linear region or the saturation region of the transfer curves. Usually the first one is extracted based on the slope (I_d/V_g) which is fitted to the linear regime of the transfer curves using the equation

$\mu=(L/WC_{ox}V_d)(I_d/V_g)$, where L and W are the channel length and width, V_d is source-drain voltage, I_d is source drain current, V_g is gate voltage and C_{ox} the gate capacitance. This equation may overestimate the true mobility when the transistor does work in the linear region if V_d is not small enough and V_g is not large enough [174, 175], or underestimate the true mobility when the area of percolating conductive paths is not taken into consideration [55]. To obtain the correct mobility the second method $\mu=(ne\rho)^{-1}$ should be used, where e is the electron charge, $\rho=RA/l$ is the sheet resistivity(Ωm), n is carrier density $n = \varepsilon_0 \varepsilon (V_g - V_{DP}) / te$ Where V_g is gate voltage, V_{DP} is the Dirac point, ε_0 and ε are the permittivities of free space and SiO_2 , respectively, t is SiO_2 layer thickness and e is the electron charge ($1.60217646 \times 10^{-19}$ coulombs) [1]. This formula is only valid in the saturation region (metallic regime) of transfer curves because only here n is uniform [98, 176] and electron hole puddles are exclusive [13]. It is a common issue that graphene and rGO transistors could not reach drain current saturation [86, 177-179] because electrodes can be easily destroyed at large gate voltage (usually range -100V~100V) and scaling method can be used to estimate the mobility [98]. Mobility values reported for rGO transistors are ~ 0.01 - $10 \text{ cm}^2/\text{Vs}$ [15, 75, 180, 181], which are far below those of devices made from CVD growth graphene and mechanically exfoliated graphene.

Cristina et al.[86] studied the electronic transport properties of FET devices made from individual single-layer or few-layer rGO sheets for the first time. Comparing with perfect graphene (ambient, similar device structure, hole mobility $\sim 40,000 \text{ cm}^2/\text{Vs}$ [182]), the rGO sheets reduced by hydrazine vapor and hydrogen plasma showed quite poor electrical properties: electrical conductivities between 0.05 and 2 S/cm, field effect mobility $0.01 \sim 1 \text{ cm}^2/\text{Vs}$ for holes and $0.003 \sim 0.2 \text{ cm}^2/\text{Vs}$ for electrons. This showed the poor efficiency of adopted reduction methods. Without undergoing thermal annealing rGO transistors always show ambipolar behavior which is more prominent under vacuum [49, 183].

Although annealing of GO at high temperature is a quite effective method for graphitization of GO, FET devices fabricated these samples usually behave strongly *p*-doped under ambient condition, which means that the Dirac point (charge neutrality point) shifts to large positive gate voltage and sometimes beyond the range of measurement [58, 102, 112]. The origin of *p*-doping is still not clear and residual hydroxyl groups with positive charges are speculated to be responsible for this phenomena [58].

Chapter 2 Aims and Motivations

2.1 Objectives and Scopes

GO has become a promising precursor for producing graphene with large-scale and high-yield. The large sheet size and high crystalline quality of GO will improve the potential applications of GO in photonic and electronic investigations. And it is also a big challenge to find a highly efficient reduction method. In this thesis we aim to find a controllable way to produce ultra-large size GO, and also use different reduction methods not only to remove the oxygen functional groups but also to repair these structural defects and vacancies inside GO. The structural evolution during graphitization will be evaluated using Raman spectroscopy and FET electrical measurements.

Based on the previously reported applications, synthesis, and reduction of GO as well as its structural characterization, we propose a controllable method to obtain ultra-large single-layer GO sheets in Chapter 4. The Hummers' method is improved by introducing an ultrasound sonication step into the pre-oxidation process of GO fabrication. The influence of sonication time on sheet size is studied, which provides a controllable way to produce large size GO sheets.

In Chapter 5 conventional methods like hydrazine reduction and thermal annealing are adopted to obtain rGO. The sheet resistance of thin-film electrodes made from ultra-large rGO exhibits sheet size dependence. Through XPS, FET electrical measurements and Raman spectroscopy, the evolution of GO structure during graphitization is clearly studied. Enhanced results are obtained by thermal annealing. However, vacancies due to carbon loss and significant amount of defects existed in these rGO samples reduced by thermal annealing. Finding ways to complete restoring the delocalized sp^2 hybridization is

challenging and of great interest. In Chapter 6 a novel method is adopted to heal the defects of rGO by alcohol-CVD method. The relation between field effect mobility and Raman spectra is established. In chapter 7 the heavily *p*-doping behavior of as-reduced graphene is studied through DMF doping and PMMA transfer of rGO sheets. The quality of alcohol-CVD graphitized graphene is further investigated by electrical measurements and Raman spectroscopy. The influence of doping on Tuinstra-Koenig (TK) relation is also studied.

2.2 Hypothesis

(1) Based on previous investigations the size and crystalline quality of GO could be controlled by using starting materials with large size and lowering the oxidation degree. We envision that the oxidation of graphite starts from the edges, and the utilization of sonication in the pre-oxidation step will help to break graphite flakes into thinner flakes with desired sizes. This will greatly facilitate the production of large size GO in following oxidation step with H_2SO_4 and KMnO_4 .

(2) We anticipate that the size of GO sheets will influence the sheet resistance of TCFs, because large sheet size will lower the inter-sheet junctions. This can be verified by measuring the sheet resistance of TCFs fabricated from different sized GO sheets. We also believe that during reduction, the removal of oxygen functional groups happens first, subsequently, the formation of carbon hexagonal rings will take place at high temperatures. This could be monitored by both electrical measurements of FETs and Raman spectroscopic study.

(3) We believe that carbon loss and vacancy defects generated during high temperature annealing may be the main cause hindering the restoration of $\text{C}=\text{C}$ π conjugation (graphitization). To repair these defects, carbon sources should be added during

graphitization treatment. As a precursor to synthesize high-purity single-walled carbon nanotube (SWNT), alcohol may also be used as the carbon source in a similar CVD process. The graphitization efficiency of alcohol could be verified by the field-effect hole mobility values from electrical measurements of FETs and the structural information obtained from Raman spectroscopic study.

(4) Based on previous works we anticipate that our rGO sample should be *p*-doped after high temperature annealing. This owes to the strong interaction between rGO sheets and silicon dioxide substrates. To minimize this interaction we can either dope as-prepared rGO sheets with electrons or transfer them to new substrates. This can allow us to obtain more information on evaluating our graphitization methods and rGO qualities.

Chapter 3 Experimental Details

In this chapter the materials used for production and graphitization of GO will be listed. The methods for fabrication of TCFs and FET devices, together with rGO characterization methods, will also be described here.

3.1 Materials

Natural graphite flakes with different sizes were purchased from NGS Naturgraphit GmbH (Germany) and used to produce GO or mechanically exfoliated graphene. To fabricate GO following chemicals were used: 98% sulfuric acid (H_2SO_4), 30% hydrogen peroxide (H_2O_2), and potassium permanganate (KMnO_4). To deposit graphene and GO, two kinds of substrates were used: silicon wafers with 300nm SiO_2 layer from MOS Group Company, quartz substrates (24.5mm in diameter; 1.00mm in thickness) from Photonik Singapore. After depositing GO on these substrates, hydrazine monohydrate from Sigma-Aldrich (65%), forming gas H_2 (20% in Ar), Ar (100%) and alcohol (99.99%) were used to reduce GO under different temperatures.

3.2 GO Deposition, Reduction and Devices Fabrication

GO with different sheet size (several hundred nm to mm) was produced on basis of a modified Hummers' method [184]. The detailed process is described in Chapter 4. To prepare TCFs on quartz substrates, the substrates were first cleansed with a standard Piranha process to obtain hydrophilic surfaces and remove organic residues. GO was dispersed in de-ionized (DI) water and then directly air-sprayed [185] onto the cleaned substrates. During the spraying process, the quartz substrate was put on a hot plate with its temperature maintained at 80-90 °C. The densities of GO on substrates were controlled

by the quantity (2 mL each time) of spraying. Depending on the GO density, the film color varied from light yellow to brown. In the end, the substrates were dried and treated by different kinds of reduction processes.

To prepare rGO FETs, single-layer GO sheets were first dip-coated onto 300nm SiO₂ substrates (cleaned by the standard Piranha process to obtain hydrophilic surfaces) in as-prepared GO solution with proper concentration. To prepare thin film electrodes on quartz with large sized GO, dip-coating method was also employed. Briefly, substrates for receiving GO sheets were immersed into GO solution (0.062 mg/mL), followed by slow pulling out (0.16 mm/sec). Then, the substrates were dried in air and treated by the corresponding reduction processes.

For hydrazine reduction (Chapter 5), samples were first put into a glass vial and a drop of 200 μ L hydrazine monohydrate was put beside the substrates, and then heated at 80 °C for 24 hr with the bottle sealed by Parafilm. For high temperature annealing, samples were put inside a quartz tube (Figure 3-1) and heated at different temperatures (400~1000 °C) for 2hr under a flow of H₂ gas (80 sccm, 20% in Ar).

For alcohol-CVD graphitization process (Chapter 6), samples were also loaded into a quartz tube (Figure 3-1). Forming gas (80 sccm, 20% in Ar) was introduced to the tube to purge undesired moisture and oxygen. After 10 mins the tube was heated to desired temperatures (600~1000 °C). And then absolute alcohol vapors were introduced into the tube with the forming gas (or 100% Ar, at 80-100 sccm) as a carrier gas bubbling through an alcohol bottle maintained at 0 °C.

Because of the large size of our GO sheets, hard mask method was adopted to fabricated FET devices from these rGO sheets. Single-layer rGO sheets were located under optical microscope (20X, Olympus) and FET devices were fabricated by evaporating Au electrodes (40 nm in thickness) on top of large-size rGO sheets with regular shape. TEM

copper grids (SPI, 200 mesh, 20 μ m spacing) were used as hard masks. Channel length of FET devices (distance between source and drain electrodes) was typically $\sim 20\text{ }\mu\text{m}$. This method avoided the resist residue and other wet-chemicals processes, which could influence the electrical characteristics.

Figure 3-1 Lindberg furnace used for GO graphitization.

3.3 Graphene by mechanically exfoliation

Single-layer graphene sheets were obtained using the “scotch-tape” method (3M scotch tape). Natural graphite flakes were purchased from NGS and were split with scotch tape for several times until the surface color of graphite residue on the tape became dark, then were pressed on 300nm SiO₂ substrates following with a gentle scrub. Single-layer graphene FETs were fabricated by the same method in section 3.2.

3.4 Optical microscopy

Despite its atomic thickness, graphene and rGO could be easily observed on 300nm SiO₂ under optical microscope. This brings great conveniences for us to identify graphene or

rGO samples. In Figure 3-2 and Figure 3-3 optical images of rGO and graphene were collected with different optical filters. The thicker the sheet is, the darker its color is. From these figures it is reasonable for observers to select proper optical filters which can improve the image contrast.

Figure 3-2 (a) and (b) Optical images of rGO sheets on SiO₂ with different filters.

Figure 3-3 (a) and (b) Optical images of micro-mechanically exfoliated graphene sheets on SiO₂ using different optical filters.

3.5 AFM

AFM images of graphene and reduced graphene samples were collected by Veeco Dimension 3100 with tapping mode under ambient conditions. Usually AFM measurements were used to confirm the thickness of graphene sheets which were first

selected under optical microscope. In Figure 3-4 an example of rGO FET was given. Its sheet height is 1.157nm, which proves that it is a single-layer sample [31]. In Figure 3-5 one graphene sample made by mechanically exfoliation is given for comparison, the height of which is $\sim 0.497\text{nm}$.

Figure 3-4 AFM image of rGO, Height $\sim 1.157\text{nm}$.

Figure 3-5 AFM image of mechanically exfoliated graphene, Height $\sim 0.497\text{nm}$.

3.6 Raman Spectroscopy

Raman spectroscopy has been proved to be a useful tool for characterizing carbon materials such as diamond, amorphous carbon, graphite, carbon nanotube as well as graphene. It can provide detailed structural and electronic information of studied graphene samples such as crystallographic quality and electron phonon interaction. Raman spectra have been used to study graphene layer numbers [186], stacking disorder [187] and interactions between graphene and surroundings such as doping and strain [188]. In our work we use Raman spectra to monitor the structural evolution of GO during graphitization treatment. Domain size can be calculated from intensity ratio of Raman D to G peaks using TK relation.

Witec alpha300 confocal microscopy instrument was used in our experiments to collect point and image Raman data from graphene samples. Its specifications are as following: excitation laser wavelength 488nm (2.54eV), gratings 300, 600, 1800 Grooves/mm, vacuum sealed thermoelectric (TE) cooling CCD. Laser beam was illuminated on samples through an 100X objective (N.A. 0.95) with spot size $\sim 0.5\mu\text{m}$ and the laser power was tuned below 1mw to avoid heating or destroying samples. The Si peak at 520.6 cm^{-1} was used as a reference for wavenumber calibration.

3.7 Electrical Measurement

All electrical measurements were performed under ambient conditions using a Keithley semiconductor parameter analyzer, model 4200-SCS. FET devices with back-gated structure were measured. Source was grounded, and Drain voltage (V_{ds}) was 0.5V. Gate voltage V_{g} ranged from -100V to 100V. Mobility was extracted from the $I_{\text{d}}-V_{\text{g}}$ transfer curve. The gate voltages at Dirac point provided the doping information of graphene samples.

3.8 UV-Vis Absorption Spectroscopy

After depositing graphene thin films on quartz substrates, transmittance measurement was done with a UV-Vis-NIR spectrophotometer (Perkin Elmer). Background calibration was carried out with two bare quartz substrates.

3.9 Sheet Resistance Measurement

Sheet resistance was measured using the four point probe method (Keithley Instrument). The sheet resistance values combined with the transmittance value at 550nm were used for comparing between different transparent thin film electrodes.

3.10 XPS

XPS measurements were carried out by a Kratos AXIS-ultra spectrometer (UK) with monochromatic Al K α X-ray radiation (1486.71 eV). XPS was used to monitor the removal of functional groups of rGO after reduction.

3.11 SEM

SEM images were collected from JEOL JSM-6700 field-emission scanning electron microanalyzer. For single-layer GO (or rGO), an accelerating voltage of 5 kV was adopted.

Chapter 4 Preparation of Ultra-Large GO

4.1 Introduction

Graphite oxide has been produced by different methods for a long time [15, 45, 46, 57], which typically involve oxidation of graphite with the aid of strong oxidants and acids for extended periods. After the discovery of graphene in 2004, people realized that atomic thin materials could exist in nature. Stankovich et al. treated graphite oxide in water with mild ultrasonic treatment and found that uniform GO sheets (~ 1 nm in thickness) existed in solutions [31]. Since then, chemical routes of producing and modifying graphene have become the research topics of chemists, materialists and physicists [189].

According to the commonly used Hummers' method [45], graphite powders were oxidized by adding oxygen functional groups onto the basal planes and edges of graphite flakes. These decorated functional groups were able to reduce the inter-planar forces and make graphite oxide easily exfoliated to single-layer sheets in aqueous media. The size of as-prepared GO sheets greatly influences the inter-sheet contact resistance in TCFs. The size of as-prepared GO sheets in most reports ranges from 100 nm to several microns [32], which will limit the application of GO in TCFs.

Theory calculation has shown that GO sheets were unzipped during oxidation, and were smaller than starting graphite flakes [190]. Recently, Luo et al. have obtained large sized single-layer GO sheets (up to $2000\ \mu\text{m}^2$ in size) by involving pre-exfoliation of graphite using microwave heating [49], which provides a hint that additional oxidation process can help to exfoliate layers of graphite flakes.

To minimize the oxidation degree and increase the sheet size of GO, in this chapter, we

modified the Hummers' method used by Xu et al [57], where a sonication process of graphite and H_2SO_4 mixture was added into the pre-oxidation step. The sonication process aimed to break graphite flakes into the smaller and thinner flakes. We found that the lateral size of single-layer GO sheets obtained after the subsequent oxidation could be adjusted by the sonication period, where shorter sonication time resulted in larger GO sheets. Fairly large sheet size ($>100\text{ }\mu\text{m}$, up to several mm in lateral size) of GO sheets has been achieved, which is quite useful for preparing devices for electrical measurements.

4.2 Procedures of Large GO Preparation

Natural graphite flakes (average size 3~5mm) were used to synthesis GO. We modified the Hummers' method used by Xu et al. [57], where graphite flakes were oxidized by concentrated H_2SO_4 only in the first pre-oxidation step (the chemical oxidation of graphite flakes using concentrated H_2SO_4 , P_2O_5 and $\text{K}_2\text{S}_2\text{O}_8$). A bath sonication process was added after the pre-oxidation. Sonication processes with different periods were carried out to adjust the size of the obtained single-layer GO.

The experiment procedures are described here in time sequence. At first graphite flakes (2 g) were mixed with concentrated H_2SO_4 (12 mL) in a glass bottle. The mixture was kept at $80\text{ }^\circ\text{C}$ on a hotplate and stirred at the same time. After 4.5hr the solution was cooled to room temperature and then put into the water sonication bath (300W, Finnsonic Model 20) for 1~6hr, which helped to break the graphite into smaller and thinner flakes. The sonication process was crucial for achieving desired large-sized GO sheetes.

The solution was then diluted with 0.5L de-ionized (DI) water and left overnight. The pre-oxidized graphite powders were obtained after removal of the residual acid by filtration the solution with porous filters (200 nm pore size). The filtered product was dried with gentle baking ($70\text{ }^\circ\text{C}$) in a dry box. To exfoliate the pre-oxidized graphite flakes into GO

sheets, they were put into concentrated H_2SO_4 (120mL), added with KMnO_4 (15 g), following by stirring at room temperature for 2 hr. The solution was diluted with DI water (250mL) and stirred for another 2 hr, and then additional 0.7L of DI water was added. Shortly, 20mL of H_2O_2 (30%) was added into the mixture. After setting overnight, upper portions of solution was collected (unreacted graphite powders precipitated in the bottom of solution) and then centrifuged (10000 rpm). These obtained powders after centrifuge were dissolved in HCl solution (1:10) and then centrifuged several times to remove residual metal ions. Finally, these powders were dissolved in DI water again and centrifuged to remove the unwanted acid. The yield of GO sheets for the whole process was ~4.3 wt%.

4.3 Results and Discussions

GO sheets could be well dispersed in water because of the oxygen functional groups at the edge of the sheets [94, 191]. Figure 4-1(a) showed a photo of brown color solution containing ultra-large GO sheets produced with 2hr sonication. In Figure 4-1(b) a single-layer GO sheet was dip-coated on a 300 nm SiO_2/Si substrate, the lateral size of which was typically ~100 μm . Figure 4-1(c) and (d) showed the AFM image and its height profile for a single-layer GO sheet. The measured thickness was ~1.07 nm, which suggested that it was a single-layer sheet.

More optical images of large GO sheets were provided in Figure 4-2. Their sizes were all around 100 μm , and even larger sheets were also observed. The improved sheet size greatly facilitated the study of GO, making it convenient for us to fast fabricate FET devices using shadow masks. This avoided the resist residues on rGO surface. And also the larger sheet size can lower the sheet resistance of rGO thin films, which will be shown in Chapter 5.

Figure 4-1 (a) As-prepared GO solution. (b) Optical image for a single-layer GO sheet (on 300 nm SiO₂) produced by the modified method (with 2 hr sonication). (c) The corresponding AFM image and (d) AFM height profile for a GO sheet. AFM measurement along the dotted line in the optical image showed that the sheet was ~1 nm thick. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.

Figure 4-2 Optical microscopy images of ultra-large GO on 300nm SiO₂ substrate. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.

4.4 Influence of Sonication Time on Sheet Size

We found that the lateral size of GO sheets was related to the length of sonication period, where longer sonication time resulted in smaller GO sheets. Interestingly, a short sonication process (1hr) allowed us to obtain ultra-large GO sheets from natural graphite flakes. Figure 4-3(a) showed the SEM and AFM images of the ultra-large GO sheets dip-coated using the GO solution with 1 hr sonication. The GO sheets were up to 3 mm in lateral size, and the magnified images show that the GO sheet had a wrinkled surface, likely unavoidable during dip-coating due to its ultra-large size. The AFM height profile from the edge of the GO sheet was shown in Figure 4-3(a). It was ~1 nm thick, suggesting that the obtained GO sheet was single-layer. Some small GO fragments could also be found on top of the large GO sheet. The two SEM images in Figure 4-3(a) together with the AFM image in Figure 4-4(b) showed that there were almost perfect connections between each flat domain without exposing the underlying substrates, implying that the ultra-large GO sheet was not composed of separate GO sheets because the dip-coating method was unlikely to achieve such a well-connected GO film.

It was shown in Figure 4-4(a) that small GO sheets (prepared with 6 hr sonication) were sparsely distributed on substrates by dip-coating, in clear contrast to the ultra-large film. It was worth noting that small GO sheets were unlikely to achieve 100% coverage on substrates even using the LB method [95]. Figure 4-3(b) showed the SEM image for the same single sheet after 800°C thermal treatment (under 20% H₂/Ar), and the large sheet broke into small domains after the high temperature process. However, these domains were still well connected after high temperature reduction, which was promising for large size and ultra-thin transparent electrodes. More photographs of ultra-large GO sheets (1 hr) were also provided in Figure 4-5. For 2 hr sonication time, the lateral size of obtained GO sheets typically ranged from 50 to 100µm, as shown in Figure 4-2 and Figure 4-3(c). The

size of the obtained GO sheets became smaller than $10\mu\text{m}$ in lateral size if the sonication time was further increased to 6hr, as shown in Figure 4-4(a).

Figure 4-3 (a) SEM and AFM images of the ultra-large GO sheets (on quartz) produced from the modified method (with 1 hr sonication). (b) SEM photo for the single sheet after the 800°C reduction process. (c) The optical micrograph for the GO sheets produced from the modified method with 2hr sonication. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.

Figure 4-4 AFM images of dip-coated (a) small GO sheets and (b) ultra-large GO sheets on 300 nm SiO_2 substrates. The domains in image (b) were tightly linked with each other. However, the small GO sheets in (a) were sparsely distributed on the substrate. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.

Figure 4-5 (a-b) SEM and (c) optical images of the ultra-large GO sheets (produced with 1hr sonication as detailed in the text) on 300nm SiO₂ substrates. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.

4.5 Conclusions

In this chapter a useful method to obtain ultra-large single-layer GO sheets (up to several mm in lateral sizes) has been demonstrated. By adding an ultrasound sonication step into the pre-oxidation process of GO production, it is able to better adjust the size of the obtained GO sheets which increases with the decreasing sonication time. These efforts will be crucial for the application of GO in electrical applications with solution compatible techniques.

Chapter 5 Graphitization by Hydrazine Reduction and Thermal Annealing

5.1 Introduction

Due to its intrinsic insulating character [181], GO need be converted back to conducting graphene through removal of oxygen-containing functional groups (reduction) and graphitization treatment. Two main approaches, including hydrazine reduction [46] and thermal annealing [18, 50], have been widely adopted. Cristina et al. explored for the first time the electrical properties of individual single-layer rGO sheet after hydrazine reduction. The field-effect hole mobility with $\sim 0.001\text{-}1\text{cm}^2/\text{Vs}$ was obtained [181]. Thermal annealing method has been demonstrated to be effective in restoring the conductivity of rGO. And hole mobility $\sim 10\text{cm}^2/\text{Vs}$ was obtained [180]. However, the relation between the degree of graphitization and carrier mobility in single-layer rGO was still unclear.

TCFs and FET devices were fabricated from the GO sheets obtained in Chapter 4. In this chapter hydrazine reduction and thermal annealing ($400\text{-}1000^\circ\text{C}$, 20% H_2/Ar) methods were adopted to study the graphitization progress and electrical properties of rGO. The TCFs made from ultra-large rGO sheets exhibited lower resistance compared with those made from small-size rGO sheets. The obtained large rGO sheets allow us to study the electrical properties and Raman characteristics easily. The transistor devices made from these single-layer rGO after 800°C thermal annealing exhibited high field-effect hole mobility with $4\text{-}12\text{ cm}^2/\text{Vs}$. The enhancement in mobility after high temperature reduction is well correlated to the removal of functional groups and graphitization of GO.

5.2 Influence of Sheet Size on Sheet Resistance

rGO has demonstrated its application in TCFs [15, 17, 18, 50, 97, 132]. Based on obtained GO with different sizes in Chapter 4, it is shown that GO sheets with larger size hold advantage over GO sheets with smaller size in the performance of TCFs. GO solution was coated on quartz substrates by air-spraying or dip-coating, and the GO films on substrates were treated by thermal annealing (800°C, 20% H₂/Ar) for 2 hrs (methods in section 3.2). The influence of sheet size on sheet resistance was shown in Figure 5-1. The electrodes using the small-size GO sheets (typical lateral size ~1μm; with 6hr sonication) gave significantly higher sheet resistance than those prepared from large size GO (typical size 20~100μm; with 2hr sonication) or those from ultra-large GO (typical size ~mm; with 1hr sonication). Only electrodes made from ultra-large single-layer GO sheets could obtain 98% transparency (2% absorption is known to be attributed to single-layer graphene), which is the advantage of using ultra-large GO sheets. It was not able to fabricate conductive electrodes with such a high transparency (98% transparency) using other two types of GO films (large and small) due to the fact that stacking of GO sheets reduced the transparency value. The resistance of the ultra-large GO transparent electrodes decreased from ~1000 kΩ/□ (800 °C annealing) to ~188 kΩ/□ (1000 °C annealing), as shown in Table 5-1. The sheet resistance for electrodes made from single-layer ultra-large GO films reduced at 1000 °C (188 kΩ/□) was already lower than (or comparable with) the 500 kΩ/□ (~95% transparency) obtained from a thicker film under vacuum annealing at higher temperature (1100 °C) [103]. Note that the sheet resistances that we have achieved, although lower than in previous works, are still too high for practical applications. Therefore, further investigations would be necessary to lower the resistance even more substantially.

Figure 5-1 Sheet resistance as function of transparency (T% at 550nm) for the electrodes prepared from ultra-large, large and small size rGO sheets after 800 oC thermal annealing (20% H₂ in Ar). Reprinted with permission from [184]. Copyright 2009, American Chemical Society.

Table 5-1 Comparison of ultra-thin electrodes prepared from various rGO sheets. Reprinted with permission from [184]. Copyright 2009, American Chemical Society.

Sample ID	Process	Transparency (% @550nm)	Resistance (KOhm/□)
1	20%H ₂ 800°C, 30min	98.0	1005
2	20%H ₂ 900°C, 30min	98.1	413
3	20%/H ₂ 1000°C, 30min	98.0	188
4*	1100°C vacuum annealing, 3hr	95.0	500

* from reference [103].

5.3 Electrical Study of rGO FETs

Electrical study on gate voltage dependant FET devices is another way to evaluate how much GO has been restored to perfect graphene after hydrazine and thermal annealing treatments. The ultra-large size of obtained GO allowed us to easily and fast fabricate FET devices on individual sheets using copper grids under optical microscope (details in section 3.2). Hydrazine treatment was first carried out to reduce GO sheets on SiO₂

substrates, and then subsequent thermal annealing (400 °C and 800 °C in 20% H₂/Ar) was performed to further improve the electrical properties of single-layer rGO sheets. The transfer curves of bottom-gated transistors were measured under ambient condition and a typical device data with hole mobility $\sim 4.6 \text{ cm}^2/\text{Vs}$ was shown in Figure 5-2. This single-layer GO sheet was treated by hydrazine vapor following 800 °C thermal annealing. Its optical image was shown in the inset of Figure 5-2(a). Only single-layer GO sheets with regular shapes and suitable size ($\sim 10\mu\text{m} \times 30\mu\text{m}$) were selected for FET devices fabrication which helped us to easily extract the effective field-effect hole mobility. From the transfer curve in Figure 5-2(a), it was seen that the ambipolar behaviour was almost disappeared and *p*-type doping was observed from drain current (I_d) vs. drain voltage (V_d) characteristics shown in Figure 5-2(b). The field-effect mobility was calculated by equation $\mu = (L/WC_{\text{ox}}V_d)(\Delta I_d/\Delta V_g)$, where the slope $\Delta I_d/\Delta V_g$ was fitted from the linear region of the transfer curve in Figure 5-2(a), *L* and *W* were channel length and width, and C_{ox} was the gate capacitance.

In this chapter three processes (hydrazine only, hydrazine+400 °C annealing and hydrazine+800 °C annealing) were performed on GO sheets. Summarization on the statistical hole mobility values was drawn in Figure 5-3. The mobility of GO devices treated by hydrazine was only $\sim 0.1 \text{ cm}^2/\text{Vs}$, similar to previous reports [181]. After thermal annealing at 400°C, the mobility was significantly enhanced around 10 times ($\sim 1.0 \text{ cm}^2/\text{Vs}$). And high mobility values ($4\sim 12 \text{ cm}^2/\text{Vs}$) were obtained after annealing at 800°C. Very small hysteresis was observed from the transfer curves of measured devices. Several examples were shown in Figure 5-4, in which the *L/W* ratios were also provided. In Table 5-2 it could be seen that there was no much difference between mobility extracted from the forward V_g scan and that obtained from the reverse scan.

Figure 5-2 (a) Optical image and transfer curve (I_d - V_g), (b) drain current vs. drain voltage for the transistor device made from a single-layer rGO sheet under different applied gate voltages. Reprinted with permission from [184]. Copyright 2009, American Chemical Society.

Figure 5-3 The statistical mobility values extracted from the transistor devices made from single-layer GO sheets treated by three processes: (1) hydrazine only, (2) hydrazine+ 400 °C annealing (20% H₂/Ar) and (3) hydrazine+800 °C annealing (20% H₂/Ar). The number in the parenthesis indicates the number of devices tested. Reprinted with permission from [184]. Copyright 2009, American Chemical Society.

Figure 5-4 Transfer curves for several devices made from rGO sheets.

XPS is a surface sensitive probe which has been used to study the change of chemical composition. C1s XPS data of GO sheets before and after various treatments were shown in Figure 5-5. There were three main components C-C (at 284.6 eV), C-O (at 286.6 eV) and C=O (at 288.5 eV) in Figure 5-5(a) [15, 46, 50, 80]. After hydrazine treatment (Figure 5-5(b)) the peak intensities of C-O and C=O peaks were reduced greatly and a new peak emerged which referred to the binding energy of C-N [15, 50]. After following thermal annealing at 400 °C and 800 °C, peak intensities of C-N, C-O and C=O lowered a little bit (Figure 5-5(c)). This is contrast to the mobility increase: almost 6 times higher for thermal annealing at 800 °C than annealing at 400 °C in Figure 5-3. This implied that the removal of heteroatoms (O or N) in basal plane of rGO might not be the only explanation for the mobility enhancements.

Figure 5-5 The XPS spectra and identified binding energies for (a) unreduced GO sheets, and the GO sheets after (b) hydrazine, (c) hydrazine + 400 °C annealing (20% H₂/Ar) and (d) hydrazine + 800 °C annealing (20% H₂/Ar). Reprinted with permission from [184]. Copyright 2009, American Chemical Society.

It was reported that hole mobility as high as $\sim 850 \text{ cm}^2/\text{Vs}$ was obtained for the GO devices [104]. It is worth noting that different method was used to extract the mobility and epitaxial graphene (EG) was used instead of metal contacts to reduced the contact barrier between GO and EG [104]. Similar enhancement in mobility was also observed where rGO thin films were used as electrodes [173]. Thus electrical data could not provide enough information on the graphitization degree of GO after different treatments. Another tool Raman spectroscopy should be involved to study the crystalline structure of rGO.

5.4 Correlation between Electrical Properties and Raman Characteristics

The relation between mobility values and crystalline structure would provide us a comprehensive view of rGO. Raman spectroscopy is the widely used tool to probe the structural information of carbon materials and then adopted here. Raman spectra shown in Figure 5-6(a) were collected directly from 5 selected transistor devices with different mobility values. The labels M0.4, M1.0, M4.6, M6.9, and M12 represented the devices with hole mobility value 0.4, 1.0, 4.6, 6.9 and $12 \text{ cm}^2/\text{Vs}$ respectively. The well-known G peak ($\sim 1585 \text{ cm}^{-1}$) means the existence of sp^2 -hybridized C-C bonds in graphene [186, 193, 194]. D peak ($\sim 1350 \text{ cm}^{-1}$) is induced by the existence of disorders or defects. The overtone of D peak, 2D peak locating at $\sim 2700 \text{ cm}^{-1}$, is from a double-resonance(DR) process like D peak [169, 170, 195, 196]. Usually the more defects existing in graphene basal plane, the higher D peak intensity is and the lower 2D peak intensity is [195]. In addition, D' peak ($\sim 1620 \text{ cm}^{-1}$) is also induced by disorder from the DR process due to intravalley scattering [128, 168]. In Figure 5-6(a) it was shown that G peak shifted to smaller wavenumbers as the increase of mobility values, which resulted that D' peak could be much easily deconvoluted (a clear shoulder in the right side of G peak). This trend could also be seen in Table 5-2 where the corresponding device hole mobility values and

G peak positions were listed together. All the spectra data were obtained by carefully peak fitting. In Table 5-2 the peak ratios of G, D, 2D peaks were also given and the trends were drawn in Figure 5-6(b).

$I(D)/I(G)$ ratio known as the TK relation is often used to estimate the graphitic domain size [46, 57, 172, 181], and usually this ratio increases with decreased domain size. Recently, Paredes et al. argued that the ratio $I(D)/I(G)$ may be invalid to serve as an indicator of structural transition from extremely amorphous to graphitic materials [125]. In Figure 5-6(b) the trend of $I(D)/I(G)$ change was not linear and first increased at low mobility regime ($0.1\sim6.9\text{ cm}^2/\text{Vs}$). This phenomena could be attributed to the structure changing of GO from amorphous and distorted states to more graphitic structures yet with significant amounts of defects [125]. In this regime TK relation is invalid. Similarly, at this low mobility regime the ratio $I(2D)/I(G)$ increased with mobility. By contrast, at a higher mobility regime ($6.9\sim12\text{ cm}^2/\text{Vs}$) the ratio $I(D)/I(G)$ decreased with mobility, $I(2D)/I(G)$ still increased with mobility. In this regime TK relation was valid and it implied that the graphitic structure was better improved after high temperature annealing. Therefore, at high mobility regime the decrease in $I(D)/I(G)$ ratio was actually well associated with the increase of the graphitic domain size. Based on Figure 5-6(b), it could be seen that the ratio $I(2D)/I(G)$ well correlated the electrical properties to their graphitic structures. Moreover, the ratio between the 2D and D+G ($\sim 2950\text{ cm}^{-1}$) peak areas, $I(2D)/I(D+G)$, might also be an valid indicator of GO structure evolutions.

Usually G peak downshift and increase of $I(2D)/I(G)$ in perfect graphene have been explained by following reasons: (1) decreasing of *p*-doping [14, 197-200] or (2) recovering of delocalized π systems (graphitization) [195]. However, the G peak positions in low mobility regime were $\sim 1596\text{ cm}^{-1}$, which strongly suggested that in this stage the structure of rGO was highly amorphous with isolated C=C bonds [128]. Therefore the graphitization

seemed to be a more reasonable explanation of the increase of $I(2D)/I(G)$.

Table 5-2 Raman characteristics for five selected transistors made from rGO. Reprinted with permission from [184]. Copyright 2009, American Chemical Society.

	Mobility (cm^2/Vs)		Pos(G) cm^{-1}	$I(D)/I(G)$	$I(2D)/I(G)$	$I(2D)/I(D+G)$
	Forward scan	Reverse scan				
M12	12.01	12.35	1586.7	1.17	0.34	1.37
M6.9	6.95	6.89	1584.7	1.55	0.25	0.93
M4.6	4.56	4.62	1597.0	1.53	0.26	0.97
M1.0	0.99	1.05	1596.9	1.38	0.22	0.75
M0.4	0.40	0.46	1596.6	1.16	0.13	0.70

Figure 5-6 (a) Raman spectra for 5 selected transistor devices with various values of effective mobility. The labels M0.4, M1.0, M4.6, M6.9, and M12 represent the devices with mobility 0.4, 1.0, 4.6, 6.9 and 12 cm^2/Vs respectively. (b) Various ratios for the integrated peak area for D, G, 2D and D+G bands. Reprinted with permission from [184]. Copyright 2009, American Chemical Society.

5.5 Conclusions

In this chapter combining hydrazine reduction with high temperature annealing, GO sheets were restored to more graphitic structures with relatively high hole mobility ($4\sim 12\text{ cm}^2/\text{Vs}$). It was also found that larger GO sheets could obtain lower sheet resistance: $\sim 188\text{ k}\Omega/\square$ with 98% transparency using ultra-large GO sheets. Sheet resistance was improved compared with previous work, yet not enough for industrial applications. Although relative high hole mobility was obtained compared with other organic materials, several issues are still left to be further investigated, including high threshold voltage, low on-off ratio, lack of ambipolar behaviour and non-saturated output curves. Therefore, further improvements in lowering sheet resistance and obtaining higher mobility will be more essential. Raman spectroscopic studies showed that the structure of the rGO sheets was converted from amorphous to more graphitic states and the ratio $I(2D)/I(G)$ was better correlated to the hole mobility of the rGO.

Chapter 6 Graphitization by Alcohol-CVD Method

6.1 Introduction

High temperature annealing under ultrahigh vacuum (UHV), inert or reducing conditions has been proved to be an efficient method for the graphitization of GO [18, 50, 184], but for individual single-layer rGO transistors on SiO₂, the highest hole mobility obtained at room temperature was $\sim 12 \text{ cm}^2/\text{Vs}$ in Chapter 5 [184], which was far below the value of $\sim 4050 \text{ cm}^2/\text{Vs}$ for graphene produced by CVD growth method [26]. Although thermal annealing could remove oxygen functional groups efficiently, the increase of mobility still not good, which probably due to carbon loss during reduction and vacancy defects left [59, 126]. Therefore, further improvements are required not only to remove of oxygen functional groups, but also to graphitize the GO hexagonal structure, i.e. increasing of crystalline size. Systematic investigations particularly on the graphitic structure-electrical property relationship are needed.

It was discovered in this chapter that alcohol vapors were more effective in improving the graphitization of GO in contrast to the methods used in Chapter 5. After alcohol-CVD treatment low sheet resistance of TCFs ($\sim 15 \text{ k}\Omega/\square$, 96% transmittance at 550 nm) was obtained. The FETs made from these alcohol-CVD treated GO sheets also exhibited high hole mobility up to $210 \text{ cm}^2/\text{Vs}$. It was discovered that most of the oxygen functional groups could be almost removed by low temperature alcohol-CVD treatment (600°C). At higher temperature ($>800^\circ\text{C}$), the increase in domain size of nano-graphitic structures was the major cause for mobility and conductivity enhancement.

6.2 Graphitization of GO Using Alcohol Vapors

Alcohol has been used as the carbon feedstock to synthesize high-purity SWNT at high temperatures (550~900 °C) with the aid of catalytic particles. The OH radicals dissociated from alcohol molecules are able to attack carbon atoms with a dangling bond, leaving SWNT to survive in the reaction conditions [201]. Here, instead of growing SWNT, alcohol was adopted as carbon source to graphitize the GO sheets. In Figure 6-1 the Raman spectra of single-layer GO sheets before and after various graphitization procedures, including hydrazine vapor soaking (Hy), H₂-annealing (900 °C; 20% H₂ in Ar), alcohol-CVD (900 °C; Ar as carrier gas) and alcohol/H₂ CVD (900 °C; 20% H₂/Ar as carrier gas), were put together for comparison. The well-known G peak (at ~1585 cm⁻¹) and 2D peak (at ~2700 cm⁻¹) are characteristic of the sp²-hybridized carbon-carbon bonds in graphene [186, 193-195]. The ratio of the 2D to G, I(2D)/I(G) has been shown to be related to the degree of recovery for delocalized π electronic structure in graphitic materials (graphitization) [184, 195]. Figure 6-1(a) clearly showed that 2D peak intensity became much higher after treated with alcohol vapors (with or without introducing H₂ gas) than that treated with H₂-annealing or hydrazine vapor. This observation proved that the restoration of π electronic structure was strongly related to the presence of alcohol vapors. Nevertheless, pure alcohol vapor without H₂ would cause some amorphous carbons deposition on reduced graphene surface due to the recombination of excess carbon radicals decomposed from alcohol. Therefore, introducing small amounts of H₂ flow during the process would be helpful to keep the process clean by suppressing the formation of amorphous carbon.

Figure 6-1 (a) Raman spectra for single-layer GO sheets before and after various reduction procedures including hydrazine vapor soaking (Hy), H₂-annealing (900 °C; 20% H₂ in Ar), alcohol reduction (at 900 °C; Ar as a carrier gas) and alcohol/H₂ reduction (900 °C; 20% H₂/Ar as a carrier gas). (b) Raman spectra for the GO sheets after alcohol reduction at 600, 700, 800, 900 and 1000 °C. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.

It was noticed from Raman measurement in Figure 6-2(a) that there was no sign of forming amorphous carbon on GO film if 20% H₂/Ar was used as a carrier gas in alcohol-CVD. If no H₂ gas was provided (only Ar as a carrier gas) amorphous carbon can sometimes be observed on surface of rGO shown in Figure 6-2(b). In both case no amorphous carbon was found on substrates. To confirm the source of amorphous carbon another control experiment was done on HOPG with alcohol vapor carried by 20% H₂/Ar. No amorphous carbon and defects were found from Raman data (Figure 6-3). Therefore, in the subsequent alcohol-CVD processes 20% H₂/Ar was used to carry alcohol vapor for performing the graphitization of GO sheets.

Figure 6-2 Raman spectra taken at the sites with and without GO on SiO₂ substrates. (a) Sample was treated by alcohol (with 20% H₂/Ar) at 900 °C. (b) Sample was treated with alcohol but no H₂ gas at 900 °C. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.

Figure 6-3 Raman spectrum taken on HOPG after it was exposed to alcohol (20% H₂/Ar) at 900 °C. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.

In Figure 6-1(b) the influence of temperature on the Raman spectra of alcohol-CVD treated samples was shown at 600, 700, 800, 900 and 1000 °C. The 2D peak started to emerge out at 700 °C and became more pronounced at 900 and 1000 °C. The ratio $I(2D)/I(G)$ even reached a value >1.4 at 1000 °C. This temperature dependence study suggested that high temperature (900-1000 °C) alcohol treatment was able to achieve

efficient restoration of graphitic structure in GO. In addition, there was almost no change for the thickness of single-layer rGO sheets from AFM measurements.

Table 6-1 Comparison of ultrathin GO electrodes treated under different conditions. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.

Sample ID	Process	Transparency (%) @550nm)	Sheet resistance (kOhm/□)
1	20% H ₂ /Ar with Alcohol 900 °C, 30mins	98.2	43
2	20 %H ₂ /Ar 900 °C, 2hr	98.1	413
3	20% H ₂ /Ar with Alcohol 1000 °C, 30mins	96.2	15
4	20% H ₂ /Ar 1000 °C, 2hr	98.0	188
5 [%]	1100 °C vacuum annealing, 3hr	95.0	500
6 [^]	Hydrazine reduction	95.4	19000

% from reference [103]. ^ from reference [95].

6.3 Electrical Properties of alcohol-CVD Treated GO

6.3.1 Sheet Resistance Measurement of TCFs

To confirm the restoration of graphitic structures in rGO films by alcohol-CVD, TCFs on quartz substrates were prepared and treated at various temperatures. Table 6-1 showed that sheet resistance of the TCFs decreased from ~43 kΩ/□ (900 °C with alcohol) to ~15 kΩ/□ (1000 °C with alcohol), where the thin films had similar transparency (T=96-98%, corresponding to 1 or 2 layer GO). Since the absorption of single-layer graphene in the visible range is 2.7 %, the deviation of transparency among reported papers may come from the discontinuous coverage of GO sheets. For comparison, the GO thin films after high temperature annealing without alcohol exhibited significantly higher sheet resistance (188-413 kΩ/□). It was noted that the sheet resistance for the alcohol-treated GO electrodes at a lower temperature 900 °C, ~ 42k Ω/□ (T ~98%), was already comparable with the 40~100 kΩ/□ (T ~95%) obtained by vacuum annealing at 1100 °C [103]. The

typical sheet resistance for hydrazine-treated GO electrodes [95] was also listed in Table 6-1 for comparison. These results suggested that alcohol vapor-assisted graphitization was highly efficient in enhancing the conductivity of GO.

6.3.2 Electrical Measurement of FET devices

In addition, bottom-gated FET devices were fabricated using the rGO sheets, which were previously deposited on SiO₂/Si substrates and treated by alcohol-CVD (method in section 3.2). Figure 6-4(a) presented a typical output characteristics (drain current I_d vs. drain voltage V_d) for the device prepared from a single-layer rGO sheet after 1000 °C alcohol graphitization. Inset showed the optical image of the device, where reduced graphene edges were indicated by dotted white lines. Only rGO sheets with regular shapes and suitable sizes were selected for transistors fabrication because it was convenient to extract their field effect carrier mobility. Figure 6-4(b) showed the transfer curves (I_d vs. V_g) for the device at gate voltage ranging from -80V to 80V. No neutrality point (Dirac-point) was observed for the as-prepared device within V_g scanning range, likely because the rGO sheet was heavily *p*-doped. The dimethylformamide (DMF) vapor soaking was performed by putting the device in a sealed vessel together with a small drop of DMF beside the device for 8 hrs. The Dirac point of the device could be shifted back to 0~30 V after it was doped by DMF vapors with electrons. In addition, it was reasonable that the I_d was consequently reduced, shown in Figure 6-4(a), because of the decrease in the hole carrier concentration. The transfer curves for several other high mobility devices were provided in Figure 6-5, from which the ambipolar behavior of rGO devices was observed. The field-effect hole mobility was extracted based on the slope $\Delta I_d / \Delta V_g$ fitted to the linear regime of the transfer curves using the equation $\mu = (L / WC_{ox} V_d) (\Delta I_d / \Delta V_g)$, where L and W were device channel length and width, and C_{ox} was gate capacitance. The field effect mobility of the alcohol treated GO sheets was up to $\sim 210 \text{ cm}^2/\text{Vs}$ in ambient condition, which was at least two

orders of magnitude higher than the reported $\sim 0.1\text{--}1\text{ cm}^2/\text{Vs}$ after hydrazine reduction [181]. Figure 6-4(c) compiled the mobility data for the devices made from single-layer rGO sheets treated at various temperatures, where the number in parenthesis indicated the number of devices tested. The statistical results clearly demonstrated that the mobility increased with temperature, consistent with the Raman results in Figure 6-1(b). Moreover, the device mobility for the rGO sheet after annealing in H_2 gas at 1000°C was much lower than those treated by alcohol-CVD at the same temperature, consistent with the conclusion from Raman studies (Figure 6-1a).

Figure 6-4 (a) Typical output characteristics (drain current I_d vs. drain voltage V_d) and (b) transfer curves for a single-layer GO sheet after 1000°C alcohol-CVD with or without DMF treatment. (c) The statistical mobility data for the devices made from single-layer GO sheets treated at various temperatures. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.

Figure 6-5 Transfer characteristics for two other devices made from alcohol treated GO sheets (1000°C). These devices were treated with DMF soaking before measurements. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.

6.4 Correlation between Spectroscopic Data and Electrical Properties

To correlate the electrical properties of the single-layer GO sheets with their structural changes, confocal Raman spectroscopy was adopted to directly characterize the rGO sheets in transistor devices with effective field-effect mobility values from 0.05 to $210 \text{ cm}^2/\text{Vs}$. The mobility values were extracted only after DMF soaking; therefore, they were used as the indices for the degree of graphitic structure restoration. The correlations of several Raman features (G peak position, 2D peak position, 2D peak width and integrated peak ratio of $I(\text{D})/I(\text{G})$, $I(2\text{D})/I(\text{G})$) with the field-effect mobility were shown in Figure 6-6,

where the Raman data before DMF soaking were also included for comparison.

Figure 6-6 The correlations of (a) G peak position, (b) 2D peak width, (c) integrated peak ratio of $I(\text{D})/I(\text{G})$ and (d) integrated peak ratio of $I(2\text{D})/I(\text{G})$ and, (e) 2D peak frequency with the field-effect hole mobility. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.

In general, the Dirac point of each device was shifted toward 0 V after DMF soaking, and the p -doping effect was reduced. The trend of n -doping of rGO by DMF was also

confirmed by the left-shift of Raman 2D frequency [197] after DMF soaking, as shown in Figure 6-6(e). Hence, the relation between Raman signatures and carrier mobility in Figure 6-6 was more informative because both sets of data (before and after DMF soaking) were included. All Raman peaks including G, D, D', 2D and other high-energy overtone bands in each spectrum were fitted with a Lorentzian function (see Figure 6-7 for an example). Figure 6-6(a) demonstrated that the peak position of the G-band initially at $\sim 1600\text{ cm}^{-1}$ was clearly downshifted to 1590 cm^{-1} with the increase of mobility in the early stage (from ~ 0.05 up to $10\text{ cm}^2/\text{Vs}$; corresponding to the graphitization performed at $\leq 800^\circ\text{C}$). It has been concluded that the downshift of G peak frequency in graphite corresponded to the development of long-range in-plane order or establishment of a three-dimensional graphite structure [170, 202]. At this stage, the chemical functional groups were being removed and six-fold graphitic rings were built up. XPS characterizations shown in Figure 6-8(a) suggested that the removal of the majority of chemical functional groups (oxygen containing species such as C-O and C=O) occurred even at a lower temperature regime ($< 600^\circ\text{C}$). With further increase in device mobility (from 10 up to $210\text{ cm}^2/\text{Vs}$; corresponding to the temperature $\geq 800^\circ\text{C}$), the G peak frequency approached to 1590 cm^{-1} and became less sensitive to the mobility. The less sensitive and lower G-band frequency corresponded well to the restoration of the graphitic structure in rGO, and similar observations for graphite have been reported [202]. This suggested that at higher temperature the growth of nano-graphitic domains became the dominant process rather than the removal of chemical functional groups [184]. Moreover, the 2D peak located at $\sim 2700\text{ cm}^{-1}$, the 2nd order Raman feature of the D peak, originated from a double-resonance process [169, 170, 195, 196]. The decrease of the 2D peak width has been used to indicate the restoration of graphitic structures in graphite [202]. Figure 6-6(b) showed that the 2D peak width decreased rapidly with mobility in the low mobility regime and approached 50 cm^{-1} in the high mobility regime, corresponding well to the evolution of the G peak

frequency in Figure 6-7(a).

Examining the evolution of $I(D)/I(G)$ with mobility (as shown in Figure 6-6(c)) would help to provide structural information of the rGO with different degree of graphitization. Ferrari et al. have reported that the development of Raman D peak indicated disordering of graphite but ordering of amorphous carbon structures [169]. We believed the model provided by Ferrari et al. can be used to interpret our Raman results (Figure 6-6(c)). For very disordered structure such as amorphous carbon or low mobility rGO the probability of finding a six-fold ring in the cluster was low and the intensity of D peak was related to the richness of aromatic rings. Meanwhile, the G peak was caused by in-plane bond stretching of sp^2 C atoms pairs, and it occurred at all sp^2 sites and was not necessarily related to the presence of a six-fold ring. Therefore, $I(D)/I(G)$ increased with mobility for rGO at low mobility regime (mobility $< 1 \text{ cm}^2/\text{Vs}$). Once the structure of reduced-GO was better (more ordered), $I(D)/I(G)$ decreased with decreasing disorder in graphitic structures. Tuinstra and Koenig (TK) had noted that $I(D)/I(G)$ varied inversely with the crystallite size L_a in graphite: $I(D)/I(G)=C(\lambda)/L_a$ [171], where $C(\lambda)$ was the constant related to the excitation wavelength used in Raman measurement. The TK relation was only valid when the aromatic domains were already present; hence, the relation was only used to estimate the crystalline domain size for the rGO sheets with high mobility ($>1 \text{ cm}^2/\text{Vs}$ in our case), where the structure of rGO was closer to the graphene structure. Figure 6-8(b) showed that the estimated nano-graphitic domain size (calculated from TK relation) increased from 1 nm to ~ 4 nm when the mobility was increased from 10 to $210 \text{ cm}^2/\text{Vs}$, where the $C(\lambda)$ for a 488 nm laser was estimated to be 4.4 nm [170, 203].

Figure 6-6(d) showed that the ratio $I(2D)/I(G)$ increased slowly in the low mobility regime and faster in the high mobility regime. Both the downshift of G peak position and the increase of the $I(2D)/I(G)$ ratio could be attributed to either (1) de-doping of p -typed

carriers in graphene [14, 197, 198] or (2) recovery of sp^2 C=C bonds (graphitization) in graphitic structures [195]. The $I(2D)/I(G)$ trend in Figure 6-6(d) was the same before and after DMF doping, although the Dirac point of these devices was greatly left-shifted, suggesting that the general observation for $I(2D)/I(G)$ was not governed by doping or de-doping here. Therefore, the graphitization appeared to be a more appropriate explanation for the increase of $I(2D)/I(G)$, corroborating the conclusion from Figure 6-6(c).

Figure 6-7 Raman (a) D, G and D', and (b) TO+LA, 2D, D+G, 2D' peaks fitted with Lorentzian peaks. The Raman spectrum was taken from a rGO sheet (alcohol-CVD at 900°C). Reprinted with permission from [192]. Copyright 2009, American Chemical Society.

Figure 6-8 (a) XPS data for the rGO sheets treated at indicated various temperatures. (b) The estimated graphene nano-graphitic size (L_a) increased with the mobility. Reprinted with permission from [192]. Copyright 2009, American Chemical Society.

6.5 Conclusions

In summary, the rGO sheets treated by high temperature alcohol-CVD exhibited highly integrated graphitic structures and excellent electrical conductivity and carrier mobility. Raman spectroscopic studies revealed that the conductivity and mobility increase in the low mobility regime was attributed to the removal of chemical functional groups and the formation of six-fold rings. In the high mobility regime, the growth of the graphitic domain size became dominant in restoring the electrical properties of rGO. More investigations are required to further suppress the Raman D peak and promote the quality of rGO sheets.

Chapter 7 Influence of Doping on Alcohol-CVD Graphitized rGO

7.1 Introduction

To improve the graphitization degree of GO we proposed an alcohol-CVD method in Chapter 6, where alcohol was used as the carbon source to heal the defects inside the GO basal plane [192]. Field-effect hole mobility as high as $\sim 210 \text{ cm}^2/\text{Vs}$ was obtained from these rGO samples. Recently similar CVD methods were also adopted to graphitize GO [98, 101, 102], and excellent electrical results were obtained. Graphitization of GO by CVD methods has great advantages over traditional reduction methods and holds the promise to fully return GO to pristine graphene [189].

Although highest mobility value was obtained from rGO graphitized by alcohol-CVD method, existed issues, including strong *p*-doping and lack of ambipolar behavior, prevented the comprehensively study of the structure and quality of reduced graphene sheets. In previous studies heavily *p*-doping behavior was also observed from rGO sheets under ambient after thermal annealing ($150 \text{ }^\circ\text{C} \sim 1000 \text{ }^\circ\text{C}$), and the ambipolar transfer curves became less pronounced or even unipolar-like [58, 98, 101, 102, 192]. This phenomenon was attributed to the existence of residual positively charged hydroxyl groups after reduction in the publication of Tung et al. [58].

In previous studies it has been shown that graphene strongly deforms and couples intensely with SiO_2 substrates after thermal annealing ($< 500 \text{ }^\circ\text{C}$) [204-206]. After alcohol-CVD treatment, strain and doping occur simultaneously in rGO, making the study of rGO complicated. Thus, it is reasonable to separate these rGO sheets from SiO_2 substrates onto new SiO_2 substrates without undergoing thermal annealing to minimize the strain and

doping effects.

The ambipolar behavior of rGO FETs recovered after DMF-doping and became more prominent after PMMA-assisted transfer [207, 208]. The Dirac transfer curves were comparable to those of mechanical exfoliated graphene (M-graphene) devices. By comparing the width, position and intensity ratio of Raman peaks before and after DMF-doping and PMMA-transfer, the reason of the heavily *p*-doping behavior occurrence was obtained, which was related to the strongly interaction between rGO and substrates. The TK relation was also found to be sensitive with doping.

7.2 Evolution of Raman Spectra of rGO by Different Graphitization Progresses

To improve the graphitization degree of GO, various methods have been adopted in our experimental works [184, 192]: hydrazine reduction, hydrazine reduction combined with thermal annealing in H₂, thermal annealing in Ar, and alcohol-CVD method. The normalized Raman spectra of rGO samples obtained by above methods were shown in Figure 7-1. The Raman data of PMMA-transferred rGO (the same sample by alcohol-CVD at 1000°C) and M-graphene samples with different defect levels were also given for comparing.

The evolution of Raman peaks (especially D and 2D peaks) was very clear in Figure 7-1. The best result was obtained by alcohol-CVD graphitization method (1000 °C). In Figure 7-1 the 2D peak height of rGO treated by alcohol-CVD was much higher than that of rGO treated by hydrazine, Ar-annealing or H₂-annealing. This observation demonstrated that the high efficiency of restoring sp² carbon network was strongly related to the presence of alcohol vapors. It could be seen that after transfer of the rGO treated by alcohol-CVD, its Raman spectrum was almost the same with that of M-graphene with large defects. In

Figure 7-1 G peak ($\sim 1585\text{ cm}^{-1}$, E_{2g} zone center mode), which is related to the sp^2 -hybridized carbon-carbon bonds in graphene, became narrower and separated from the D' peak ($\sim 1620\text{ cm}^{-1}$, from intravalley (DR) Raman scattering) [170]. The position and width of G peak can be strongly influenced by doping and strain, which will be discussed later. The D peak ($\sim 1350\text{ cm}^{-1}$) originates from intervalley DR Raman scattering, and the ratio $I(D)/I(G)$ has been used to estimate the crystalline size of graphene domain (TK relation) [171]. After PMMA transfer the intensity of D peak increased and its width narrowed. It is shown here that $I(D)/I(G)$ is influenced by doping or strain. Thus the domain size calculated from TK relation may not be precise.

Figure 7-1 Raman spectra evolution of rGO under different reduction methods: hydrazine vapor (Hy), hydrazine following thermal annealing in H_2 (Hy+ H_2), annealing in Argon (Ar), alcohol-CVD graphitization (A-CVD). Mechanically exfoliated graphene (M-graphene) with different defect levels and Transferred A-CVD (the same A-CVD sample after PMMA transfer) Raman spectra were also listed for comparison. The numbers in parentheses denotes the reduction temperature ($^{\circ}C$).

2D peak ($\sim 2700\text{ cm}^{-1}$) is the overtone of D peak and is extremely sensitive to the delocalized π electronic structure. The Intensity ratio $I(2D)/I(G)$ can be used to monitor the doping of graphene [14] or restoration of aromatic rings [195]. For the same sample A-CVD (1000), after PMMA-transfer, 2D became much higher and narrower and the value

of $I(2D)/I(G)$ reached ~ 1.85 , which is comparable with that of M-graphene with large defects (~ 1.76). The highest value of $I(2D)/I(G)$ obtained was ~ 2.85 , close to that of M-graphene with small defects (~ 3.4). The effect of PMMA transfer on Raman spectra would be discussed later. All these data showed that the amorphous structure of GO was greatly removed after alcohol-CVD graphitization.

7.3 Raman Spectroscopic Study of Doped and Transferred Graphene

After high temperature annealing and cooling processes, compression and ripples can be formed in graphene because of its negative thermal expansion coefficient (TEC) [204]. In detail when a graphene sample is heated, the substrate expands and graphene contracts. When the sample is cooled down, graphene expands while the substrate contracts. From AFM measurements dome-like islands with a lateral size of several nm are often observed, which indicates that rGO sheets deform significantly after alcohol-CVD process. Compressive strain in graphene and strong interactions between graphene and the substrates can be generated. Thus, the Raman spectra and electrical properties of rGO sheets by alcohol-CVD will be influenced by either doping or strain.

To study this issue, PMMA-transfer process was performed on as-reduced rGO sheets and rGO FET devices with Au electrodes. PMMA was spin coated onto substrates and 1M KOH solution was used to etch away the silicon dioxide layers. After peeled off, graphene-PMMA films were washed by DI water and put onto new SiO_2 substrates carefully. After drying without any heating process, PMMA was washed away by large amount of acetone. Gold electrodes were coated on top of transferred rGO sheets by hard mask method (details in section 3.2). For those samples transferred with their electrodes, the transferred electrodes can still be used for electrical measurements.

In Figure 7-1 it can be seen that the position and intensity of Raman D, G, 2D peaks changed greatly after PMMA transfer. The main influencing factor (either strain or doping) needs to be investigated. The 2D peak position as a function of G peak position before and after PMMA transfer was shown in Figure 7-2. These Raman spectra were collected from rGO samples graphitized by alcohol-CVD at 900 °C. The G peak positions of as-reduced rGO samples all located at above 1600 cm^{-1} and down-shifted 3~18 cm^{-1} after PMMA transfer. After thermal annealing, the up-shift of G peak was found to be related to hole doping instead of compressive strain [205]. The doping can be controlled by two independent factors: the degree of graphene coupling to the substrate and exposure to oxygen and moisture. For the positions of 2D peak, downshifts were observed at 7~32 cm^{-1} after PMMA transfer. Biaxial strain (compress) can induce shifts of G and 2D peaks, but it does not influence the electronic properties of graphene [209]. And in our former electrical studies heavily *p*-doping behavior was observed in rGO samples by alcohol-CVD graphitization [192]. After transfer the *p*-doping is minimized (Dirac points approaching 0 V). So we attribute doping to be the main factor inducing Raman peak shifts and electronic properties.

In Figure 7-3 the ratio $I(2D)/I(G)$ as a function of $\text{Pos}(G)$ was plotted. It was clearly seen that after PMMA transfer the intensity ratio of 2D to G increased up to ~1.6, accompanying with the down-shift of G peak position. However, the softening of G peak (G width increase) was observed with the up-shift of G peak position, as shown in Figure 7-4. This phenomenon was contrary to that of M-graphene, yet it was consistent with that of nano-graphite, indicating that the structure of our rGO samples is nano-graphite like with lots of structural disorders [199].

Figure 7-2 2D peak position $\text{Pos}(2D)$ as a function of G peak position $\text{Pos}(G)$ before and after PMMA transfer.

Figure 7-3 $I(2D)/I(G)$ ratio as a function of G peak position $\text{Pos}(G)$.

Figure 7-4 G peak width $\text{FWHM}(G)$ as a function of G peak position $\text{Pos}(G)$.

To lower the p -doping, DMF was used to dope some of our rGO samples with electrons. And these DMF-doped rGO samples were also transferred to new SiO₂ substrates. In Figure 7-5 we summarized the peak width of D and 2D as a function of graphitization temperatures after DMF doping and PMMA transfer. In Figure 7-6 $I(D)/I(G)$ and $I(2D)/I(G)$ as a function of graphitization temperatures after DMF doping and PMMA transfer were drawn. Their average FET mobility values were also listed in top [192]. In Figure 7-5(a) it was shown that the D peak width decreased with graphitization temperatures. It became narrower after DMF doping, and further decreased after PMMA transfer. Correspondingly $I(D)/I(G)$ in Figure 7-6(a) increased (600 °C ~800 °C) and then decreased (800 °C ~1000 °C). $I(D)/I(G)$ was also found to increase after DMF doping and PMMA transfer, which means that doping can influence the value of $I(D)/I(G)$. Thus the crystalline size calculated from the TK relation will be overestimated. The narrowing of D peak width has been found to be related to the increase of graphene domain size [210], and the increase of D peak intensity has been related to the enlargement of aromatic domain size within sp^3 carbon matrix [211].

Figure 7-5 (a) D, (b) 2D peak width as a function of graphitization temperatures after DMF doping and PMMA transfer.

Figure 7-6 (a) $I(D)/I(G)$, (b) $I(2D)/I(G)$ as a function of graphitization temperatures.

2D peak is extremely sensitive to the delocalized π electronic structure. Figure 7-5(b) shows that the 2D peak width decreased rapidly with graphitization temperatures. The decrease of the 2D peak width has been used to indicate the restoration of graphitic structures in graphite [202]. In Figure 7-6(b) $I(2D)/I(G)$ increased with graphitization temperatures. At specific temperatures, $I(2D)/I(G)$ ratio increased after n -doping by DMF, and further increased after PMMA transfer, indicating the strong interaction between rGO and substrates and heavily p -doping are minimized. The increase of the $I(2D)/I(G)$ ratio has been related to de-doping of p -typed carriers in graphene [14, 198]. Overall, the increase of $I(2D)/I(G)$ with graphitization temperatures means that the graphitic structures are greatly recovered in our rGO samples [192, 195].

7.4 Electrical Properties of Transferred rGO

There are two kinds of methods to calculate the field effect mobility: the first formula is: $\mu = (L/WC_{\text{ox}}V_d)(I_d/V_g)$, where L and W are the channel length and width, V_d is source-drain voltage, I_d is source drain current, V_g is gate voltage and C_{ox} the gate capacitance; The second method $\mu = (nep)^{-1}$ is only valid in the saturation region (metallic regime) of transfer curve because only here n is uniform [1, 98, 176] and exclusive of electron hole puddles

[13]. e is the electron charge, ρ is the sheet resistivity, n is carrier density [1].

In Figure 7-7(a) two typical Dirac curves of FET devices made from PMMA-transferred rGO samples were shown. After PMMA transfer ambipolar behavior was recovered with Dirac points located at $\sim 12\text{V}$ and $\sim 43\text{V}$, and the Dirac curve of sample 1 even reached to the metallic regime similar with that of M-graphene, as shown in Figure 7-7(b). The mobility calculated from the second formula is more precise [1, 98, 176]. For our rGO samples, additional method like scaling of the transfer curve was not needed to calculate the mobility in the saturation area [98]. We calculated hole mobility with the above two formulas and obtained mobility values of sample 1: $116.05\text{ cm}^2/\text{Vs}$ by the first formula and $252.3\text{ cm}^2/\text{Vs}$ by the second formula. The difference between the two mobility values need be further studied.

Figure 7-7 Resistance as a function of gate voltage V_g for (a) different alcohol-CVD graphitized graphene samples, (b) mechanically exfoliated graphene (M-graphene) and alcohol-CVD graphitized graphene.

7.5 Comparing Alcohol-CVD with Other CVD Methods

In these similar CVD graphitization methods, acetylene (C_2H_2) [102], ethylene (CH_4) [98], and ammonia (NH_3) [101] were used as carbon sources. In all the works, the detailed

Raman spectra data was not provided, and especially the information of 2D peak was lack. So we only summarized their reaction conditions and FET mobility values in Table 7-1 and Figure 7-8. From Table 7-1 it could be seen that the highest mobility value ($\sim 210 \text{ cm}^2/\text{Vs}$) was obtained by alcohol-CVD, which indicated that the graphitic structure of our GO was best recovered among these CVD methods. For ammonia-CVD the mobility value was not calculated in their work and should be low because that carbon atoms of GO were replaced by nitrogen [101]. In Figure 7-8, it was seen that at 700°C , mobility value with $\sim 12 \text{ cm}^2/\text{Vs}$ was obtained by ethylene-CVD, which was close to that of alcohol-CVD ($\sim 10 \text{ cm}^2/\text{Vs}$) [98]. And the mobility value obtained by acetylene-CVD was $\sim 50 \text{ cm}^2/\text{Vs}$ at 800°C , which was higher than that of alcohol-CVD ($\sim 12 \text{ cm}^2/\text{Vs}$) [102]. However at higher temperatures ($>800^\circ\text{C}$) this value was not improved for acetylene-CVD [102].

Table 7-1 Summarizing of different CVD graphitization methods

Sample ID	Hole mobility (cm^2/Vs)	CVD condition
1[98]	12	ethylene(C_2H_4), 700°C , 90mins
2[102]	1~50	acetylene (C_2H_2), 800°C , 3mins
3[101]	N.A.	ammonia(NH_3), $500\sim 1100^\circ\text{C}$, 10mins
4[192]	0.1~210	alcohol($\text{C}_2\text{H}_5\text{OH}$), $600\sim 1000^\circ\text{C}$, 30mins

Figure 7-8 Comparing FET mobility values between alcohol-CVD and other CVD methods.

The dependence of FET mobility on alcohol-CVD graphitization temperatures was observed in Figure 7-8, while was not observed in ethylene-CVD and acetylene-CVD. To be mentioned, the other three methods were carried out with low pressures, while our method was performed at ambient conditions. To understand these discrepancies and the high graphitization efficiency of alcohol-CVD, the reaction mechanisms need be studied in future work.

Usually *p*-doping behavior is observed in M-graphene after thermal annealing under vacuum or buffer gas atmosphere [205]. The rGO samples by ethylene-CVD method showed less *p*-doping behavior in air, which was interesting [98]. These results indicated that the surface chemistry of substrates might be different under different CVD gas atmospheres, which was related to the doping behavior. One possible explanation was that the surfaces of SiO₂ substrates were hydrophobic under acetylene-CVD, and hydrophilic under alcohol-CVD. Doping of graphene can be reduced by putting graphene on hydrophobic surfaces [212]. *p*-doping was not observed (Dirac point at ~0V) under vacuum for rGO reduced by H₂ annealing [101]. Thus, the existence of residual positively charged hydroxyl groups after reduction [58] should not be responsible for the *p*-doping behavior.

7.6 Conclusions

The heavily *p*-doping behavior of rGO by alcohol-CVD was studied. The obvious changes of Raman peaks in width, position and intensity were observed from DMF-doped and PMMA-transferred rGO. Comparing to other CVD methods, rGO with better crystalline structures was obtained by alcohol-CVD method. This was confirmed by the excellent electrical data with ambipolar behavior and transfer curve approaching to the saturation regime. The ratio $I(D)/I(G)$ can be influenced by doping, thus doping effect must be considered when TK relation is used to evaluate the domain size of graphene samples.

Chapter 8 Conclusions and Future Recommendations

8.1 Conclusions

Comprehensive studies on graphitization of GO have been performed in this thesis. Traditional methods like hydrazine reduction, thermal annealing and a novel alcohol-CVD method were carried out to improve the crystalline structure of GO. A controllable method to produce ultra-large GO was put forward. The quality of reduced graphene was evaluated by Raman spectroscopy, FETs measurements, TCFs measurements and XPS measurements. Promising results have been obtained and these contributions can be summarized as follows:

(1) A sonication step was introduced into the pre-oxidation step of a modified Hummers' method, which could adjust the sheet size of produced GO. Lateral size up to 3mm was obtained.

(2) Hydrazine reduction and thermal annealing under H_2 were adopted to obtain rGO. Field-effect hole mobility with $\sim 12 \text{ cm}^2/\text{Vs}$ was obtained. TCFs made from ultra-large rGO sheets exhibited lower sheet resistance compared with those made from small-size rGO sheets. And Raman peak ratio $I(2D)/I(G)$ was found to be well correlated to the structure transition of rGO from amorphous to graphitic states.

(3) Alcohol-CVD method was first adopted to repair the defects inside GO basal plane and improve the crystalline size of rGO. Alcohol vapor was served as carbon source. Field-effect hole mobility as high as $210 \text{ cm}^2/\text{Vs}$ was obtained. The sheet resistance of TCFs was lowered to $15 \text{ k}\Omega/\square$ at $>96\%$ transparency.

(4) Raman spectra of alcohol-CVD graphitized rGO were correlated to the field-effect hole mobility and graphitic domain size. The increase of conductivity in the low mobility regime was attributed to the removal of chemical functional groups and the formation of six-fold rings. In the high mobility regime, the growth of the graphitic domain size became dominant for enhancing its electrical conductivity. The obtained rGO sheets with excellent electrical and structural properties show great promise for potential electrical applications.

(5) The *p*-doping behavior of rGO was studied by Raman spectroscopic and electrical measurements of DMF-doped and PMMA-transferred rGO. It was concluded that after high temperature treatment rGO sheets coupled closely with underlying SiO₂ substrate. The rGO was activated to donate electrons to surrounding environments like oxygen molecular and water moisture, which induced the heavily *p*-doping behavior.

(6) After PMMA-transfer, the Dirac transfer curves of rGO FETs showed obvious ambipolar behavior under ambient and I(2D)/I(G) ratio as high as ~2.85 was obtained. All these results revealed that better crystalline quality was obtained by alcohol-CVD graphitization method. Comparing with those rGO produced by other CVD graphitization methods, the efficiency of alcohol vapor was shown to be the highest.

(7) TK relation of rGO was found to be sensitive to doping. Thus the doping effect need be considered when TK relation is used to estimate the domain size of disordered graphene.

8.2 Future Recommendations

8.2.1 Increasing the Quality and Size of rGO

Although GO sheets with size up to 3mm were obtained in Chapter 5, the yield of them is

quite low. The defects in rGO arise from the oxidation and reduction procedures. To obtain GO with better quality (less defects), the oxidation time or degree should be lowered. So in the next step, we will try to find a way to oxidize graphite flakes moderately and increase sheet size of GO simultaneously. Another crucial issue is to understand the oxidation mechanisms which will help us to fabricate better graphene based composites and thin films. Thus, following steps are suggested:

Step 1: Reduce sonication power in the pre-oxidation step. Strong sonication power will break graphite into small pieces. A soft power will be used in order to keep graphite larger.

Step 2: Additional surfactant is added before KMnO_4 . Surfactant, like sodium dodecyl sulfate (SDS) which is used for wrapping carbon nanotubes, is selected to avoid further oxidation of GO.

Step 3: Reduce the oxidation degree of GO by control the amount of KMnO_4 . In the experiment, the proper amount of KMnO_4 need to be found, in order to avoid the heavy breakage of the aromaticity on the basal plane of GO.

8.2.2 Study the Mechanism of alcohol-CVD Graphitization

Up to now, a lot of experimental and theoretical studies have been done to reduce GO by hydrazine and thermal annealing, however, the mechanism of CVD-repair method is still not every clear. Our experimental results and other published results all prove that CVD method has the advantage to produce graphene with excellent electrical properties for electronic applications. So we suggest to study the reduction protocols by simulation, in order to get better understanding about how alcohol could graphitize GO under high temperature and which conditions can be used improve this process. Several experiments can be carried out to get high quality graphene, such as control the pressure of CVD process, change of the concentration of hydrogen carrier gas, etc.

8.2.3 Fabrication of Suspended rGO FET Devices

In chapter 6 and 7 after we transfer as-reduced graphene to new substrates, undesirable doping during transferring may happen. In the studies about mechanically exfoliated graphene, suspended graphene FET devices have provided a lot of useful information on the structure and electrical properties of graphene. So if suspended rGO FET devices could be the fabricated, the electrical conduction mechanisms of rGO will be clear. We suggest using the buffered oxide etching (BOE) method which is controllable and fast. Higher mobility than $210 \text{ cm}^2/\text{Vs}$ should be obtained from suspended rGO FET devices.

Reference

1. Novoselov, K.S., et al., *Electric Field Effect in Atomically Thin Carbon Films*. Science, 2004. **306**(5696): 666-669.
2. Novoselov, K.S., et al., *Two-dimensional gas of massless Dirac fermions in graphene*. Nature, 2005. **438**(7065): 197-200.
3. Novoselov, K.S., et al., *Two-dimensional atomic crystals*. Proceedings of the National Academy of Sciences of the United States of America, 2005. **102**(30): 10451-10453.
4. Bolotin, K.I., et al., *Ultrahigh electron mobility in suspended graphene*. Solid State Communications, 2008. **146**(9-10): 351-355.
5. Ozyilmaz, B., et al., *Electronic Transport and Quantum Hall Effect in Bipolar Graphene p-n-p Junctions*. Physical Review Letters, 2007. **99**(16): 166804-4.
6. Zhang, Y., et al., *Experimental observation of the quantum Hall effect and Berry's phase in graphene*. Nature, 2005. **438**(7065): 201-204.
7. Han, M.Y., et al., *Energy Band-Gap Engineering of Graphene Nanoribbons*. Physical Review Letters, 2007. **98**(20): 206805-4.
8. Zhang, Y., et al., *Direct observation of a widely tunable bandgap in bilayer graphene*. Nature, 2009. **459**(7248): 820-823.
9. Lee, C., et al., *Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene*. Science, 2008. **321**(5887): 385-388.
10. Balandin, A.A., et al., *Superior Thermal Conductivity of Single-Layer Graphene*. Nano Letters, 2008. **8**(3): 902-907.
11. Chen, Z., et al., *Graphene nano-ribbon electronics*. Physica E: Low-dimensional Systems and Nanostructures, 2007. **40**(2): 228-232.
12. Lemme, M.C., et al., *A Graphene Field-Effect Device*. Electron Device Letters, IEEE, 2007. **28**(4): 282-284.
13. Martin, J., et al., *Observation of electron-hole puddles in graphene using a scanning single-electron transistor*. Nat Phys, 2008. **4**(2): 144-148.
14. Das A, et al., *Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor*. Nat Nano, 2008. **3**(4): 210-215.
15. Eda, G., G. Fanchini, and M. Chhowalla, *Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material*. Nat Nano, 2008. **3**(5): 270-274.
16. Wang, Y., et al., *Large area, continuous, few-layered graphene as anodes in organic photovoltaic devices*. Applied Physics Letters, 2009. **95**(6): 063302-3.

17. Tung, V.C., et al., *Low-Temperature Solution Processing of Graphene-Carbon Nanotube Hybrid Materials for High-Performance Transparent Conductors*. Nano Letters, 2009. **9**(5): 1949-1955.
18. Wang, X., L. Zhi, and K. Mullen, *Transparent, Conductive Graphene Electrodes for Dye-Sensitized Solar Cells*. Nano Letters, 2007. **8**(1): 323-327.
19. Chen, C., et al., *Performance of monolayer graphene nanomechanical resonators with electrical readout*. Nat Nano, 2009. **4**(12): 861-867.
20. Stankovich, S., et al., *Graphene-based composite materials*. Nature, 2006. **442**(7100): 282-286.
21. Xie, S.H., Y.Y. Liu, and J.Y. Li, *Comparison of the effective conductivity between composites reinforced by graphene nanosheets and carbon nanotubes*. Applied Physics Letters, 2008. **92**(24): 243121-3.
22. Yoo, E., et al., *Large Reversible Li Storage of Graphene Nanosheet Families for Use in Rechargeable Lithium Ion Batteries*. Nano Letters, 2008. **8**(8): 2277-2282.
23. Eizenberg, M. and J.M. Blakely, *Carbon monolayer phase condensation on Ni(111)*. Surface Science, 1979. **82**(1): 228-236.
24. Kim, K.S., et al., *Large-scale pattern growth of graphene films for stretchable transparent electrodes*. Nature, 2009. **457**(7230): 706-710.
25. Sutter, P.W., J.-I. Flege, and E.A. Sutter, *Epitaxial graphene on ruthenium*. Nat Mater, 2008. **7**(5): 406-411.
26. Li, X., et al., *Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils*. Science, 2009. **324**(5932): 1312-1314.
27. Bae, S., et al., *Roll-to-roll production of 30-inch graphene films for transparent electrodes*. Nat Nano, 2010. **5**(8): 574-578.
28. Berger, C., et al., *Ultrathin Epitaxial Graphite: 2D Electron Gas Properties and a Route toward Graphene-based Nanoelectronics*. The Journal of Physical Chemistry B, 2004. **108**(52): 19912-19916.
29. Berger, C., et al., *Electronic Confinement and Coherence in Patterned Epitaxial Graphene*. Science, 2006. **312**(5777): 1191-1196.
30. Emtsev, K.V., et al., *Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide*. Nat Mater, 2009. **8**(3): 203-207.
31. Stankovich, S., et al., *Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate)*. Journal of Materials Chemistry, 2006. **16**(2): 155-158.
32. Park, S. and R.S. Ruoff, *Chemical methods for the production of graphenes*. Nat Nano, 2009. **4**(4): 217-224.
33. Dikin, D.A., et al., *Preparation and characterization of graphene oxide paper*. Nature, 2007. **448**(7152): 457-460.

34. Wang, H., et al., *Solvothermal Reduction of Chemically Exfoliated Graphene Sheets*. Journal of the American Chemical Society, 2009. **131**(29): 9910-9911.
35. Peierls, R.E., *Quelques proprietes typiques des corps solides*. Ann. I. H. Poincare, 1935. **5**: 177-222.
36. Landau, L.D., *Zur Theorie der phasenumwandlungen* Phys. Z. Sowjetunion II, 1937. **11**: 26-35.
37. Venables, J.A., G.D.T. Spiller, and M. Hanbucken, *Nucleation and growth of thin films*. Reports on Progress in Physics, 1984(4): 399.
38. Evans, J.W., P.A. Thiel, and M.C. Bartelt, *Morphological evolution during epitaxial thin film growth: Formation of 2D islands and 3D mounds*. Surface Science Reports, 2006. **61**(1-2): 1-128.
39. Jung, I., et al., *Simple Approach for High-Contrast Optical Imaging and Characterization of Graphene-Based Sheets*. Nano Letters, 2007. **7**(12): 3569-3575.
40. Meyer, J.C., et al., *The structure of suspended graphene sheets*. Nature, 2007. **446**(7131): 60-63.
41. Dreyer, D.R., et al., *The chemistry of graphene oxide*. Chemical Society Reviews, 2010. **39**(1): 228-240.
42. Eda, G., et al., *Blue Photoluminescence from Chemically Derived Graphene Oxide*. Advanced Materials, 2010. **22**(4): 505-509.
43. Brodie, B.C., *On the atomic weight of graphite*. Proceedings of the royal society of London(1859-1860), 1859. **10**: 11-12.
44. Staudenmaier, L., *Verfahren zur darstellung der graphitsaure*. Ber Dtsch Chem Ges, 1898. **31**: 1481-1499.
45. Hummers, W.S. and R.E. Offeman, *Preparation of Graphitic Oxide*. Journal of the American Chemical Society, 1958. **80**(6): 1339-1339.
46. Stankovich, S., et al., *Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide*. Carbon, 2007. **45**(7): 1558-1565.
47. Jung, I., et al., *Tunable Electrical Conductivity of Individual Graphene Oxide Sheets Reduced at "low" Temperatures*. Nano Letters, 2008. **8**(12): 4283-4287.
48. Park, S., et al., *Colloidal Suspensions of Highly Reduced Graphene Oxide in a Wide Variety of Organic Solvents*. Nano Letters, 2009. **9**(4): 1593-1597.
49. Luo, Z., et al., *High Yield Preparation of Macroscopic Graphene Oxide Membranes*. Journal of the American Chemical Society, 2009. **131**(3): 898-899.
50. Becerril, H.A., et al., *Evaluation of Solution-Processed Reduced Graphene Oxide Films as Transparent Conductors*. ACS Nano, 2008. **2**(3): 463-470.
51. Li, D., et al., *Processable aqueous dispersions of graphene nanosheets*. Nat Nano,

2008. **3**(2): 101-105.
52. Pham, V.H., et al., *Fast and simple fabrication of a large transparent chemically-converted graphene film by spray-coating*. Carbon, 2010. **48**(7): 1945-1951.
53. Zhao, J., et al., *Efficient Preparation of Large-Area Graphene Oxide Sheets for Transparent Conductive Films*. ACS Nano, 2010. **4**(9): 5245-5252.
54. Matyba, P., et al., *Graphene and Mobile Ions: The Key to All-Plastic, Solution-Processed Light-Emitting Devices*. ACS Nano, 2010. **4**(2): 637-642.
55. Eda, G. and M. Chhowalla, *Chemically Derived Graphene Oxide: Towards Large-Area Thin-Film Electronics and Optoelectronics*. Advanced Materials, 2010. **22**(22): 2392-2415.
56. Kovtyukhova, N.I., et al., *Layer-by-Layer Assembly of Ultrathin Composite Films from Micron-Sized Graphite Oxide Sheets and Polycations*. Chemistry of Materials, 1999. **11**(3): 771-778.
57. Xu, Y., et al., *Flexible Graphene Films via the Filtration of Water-Soluble Noncovalent Functionalized Graphene Sheets*. Journal of the American Chemical Society, 2008. **130**(18): 5856-5857.
58. Tung, V.C., et al., *High-throughput solution processing of large-scale graphene*. Nat Nano, 2009. **4**(1): 25-29.
59. Schniepp, H.C., et al., *Functionalized Single Graphene Sheets Derived from Splitting Graphite Oxide*. The Journal of Physical Chemistry B, 2006. **110**(17): 8535-8539.
60. McAllister, M.J., et al., *Single Sheet Functionalized Graphene by Oxidation and Thermal Expansion of Graphite*. Chemistry of Materials, 2007. **19**(18): 4396-4404.
61. Marcano, D.C., et al., *Improved Synthesis of Graphene Oxide*. ACS Nano, 2010. **4**(8): 4806-4814.
62. Paredes, J.I., et al., *Graphene Oxide Dispersions in Organic Solvents*. Langmuir, 2008. **24**(19): 10560-10564.
63. De, S. and J.N. Coleman, *Are There Fundamental Limitations on the Sheet Resistance and Transmittance of Thin Graphene Films?* ACS Nano, 2010. **4**(5): 2713-2720.
64. Moon, I.K., et al., *Reduced graphene oxide by chemical graphitization*. Nat Commun, 2010. **1**(6): 73.
65. Rogers, J.A., *Electronic materials: Making graphene for macroelectronics*. Nat Nano, 2008. **3**(5): 254-255.
66. Ganhua, L. and et al., *Reduced graphene oxide for room-temperature gas sensors*. Nanotechnology, 2009. **20**(44): 445502.

67. Robinson, J.T., et al., *Reduced Graphene Oxide Molecular Sensors*. Nano Letters, 2008. **8**(10): 3137-3140.
68. Fowler, J.D., et al., *Practical Chemical Sensors from Chemically Derived Graphene*. ACS Nano, 2009. **3**(2): 301-306.
69. Jung, I., et al., *Effect of Water Vapor on Electrical Properties of Individual Reduced Graphene Oxide Sheets*. The Journal of Physical Chemistry C, 2008. **112**(51): 20264-20268.
70. Cai, D., M. Song, and C. Xu, *Highly Conductive Carbon-Nanotube/Graphite-Oxide Hybrid Films*. Advanced Materials, 2008. **20**(9): 1706-1709.
71. Robinson, J.T., et al., *Wafer-scale Reduced Graphene Oxide Films for Nanomechanical Devices*. Nano Letters, 2008. **8**(10): 3441-3445.
72. Hernandez, Y., et al., *High-yield production of graphene by liquid-phase exfoliation of graphite*. Nat Nano, 2008. **3**(9): 563-568.
73. Geim, A.K., *Graphene: Status and Prospects*. Science, 2009. **324**(5934): 1530-1534.
74. Cai, D. and M. Song, *Preparation of fully exfoliated graphite oxide nanoplatelets in organic solvents*. Journal of Materials Chemistry, 2007. **17**(35): 3678-3680.
75. Eda, G. and M. Chhowalla, *Graphene-based Composite Thin Films for Electronics*. Nano Letters, 2009. **9**(2): 814-818.
76. RamanathanT, et al., *Functionalized graphene sheets for polymer nanocomposites*. Nat Nano, 2008. **3**(6): 327-331.
77. Verdejo, R., et al., *Functionalized graphene sheet filled silicone foam nanocomposites*. Journal of Materials Chemistry, 2008. **18**(19): 2221-2226.
78. Liang, J., et al., *Molecular-Level Dispersion of Graphene into Poly(vinyl alcohol) and Effective Reinforcement of their Nanocomposites*. Advanced Functional Materials, 2009. **19**(14): 2297-2302.
79. Villar-Rodil, S., et al., *Preparation of graphene dispersions and graphene-polymer composites in organic media*. Journal of Materials Chemistry, 2009. **19**(22): 3591-3593.
80. Watcharotone, S., et al., *Graphene-Silica Composite Thin Films as Transparent Conductors*. Nano Letters, 2007. **7**(7): 1888-1892.
81. Liu, Z., et al., *Organic Photovoltaic Devices Based on a Novel Acceptor Material: Graphene*. Advanced Materials, 2008. **20**(20): 3924-3930.
82. Eda, G., et al., *Field emission from graphene based composite thin films*. Applied Physics Letters, 2008. **93**(23): 233502-3.
83. Watcharotone, S., R.S. Ruoff, and F.H. Read, *Possibilities for graphene for field emission: modeling studies using the BEM*. Physics Procedia, 2008. **1**(1): 71-75.

84. Fowler, R.H. and L. Nordheim, *Electron Emission in Intense Electric Fields*. Proceedings of the Royal Society of London. Series A, 1928. **119**(781): 173-181.
85. Rafiee, M.A., et al., *Enhanced Mechanical Properties of Nanocomposites at Low Graphene Content*. ACS Nano, 2009. **3**(12): 3884-3890.
86. Gomez-Navarro, C., et al., *Electronic Transport Properties of Individual Chemically Reduced Graphene Oxide Sheets*. Nano Letters, 2007. **7**(11): 3499-3503.
87. Loh, K.P., et al., *Graphene oxide as a chemically tunable platform for optical applications*. Nat Chem, 2010. **2**(12): 1015-1024.
88. Pan, D., et al., *Hydrothermal Route for Cutting Graphene Sheets into Blue-Luminescent Graphene Quantum Dots*. Advanced Materials, 2010. **22**(6): 734-738.
89. Luo, Z., et al., *Photoluminescence and band gap modulation in graphene oxide*. Applied Physics Letters, 2009. **94**(11): 111909-3.
90. Cuong, T.V., et al., *Photoluminescence and Raman studies of graphene thin films prepared by reduction of graphene oxide*. Materials Letters, 2010. **64**(3): 399-401.
91. Chen, J.-L. and X.-P. Yan, *A dehydration and stabilizer-free approach to production of stable water dispersions of graphene nanosheets*. Journal of Materials Chemistry, 2010. **20**(21): 4328-4332.
92. Subrahmanyam, K.S., et al., *Blue light emitting graphene-based materials and their use in generating white light*. Solid State Communications, 2010. **150**(37-38): 1774-1777.
93. Gao, W., et al., *New insights into the structure and reduction of graphite oxide*. Nat Chem, 2009. **1**(5): 403-408.
94. Kim, J., et al., *Graphene Oxide Sheets at Interfaces*. Journal of the American Chemical Society, 2010. **132**(23): 8180-8186.
95. Cote, L.J., F. Kim, and J. Huang, *Langmuir-Blodgett Assembly of Graphite Oxide Single Layers*. Journal of the American Chemical Society, 2009. **131**(3): 1043-1049.
96. Shin, H.-J., et al., *Efficient Reduction of Graphite Oxide by Sodium Borohydride and Its Effect on Electrical Conductance*. Advanced Functional Materials, 2009. **19**(12): 1987-1992.
97. Si, Y. and E.T. Samulski, *Synthesis of Water Soluble Graphene*. Nano Letters, 2008. **8**(6): 1679-1682.
98. Gengler, R.Y.N., et al., *Large-Yield Preparation of High-Electronic-Quality Graphene by a Langmuir-Schaefer Approach*. Small, 2010. **6**(1): 35-39.
99. Wang, G., et al., *Facile Synthesis and Characterization of Graphene Nanosheets*. The Journal of Physical Chemistry C, 2008. **112**(22): 8192-8195.

100. Hofmann, U. and A. Frenzel, *The reduction of graphite oxide with hydrogen sulphide*. Kolloid-Zeitschrift, 1934. **68**(2): 149-151.
101. Li, X., et al., *Simultaneous Nitrogen Doping and Reduction of Graphene Oxide*. Journal of the American Chemical Society, 2009. **131**(43): 15939-15944.
102. López, V., et al., *Chemical Vapor Deposition Repair of Graphene Oxide: A Route to Highly-Conductive Graphene Monolayers*. Advanced Materials, 2009. **21**(46): 4683-4686.
103. Wu, J., et al., *Organic solar cells with solution-processed graphene transparent electrodes*. Applied Physics Letters, 2008. **92**(26): 263302-3.
104. Wu, X., et al., *Epitaxial-Graphene/Graphene-Oxide Junction: An Essential Step towards Epitaxial Graphene Electronics*. Physical Review Letters, 2008. **101**(2): 026801-4.
105. Williams, G., B. Seger, and P.V. Kamat, *TiO₂-Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide*. ACS Nano, 2008. **2**(7): 1487-1491.
106. Cote, L.J., R. Cruz-Silva, and J. Huang, *Flash Reduction and Patterning of Graphite Oxide and Its Polymer Composite*. Journal of the American Chemical Society, 2009. **131**(31): 11027-11032.
107. Wang, Z., et al., *Direct Electrochemical Reduction of Single-Layer Graphene Oxide and Subsequent Functionalization with Glucose Oxidase*. The Journal of Physical Chemistry C, 2009. **113**(32): 14071-14075.
108. Ramesha, G.K. and S. Sampath, *Electrochemical Reduction of Oriented Graphene Oxide Films: An in Situ Raman Spectroelectrochemical Study*. The Journal of Physical Chemistry C, 2009. **113**(19): 7985-7989.
109. An, S.J., et al., *Thin Film Fabrication and Simultaneous Anodic Reduction of Deposited Graphene Oxide Platelets by Electrophoretic Deposition*. The Journal of Physical Chemistry Letters, 2010. **1**(8): 1259-1263.
110. Pei, S., et al., *Direct reduction of graphene oxide films into highly conductive and flexible graphene films by hydrohalic acids*. Carbon, 2010. **48**(15): 4466-4474.
111. Zhou, Y., et al., *Hydrothermal Dehydration for the "Green" Reduction of Exfoliated Graphene Oxide to Graphene and Demonstration of Tunable Optical Limiting Properties*. Chemistry of Materials, 2009. **21**(13): 2950-2956.
112. Gilje, S., et al., *A Chemical Route to Graphene for Device Applications*. Nano Letters, 2007. **7**(11): 3394-3398.
113. Wei, Z., D.E. Barlow, and P.E. Sheehan, *The Assembly of Single-Layer Graphene Oxide and Graphene Using Molecular Templates*. Nano Letters, 2008. **8**(10): 3141-3145.
114. Stankovich, S., et al., *Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets*. Carbon, 2006. **44**(15): 3342-3347.

115. Bourlinos, A.B., et al., *Graphite Oxide: Chemical Reduction to Graphite and Surface Modification with Primary Aliphatic Amines and Amino Acids*. Langmuir, 2003. **19**(15): 6050-6055.
116. Boukhvalov, D.W. and M.I. Katsnelson, *Modeling of Graphite Oxide*. Journal of the American Chemical Society, 2008. **130**(32): 10697-10701.
117. Cecilia, M., et al., *Evolution of Electrical, Chemical, and Structural Properties of Transparent and Conducting Chemically Derived Graphene Thin Films*. Advanced Functional Materials, 2009. **19**(16): 2577-2583.
118. Yan, J.-A. and M.Y. Chou, *Oxidation functional groups on graphene: Structural and electronic properties*. Physical Review B, 2010. **82**(12): 125403.
119. Yan, J.-A., L. Xian, and M.Y. Chou, *Structural and Electronic Properties of Oxidized Graphene*. Physical Review Letters, 2009. **103**(8): 086802-4.
120. Gómez-Navarro, C., et al., *Atomic Structure of Reduced Graphene Oxide*. Nano Letters, 2010. **10**(4): 1144-1148.
121. Nakajima, T., A. Mabuchi, and R. Hagiwara, *A new structure model of graphite oxide*. Carbon, 1988. **26**(3): 357-361.
122. Lerf, A., et al., *Structure of Graphite Oxide Revisited*. The Journal of Physical Chemistry B, 1998. **102**(23): 4477-4482.
123. He, H., et al., *A new structural model for graphite oxide*. Chemical Physics Letters, 1998. **287**(1-2): 53-56.
124. Mkhoyan, K.A., et al., *Atomic and Electronic Structure of Graphene-Oxide*. Nano Letters, 2009. **9**(3): 1058-1063.
125. Paredes, J.I., et al., *Atomic Force and Scanning Tunneling Microscopy Imaging of Graphene Nanosheets Derived from Graphite Oxide*. Langmuir, 2009. **25**(10): 5957-5968.
126. Bagri, A., et al., *Structural evolution during the reduction of chemically derived graphene oxide*. Nat Chem, 2010. **2**(7): 581-587.
127. Szabó, T., et al., *Evolution of Surface Functional Groups in a Series of Progressively Oxidized Graphite Oxides*. Chemistry of Materials, 2006. **18**(11): 2740-2749.
128. Kudin, K.N., et al., *Raman Spectra of Graphite Oxide and Functionalized Graphene Sheets*. Nano Letters, 2008. **8**(1): 36-41.
129. De La Cruz, F.A. and J.M. Cowley, *Structure of Graphitic Oxide*. Nature, 1962. **196**(4853): 468-469.
130. De La Cruz, F.A. and J.M. Cowley, *An electron diffraction study of graphitic oxide*. Acta Crystallographica, 1963. **16**(6): 531-534.
131. Yamaguchi, H., et al., *Highly Uniform 300 mm Wafer-Scale Deposition of Single and Multilayered Chemically Derived Graphene Thin Films*. ACS Nano, 2010.

- 4(1): 524-528.
132. Shuping, P., et al., *Patterned Graphene Electrodes from Solution-Processed Graphite Oxide Films for Organic Field-Effect Transistors*. Advanced Materials, 2009. **21**(34): 3488-3491.
133. Li, X., et al., *Highly conducting graphene sheets and Langmuir-Blodgett films*. Nat Nano, 2008. **3**(9): 538-542.
134. Mattevi, C., et al., *Evolution of Electrical, Chemical, and Structural Properties of Transparent and Conducting Chemically Derived Graphene Thin Films*. Advanced Functional Materials, 2009. **19**(16): 2577-2583.
135. Eda, G., et al., *Transparent and conducting electrodes for organic electronics from reduced graphene oxide*. Applied Physics Letters, 2008. **92**(23): 233305-3.
136. Zhu, Y., et al., *Transparent self-assembled films of reduced graphene oxide platelets*. Applied Physics Letters, 2009. **95**(10): 103104-3.
137. Chen, C., et al., *Self-Assembled Free-Standing Graphite Oxide Membrane*. Advanced Materials, 2009. **21**(29): 3007-3011.
138. De, S., et al., *Flexible, Transparent, Conducting Films of Randomly Stacked Graphene from Surfactant-Stabilized, Oxide-Free Graphene Dispersions*. Small, 2010. **6**(3): 458-464.
139. Teweldebrhan, D. and A.A. Balandin, *Modification of graphene properties due to electron-beam irradiation*. Applied Physics Letters, 2009. **94**(1): 013101-3.
140. Moser, J., A. Barreiro, and A. Bachtold, *Current-induced cleaning of graphene*. Applied Physics Letters, 2007. **91**(16): 163513-3.
141. Bolotin, K.I., et al., *Temperature-Dependent Transport in Suspended Graphene*. Physical Review Letters, 2008. **101**(9): 096802-4.
142. Kim, T.-W., et al., *Graphene oxide nanosheets based organic field effect transistor for nonvolatile memory applications*. Applied Physics Letters, 2010. **97**(2): 023310-3.
143. Dong, X., W. Huang, and P. Chen, *In Situ Synthesis of Reduced Graphene Oxide and Gold Nanocomposites for Nanoelectronics and Biosensing*. Nanoscale Research Letters, 2010: 1-6.
144. Dong, X., et al., *Ultra-large single-layer graphene obtained from solution chemical reduction and its electrical properties*. Physical Chemistry Chemical Physics, 2010. **12**(9): 2164-2169.
145. Wang, H., et al., *Hysteresis of Electronic Transport in Graphene Transistors*. ACS Nano, 2010. **4**(12): 7221-7228.
146. Ishigami, M., et al., *Atomic Structure of Graphene on SiO₂*. Nano Letters, 2007. **7**(6): 1643-1648.
147. Dan, Y., et al., *Intrinsic Response of Graphene Vapor Sensors*. Nano Letters, 2009.

- 9(4): 1472-1475.
148. Roddaro, S., et al., *The Optical Visibility of Graphene: Interference Colors of Ultrathin Graphite on SiO₂*. Nano Letters, 2007. 7(9): 2707-2710.
149. Kikuo, H. and et al., *Novel electronic wave interference patterns in nanographene sheets*. Journal of Physics: Condensed Matter, 2002. 14(36): L605.
150. Nemes-Incze, P., et al., *Anomalies in thickness measurements of graphene and few layer graphite crystals by tapping mode atomic force microscopy*. Carbon, 2008. 46(11): 1435-1442.
151. Pandey, D., R. Reifengerger, and R. Piner, *Scanning probe microscopy study of exfoliated oxidized graphene sheets*. Surface Science, 2008. 602(9): 1607-1613.
152. Stolyarova, E., et al., *High-resolution scanning tunneling microscopy imaging of mesoscopic graphene sheets on an insulating surface*. Proceedings of the National Academy of Sciences, 2007. 104(22): 9209-9212.
153. Meyer, J.C., et al., *Imaging and dynamics of light atoms and molecules on graphene*. Nature, 2008. 454(7202): 319-322.
154. Wilson, N.R., et al., *Graphene Oxide: Structural Analysis and Application as a Highly Transparent Support for Electron Microscopy*. ACS Nano, 2009. 3(9): 2547-2556.
155. Wilson, N.R. and et al., *On the structure and topography of free-standing chemically modified graphene*. New Journal of Physics, 2010. 12(12): 125010.
156. Takahiro, K., et al., *Amorphization of carbon materials studied by X-ray photoelectron spectroscopy*. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2006. 242(1-2): 445-447.
157. Filik, J., et al., *XPS and laser Raman analysis of hydrogenated amorphous carbon films*. Diamond and Related Materials, 2003. 12(3-7): 974-978.
158. Titantah, J.T. and D. Lamoen, *sp^3/sp^2 characterization of carbon materials from first-principles calculations: X-ray photoelectron versus high energy electron energy-loss spectroscopy techniques*. Carbon, 2005. 43(6): 1311-1316.
159. Yang, D., et al., *Chemical analysis of graphene oxide films after heat and chemical treatments by X-ray photoelectron and Micro-Raman spectroscopy*. Carbon, 2009. 47(1): 145-152.
160. Li, Z.Q., et al., *X-ray diffraction patterns of graphite and turbostratic carbon*. Carbon, 2007. 45(8): 1686-1695.
161. Kim, H., A.A. Abdala, and C.W. Macosko, *Graphene/Polymer Nanocomposites*. Macromolecules, 2010. 43(16): 6515-6530.
162. Eda, G., et al., *Insulator to Semimetal Transition in Graphene Oxide*. The Journal of Physical Chemistry C, 2009. 113(35): 15768-15771.

163. Jeong, H.K. and et al., *Tailoring the characteristics of graphite oxides by different oxidation times*. Journal of Physics D: Applied Physics, 2009. **42**(6): 065418.
164. Bonaccorso, F., et al., *Graphene photonics and optoelectronics*. Nat Photon, 2010. **4**(9): 611-622.
165. Avouris, P., *Graphene: Electronic and Photonic Properties and Devices*. Nano Letters, 2010: null-null.
166. Subrahmanyam, K.S., et al., *A study of graphenes prepared by different methods: characterization, properties and solubilization*. Journal of Materials Chemistry, 2008. **18**(13): 1517-1523.
167. Thomsen, C. and S. Reich, *Double Resonant Raman Scattering in Graphite*. Physical Review Letters, 2000. **85**(24): 5214.
168. Saito, R., et al., *Probing Phonon Dispersion Relations of Graphite by Double Resonance Raman Scattering*. Physical Review Letters, 2001. **88**(2): 027401.
169. Ferrari, A.C. and J. Robertson, *Interpretation of Raman spectra of disordered and amorphous carbon*. Physical Review B, 2000. **61**(20): 14095-14107.
170. Ferrari, A.C., *Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects*. Solid State Communications, 2007. **143**(1-2): 47-57.
171. Tuinstra, F. and J.L. Koenig, *Raman Spectrum of Graphite*. The Journal of Chemical Physics, 1970. **53**(3): 1126-1130.
172. Park, S., et al., *Aqueous Suspension and Characterization of Chemically Modified Graphene Sheets*. Chemistry of Materials, 2008. **20**(21): 6592-6594.
173. Wang, S., et al., *High Mobility, Printable, and Solution-Processed Graphene Electronics*. Nano Letters, 2009. **10**(1): 92-98.
174. Stassen, A.F., et al., *Influence of the gate dielectric on the mobility of rubrene single-crystal field-effect transistors*. Applied Physics Letters, 2004. **85**(17): 3899-3901.
175. Rost, C., et al., *Ambipolar light-emitting organic field-effect transistor*. Applied Physics Letters, 2004. **85**(9): 1613-1615.
176. Régis, Y.N.G. and et al., *A roadmap to high quality chemically prepared graphene*. Journal of Physics D: Applied Physics, 2010. **43**(37): 374015.
177. Schwierz, F., *Graphene transistors*. Nat Nano, 2010. **5**(7): 487-496.
178. Perebeinos, V. and P. Avouris, *Inelastic scattering and current saturation in graphene*. Physical Review B, 2010. **81**(19): 195442.
179. Meric, I., et al., *Current saturation in zero-bandgap, top-gated graphene field-effect transistors*. Nat Nano, 2008. **3**(11): 654-659.
180. Wang, S., et al., *Band-like Transport in Surface-Functionalized Highly*

- Solution-Processable Graphene Nanosheets*. Advanced Materials, 2008. **20**(18): 3440-3446.
181. Gomez-Navarro, C., et al., *Electronic Transport Properties of Individual Chemically Reduced Graphene Oxide Sheets*. Nano Letters, 2009. **9**(5): 2206-2206.
182. Chen, J.-H., et al., *Intrinsic and extrinsic performance limits of graphene devices on SiO₂*. Nat Nano, 2008. **3**(4): 206-209.
183. Meihua, J., et al., *Graphene oxide thin film field effect transistors without reduction*. Journal of Physics D: Applied Physics, 2009(13): 135109.
184. Su, C.-Y., et al., *Electrical and Spectroscopic Characterizations of Ultra-Large Reduced Graphene Oxide Monolayers*. Chemistry of Materials, 2009. **21**(23): 5674-5680.
185. Tantang, H., et al., *Using oxidation to increase the electrical conductivity of carbon nanotube electrodes*. Carbon, 2009. **47**(7): 1867-1870.
186. Ferrari, A.C., et al., *Raman Spectrum of Graphene and Graphene Layers*. Physical Review Letters, 2006. **97**(18): 187401.
187. Hao, Y., et al., *Probing Layer Number and Stacking Order of Few-Layer Graphene by Raman Spectroscopy*. Small, 2010. **6**(2): 195-200.
188. Ferralis, N., *Probing mechanical properties of graphene with Raman spectroscopy*. Journal of Materials Science, 2010. **45**(19): 5135-5149.
189. Ruoff, R., *Graphene: Calling all chemists*. Nat Nano, 2008. **3**(1): 10-11.
190. Li, J.-L., et al., *Oxygen-Driven Unzipping of Graphitic Materials*. Physical Review Letters, 2006. **96**(17): 176101-4.
191. Kim, F., L.J. Cote, and J. Huang, *Graphene Oxide: Surface Activity and Two-Dimensional Assembly*. Advanced Materials, 2010. **22**(17): 1954-1958.
192. Su, C.-Y., et al., *Highly Efficient Restoration of Graphitic Structure in Graphene Oxide Using Alcohol Vapors*. ACS Nano, 2010. **4**(9): 5285-5292.
193. Gupta, A., et al., *Raman Scattering from High-Frequency Phonons in Supported n-Graphene Layer Films*. Nano Letters, 2006. **6**(12): 2667-2673.
194. Graf, D., et al., *Spatially Resolved Raman Spectroscopy of Single- and Few-Layer Graphene*. Nano Letters, 2007. **7**(2): 238-242.
195. Krauss, B., et al., *Laser-induced disassembly of a graphene single crystal into a nanocrystalline network*. Physical Review B (Condensed Matter and Materials Physics), 2009. **79**(16): 165428-9.
196. Pimenta, M.A., et al., *Studying disorder in graphite-based systems by Raman spectroscopy*. Physical Chemistry Chemical Physics, 2007. **9**(11): 1276-1291.
197. Xiaochen, D., et al., *Doping Single-Layer Graphene with Aromatic Molecules*.

- Small, 2009. **5**(12): 1422-1426.
198. Yan, J., et al., *Electric Field Effect Tuning of Electron-Phonon Coupling in Graphene*. Physical Review Letters, 2007. **98**(16): 166802-4.
199. Casiraghi, C., et al., *Raman fingerprint of charged impurities in graphene*. Applied Physics Letters, 2007. **91**(23): 233108-3.
200. Stampfer, C., et al., *Raman imaging of doping domains in graphene on SiO₂*. Applied Physics Letters, 2007. **91**(24): 241907-3.
201. Maruyama, S., et al., *Low-temperature synthesis of high-purity single-walled carbon nanotubes from alcohol*. Chemical Physics Letters, 2002. **360**(3-4): 229-234.
202. Chieu, T.C., M.S. Dresselhaus, and M. Endo, *Raman studies of benzene-derived graphite fibers*. Physical Review B, 1982. **26**(10): 5867-5877.
203. Matthews, M.J., et al., *Origin of dispersive effects of the Raman D band in carbon materials*. Physical Review B, 1999. **59**(10): R6585-R6588.
204. Chen, C.-C., et al., *Raman Spectroscopy of Ripple Formation in Suspended Graphene*. Nano Letters, 2009. **9**(12): 4172-4176.
205. Ryu, S., et al., *Atmospheric Oxygen Binding and Hole Doping in Deformed Graphene on a SiO₂ Substrate*. Nano Letters, 2010. **10**(12): 4944-4951.
206. Liu, L., et al., *Graphene Oxidation: Thickness-Dependent Etching and Strong Chemical Doping*. Nano Letters, 2008. **8**(7): 1965-1970.
207. Reina, A., et al., *Transferring and Identification of Single- and Few-Layer Graphene on Arbitrary Substrates*. The Journal of Physical Chemistry C, 2008. **112**(46): 17741-17744.
208. Jiao, L., et al., *Creation of Nanostructures with Poly(methyl methacrylate)-Mediated Nanotransfer Printing*. Journal of the American Chemical Society, 2008. **130**(38): 12612-12613.
209. Yang, R., et al., *Substrate doping effects on Raman spectrum of epitaxial graphene on SiC*. Journal of Applied Physics, 2010. **107**(3): 034305-5.
210. Jorio, A., et al., *Measuring disorder in graphene with the G and D bands*. physica status solidi (b), 2010. **247**(11-12): 2980-2982.
211. Jin, C., et al., *In situ Raman spectroscopy of annealed diamondlike carbon-metal composite films*. Applied Surface Science, 2007. **253**(15): 6487-6492.
212. Lafkioti, M., et al., *Graphene on a Hydrophobic Substrate: Doping Reduction and Hysteresis Suppression under Ambient Conditions*. Nano Letters, 2010. **10**(4): 1149-1153.

List of Publications

1. **Xu Y. P.**, Zhang H., In preparation.
2. Su, C.-Y.[#]; **Xu, Y. P.**[#]; Zhang, W.; Zhao, J.; Liu, A.; Tang, X.; Tsai, C.-H.; Huang, Y.; Li, L.-J., Highly Efficient Restoration of Graphitic Structure in Graphene Oxide Using Alcohol Vapors. *ACS Nano* 2010, 4, 5285-5292. **(Equally contributed)**
3. Su, C.-Y.[#]; **Xu, Y. P.**[#]; Zhang, W.; Zhao, J.; Tang, X.; Tsai, C.-H.; Li, L.-J., Electrical and Spectroscopic Characterizations of Ultra-Large Reduced Graphene Oxide Monolayers. *Chemistry of Materials* 2009, 21, 5674-5680. **(Equally contributed)**
4. Su, C.-Y., Lu, A.-Y., **Xu Y. P.**, Chen F., Khlobystov A. N., Li, L.-J., High quality thin graphene films from fast electrochemical exfoliation. *ACS Nano* 2010.
5. Gui, E.L., Li L.J., Zhang K. K., **Xu Y. P.**, Dong X.C., Ho X.N., Lee P.S., Kasim J., Shen Z.X., Rogers J.A., and Mhaisalkar S.G., DNA sensing by field-effect transistors based on networks of carbon nanotubes. *JACS*, 2007, 29, 14427-14432.
6. Fu, D.L., **Xu Y. P.**, Li L.J., Chen Y., Mhaisalkar S.G., Boey F.Y.C., T.W. Lin, and S. Mookhala, Electrical detection of nitric oxide using single-walled carbon nanotube network devices. *Carbon*, 2007. 45, 1911-1914.
7. Kloc, C., Tan K., Toh M., Zhang K., and **Xu Y. P.**, Purity of rubrene single crystals. *Applied Physics A: Materials Science & Processing*, 2009, 95, 219-224.
8. Xi, L.F., Lam Y.M., **Xu Y. P.**, and L.J. Li, Synthesis and characterization of one-dimensional CdSe by a novel reverse micelle assisted hydrothermal method. *Journal of Colloid and Interface Science*, 2008, 320, 491-500.

9. Ong, H.G, Cheah J.W., Chen L., TangTang H., **Xu Y. P.**, Li B., Zhang H., Li L.J., and Wang J.L., Charge injection at carbon nanotube-SiO₂ interface. *Applied Physics Letters*, 2008, 93, 093509-3.