Graphene oxide-based nanomaterials : synthesis, optical characterisation and supercapacitor

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**GRAPHENE OXIDE-BASED NANOMATERIALS:
SYNTHESIS, OPTICAL CHARACTERIZATION AND
SUPERCAPACITOR**

YANG HUANPING

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2012

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Summary

This thesis concerns the study of effect of functional groups on graphene oxide (GO). Functional groups strongly affect the optical properties of GO and they can be used to facilitate the preparation of GO derivatives. This thesis systematically investigates the synthesis, optical characterization and applications of GO-based materials, with an emphasis on the influence of the oxygen-containing groups on their chemical and optical properties. The research can be divided into three sections as shown below.

First, the identification of the thickness of GO by white light contrast spectroscopy, which is discussed in Chapter 4. This topic has rarely been studied because of the weak optical absorbance that originates from both the large optical gap caused by sp^3 hybridization of the functional groups and the adsorbed water on GO sheets. In our work, we have successfully identified the number of layers of GO (≤ 10 layers) and deduced the complex refractive index of GO sheets (≤ 10 layers) as $n_{GO} = 1.2 - 0.24i$. For GO sheets of a few layers (≤ 10 layers), both the optical contrast (at ~ 580 nm) and the G band intensity increase linearly with the thickness. In comparison with Raman spectroscopy, in which laser-induced reduction of GO cannot be absolutely avoided, contrast spectroscopy is a non-destructive and more efficient approach. Simulation results based on Fresnel's equations agree well with the evolution of the optical contrast and the trend of G band intensity in accordance with the number of layers. The refractive index of GO can be precisely calculated by this method, which can subsequently be used as a basis for further examination of the optical properties of GO. Overall, we proposed a simple and rapid approach to determine the number of layer of GO on the Si/SiO₂ substrate by measuring the optical contrast values, which can also be applied to other graphene-based and two-dimensional materials.

Second, GO-based nanomaterials as surface-enhanced Raman spectroscopy (SERS) substrates, which are discussed in Chapters 5 and 6. Different surface chemistry of GO, reduced graphene oxide (r-GO) and graphene, give rise to different interactions between the substrates and rhodamine 6G (R6G); therefore, varying Raman enhancement effects are produced. Comparing the Raman signals of molecules on these substrates, we observe that the Raman intensity is the strongest on single-layer graphene (SLG) and that different substrates give varying relative Raman signal ratios because of their particular fluorescence quenching capability. The Raman enhancement efficiency is also quite different for the various Raman bands of the molecule, for instance the π -conjugation network and the local chemical groups of these substrates affect the adsorption behaviour of the R6G molecule and hence induce different Raman enhancement efficiency. Notably, the enhancement factors are dependent on the thickness of the substrates, i.e., the Raman signals of the molecules increase with the number of GO layers while an inverse trend is apparent for graphene and r-GO substrates. This prominent SERS effect of r-GO and GO will expand the application of r-GO and GO as good SERS substrates because of their solubility, easy availability, light weight, low cost and good stability.

To combine the fluorescence quenching effect of GO and the electromagnetic enhancement effect of metal nanoparticles (NPs), Au NP-decorated r-GO was synthesized and developed as a hybrid SERS substrate. To successfully synthesize the composite material, GO sheets were covalently bonded with 1-(3-aminopropyl) imidazole to allow the loading of AuCl_4^- ions onto the GO sheets via anion exchange. The AuCl_4^- ions and GO were then reduced in a single step to produce Au NP-decorated r-GO sheets. The Au NP-decorated r-GO sheet prepared in this manner was utilized as a SERS substrate. The obtained SERS spectra demonstrate a weak

fluorescence background and a strong Raman signal for R6G on the Au NP-decorated r-GO sheet substrate caused by the energy/charge transfer between R6G and r-GO. The weak molecule fluorescence background and the relatively strong Raman signal show that the Au NP-decorated r-GO sheet is a promising SERS substrate.

Last, the electrochemical performances of GO/r-GO-based composites, which are investigated in Chapters 7 and 8. The morphology of the MnO₂ nanomaterials deposited on GO are affected by the oxidation degree of GO, which has a notable effect on the electrochemical performances of the GO-based composites. Our results demonstrate that GO that is synthesized by commercial expanded graphite (denoted as GO1) owns more functional groups and a larger inter-layer distance when compared with GO from commercial graphite powder (denoted as GO2). The surface chemistry of GO has significant effects on the morphology of MnO₂, which leads to a dramatic difference in the electrochemical performance of the resulting GO-MnO₂ composites. This is supported by the fact greater loading weight ratio of MnO₂ on GO1 that is much higher than that on GO2, which was confirmed by Inductively Coupled Plasma Optical Emission Spectroscopy (IC-OES). When used as an electrode for a supercapacitor, the MnO₂-GO1 nanocomposite shows a larger capacitance (307.7 F g⁻¹) and a better rate performance than MnO₂-GO2 because of the high loading efficiency and homogeneous distribution of MnO₂ on the GO1 sheets.

To further elucidate the influences of the surface chemistry of graphene on the electrochemical performance of their composites, polypyrrole (PPy) was chemically polymerized in-situ onto four types of functionalized graphene: amine-modified graphene (NH₂-G), nitrogen-doped graphene (N-G), pristine graphite oxide (GTO) and reduced graphite oxide (RGO). A series of electrodes were synthesized through the four types of graphene/PPy composites that are supplied to the active substance

for supercapacitors. The specific capacitances of N-G, NH₂-G, RGO and GTO are 393.67, 225.33, 150 and 165 F g⁻¹, respectively, with a sample loading of 20 mg on 0.5 cm × 0.5 cm nickel foam using 6 M KOH as the electrolyte. The NG-PPy electrodes show the best capacitive performance when compared with the other three composites due to the introduction of nitrogen doping in the graphene network. The nitrogen doping can improve the electrical properties of graphene and facilitate the uniform growth of polypyrrole on both sides of the graphene. Therefore, the largest synergistic effect can be achieved from pseudocapacitance generation in uniform polypyrrole coating layers, and the improved charge transfer efficiency from the nitrogen doping induced excellent conductivity. The improved nitrogen doping-induced capacitance is also applicable to other graphitic material/conducting polymer composite preparations that show promise in energy-storage applications. Graphene surface chemistry is important for the preparation of graphene/PPy composite electrodes for supercapacitor applications.

Publications

1. **Huanping Yang**, Hailong Hu, Zhenhua Ni, Ting Yu. “Comparison of SERS Measurements on Graphene oxide, Reduced Graphene oxide and Graphene Surfaces” (submitted)
2. **Huanping Yang**, Hailong Hu, Yingying Wang, Ting Yu. “Rapid and Non-Destructive Identification of Graphene Oxide Thickness Using Contrast Spectroscopy” Carbon (2013) 52, 528-534.
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Abbreviations

Graphene oxide (GO)

Surface-enhanced Raman spectroscopy (SERS)

Polypyrrole (PPy)

Nanoparticles (NPs)

Amine-modified graphene (NH₂-G)

Nitrogen-doped graphene (N-G)

Pristine graphite oxide (GTO)

Chemically modified graphene (CMG)

Graphite intercalation compound (GIC)

Chemical-reduced graphene oxide (CReGO)

3, 4, 9, 10-perylene tetracarboxylic acid (PTCA)

Amino-terminated ionic liquid (IL-NH₂)

3-aminopropyltriethoxysilane (APTES)

Poly-(vinyl alcohol) (PVA)

Polyaniline (PANI)

Polyurethane (PU)

Polycaprolactone (PCL)

Poly (methyl methacrylate) (PMMA)

Polyethylene terephthalate (PET)

Carbon nano-tubes (CNT)

Carbon nano-wires (CNW)

Electromagnetic (EM)

Chemical enhancement mechanisms (CM)

Chemical charge transfer (CT)

Mildly reduced graphene oxide (MR-GO)

Rhodamine 6G (R6G)

Rhodamine B (RhB)

Three-dimensional (3D)

Ionic liquid (IL)

Room-temperature ionic liquids (RTILs)

Pt nano-particles (PtNPs)

Double resonance (DR)

Micromechanical exfoliation (ME)

Highly oriented pyrolytic graphite (HOPG)

Single-layer graphene (SLG)

Bi-layer graphene (BLG)

Charge-coupled-device (CCD)

Cyclic voltammetry (CV)

Electrochemical impedance spectroscopy (EIS)

Commercial expanded graphite (CEG)

Commercial graphite powder (CGP)

Reduced graphite oxide (RGO)

Specific surface area (SSA)

Graphene-based materials (GBMs)

Electric double-layer capacitor (EDLC)

Reduced graphene oxide (r-GO)

Tetrahydrofuran (THF)

Ionic liquid functionalized GO (ILGO)

N, N'-dicyclohexylcarbodiimide (DCC)

Polytetrafluorene-ethylene (PTFE)

Brunauer–Emmett–Teller (BET)

Barrett–Joyner–Halenda (BJH)

Transmission electron microscopy (TEM)

Scanning electron microscopy (SEM)

Energy Dispersive X-ray Detector (EDX)

X-ray diffraction (XRD)

X-ray photoelectron spectroscopy (XPS)

Fourier transform infrared spectrometer (FT-IR)

High resolution transmission electron microscopy (HRTEM)

Energy dispersive X-ray analysis (EDXA)

X-ray photoelectron spectra (XPS)

X-ray diffraction (XRD)

Nuclear Magnetic Resonance (NMR)

Inductively Coupled Plasma Optical Emission Spectroscopy (IC-OES)

Fluorescence quenching microscopy (FQM)

Chapter 1

Introduction

1.1 Issues regarding the surface chemistry of graphene oxide /graphite oxide

Graphene oxide (GO), an excellent substrate for various chemical transformations, has attracted much attention during the last half decade. After chemical modification, the chemically modified graphene oxide can be widely used in sensors, field-effect transistors, energy-related materials, biomedical applications, and so on. The production of GO in large quantities from graphite oxide using a chemical method is well known. Although the study of the chemistry of graphite oxide can be traced back many decades, the exact surface chemistry and structure of graphite oxide/GO is still under debate. Many factors inhibit the elucidation of the chemistry of graphite oxide/GO, primarily as a result of the complexity of the properties of graphite oxide/GO. Such as the amorphous nature and berthollide character (nonstoichiometric atomic composition) of the material that differs between samples. Another primary cause is the lack of accurate analytical techniques to properly characterize the chemically modified graphene oxide.

The surface chemistry of materials can significantly affect their optical and electrical properties, as well as their chemical activity. Therefore, strong research efforts are afforded to explore the precise surface chemistry and structure of graphite oxide/GO.

1.2 The motivation and significance of the thesis

This PhD project focuses on the investigation of surface chemistry of GO-based materials by the following three approaches discussed in the following three sections:

Section 1: To study the optical properties of GO and identify the GO layers.

Section 2: To investigate the SERS effect of GO and GO-Au composites.

Section 3: To explore the supercapacitor performances of GO-MnO₂ and graphene-polypyrrole (PPy) composites

The motivation and significance of the Section 1

Because of the chemical functional groups on GO basal planars, which strongly modify the electronic structure of graphene and introduce many insulating states or impurity states, GO possesses a much poorer optical contrast than graphene. The binding of these chemical groups to GO sheets primarily includes covalent or non-covalent (for example, π - π stacking) functionalization, which leads to the weak thermal stability of GO. Thus, the Raman spectroscopy used for graphene is not appropriate for the direct and accurate identification of the thickness of GO sheets. Therefore, we use white light contrast spectroscopy to determine the number of GO layers (≤ 10 layers) and determine a refractive index of GO sheets (≤ 10 layers) of $n_{GO} = 1.2-0.24i$. The contrast value at ~ 580 nm wavelength and the G band intensity of the GO sheets possessing a few layers (≤ 10 layers) linearly increase with the thickness of GO. Because of the laser-induced heating effects and the need for a reference Raman spectrum in Raman spectroscopy, contrast spectroscopy is less destructive and more efficient. The good agreement between the calculated and experimental results for both the contrast and G band intensity suggests that this refractive index can be

widely adopted in future studies of GO. Our contrast mapping further confirms that this method is a convenient, yet powerful, probe for the rapid visualization of GO sheets with varying thicknesses. As more promising properties have been discovered or proposed for single layer and few layered GO sheets, contrast spectroscopy will be very useful for future fundamental and practical studies, because it is an accurate, facile and efficient method for determining the thickness of GO layers (≤ 10 layer).

Scientists can directly use our experimental contrast values as a standard to determine the thickness of GO on SiO₂/Si substrates (300 nm SiO₂ capping layer), which is a novel process for optical research and future applications of graphene-based materials.

The motivation and significance of the Section 2

There are many functional groups present on the GO sheets, such as carboxyl groups, carbonyl groups, hydroxyl groups and epoxides. These functional groups not only provide a significant local electric field but also can be selectively modified. In this section we will investigate the impacts of the local chemical groups of GO and further explore the SERS properties of the r-GO-Au composites which are produced by selective functionalization of the carboxyl groups.

1. Using the probing molecule R6G, we successfully demonstrated the different interactions between R6G and GO, r-GO and graphene, which can be affected by the geometrical or electronic structure of the adsorbed molecules. Notably, not only the local chemical groups of GO and r-GO but also the global π -conjugation network of GO, r-GO and graphene are important in determining the geometry of the R6G molecule on the substrate, which leads to changes in the Raman signal of the R6G molecule and differing enhancement abilities. Because of the strong π - π interactions

between the single-layer graphene (SLG) and the molecules, the primary effect on the largest observed Raman enhancement for SLG is from π - π stacking. Although the primary effect for the larger observed Raman enhancement for r-GO is also π - π stacking, the higher number of local electronegative oxygen species also contributes to the Raman enhancement and the various relative peak intensities. Compared with r-GO, GO has fewer local electronegative oxygen species and a lower π - π stacking interaction, which causes the smallest Raman enhancement and Raman signal intensity change. Moreover, the thickness-dependent Raman enhancement of the three kinds of substrates shows different trends. On the GO surface, the Raman signals of R6G increase with an increasing number of layers because of the multiple reflections of the Raman signal. In contrast, the Raman signals of R6G decrease with the number of layers on the graphene and r-GO surface because of the lack of multiple reflections of the Raman signal. Although we do not know the exact reasons and more research should be carried out in this new area, we believe that this discovery will expand the useful applications of GO in life science and food safety, because of the peculiar advantages of solubility, high-fidelity, large enhancement and non-destructive characteristics.

2. We produce the uniform gold nano-particles on r-GO sheets via a simple method that employs ionic liquid functionalization. The modified GO with ionic liquid is achieved by selectively covalently bonding 1-(3-aminopropyl) imidazole with the carboxyl group of the GO sheets. The mechanism of the formation of the r-GO sheets with Au nano-particles is proposed as follows: AuCl_4^- was first loaded onto the GO sheets via anion exchange, and the AuCl_4^- was then reduced to Au NPs while the GO sheets were simultaneously converted to r-GO sheets by a single-step procedure. The presence of Au NPs is shown well by EDS, HRTEM and XPS. Subsequently, the r-

GO-supported Au NPs were used as a SERS substrate. Strong and detectable Raman signals of the R6G molecules were provided, which indicates that the r-GO-supported Au NPs are a promising SERS substrate and that they would be useful to the researchers in nanotechnology.

The motivation and significance of Section 3

1. We investigated the influence of the amount of GO functional groups and the inter-lamellar spacing of GO on the morphology of the loaded MnO_2 particles on GO. The electrochemical performances of various MnO_2 -GO composites as supercapacitor electrodes were also studied. The results show that the GO1 fabricated from commercial expanded graphite possesses more functional groups and a larger inter-planar gap compared with GO2 fabricated from commercial graphite powder, which lead to a higher loading and more homogeneous distribution of MnO_2 on GO1 than on GO2. Therefore, as the electrode of a supercapacitor, MnO_2 -GO1 composites show a larger capacitance (307.7 Fg^{-1}) and better electrochemical activity than MnO_2 -GO2.

We can conclude that the surface chemistry and structural properties of GO are important for a carrier of nano-particles in various applications, such as catalysts and energy storage devices.

2. The surface chemistry of graphene is found to be important for PPy growth and the electrochemical performance of the PPy/graphene composite. High specific capacitance has been achieved by N-doped graphene/polypyrrole (NG-PPy) electrodes with a value of 393.67 Fg^{-1} , which is larger than those of $-\text{NH}_2$ modified graphene/PPy (225.33 Fg^{-1}), graphite oxide/PPy (165.25 Fg^{-1}), and reduced graphene oxide/PPy electrodes (150.00 Fg^{-1}) under the same experimental conditions. Incorporating of N into the graphene network induces enhanced electronic transfer

efficiency and improves the wettability of the graphene surface. Therefore, the largest synergistic effect is achieved on NG-PPY. Our work demonstrates that the introduction of N doping to graphitic material before the growth of the conducting polymer is essential for the preparation of graphitic-conducting polymer composites with a high cycling stability and specific capacitance for supercapacitor applications.

1.3 Structure of the thesis

Chapter 1 presents a brief introduction and discusses the background of this thesis. A comprehensive literature review on graphene-based materials and the technology that was utilized is given in Chapter 2. Chapter 3 describes the experimental methods used in this thesis. Chapter 4 discusses the identification of the number of GO layers (≤ 10 layers) using contrast spectroscopy. Simultaneously, we obtained a refractive index for GO, which can be widely used to further study GO. The different R6G Raman signals on graphene, GO and r-GO caused by the different orientations of the adsorbed molecules is discussed in Chapter 5. Chapter 6 discusses the R6G Raman signals on r-GO-Au nanoparticles and Chapter 7 describes the immense effects of different oxidation degrees of GO on the quantity and morphology of the loaded MnO_2 , which affects the electrochemical performances of the prepared composites. Chapter 8 discusses the influence of the four kinds of surface chemistry of graphene on the performance of Graphene/Polypyrrole electrochemical supercapacitors. Finally, the main conclusions of the thesis and future research directions are presented in Chapter 9.

Chapter 2

Literature Review

2.1 Introduction of GO

The 2010 Nobel Prize in Physics was awarded jointly to Andre K. Geim and Konstantin S. Novoselov for their pioneering work on graphene,¹ which is the thinnest material ever created by scientists. The wondrous properties of the material (high Young's modulus (~ 1.0 TPa),² theoretical specific surface area ($2630 \text{ m}^2\text{g}^{-1}$),³ electrical conductivity,⁴ optical transmittance ($\sim 97.7\%$),⁴ thermal conductivity ($\sim 5000 \text{ Wm}^{-1}\text{K}^{-1}$),⁵ fracture strength (126GPa)^{2,6} and intrinsic mobility ($200\,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$)^{7,8}) will have a tremendous impact on our lives in the future. Graphene and chemically modified graphene (CMG) are promising components for applications such as liquid crystal devices,⁹ polymer composites,^{10,11} mechanical resonators¹² and energy-storage materials.³

From a practical perspective, one of the important issues is the creation of graphene in large quantities. Chemically derived graphene oxide (GO) is an atomically thin sheet of graphite that has traditionally served as a precursor for graphene, which can be supplied at a ton scale,¹³ and is cost-effective for the large-scale production of graphene-based materials.⁶ Due to the ease of processability and the compatibility with various substrates, GO is considered to be an attractive candidate for the high-yield manufacture of graphene-based electronic and optoelectronic devices, such as field-effect transistors, chemical/bio sensors, organic solar cells and transparent electrodes in photovoltaic devices. However, it is worth clarifying that GO is related to graphite oxide. From the chemical point of view, GO is generated from graphite

oxide. Unlike graphite oxide, which possesses a stacked structure, GO is composed of a monolayer or a few stacked-layers. Therefore, several graphite oxide properties can be used to provide information about GO.

2.1.1 Structure of GO/graphite oxide

Although graphite oxide was first prepared 150 years ago,¹⁴ its precise chemical structure remains ambiguous. The accurate chemical structure of GO, which is single- or few-layered of graphite oxide, also has been debated over years, and a clear model remains to be provided. Many techniques have been used to characterize the structure of GO, such as X-ray photoelectron spectra (XPS), X-ray diffraction (XRD), elemental analysis, Nuclear Magnetic Resonance (NMR) and infrared spectroscopy. The structural analysis of GO is difficult^{15,16} for the following reasons: (1) GO is a complex material due to the variety of preparation-dependent compositions (i.e., nonstoichiometric atomic composition), (2) GO slowly decomposes in air at temperatures above 60-80°C and (3) GO strongly adsorbs water and other materials from the air. Precise analytical techniques do not exist for characterizing such materials (or mixtures of materials). Despite such obstacles, researchers have expended significant efforts to understand the structure of GO, which many efforts have achieved great success.

Scheme 2.1 shows several previously proposed structural models of graphite oxide. Hofmann and Holst¹⁷ suggested that the structure of graphite oxide (labeled in Scheme 2.1 as Hoffmann) is composed of epoxy (1,2-ether) groups on the basal planars of graphite, and the ideal molecular formula is C-O-C. In 1946 Ruess¹⁸ proposed that the structure of graphite oxide (labeled in Scheme 2.1 as Ruess) consists of hydroxyl groups in the basal planar, which would explain the hydrogen content

observed in graphite oxide. Ruess also introduced sp^3 hybridization into the basal planar structure of graphite oxide. Ten years later, Clauss and co-workers¹⁹ proposed that enolic groups, ketones and C=C double bonds should be added to Ruess' model. In 1969, Scholz and Boehm²⁰ modified Clauss' model to account for stereochemistry (labeled in Scheme 2.1 as Scholz-boehm), in which the epoxide and ether groups were replaced with regular quinoidal species in a wrinkled carbon network. Nakajima and Matsuo²¹ suggested a remarkable model (labeled in Scheme 2.1 as Nakajima-Matsuo) in the form of a stage 2 graphite intercalation compound (GIC) that had a lattice framework similar to poly (dicarbon monofluoride), $(C_2F)_n$. Recently, the nonstoichiometric nature of graphite oxide caused many researchers to reject the lattice-based model and propose new models for the structure of graphite oxide. Among the proposed models, the model proposed by Lerf and Klinowski^{22,23} (labeled in Scheme 2.1 as Lerf-Klinowski), is the most widely cited in contemporary literature. NMR spectroscopy was used to investigate the structure of graphite oxide, which was determined to be composed of C=C, C-OH, and ether groups on the basal planar, while C-OH and COOH groups were identified on the edge. Flat unoxidized benzene rings and wrinkled alicyclic six-member rings were observed to be randomly distributed on the basal planar.

However, Dékány and coworkers¹⁵ proposed a similar model to Scholz's model to describe the structure of graphite oxide (shown in Scheme 2.2). The graphite oxide structure was proposed to consist of trans-linked cyclohexyl species dotted with tertiary alcohols, 1, 3-ethers, and a plicate network of keto/quinoidal species.^{15,16} No carboxyl groups were proposed to be on the structure of graphite oxide. The alkenes of the quinines were replaced by 1, 2-ethers as the degree of oxidation increased.

Scheme 2.1 Summary of several previously proposed structural models of graphite oxide (adapted from ref. 16).

Using different graphite sources and tuning the degree of oxidation can significantly affect the structure and properties of GO. Scientists endeavor to utilize this method to decorate GO sheets with metal/metal oxide/polymer.

Scheme 2.2 Structural model of graphite oxide: (a) the surface species and (b) folded carbon skeleton (adapted from ref. 16).

2.1.2 Synthesis of GO/graphite oxide

According to the discussion above, the various forms of nonstoichiometric GO are obtained using strong oxidizing agents. Though the precise structure of GO is difficult to identify, it is obvious that there are epoxides, alcohols, ketone carbonyls, and carboxylic groups.²³⁻²⁵ The inter-layer spacing increases from 0.335 nm for graphite to more than 0.625 nm for GO.²⁶ Reports of the synthesis of graphite oxide can be traced back more than a century. The first notable approach was reported in 1859 when Brodie¹⁴ demonstrated the synthesis of graphite oxide by oxidizing flake graphite with, fuming nitric acid. Potassium chlorate was subsequently added into the

graphite-containing slurry. The molecular weight of graphite was proposed to be 33, Brodie said the following regarding the material:

“This form of carbon should be characterized by a name marking it as a distinct element. I propose to term it Graphon.”

“Graphene” is currently the recipient of significant attention in materials science.

Graphite oxide is a nonstoichiometric material. However, Brodie incorrectly determined the molecular formula for graphite. Almost 40 years later, L. Staudenmaier improved Brodie’s experimental procedure by adding multiple aliquots of chlorate over the course of the reaction.²⁷ In addition, the concentrated sulfuric acid was added to improve the acidity of the mixture. Even though the procedural changes were small, an effective approach to produce highly oxidized graphite oxide in a single reaction vessel was achieved. In 1958, Hummers and Offeman developed a method to produce graphite oxide, which is currently the most commonly used method. Graphite is oxidized with KMnO_4 and NaNO_3 in concentrated H_2SO_4 .²⁸ All three procedures achieve similar levels of oxidation and generate toxic gases (NO_2 , N_2O_4 and/or ClO_2); Furthermore, Hummers’ method is explosive. In addition to the oxidant, researchers subsequently discovered that the graphite source and reaction conditions can greatly affect the graphite oxide structure. Because the immediate mechanisms related to these procedures are not well understood, it is necessary to consider the reactivity of these chemicals in more easily investigated systems.

The commonly used oxidant in Hummers’ method was potassium permanganate. However, the reaction between potassium permanganate with sulfuric acid produces diamanganese heptoxide (Scheme 2.3) and bimetallic heptoxide, which are more reactive and explosive than potassium permanganate.²⁹ By studying the oxidative

ability of Mn_2O_7 , Trömel and Russ determined that unsaturated aliphatic double bonds are preferentially oxidized over aromatic double bonds. These exciting observations are useful for investigating the structure of graphite and the reaction route(s) that occur during the oxidation process.³⁰

Scheme. 2.3 Formation of dimanganese heptoxide (Mn_2O_7) from KMnO_4 in the presence of a strong acid (adapted from ref. 29).

Generally, the commonly used precursors for chemical reactions are natural minerals, which are purified to remove hetero-atomic contaminants.³¹ Numerous localized defects in the π - π structure can act as active sites for the oxidation process. If the oxidation conditions used by Trömel and Russ to form graphite oxide are used on styrene as a model compound, then the preferential oxidation of the aromatic systems over isolated alkenes is observed. However, an accurate explanation of the oxidation mechanisms remains challenging due to the complexity of graphite and the various defects present in natural sources. Researchers tried other oxidants to synthesize graphite oxide. For example, Jone obtained expanded graphite (a partially oxidized intermediate state between graphite and true graphite oxide) using an $\text{H}_2\text{CrO}_4/\text{H}_2\text{SO}_4$ solution.³² Due to the hydrophilicity of the functional groups and electrostatic repulsion, the platelet–platelet interactions were greatly weakened. Therefore, a variety of approaches (e.g., thermal and mechanical methods) were used to prepare GO from the exfoliation of graphite oxide. Ultrasonication and/or stirring graphite oxide in water is the most commonly used exfoliation technique. The ultrasonication

of graphite oxide in water or a polar organic media results in a faster and more efficient preparation of GO than mechanical stirring. However, ultrasonication can damage the GO platelets,³³ break the graphitic structure into smaller fragments^{34,35} and diminish the dimensions of GO to different sizes, which leads to a larger size distribution.^{10,36,37}

Recently, an improved method was developed by James M. Tour's group. More highly oxidized graphite oxide was generated by combining a 9:1 H₂SO₄/H₃PO₄ solution with graphite, and no toxic gases were released.³⁸ Wissler's review elaborates on the use of various graphite and/or carbon sources, and the corresponding terminology regarding the preparation of GO sheets.³¹

2.1.3 Chemical reactivity of GO/graphite oxide

2.1.3.1 Reductions

GO/graphite oxide is an insulator because the sp² carbon networks are damaged. The electrical conductivity of graphite oxide and GO can be effectively recovered by restoring the π -network of the basal planar. Therefore, GO reduction is of significant importance for further application in various fields. Due to the similarities between the product of reduced graphene oxide and scotch tape-prepared graphene, the former material is named chemical-reduced graphene oxide (CReGO) or reduced graphene oxide (r-GO) because it originated from GO. The reduction of GO is the most obvious and desirable method to prepare graphene-like materials in a large scale. Scientists and engineers determined that r-GO has superior performance as energy storage³⁹ and high-capacity hydrogen storage^{40,41} due to a high surface area and conductivity. Chemical, thermal and electrochemical reductions are the current approaches to

reduce GO. The reduction process restores the electrical, mechanical, and thermal properties as well as the surface morphology.

2.1.3.2 Chemical functionalization

The previous section discussed the elimination of the functional groups from GO (reduction). In this section the functionalization of GO platelets will be discussed. Functional groups are added to the GO sheets through covalent or non-covalent interactions, which result in more versatile composite materials for applications.

GO contains a number of chemically reactive groups, which are located on the edges (carboxylic acid) or on the basal planars (epoxy and hydroxyl). The main challenge of the chemical modification of GO is to selectively functionalize one group at a time. However, the reactions occur on multiple functionalities in most cases. The reactions reported for our work will be discussed later in the thesis.

2.1.4 GO/r-GO-based Composites

Scientists have attempted to synthesize graphite oxide-based inorganic compounds or polymer composites for 30 years.⁴²⁻⁴⁴ An early study shows monolayer and few-layered graphite oxide (i.e., GO; however, the structure was not clearly described at that time) can be facilely exfoliated into thin-layered structures using sonication in water. Kotov and Fendler *et. al.* first reported the in situ reduction of a graphite oxide/polyelectrolyte composite film prepared by LBL assembly,⁴⁵ which formed a conductive 1.8-2.8 nm-thick composite after the graphite oxide sheets were reduced. The reduced graphite oxide sheets were less than three layers. However, some reports concentrated on the investigation of layer-by-layer composite films^{46,47} and intercalated composites, but rarely explored applications for the materials at that time.⁴⁸⁻⁵² The lack of chemical and physical understanding of graphene has restricted

research for many years. Until 2006, Ruoff *et al.* prepared large quantities of GO/r-GO sheets by exfoliating finely dispersed graphite oxide in water or organic solvents,^{10,25,53} which enables a one-step solution-based process to combine GO/r-GO sheets with organic molecules, polymers or inorganic nanostructures.⁵⁴⁻⁵⁷ Due to the development of this excellent method, many contributions to the synthesis and exploration of applications for GO/r-GO-based composites occurred. Generally, GO/r-GO-based composites are used as a functional component or a substrate to immobilize other components. The obtained composites can potentially be used in applications including microelectronic devices,⁵⁸ fuel cell bipolar plates,^{59,60} hydrogen storage,⁶¹ energy,⁶² transparent conductors,⁶³ and dye-sensitized solar cells.⁶⁴

2.1.4.1 GO/r-GO Metal Nanoparticle Composites

Many noble metal nanoparticles have a long history in terms of synthesis, characterization and applications. Graphene-based metal nanoparticle composites were broadly studied, such as Au,⁶⁵⁻⁷³ Cu,⁷¹ Ni,⁷⁴ Pt,^{67,68} Pd,^{68,71,73} and Ag.⁷⁵⁻⁷⁷ These composites can be used in surface-enhanced Raman scattering (SERS),^{65,70} electrochemical sensing⁷² and catalysis⁷³ experiments due to the various properties of the metallic nanomaterials. To prepare these fascinating composites, many synthetic methods have been developed including microwave-assisted synthesis,⁷¹ chemical reduction,^{66,68,69} electroless metallization⁶⁵ and photo-chemical synthesis.⁷⁸

There are numerous defects and oxygenic functional groups on GO sheets, which can behave as active sites for decorating metallic nanostructures. Thus, the most direct method to obtain GO/r-GO-metal composites is to reduce the metal precursors in a GO-containing solution. For example, a Pd²⁺-GO solution enabled Pd NPs to be grafted on GO sheets.⁷³ The resultant composites showed higher catalytic activities

than traditional Pd/carbon catalysts. To improve the solubility and processability of the GO/r-GO-metal composites in polar solvents, GO sheets were primarily covalently bonded with 3, 4, 9, 10-perylene tetracarboxylic acid (PTCA) and then reduced to r-GO by hydrazine. Finally, r-GO sheets were decorated with uniform sized Au NPs by reducing HAuCl_4 with an amino-terminated ionic liquid (IL-NH_2).

Microwave-assisted synthesis,⁷¹ electroless metallization⁶⁵ and photo-chemical synthesis⁷⁸ were also used to produce GO/r-GO-metal composites. For example, GO and r-GO films were decorated with Ag NPs using the electroless metallization⁶⁵ method. GO and r-GO films were absorbed onto Si/SiO_x substrates modified with 3-aminopropyltriethoxysilane (APTES) before being heated in an aqueous AgNO_3 solution. Comparing the number density and size of the Ag NPs bonded to the GO and r-GO sheets results in the observation, that the Ag NPs on GO sheets have a higher number density and smaller size than particles on the r-GO sheets due to the larger quantity of functional groups on GO sheets. Dai et al. reported a similar phenomenon on Ni nanocrystals deposited on GO/r-GO sheets. The higher degree of oxidation of GO sheets resulted in a higher density of Ni NPs.⁷⁴ These phenomena indicate that the number density of metal NPs is significantly influenced by the surface chemistry of GO/r-GO, which is the core of this thesis.

2.1.4.2 GO/r-GO Semiconductor Nano-material Composites

Due to the promising application of semiconductor nano-material in solar cells, optics, electronics, supercapacitors and other materials, scientists are interested in the deposition of various semiconductor nano-material on GO/r-GO/graphene, such as MnO_2 ,⁷⁹⁻⁸¹ RuO_2 ,^{82,83} Cu_2O ,⁸⁴ CdS ,⁸⁵ CdSe ,⁸⁶ NiO ,⁸⁷ Fe_2O_3 ,⁸⁸ TiO_2 ,⁸⁹ ZnO_2 ,⁹⁰ SnO_2 .⁹¹ Generally, the methods for synthesizing GO/r-GO semiconductor nano-material

composites are accomplished via vapour deposition,⁸⁷ in-situ crystallization,⁹² solution mixing,⁹³ electrochemical deposition⁹⁰ and microwave-assisted growth.⁹⁴

The in-situ crystallization method has been widely used to obtain GO/r-GO semiconductor nano-material composites. For example, MnO₂ nano-needles⁷⁹ were grafted on GO sheets through a simple crystallization method at low temperature. The resultant composites possessed good electrochemical behaviour, which may potentially be used as electrode materials for supercapacitors.

Other efficient and direct methods can be used in the preparation of GO/r-GO semiconductor nano-material composites. For example, the solution mixing method^{93,95-98} uses benzyl mercaptan molecules to functionalize pre-synthesized CdS NPs. Due to the π - π interactions of the benzyl mercaptan-capped CdS, NPs are absorbed on the r-GO sheets.

2.1.4.3 GO/r-GO Polymer Composites

Recently, 3-dimensional macroporous GO/r-GO polymer composites attracted significant attention due to their promising applications as novel materials of highly conductive; high electrochemical capacity, high mechanical strength and good thermal stability.⁹⁹⁻¹⁰² The hydrophilic nature of GO sheets impedes its applications as a filler material for polymer composites because of its electrical insulation properties and incompatibility with most organic polymers. Interestingly, the electrical conductivity and dispersibility in a polymer matrix can be accomplished through the chemical functionalization of GO,^{10,25,45,52,53,103} which changes the surface properties. Many factors can affect the performance and properties of the GO/r-GO polymer composites such as the characteristics of the GO/r-GO filler and polymer matrix, the binding between the GO/r-GO filler and polymer matrix, the degree of dispersion the

of GO/r-GO filler in the polymer matrix and the ratio of GO/r-GO filler to the polymer matrix. The factors can be decided during the fabrication procedure. Conventional approaches to prepare polymer composites are used such as in-situ polymerization,¹⁰⁴⁻¹⁰⁷ solution mixing^{11,54,108-111} and melt blending.¹¹²⁻¹¹⁴

One large-scale and straightforward method for preparing polymer composites is solution mixing. The greatest challenge of this method is dispersing the GO/r-GO sheets in the polymer solution. Water-soluble polymers, such as poly-(vinyl alcohol) (PVA), are desirable because the polymer and GO can be mixed in aqueous solutions at any concentration.^{108,115} However, most polymers cannot dissolve in water, while GO/r-GO has low solubility in organic solvents. Many methods have been investigated in attempt to solve this problem. The most popular method is ultrasonication, which results in a short-lived metastable dispersion of GO or r-GO. The dispersions of GO or r-GO can be mixed with polyaniline (PANI),⁵⁴ polyurethane (PU),^{110,116} polycaprolactone (PCL),¹⁰⁹ and poly (methyl methacrylate) (PMMA).¹¹¹ Nevertheless, GO/r-GO aggregation occurs during solvent evaporation, which prohibits the use of this method. Therefore, GO/r-GO sheets require modification with functional molecules to increase the solubility in a wide variety of solvents.

Melt blending is commonly used to produce high-yield polymer composites in industry. For example, Yu *et. al.*¹¹³ use thermal exfoliation and reduction of GO to synthesis polyethylene terephthalate (PET)/graphene nanocomposites through melt compounding method.

Another popular method to produce GO/r-GO polymer composites is in-situ polymerization, in which a monomer solution mixed with suspensions GO/r-GO-based materials are polymerized under suitable reaction conditions in the presence of

a catalyst. Polyaniline (PANI) is a representative polymer suitable for preparing composite materials using the in-situ polymerization method.^{107,117,118} For instance, the polymerization of PANI is achieved by adding ammonium persulfate into a mixture of aniline monomers and graphene nanosheets.¹¹⁸

Polypyrrole (PPy) is a promising supercapacitor electrode material developed during the last decade,¹¹⁹ which composites are prepared with carbon materials to improve the mechanical and electrochemical properties of electrodes. The surface and electrical properties of graphene are important for carbon-based supercapacitors. The combination of a conducting polymer and GO-based materials to form nano-composite hybrid materials represents an opportunity for the design of novel materials with significantly improved electrochemical supercapacitors performance. For the carbon-based PPy supercapacitors, the introduction of nitrogen in carbon precursors improves the electrical properties of graphene, as well as the adsorption of monomers; therefore, a large synergistic effect can be achieved.

2.1.4.4 Other GO/r-GO based Composites

Recently, organic nanowires,^{120,121} carbon nanotubes (CNT)¹²²⁻¹²⁵ and carbon nanowires (CNW)¹²⁶ were used to decorate GO/r-GO sheets. It has been demonstrated that many small organic molecules can be deposited on GO/r-GO sheets to form core-shell structures through non-covalent interactions, which can be used as supercapacitor electrodes.^{126, 127} It should be noted that GO/r-GO sheets with small organic molecules result in a material with poor electronic properties due to defects and oxygen groups on the chemically converted graphene. To overcome this problem, CNT/CNW was grafted on GO/r-GO, which resulted in a material with excellent

performance on applications such as supercapacitors,^{124,125} Li ion batteries¹²³ and transparent conductors.¹²²

2.1.5 Applications of GO and GO-based materials

GO and GO-based materials show promise in a variety of applications (e.g., field-effect transistors,¹²⁷⁻¹²⁹ memory devices,¹³⁰⁻¹³² photovoltaic devices,^{90,92,93,96} and sensing platforms¹³³⁻¹³⁵). This thesis focuses on surface-enhanced Raman scattering (SERS) and supercapacitors applications.

2.2 Introduction of Raman spectroscopy

Raman spectroscopy is widely used to detect the vibrations in molecules, which provides information regarding the chemical structures of molecules and physical form. The technique is based on the Raman scattering effect, which is an inelastic scattering of light first theorized by Smekal¹³⁶ in 1923. This phenomenon was experimentally observed by the Indian physicist C. V. Raman¹³⁷ in 1928, for which he was awarded the Nobel Prize in Physics in 1930. This phenomenon was known as Raman spectroscopy or the Smekal-Raman effect from that point onward. The emergence of lasers led to the further development of the Raman technique, which caused the technique to be a powerful tool to investigate molecular structures. With the development of lasers and highly efficient signal detector, Raman spectroscopy is an effective means of detecting the structure of materials, which allowed the technique to have more extensive and practical applications in the chemical, physical, biological and medical fields.

2.2.1 Basic principles of Raman scattering

When matter is irradiated by monochromatic light of a specific frequency (ν_0) (generally, the visible, near ultraviolet and near infrared ranges are used), the photons are scattered from an atom or molecule. Most photons are elastically scattered at the original frequency (ν_0), while a small population of the scattered photons are inelastically scattered at a different frequency ($\nu_0 \pm \Delta\nu$). These two types of scattering processes are shown in Scheme 2.4. The elastic and inelastic scattering processes are also called Rayleigh and Raman scattering, respectively. In practice, Raman scattering includes anti-Stokes scattering (the incident light frequency is lower than that of the scattered light, $\nu_0 + \Delta\nu$) and Stokes scattering (the incident light frequency is higher than that of the scattered light, $\nu_0 - \Delta\nu$). Virtual excited states cause normal Raman scattering to be weak (only 10^{-6} of the incident radiation is detected).

Excited states that are real electronic states are in resonance with a Raman scattering process. Compared to normal scattering, the Raman scattering can be greatly enhanced by 10^3 - 10^6 ,¹³⁸ which enables more molecular information to be obtained regarding the vibrations of complex systems.¹³⁸ However, as electrons are excited to a real electronic state, molecular fluorescence can also occur simultaneously, which results in a very broad and noisy background. In that case, the background can be a major problem in the Raman measurements, which the Raman signals become swamps or obscures. For example, it is extremely difficult to obtain a Raman spectrum for the dye rhodamine 6G (R6G) with 532 nm green lasers as the excitation source,¹³⁹ because of a noisy background caused by high fluorescence background. To solve this problem, scientists have used a variety of methods. Surface-enhanced Raman scattering (SERS) is the most outstanding method.

Scheme 2.4 Schematic diagram of the different light scattering processes: Rayleigh scattering, anti-stokes/stokes Raman scattering and resonance Raman scattering.

2.2.2 Surface-enhanced Raman scattering

Metal nanoparticles can enhance Raman signals of dye molecules, which is a phenomenon called SERS.¹³⁹⁻¹⁴³ SERS can provide a significant enhancement in sensitivity and a wide range of molecules can be investigated.

In 1974, strong Raman signals of pyridine were initially observed by Fleischman et al. using a rough silver electrode.¹⁴⁴ The authors believed that the electrode surface areas were greatly increased as a result of the roughening process, which led to additional adsorption of pyridine molecules to the electrode surface. In 1977, Van Duyne¹⁴⁵ repeated Fleischman's experiment. Theoretical calculation indicated that the Raman signals on the Ag electrodes were approximately six orders of magnitude greater than that of pyridine solution. The dramatic enhancement could not be explained by the increase of molecular concentration. Henceforward, a vast amount of experimental and theoretical research investigated this phenomenon. By the year 1997,

SERS of single molecules adsorbed on Ag nano-crystals with similar cross sections were independently reported by two groups.^{146,147} The SERS enhancement was ~14 orders of magnitude for single molecules, which demonstrated that SERS had the potential to be a method for single molecule detection. Despite extensive research of SERS since its discovery, the mechanisms of enhancement are still controversial. SERS has been described in terms of electromagnetic (EM) and chemical enhancement mechanisms (CM).^{140,142,143,148} Generally, these two mechanisms are concomitant. In many cases, SERS is primarily based on EM, which includes CM as a secondary mechanism.

The main contribution to the EM is through surface plasmon resonance that occurs during excitation from incident light, in which a significant increase in the Raman cross section is obtained. It is necessary to generate a strong local electromagnetic field. Metals with appropriate surface morphologies are most commonly used to enhance the Raman signals of a molecule through the EM.^{146,149-152} In contrast, the CM^{153,154} changes the electronic structure of adsorbed molecules due to charge transfer between the molecule and the substrate. intramolecular separation of positive and negative charges can increase the polarizability of the molecule, which resulting an increase in the Raman cross section. EM is a long-range effect, which requires a rough substrate. The location between two particles is called “hot spots”. However, CM occurs on the molecular scale; therefore, CM is a short-range effect (i.e., the molecule should be in contact or be very close to the substrate). Thus, the charge transfer between the molecule and the substrate can easily occur.

Recently, Zhang *et. al.* used graphene as an active SERS substrate to greatly suppress the fluorescence of R6G molecules and dramatically enhance the Raman signals.¹⁵³⁻¹⁵⁵ This work is significant and interesting because carbon materials were

demonstrated to be SERS substrates, and EM and CM, which are often mixed using noble metal substrates, were completely separated. The enhancement caused by graphene was attributed to electron transfer between the graphene and the molecules adsorbed on the surface.^{153,156} As described in the introduction of GO, graphene can possibly be used as a good platform for studying chemical enhancement because the structure of graphene can be easily modified and controlled through either physical or chemical treatments. However, the charge-transfer process and the exact mechanism of SERS using graphene as a substrate are not well understood. Recently GO/r-GO was used to investigate the SERS of graphene-based materials.¹⁵⁷ As a derivative of graphene, GO/r-GO has a rich/controllable chemical structure, with numerous active oxygen sites. These sites can enhance the graphene-metal/molecule binding^{70,157} and provide a useful way to study the impacts of local chemical groups. Additionally, the global π -conjugation network can be used to study the SERS of molecules.

2.2.3 Rhodamine 6G (R6G)

In our work, rhodamine 6G (R6G) is used to chemically decorate graphene-based materials. It is a chemical compound and a dye which is often used as a tracer dye within water to determine the rate and direction of flow and transport. It is also used as a laser dye, or gain medium, in dye lasers, and is pumped by the 2nd (532 nm) harmonic from an Nd:YAG laser or nitrogen laser. It has remarkably high photostability, high quantum yield of 0.95, low cost, and its lasing range is 555 to 585nm with a maximum at 566, which is close to its absorption maximum of approximately 530nm (figure 2.1). R6G usually comes in three different forms: rhodamine 6G chloride ($C_{27}H_{29}ClN_2O_3$), rhodamine 6G perchlorate ($C_{27}H_{29}ClN_2O_7$) as well as rhodamine 6G tetrafluoroborate ($C_{27}H_{29}BF_4N_2O_3$). R6G used in this project is a bronze/red powder with the molecular formula $C_{28}H_{31}N_2O_3Cl$ and a molar mass

of 479.02 g/mol (Figure 2.2). Its density is 1.26 g/cm³. This formulation is highly corrosive, but also highly soluble. The solubility in water is 20 g/l at 25 °C.

Figure 2.1 Rhodamine 6G¹⁵⁸ Chloride powder mixed with methanol, emitting yellow light under green laser illumination. (adapted from ref. 158)

Figure 2.2 Rhodamine 6G¹⁵⁸ (hydrochloride). (adapted from ref. 158)

2.2.4 Raman spectroscopy of GO and r-GO

Figure 2.3 shows typical Raman spectra of GO and r-GO, where four prominent peaks can be observed in both: D band (1342 cm⁻¹), G band (1589 cm⁻¹), 2D band (2684 cm⁻¹), and D+G band (2932 cm⁻¹). The D band originates from a double resonance (DR) Raman process involving the iTO phonon and defects. The G band

originates from an in-plane vibration of sp^2 carbon atoms, which is a doubly degenerate (iTO and LO) phonon mode (E_{2g} symmetry) at the Brillouin zone center (Γ point). The 2D band is derived from a double-phonon resonant scattering procedure and is usually regarded as an overtone of the defect-mediated D band.¹⁵⁹ The combination mode of D + G is induced by disorder.^{160,161} In Figure 2.3, the intensity ratios of the D to G bands (I_D/I_G) for r-GO and GO are different. Normally, the I_D/I_G ratio indicates the average size of the sp^2 C domain.¹⁶²⁻¹⁶⁴ The increase in the I_D/I_G ratio is of GO over r-GO is normally attributed to a decrease in the mean crystallite size of GO. After removing the oxygen-containing functional groups in the GO sheets by reduction, the size of the re-established graphene network is smaller than the original one, which leads to an increase in the I_D/I_G ratio.¹⁶⁴⁻¹⁶⁶

Figure 2.3 Raman spectra for GO (black) and tRGO (red) excited by various excitation laser energies (wavelengths): (a) 1.58 eV (785 nm), (b) 2.33 eV (532 nm), and (c) 3.81 eV (325 nm). Insets are 2D and D + G range for GO and tRGO (background removed) (adapted from ref. 161).

2.3 Introduction to contrast spectroscopy

The contrast spectroscopy discussed in this section is acquired from confocal white light reflection microscopy.¹⁶⁷ This fast and user-friendly technique has been widely adopted to perform a variety of characterizations including metal nanostructures,¹⁶⁸

material morphologies,¹⁶⁹ refractive index profiles of fibers,¹⁷⁰ and determination of the thickness of graphene.^{167,171}

2.3.1 Experimentally obtained Contrast spectra

Figure 2.4 presents a schematic diagram of contrast spectroscopy. The contrast spectrum can be defined according to Eq. 2.1,

$$C(\lambda) = \frac{R_0(\lambda) - R(\lambda)}{R_0(\lambda)} \quad (2.1)$$

where $C(\lambda)$ is the contrast spectrum of the sample, and $R_0(\lambda)$ and $R(\lambda)$ are the reflection spectra of the sample and substrate, respectively. In this thesis, the sample was chosen to be GO supported by a SiO_2/Si substrate; therefore, $R_0(\lambda)$ and $R(\lambda)$ refer to the reflection spectra of the GO and SiO_2/Si substrate, respectively.

Figure 2.4 Diagram of the contrast measurements process.

2.3.2 Theoretical calculation of contrast spectra

The $C(\lambda)$ can be calculated for GO on SiO_2/Si using Fresnel's equation. As incident light shines on the interfaces of air/GO and GO/ SiO_2 , most of the beam is transmitted, while some of the beam is reflected. Therefore, an unlimited number of optical paths can occur as shown in Figure 2.5. For example, the amplitudes of the reflected waves for the air/GO/ SiO_2/Si system are individually, r_{02} , $t_{02} \cdot r_{23} \cdot t'_{02} \cdot e^{-2i\phi_2}$, $t_{02} \cdot r_{23} \cdot t'_{02} \cdot (r_{23} r'_{02}) e^{-2 \cdot 2i\phi_2}$, ...

Therefore, the total reflected amplitude from the system is governed by Eq. 2.2,

$$\begin{aligned} r &= r_{02} + t_{02} \cdot r_{23} \cdot t'_{02} \cdot e^{-2i\phi_2} + t_{02} \cdot r_{23} \cdot t'_{02} \cdot (r_{23} r'_{02}) e^{-2 \cdot 2i\phi_2} + \dots \\ &= r_{02} + \frac{r_{23} \cdot (1 - r_{02}^2) \cdot e^{-2i\phi_2}}{1 + r_{02} \cdot r_{23} \cdot e^{-2i\phi_2}} \quad (\text{Eq. 2.2 adapted from ref. 171}) \\ &= \frac{r_{02} + r_{23} \cdot e^{-2i\phi_2}}{1 + r_{02} \cdot r_{23} \cdot e^{-2i\phi_2}} \end{aligned}$$

In Eq. 2.2 r_{02}/t_{02} , r'_{02}/t'_{02} and r_{23}/t_{23} are the reflection/transmission coefficients at the air/ SiO_2 , SiO_2/air and SiO_2/Si interfaces, respectively. Meanwhile, $\phi_2 = \frac{2\pi \cdot n_2 \cdot d_2}{\lambda}$ is the phase difference as light passes through the SiO_2 layers and d_2 is the thickness of the SiO_2 layer. Under normal incidence of light, $r_{02} = \frac{n_0 - n_2}{n_0 + n_2}$, $r_{23} = \frac{n_2 - \tilde{n}_3}{n_2 + \tilde{n}_3}$ with n_0 , n_2 and $\tilde{n}_3$ being the refractive indices of air, SiO_2 , and Si, respectively. The reflection spectrum $R_0(\lambda)$, obtained from the interface of air/ SiO_2/Si , can be calculated using Eq. 2.3

$$R_0(\lambda) = |r|^2 \quad (\text{Eq. 2.3 adapted from ref. 171})$$

For the air/GO/SiO₂/Si system, the calculation of the $R(\lambda)$ is described as follows. First, the reflection amplitude from the GO/SiO₂/Si interface is calculated using Eq. (2.2),

$$r' = \frac{r_{12} + r_{23} \cdot e^{-2i\phi_2}}{1 + r_{12} \cdot r_{23} \cdot e^{-2i\phi_2}} \quad (\text{Eq. 2.4 adapted from ref. 171})$$

where, r' and $r_{12} = \frac{n_1 - n_2}{n_1 + n_2}$ are the reflection coefficients at the GO/SiO₂/Si and GO/SiO₂ interfaces, respectively, and n_l is the refractive index of GO. Secondly, the reflection amplitude from the air/GO/SiO₂/Si system is calculated by Eq. 2.5,

$$r'_g = \frac{r_{01} + r' \cdot e^{-2i\phi_1}}{1 + r_{01} \cdot r' \cdot e^{-2i\phi_1}} \quad (\text{Eq. 2.5 adapted from ref. 171})$$

Here, r' is calculated from Eq. (2.5). $\phi_1 = \frac{2\pi \cdot n_1 \cdot d_1}{\lambda}$ is the phase difference as the light passes through the GO layer (d_1 is the thickness of the GO layer) and $r_{01} = \frac{n_0 - n_1}{n_0 + n_1}$ is the reflection coefficient at the air/GO interface. The reflection spectrum $R(\lambda)$ from the air/GO/SiO₂/Si system can be calculated using Eq. 2.6

$$R(\lambda) = |r'_g|^2 \quad (\text{Eq. 2.6 adapted from ref. 171})$$

It should be noted that this calculation method is also applicable to any other thin-film materials and the calculations of the contrast spectra can be obtained for GO samples on any substrate as well. Figure 2.6 presents the calculated results of the contrast spectra of GO samples with a varied number of layers (1, 2, 3, 4, 5, 7 and 8 layers) on a SiO₂ (300 nm)/Si substrate under normal incidence of light. Two contrast peaks were observed at 362 nm and 590 nm, respectively. As the numbers of layers of GO increased, the intensity of the contrast peak increased too. A one to one

correspondence between the intensity of the contrast peak and number of layers of GO enabled the determination of the number of layers possible.

Figure 2.5 Multiple beam reflections and transmissions from the air/SiO₂/Si and air/GO/SiO₂/Si systems.

Figure 2.6 Theoretical calculation of contrast spectra of GO samples with a varied number of layers on a SiO₂ (300 nm)/Si substrate.

2.4 Introduction to graphene-based materials as supercapacitor electrodes

2.4.1 Supercapacitor

As a temporary energy storage device, supercapacitors can complement the deficiencies of high-energy batteries or fuel cells due to a high-power capability to store brake energies. Supercapacitors are capable of having comparably significant applications in energy storage systems. From an energy storage mechanism point of view, supercapacitors¹⁷² are usually classified into two categories: an electrical double layer capacitor (EDLC) and a pseudo-capacitor. For the EDLC, the pure electrostatic charge, which accumulates at the interface between the electrode and the electrolyte, is the main contributor for the capacitance. Therefore, electrode materials with higher surface area will have greater access to electrolyte ions. The capacitance of the pseudo-capacitor is based on the fast and reversible faradic processes of an electro-active species. Depending on the characteristics of the electrode material, the two mechanisms can occur individually or simultaneously.

2.4.2 Carbon-based materials as supercapacitor electrodes

The fascinating physical and chemical properties of carbon-based materials (e.g., carbon nano-tubes (CNTs), GO, r-GO, activated carbons (ACs)) caused these materials to be the most commonly used electrodes. The desirable performances properties include ease of preparation and modification, various morphologies (e.g., tubes, fibers, composites, and powders), high surface areas, tailored porosity to the size of the ions, a variety of electrocatalytic active sites and reversibly inert electrochemistry.¹⁷³⁻¹⁷⁵ High performance supercapacitors have properties that include a high power delivery rate and large energy storage capacity, which are related to a

high surface area and a pore size that can be tailored to allow the electrolyte ions to freely enter and exit. ACs are the most commonly used electrode material and are also considered to be EDLC electrode materials due to their high power delivery rate and large energy storage capacity. Subsequently, porous carbons^{176,177} and CNTs^{178,179} became of particular interest in the development of supercapacitor electrodes due to their unique porous structures and superior electrical properties, which lead to fast ion and electron transportation. To enhance the capacitance of supercapacitors, other electro-active species capable of being pseudo-capacitor can be introduced into the porous carbon framework. The materials should have fast and reversible faradic reactions, such as nitrogen¹⁸⁰⁻¹⁸⁷ or oxygen-containing¹⁸² functional groups, transition metal oxides^{83,178,188-193} and conducting polymers.^{119,185,187,190,194} Based on a literature survey, Table 2.1 shows a summary of the capacitive performances and characteristics of various carbon and carbon-based electrode materials. The data indicate that high-capacitance materials require high surface area or the addition of the pseudo-active species to generate a high energy density.

Table 2.1 The supercapacitor performance of electrode materials based on various carbon and carbon-based materials (adapted from ref.173)

Materials	Specific surface area/m ² g ⁻¹	Density/g cm ⁻³	Aqueous electrolyte		Organic electrolyte	
			/F g ⁻¹	/F cm ⁻³	/F g ⁻¹	/F cm ⁻³
Carbon materials						
Commercial activated carbons (ACs)	1000–3500	0.4–0.7	< 200	< 80	< 100	< 50
Particulate carbon from SiC/TiC	1000–2000	0.5–0.7	170–220	< 120	100–120	< 70
Functionalized porous carbons	300–2200	0.5–0.9	150–300	< 180	100–150	< 90
Carbon nanotube (CNT)	120–500	0.6	50–100	< 60	< 60	< 30
Templated porous carbons (TC)	500–3000	0.5–1	120–350	< 200	60–140	< 100
Activated carbon fibers (ACF)	1000–3000	0.3–0.8	120–370	< 150	80–200	< 120
Carbon cloth	2500	0.4	100–200	40–80	60–100	24–40
Carbon aerogels	400–1000	0.5–0.7	100–125	< 80	< 80	< 40
Carbon-based composite materials						
TC–RuO ₂ composite	600	1	630	630	—	—
CNT–MnO ₂ composite	234	1.5	199	300	—	—
AC–polyaniline composite	1000	—	300	—	—	—

The energy density and the power capability are the decisive factors for high performance supercapacitors. Therefore, the energy density should be increased,

while the power capability is maintained. Graphene, a rising star in materials, is considered to be the basic building block of all-dimensional graphitic materials^{195,196} and has a huge specific surface area (SSA);³ these characteristics contribute to its promise as a supercapacitor electrode material. Therefore, graphene-based materials (GBMs) have attracted a great amount of attention over the last several years in the field of supercapacitors.^{197,198}

2.4.3 Graphene-based materials as supercapacitor electrodes

Graphene has a large particular surface area and singularly high electronic features, which are suitable properties for electric double-layer capacitor (EDLC) electrode materials. However, the lack of synthetic methods to produce high-quality and large-scale graphene has restricted potential application of graphene for supercapacitors.¹⁹⁵ This problem was partly resolved when GO and reduced graphene oxide (r-GO) were synthesized on a large-scale.²⁵ Table 2.2 and 2.3 present the supercapacitor performance of various carbon-based materials that were used as electrode materials. According to the Tables, although graphene has a high theoretical SSA, obtaining high-yield and high-quality graphene is difficult. In contrast, GBMs can be synthesized on a large-scale at a low cost and also show good supercapacitor performance. Therefore, GO-based polymers,¹⁹⁹ carbon nano-tubes,¹²⁵ transition metal oxides^{79,83,200-203} and other composites were explored to achieve wonderful supercapacitor performance.

Table 2.2 Comparison between various carbon materials used as supercapacitor electrodes.^{173,175,198,204} (adapted from ref.198)

Carbon	Specific surface area/m ² g ⁻¹	Density/g cm ⁻³	Electrical conductivity/S cm ⁻¹	Cost	Aqueous electrolyte		Organic electrolyte	
					F g ⁻¹	F cm ⁻³	F g ⁻¹	F cm ⁻³
Fullerene	1100–1400 ¹⁷	1.72	10 ⁻⁸ –10 ⁻¹⁴¹⁸	Medium				
CNTs	120–500	0.6	10 ⁴ –10 ⁵¹⁹	High	50–100	< 60	< 60	< 30
Graphene	2630 ²⁰	>1	10 ⁶	High	100–205 ^{21,22}	>100–205	80–110 ²¹	>80–110
Graphite	10 ²⁰	2.26 ¹⁹	10 ⁴²³	Low				
ACs	1000–3500	0.4–0.7	0.1–1	Low	< 200	< 80	< 100	< 50
Templated porous carbon	500–3000	0.5–1	0.3–10 ²⁴	High	120–350	< 200	60–140	< 100
Functionalized porous carbon	300–2200	0.5–0.9	> 300	Medium	150–300	< 180	100–150	< 90
Activated carbon fibers	1000–3000	0.3–0.8	5–10	Medium	120–370	< 150	80–200	< 120
Carbon aerogels	400–1000	0.5–0.7	1–10	Low	100–125	< 80	< 80	< 40

Table 2.3 Comparison between various carbon materials used as the EDLC electrodes.^{173,175,198,204} (adapted from ref.197)

Carbon based EDLC materials	SSA (m ² g ⁻¹)	C _m (F g ⁻¹)
Activated carbon	1000~3500	< 200
Activated carbon fiber	1000~3000	120~370
Templated carbon	500~3000	100~350
Carbon aerogel	400~1000	100~125
Carbon nanotube	120~500	15~135
GBMs	<1500	14~264

Chapter 3

Experimental techniques

3.1 Reagents and apparatus

Table 3.1 lists the chemicals and reagents used in the thesis including the purity and source of the material.

Table 3.1 Reagents used for synthesis of GO-based materials.

Chemical	Grade	Supplier
Commercial Graphite powder(CGP)	99.90%	Sigma-Aldrich
Commercial expanded graphite(CEG)	99.90%	Sigma
H ₂ SO ₄	98%	Sigma-Aldrich
H ₂ O ₂	30%	Sigma-Aldrich
H ₃ PO ₄	85%	Sigma-Aldrich
Potassium permanganate	98%	Sigma-Aldrich
Rhodamine 6G (R6G)	99%	Aldrich
1-(3-Aminopropyl) imidazole	98%	Aldrich
Anhydrous Tetrahydrofuran	99.90%	Sigma-Aldrich
N,N'-dicyclohexyl-carbodiimide (DCC)	99%	Aldrich
Chloroauric acid	99.90%	Sigma-Aldrich
NaNO ₃	99%	Sigma-Aldrich
NaOH	99%	Merck
NaBH ₄	98%	Aldrich
1-bromobutane	99.00%	Sigma-Aldrich
Ethylene glycol	99.80%	Sigma-Aldrich
Ammonia	99.90%	Aldrich
NH ₃ gas	10%	soxal
Pyrrole	98%	Aldrich
FeCl ₃	98%	Sigma-Aldrich
Methanol	99.90%	Merck
Ethanol	99.90%	Merck
Acetone	99.90%	Merck
HCl	37%	Sigma-Aldrich
Polytetrafluorene-ethylene (PTFE)	60%	Sigma-Aldrich

Table 3.2 presents the general equipment used for preparation of the materials and electrochemical measurements.

Apparatus	Model or Specification	Manufacturer
Hot Plate & stirrer	HP 220	SPECTRA-TEKNIK(S) PTE LTD
Ultrasonicator	Transsonic 460/H	ACHEMA
Autoclave	Stainless steel lined with Teflon	Self-made
Balance	HR-200	A&D Company Limited
Oven	100-800	Memmert
Vacuum Oven	OV-11	PALICO BIOTECH PTE LTD
Electrochemical Workstation	CHI760D	CH Instruments, Inc.
pH meter	Ioncheck 10	Radiometer Analytical
Freezing drying	RLPHR 1-2 LD plus	CHRIST

3.2 Samples and sample preparation

The samples were prepared using two different methods: the micromechanical exfoliation (ME) of highly oriented pyrolytic graphite (HOPG) and the oxidation of graphite by a modified Hummers method.²⁸

3.2.1 Fabrication of graphene sheets via micromechanical exfoliation of highly oriented pyrolytic graphite

Graphene was prepared using ME of HOPG of about a few hundred micrometers in size,¹⁹⁶ which was sufficiently large for the purpose of this experiment. Figure 3.1 shows the schematic of the fabrication process of graphene samples with the 300 nm silicon oxide layer capping the Si substrate. The substrates were washed by acetone, ethanol and distilled water in sequence. Scotch tape was attached to the surface of the HOPG or natural graphite (Figure 3.1a). Thin graphite (maybe 50~1000 layers) was successively exfoliated, and the peeling process was repeated until the contrast on the tape was light gray. Subsequently, this exfoliated sample of adhesive tape was transferred to the substrate using hand or tool pressure (Figure 3.1b). Finally, different

layers of graphene were obtained on the substrate (Figure 3.1c). A similar process was used to transfer the graphene to different substrates, such as PMMA, glass, metal foil, silicon and silicon. The best optical contrast between graphene and the substrate is given by green light, which is most comfortable for our eyes, as well as in white light.²⁰⁵ The silicon substrate covered by a 300 nm silicon oxide layer was selected (300 nm SiO₂/Si) (Figure 3.1d).

Figure 3.1 Schematic diagram of production of graphene sheets by ME of HOPG or natural graphite. (a) Using Scotch tape, multilayer graphene can be peeled away from HOPG or natural graphite. (b) Adhere the tape together with multilayer graphene on a 300 nm SiO₂/Si substrate (c) Gently remove the tape and searching for graphene sheets. (d) Optical image of SLG, bi-layer graphene (BLG), four-layer graphene and few-layer graphene on 300 nm SiO₂/Si.

3.2.2 Fabrication of graphene oxide sheets via modified Hummers method

3.2.2.1 Synthesis of GO

Figure 3.2 shows the schematic diagram of the fabrication process of GO samples. Commercial expanded graphite (CEG) was used to synthesize GO with a modified Hummers method.^{28,206,207} In a different manner from our previous work,⁸¹ 3 g of CEG was added into a 9:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (360:40 mL) in a flask, which was immersed in an ice bath. Afterwards, 15 g of KMnO_4 was slowly added to the solution. Meanwhile, the temperature of the mixed solution was maintained below 20 °C for 2 h to avoid overheating and explosion. The mixture was stirred for 5 days. Subsequently, 10 mL of 30% H_2O_2 was added to the solution to completely react with the remaining KMnO_4 , resulting in a bright yellow solution. Finally, the mixture was washed with H_2O until the pH of the solution was approximately 5. The cotton-like GO sample was obtained after freeze drying the suspension.

Figure 3.2 Schematic diagram of the preparation of the GO sample

3.2.2.2 Preparation of GO Thin-Film

Figure 3.3 shows the schematic diagram of the fabrication process of GO films on the 300 nm silicon oxide layer capping above the Si substrate. The Si wafer with a 300 nm SiO_2 (SiO_2/Si) capping layer was used as the substrate to prepare GO films. The SiO_2/Si substrates were cleaned in piranha solution²⁰⁸ (a 3:1 mixture of concentrated 98% sulfuric acid and 30% hydrogen peroxide) at 100 °C for 1h (Figure 3.3a). The surfaces became hydrophilic after the piranha treatment. The GO films were deposited onto the SiO_2/Si substrates by the dip-coating method (Figure 3.3b). The contrast of GO on SiO_2/Si substrates was weaker than graphene because of the functional groups (Figure 3.3d).

Figure 3.3 Schematic diagram of the preparation of the thin film GO. (a) Washing the substrate. (b) Using the dip-coating method to deposit the GO thin film onto the SiO_2/Si substrate. (c) Drying the sample at room temperature. (d) Optical image of different layers of GO on a 300 nm SiO_2/Si substrate.

3.2.3 Fabrication of graphene oxide based materials

3.2.3.1 Preparation of Thin-Film r-GO

The r-GO film was produced by heating the previously prepared thin-film GO at 400°C in a tube furnace for 2 h. The ratio of H₂/Ar is 1:5 as controlled by a mass flow controller.

3.2.3.2 Preparation of r-GO-Au nanoparticles

3.2.3.2.1 Synthesis of GO

GO was synthesized using a modified Hummer's method.^{28,206,207} Briefly, 2g of graphite and 1.5 g of NaNO₃ were added into 150 mL of 98% H₂SO₄ solution in a flask that was immersed in an ice bath. A 9 g portion of KMnO₄ was then slowly added into the solution, while the temperature of the mixed solution was maintained below 20 °C for 2 h to avoid overheating and explosion. After the mixture was stirred for 5 days, 10 mL of 30% H₂O₂ was added into the solution to completely react with the remaining KMnO₄, and a bright yellow solution was obtained. Finally, the resulting mixture was washed with 3 % H₂SO₄ and then H₂O until the pH of the solution was 5~6. GO powder was obtained after freeze drying the suspension.

3.2.3.2.2 Preparation of ionic liquid functionalized GO (ILGO)

Initially, the GO sheets and 1-(3-aminopropyl)-imidazole were dispersed into anhydrous tetrahydrofuran (THF) with sonication for 20 minutes. Subsequently, the N, N'-dicyclohexylcarbodiimide (DCC) solution was slowly added into the mixture, and the mixture was stirred under a nitrogen atmosphere for 6 hours. 1-Bromobutane was then added into the above mixture. Finally, the homogeneous solution was vigorously stirred at 80 °C under a nitrogen atmosphere for 24 h. The resulting chemically

converted GO sheets (labelled as ILGO) were subsequently centrifuged, washed with water, and air-dried.

3.2.3.2.3 Process of anion exchange (GO-AuCl⁴⁻)

Initially, the ionic liquid-functionalized GO was dispersed in DI water and sonication for 20 minutes. Aqueous HAuCl₄ solution was subsequently added to the solution. Subsequently the mixture was stirred vigorously for 24 h. Finally, the sample was washed with DI water several times to remove the residual AuCl₄⁻ ions. The anion exchange mixture was labelled GO-AuCl₄⁻.

3.2.3.2.4 Preparation of the composite (r-GO-Au)

The AuCl₄⁻ ions and GO sheets were reduced with NaBH₄ in this step. The AuCl₄⁻ ions were reduced to gold nanoparticles. The GO sheets were also reduced to r-GO. The r-GO acted as a supporter to stabilize the gold nanoparticles. The nano-composites were labelled r-GO-Au.

3.2.3.3 Preparation of MnO₂-GO nanocomposites

3.2.3.3.1 Synthesis of GO

Two kinds of graphite were utilized in synthesizing GO using a modified Hummers method.^{28,206,207} The method was similar to that described in 3.2.3.1.1.

3.2.3.3.2 Synthesis of MnO₂-GO nanocomposites

The MnO₂-GO nanocomposites were prepared by an in situ reduction method.²⁰⁹ The detailed procedure was as follows. A 200 mg sample of GO1 (or GO2) was blended with 150 mL of 0.02 M KMnO₄ solution in a three-necked round-bottomed flask. This mixture was refluxed at 120 °C for 12 h with sustained magnetic stirring. The nano-

composites, labelled MnO₂-GO1 (or MnO₂-GO2), were then centrifuged, washed, and dried in air at 55 °C overnight.

3.2.3.4 Preparation of graphene/PPy

3.2.3.4.1 Synthesis of GTO

GTO was prepared from natural flake graphite powder as reported previously.²⁸ Briefly, 5 g of graphite and 3.5 g of NaNO₃ were placed in a flask. Subsequently, 350 mL of H₂SO₄ was added with stirring in an ice-bath environment, and 10 g of KMnO₄ was added with vigorous stirring for 2 h and kept for 6 days at room temperature. 200 mL of 5 wt% H₂SO₄ was added to this mixture, and the temperature was maintained at 98 °C under heating for 2 h. When the temperature was reduced to 50 °C, 10 mL of H₂O₂ (30 wt% aqueous solution) was added to terminate the reaction. The resultant mixture was purified by repeating the following procedures until the supernatant was colourless: washing (1 L 3 wt% H₂SO₄/H₂O), ultra-sonication dispersing (140 W for 30 min), and centrifugation (6000 rpm for 30 min). The dark precipitate was collected and freeze dried for 2 days.

3.2.3.4.2 Synthesis of NH₂-G

NH₂-G was prepared by the method developed in our group.²¹⁰ Initially, 100 mg of GTO was added to 40 mL of ethylene glycol under ultrasonication. After further addition of 1 mL of ammonia water, the dark brown solution was transferred to a Teflon lined autoclave for a solvothermal reaction at 180 °C for 10 hours. After the reaction, the precipitate was filtered, washed repeatedly with distilled water, and dried at 60 °C for 24 h before being used further.

3.2.3.4.3 Synthesis of N-G

N-G was prepared from the annealing of GTO at 550 °C under NH₃ gas with flow rate of 2.5 ccm/s. Briefly, 500 mg of graphite oxide was placed in a tube furnace with an Ar flow of 50 sccm (5% NH₃). The temperature was increased to 550 °C over 20 min, and then maintained for 30 min. The obtained sample was ground and washed repeatedly with distilled water, and dried at 60 °C for 24 h before being used further.

3.2.3.4.4 Synthesis of RGO

RGO was prepared by chemical reduction. A 500 mg sample of GTO was dipped in an aqueous NaBH₄ (50 mM) solution for 2 h. The resulting sample was washed repeatedly with distilled water and dried at 60 °C for 1 h.

3.2.3.4.5 Synthesis of PPy/graphene composite

The chemical polymerization of pyrrole on various surface-functionalized graphene was performed with FeCl₃ as an oxidant. Samples of 200 mg of various graphene were ultrasonically dissolved in 20 mL of methanol, and 3.31 mL of 0.1 M pyrrole in methanol was added drop-wise. After 10 min, 6.62 mL of a 0.2 M FeCl₃ solution was added drop-wise. The solution was shielded from light and kept in an ice bath with magnetic stirring for 8 h to fully polymerize. The product was washed with a large amount of water and subsequently rinsed several times with ethanol and acetone to remove the residual oxidant. All of the composites were dried at 60 °C. The loading ratio of polypyrrole was ~ 9 wt%, after taking into consideration the 1% unpolymerized pyrrole monomer.

3.2.4 Sample preparation of SERS

R6G, which is a common probe molecule in SERS experiments, was used to test the efficiency of four kinds of substrates. In a typical preparation, the thin-film GO, thin-film r-GO, SLG and r-GO-Au nano-particle were initially soaked in a 10⁻⁵ M R6G

solution for about 1 h, then washed with distilled water to remove those unabsorbed molecules, and dried in air.

3.3 Characterization

3.3.1 Confocal Raman / White Light Microscope

The WITEC CRM200 Raman system was used in our experiments. Figure 3.4 shows the schematic diagram of the WITEC CRM200 system. Both contrast and Raman spectra were measured on the same WITEC CRM200 Raman system with a $100\times$ objective. For contrast measurement, we used a normal white light (tungsten halogen lamp, excitation range from 400 to 800 nm, across a 1 mm slit) as the emission source of the incident light. The reflected light was collected via a backscattering configuration (with a 100 μm pinhole), directed to a 150 lines/mm grating and detected with a TE-cooled charge-coupled-device (CCD). The reflection spectra obtained from the GO sheets were compared with those from a background spectrum of SiO_2/Si to generate the contrast spectra. For Raman measurement, the excitation source was 532 nm with a laser power of 0.1 mW. A short integration time of 3s was used in our measurement to reduce the effect of laser-induced heating as much as possible. The contrast and Raman images were obtained by scanning the sample on a piezostage under illumination with white light and laser, respectively. The ScanCtrl Spectroscopy Plus software (WITec GmbH, Germany) controlled the stage movement and recorded the data point by point. WITec Project software was used to perform the analysis of the spectra and mapping images.

Figure 3.4 Schematic diagram of the confocal Raman/white light system.

3.3.2 Electrochemical Measurements

Cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) were used to characterize the electrodes using 6/3 M KOH as the electrolyte in a three-electrode cell at a CHI electrochemical workstation. CV characteristics of the composites were recorded at various scan rates from 2 to 50 mV/s. Galvanostatic charge/discharge tests were carried out under various current densities with a sampling rate of 20 mA/s. EIS measurements were carried out in the frequency range from 10 k Hz to 10 m Hz. The applied voltage was 10 mV.

The working electrode of the electrochemical capacitors was fabricated by mixing about 85 wt. % of nano-composites, 10 wt. % of acetylene black and 5 wt. % of polytetrafluorene-ethylene (PTFE) (Figure 3.5a). A small amount of ethanol was added to the mixture to form a more homogeneous paste. Before use, the Ni foams were carefully washed with acetone, 0.1 M HCl and distilled water and then dried in a vacuum oven (Figure 3.5b). One of the Ni foams was covered by the mixture, and another was not covered with the mixture as the control experiment (Figure 3.5c).

Subsequently, the mixture was pressed into Ni foam and further dried to form the electrodes (Figure 3.5d). Electrochemical characterizations were carried out in a conventional three-electrode cell with different types of electrolytes (Figure 3.5e). A platinum foil and saturated Ag/AgCl electrode were used as the counter and reference electrode, respectively. All electrochemical measurements were conducted using a CHI 660 electrochemical workstation.

Figure 3.5 Schematic diagram of the preparation of the supercapacitor working electrode. (a) Mix of the electrode materials. (b) Wash the substrate. (c) Place the mixture on the Ni foam and then cover it with the other Ni foam. (d) Make electrodes. (e) Image of working electrode after the electrochemical measurement.

3.3.3 X-ray photoelectron spectroscopy (XPS) Measurements

XPS measurement was carried out on a Thermo VG Scientific ESCALAB 250 (Thermo Fisher Scientific, UK).

3.3.4 X-ray diffraction (XRD) Measurements

The XRD studies were characterized using a Bruker D8 ADVANCE XRD (Bruker AXS, Germany).

3.3.5 Physical adsorption of N₂ Measurements

Nitrogen adsorption–desorption experiments were investigated at 77 K on an automatic volumetric sorption analyzer (Quantachrome, NOVA1200; Micromeritics, USA). The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. Pore-size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method using the adsorption branches.

3.3.6 Scanning electron microscopy (SEM) and Energy Dispersive X-ray Detector (EDX) Measurements

SEM and EDX images were obtained on a field-emission scanning electron microscope (FE-SEM JEOL JSM-6700F; JEOL, Tokyo, Japan).

3.3.7 Transmission electron microscopy (TEM) Measurements

TEM analyses were performed using an electron microscope (JEM 2010F; JEOL, Tokyo, Japan) operating at 120 kV.

3.3.8 Elemental analysis Measurements

Quantitative elemental determinations were performed by initially dissolving the solid samples with a CEM Mars microwave digester, followed by analysis with a Thermo Scientific iCAP 6000 series ICP-OES (Thermo Scientific, England).

3.3.9 Fourier transform infrared spectrometer (FT-IR) Measurements

In this thesis, the FTIR was recorded on FT-IR spectrum one, which reports the chemical functional groups of the samples and determines the chemical structure of the sample. KBr and the powder sample were mixed in a weight ratio of 1:99 and then pelleted by a HYDRAULIC PRESS specac.

Chapter 4

Rapid and Non-Destructive Identification of Graphene Oxide Thickness Using White light Contrast Spectroscopy

4.1 Introduction

Graphene oxide (GO) sheets, free-standing two-dimensional compounds with a variable ratio of carbon, oxygen and hydrogen, have attracted significant attention because GO sheets can be used for highly sensitive bio-sensing,²¹¹ biocompatible drug delivery,²¹² energy^{39,213} and high-capacity hydrogen storage.^{40,41} The electrical, mechanical, thermal and optical properties of GO are strongly dependent on the chemical and atomic structure,^{36,161,208,214,215} which can cover a broad scope via chemical approaches. However, the determination of number of GO layers remains to challenge to fully understand and further develop potential applications for GO sheets. A fast and accurate method for identifying the thickness of GO sheets will intensify the study and exploration of GO sheets. In the past few years, many methods^{196,216-220} have been developed to identify the number of graphene layers, but only the optical methods are non-destructive and facile, such as Raman spectroscopy,^{217,221-225} contrast spectroscopy,¹⁶⁷ Rayleigh spectroscopy²²⁶ and optical microscopy.^{160,165,169} Due to the weak optical absorbance that originates from both the large optical gap caused by sp^3 hybridization of the functional groups and the adsorbed water on GO sheets, the identification of the thickness of GO sheets has been only rarely studied. Compared to graphene, GO sheets have a paler color and weaker optical absorbance.²²⁷ Some optical microscopy, which is used to characterize graphene,^{160,165,169} is not an ideal method to directly and accurately identify the thickness of GO sheets. Up to now,

only a few papers reported the visualization of GO sheets by fluorescence quenching microscopy (FQM),²²⁸⁻²³¹ which was not capable of identifying the number of GO layers. For the accurate identification of the GO thickness, a more direct and efficient method is desirable. Jung *et. al.*²²⁷ utilized a laser source with three different wavelengths to obtain a high-contrast optical image of GO sheets. However, the three individual contrast values could not provide a complete response of GO layers over the entire optical region, which may limit the general adaptation of this method due to the strict requirements of laser sources. In addition, in contrast to graphene or reduced GO sheets, GO is very sensitive to laser irradiation and easily damaged by the laser-induced heating.^{159,232} low-power-based optical contrast spectroscopy, with its advantages of rapid and non-destructive, is a unique technique for identifying GO sheets. In this work, a white light source is used to identify the number of GO layers. This technique enables a contrast spectrum to be acquired ranging from 420 to 800 nm. In comparison, Raman spectroscopy is employed to determine the number of GO layers. While accounting for the laser heating and the requirement of a reference spectrum for the Raman spectroscopy, the contrast spectra and images can accurately and directly determine the thickness of GO sheets. To further understand the contrast spectra of GO sheets, Fresnel's equations are used to simulate the contrast of GO sheets.¹⁶⁷ The simulation results are well-matched with the experimental data within the range of 520 to 800 nm. The experimental data can be used as a criterion to determine the number of GO layers accurately and directly.

4.2 Results and discussions

4.2.1 Raman Spectroscopy of 1-5 layers GO

Figure 4.1a presents an optical image of a GO sheet on a SiO₂/Si substrate. The GO sheet shows five areas of different contrast, which are likely due to five different thicknesses. The thicknesses of the GO sheets are further investigated by tapping mode AFM and the image is shown in Figure 4.1b. From the inset of the height profiles in Figure 4.1b, the thickness of single-layer GO sheet is observed to be approximately 1 nm (the inset of the height profile with white colour).^{214,233-235} As the number of layers increases, the thickness linearly increases. For example, 2.1 nm, 3.2 nm, 4.2 nm and 5.3 nm correspond to two, three, four and five layers, respectively (the inset of the height profile with green colour). Figure 4.1c displays the typical Raman spectra of a GO sheet with a single-layer to five-layer sample, which were measured under the same conditions. The two main peaks observed at 1342 cm⁻¹ and 1589 cm⁻¹ are D and G bands respectively.¹⁵⁹ As shown in the inset graph in Figure 4.1c, the intensity of the G band increases linearly as the number of GO layers increases, which is similar to observations reported in previous work.²³² Figure 4.1d shows the typical Raman mapping of a GO sheet with a single-layer to five-layer sample plotted against the G band intensity of the GO sheet. It clearly presents five different intensities.

To further extend the scope of the above-mentioned G-intensity method, a thicker GO sheet (≥ 5 layers) was studied. The thicknesses of the GO layers were characterized by AFM (Figure 4.2a). Figure 4.2b shows the optical image of the homologous GO sheets, which are labeled by the number of the layers according to the corresponding z-profiles from the AFM image. Similar to the 1 to 5 layered GO

sheets, the Raman intensity of G band was observed to linearly increase as the number of GO sheets increased to 10 layers, and similar observations were made for few-layered graphene.²³⁶ For more than 10 layers, the intensity of the G band slightly increases (10-27 layers), and then decreases as the number of GO layers increases. Although the linear relationship between the G band intensity and GO sheet thickness (≤ 10 layers) exists, the precise identify the number of layers of the GO sheet cannot be identified, because the absolute Raman band intensity can be affected by many factors. To use this method, a pre-determined single layer GO is required as a reference. In addition to the lack of a reference spectrum, the laser-induced heating is another major impediment, which will be discussed later.

Figure 4.1 (a) and (b) Optical and cross-sectional AFM images of GO sheets with 1 to 5 layers respectively. The inset curves in (b) represent the z-profiles. (c) The Raman spectra as a function of the number of layers, which shows a linear relationship between the G band intensity and the number of GO layers. (d) The Raman image plotted against the G band intensity of the GO sheet.

Figure 4.2 (a) AFM image of GO sheets with various thicknesses, (b) The corresponding optical image of the GO, which is by the number of the layers identified by AFM. (c) The optical image of the GO sheets after Raman measurements. The green circles show the area reduced by the laser.

During the Raman measurements, the areas irradiated by the laser beam were observed to darken in the optical image as shown in Figure 4.2c, and marked by green circles.

To investigate the effects of laser-induced heating on GO sheets, two-step Raman mapping was performed. Firstly, a $4 \times 4 \mu\text{m}$ square region was scanned at a laser power of 0.1 mW, and the integration time for each spectrum was 0.5 s. These conditions were used because the laser-induced heating effects were minimal and an acceptable Raman signal to noise ratio was achieved. Subsequently, a larger area, which included the square area previously mapped, was mapped under the same condition as in the first step (Figure 4.3a). Although a very low laser power and short integration time were used for the acquisition of Raman measurements, reduction²³² of the GO sheets by the laser irradiation was unavoidable. The dark area highlighted by the dash line in Figure 4.3a provides evidence for this effect.^{159,232} As shown in Figure 4.3b, the decrease in the Raman intensity before and after Raman mapping is obvious, which indicates that laser irradiation greatly influences the GO sheets. The decrease of

intensity of the Raman modes is due to the partial removal of functional groups from the GO with the laser irradiation during the Raman measurements. These effects prohibit the use of Raman spectroscopy as a reliable method to identify the thickness of GO sheets.

Figure 4.3 (a) The Raman image acquired by the intensity of the G band of the GO sheets. The area marked by the black dashed line was scanned twice. (b) Raman spectra of the single layer GO sheet (black curve) and laser-reduced GO sheet (red curve).

4.4.2 Contrast Spectroscopy of 1-5 layers GO

Because the Raman measurements always reduce the GO sheets due to laser-heating, contrast spectroscopy and mapping under white light illumination were exploited to determine the thickness of GO sheets.

Figure 4.4 shows the contrast spectra for GO sheets of various thicknesses on a SiO₂/Si substrate. The contrast spectrum was achieved using the formula, $C(\lambda) = (R_o(\lambda) - R(\lambda)) / R_o(\lambda)$,¹⁶⁷ where $R_o(\lambda)$ and $R(\lambda)$ are the reflection spectra from the SiO₂/Si substrate and GO sheets, respectively. A peak at approximately 588 nm (in the visible range) was observed in the contrast spectrum of a single-layered

GO sheet, which almost maintains a constant value as the number of layers (within 10 layers) increased. The contrast value for the single-layer GO sheet was approximately 0.035 ± 0.005 and increased as the number of layers increased. For thicker GO sheets (> 10 layers), the contrast peaks show a red shift. The shift is caused by the different phase differences, which are determined by the path difference of two neighbouring light beams that have interference ($\delta = 2n(d/\lambda)$).¹⁶⁷ Where n is the refractive index of GO and d is the thickness of GO, which can be estimated as $d = N\Delta d$ ($\Delta d=1\text{nm}$). Fresnel's equations are used to explain the evolution of the contrast values. The simulation results are discussed below.

Figure 4.4 The contrast spectra of GO sheets with different thicknesses.

Regarding the incident light into the trilayered system (air to the GO sheet to the SiO_2/Si), the contrast spectrum was calculated. The thickness of the SiO_2 was 300 nm and the Si substrate was assumed to be semi-infinite. The thickness of GO sheets was estimated to be $N \cdot \Delta d$, where $\Delta d=1$ nm, the average thickness of a single layer of GO and N is the number of layers. The refractive indices of the materials are $n_{\text{air}} \approx 1$, n_{SiO_2}

$= 1.46$ and $n_{Si} = 4.15 - 0.044i$ in the white light region ranging from 400-800 nm. Firstly, the refraction index $n_{GO} = 1.7 - 0.2i$ (blue line in Figure 4.5) was used as suggested previously.²³⁷ The results of the calculations showed large deviations from experimental data. Modification of the refractive index was performed to have a better fit with the experiment results. The optimized refractive index of a single-layer of a GO sheet was determined to be $n_{GO} = 1.2 - 0.24i$ (red line in Figure 4.5). This refractive index was also used to fit the spectra of few-layered GO sheets. The close agreement between the simulated results and experimental results supports the accuracy of the refractive index (Figure 4.6).

Figure 4.5 Typical contrast spectra of a single-layered GO sheet obtained from experiment (black line), the calculation using $n=1.2-0.24i$ (red line) and $n=1.7-0.2i$ (blue line).

A disagreement between the simulated and experimental results can be observed in the range of 420-520 nm. The reason for the deviation is not clear. One possibility is that when the contrast of the GO was calculated, the influence of the functional

groups and water on the GO sheets was not considered. The contrast of the GO sheet may be influenced. Further investigation is required.

Figure 4.6 The contrast values of experimental data (black square) and the simulated results using $n=1.2-0.24i$ (red sphere) for 1-8 layers of GO sheets.

For the identification of the thickness of a GO sheet, the accurate and effective way is to use the contrast spectra in the range 520-800 nm.

Because the Raman band intensities of multiple layer structures are sensitive to the refractive index, the refractive index ($n_{GO} = 1.2-0.24i$) was used to fit the intensity of the Raman G band based on the Fresnel's equations (shown in Figure 4.7). Good agreement between the experimental data and the simulation curve can be clearly observed in figure 4.7. The significant improvement over previously reported values indicates that the refractive index of GO determined in this work could be widely used in the future study of GO sheets. For a GO sheet of unknown thickness, contrast spectroscopy can directly determine the thickness by comparing the contrast value

with the standard values shown in Figure 4.6. Alternatively, the thickness can also be obtained from our empirical equation.

$$C = 0.01393 + 0.02264N + 0.000818037N^2 \quad (1)$$

where N (≤ 10) is the number of layers of GO. Eq (1) was obtained by fitting the experimental data.

Figure 4.7 The experimental (the blue dash-dot line curve is a guide for the eye) and calculated results of the G band intensity as a function of number of layers using $n=1.2-0.24i$ (black line) and $n=1.7-0.2i$ (red line)

To further confirm the effectiveness of the contrast spectra for the determination of the thickness of GO sheets, contrast mapping was performed. Figure 4.8 shows the contrast image of the same sample shown in Figure 4.2. It is worth noting that the contrast image provides a better perspective view of the sample. As was observed in the Raman image plotted by the intensity of the G band, thicker GO sheets resulted in a higher contrast. Figure 4.8b shows the contrast image of the same sample collected

after the single Raman spectrum measurement with a laser power of 0.1 mW and integration time of 3 s. The obvious change in the contrast image of the GO before and after laser irradiation indicates that Raman spectroscopy is inappropriate for thickness determination. Moreover, a high-quality contrast image can be acquired more quickly than a Raman image, which results in a high-throughput method relative to the Raman method. Contrast spectroscopy and mapping can enable a non-destructive and more efficient way to characterize the thickness of GO sheets to be achieved without changing the sample.

Figure 4.8 (a) The contrast image of GO sheets with a varied number of layers before laser exposure. (b) The contrast image of the sample after the collection of a single Raman spectrum.

4.3 Conclusion

In conclusion, the facile and effective determination of the number of GO layers was demonstrated using contrast spectroscopy. A refractive index for GO sheets (≤ 10 layer) was obtained ($n_{\text{GO}} = 1.2 - 0.24i$). The agreement between the simulated results and experimental data, for both the contrast and G band intensities suggests that this refractive index can be used in further GO studies. Contrast mapping further

demonstrated that this method is a convenient and powerful probe for the quick visualization of GO sheets of different thicknesses. As additional properties are discovered and new applications are proposed for single- and few-layer GO sheets, contrast spectroscopy (an accurate, easy-to-achieve and fast method to determine the thickness of GO layers less than 10 layers thick) will become very useful for future fundamental and practical studies.

Chapter 5

Comparison of SERS Measurements on Graphene Oxide, Reduced Graphene Oxide and Graphene Surfaces

5.1 Introduction

Surface-enhanced Raman scattering (SERS) is one of most important and powerful technique to probe the chemical interaction between the adsorbing molecules and the surface of noble metal, which is normally able to amplify the Raman signals of adsorbing molecules by 6~10 orders of magnitude.^{140,142,143,148} It is well-known that there are two main contributions for this huge enhancement, namely, electromagnetic (EM) and chemical charge transfer (CT) enhancements. The latter one can offer much information about the adsorbent molecules, in particular, the adsorption orientation.^{147,152} However, the fact that these two inseparable mechanisms are always concomitant in practice and the EM one plays a dominant role suggests SERS substrate with pure CT enhancement is highly demanding.

Recently, few layer graphene has been demonstrated as an active SERS substrate that drastically quenching fluorescence background of R6G and also enhancing the Raman signals. Significantly, such enhancement by graphene substrates is considered as the consequence of charge transfer between R6G and graphene, totally excluding the contribution of EM. These successes provide a direct and convincing way to understand the exact role of CT without the interruption of EM. Meanwhile, as derivatives of graphene, both graphene oxide (GO) and partially reduced GO (r-GO) possess some active oxygen sites, which were observed to notably enhance the binding between graphene and metal/molecule.^{70,157} Moreover, it is worth noting that

these three graphene-based substrates have the great potential to be as benchmarks of SERS substrate, as all of them are easy to be fabricated with large scale, high repeatability and reproducibility. To our best knowledge, a systematic investigation about the SERS effect of these three substrates is still lack.

In this chapter, we have conducted a systematic comparison of SERS effect on graphene and its derivatives (i.e., GO and r-GO). R6G was used as a probe molecule to identify the different interactions between molecules and these three substrates. We found that all of them can produce obvious Raman enhancement of R6G but with different spectral features, i.e., selectively amplifying certain vibration modes. The selectivity in signal enhancement should be ascribed to the difference orientation of the adsorbing R6G molecules on these substrates, resulting from the local chemical groups on GO and r-GO and the global π -conjugation network of GO, r-GO and graphene. Moreover, we found that with increasing the layers of these three substrates, the Raman signal of R6G on GO increased, while both graphene and r-GO substrates show inverse trends. The possible reason could be due to the different interference effect induced by different layers of graphene, r-GO and GO. The spectral comparison of R6G adsorbed on these three substrates could provide relative comprehensive understanding of SERS effects produced by graphene-based substrates. Meanwhile, this comparison will also benefit to revealing the chemical interaction between molecules and carbon materials.

5.2 Results and Discussion

5.2.1 The typical R6G Raman spectra and mapping on single-layered GO, single-layered r-GO and SLG

Figure 5.1 presents the typical Raman spectra and mapping of R6G molecules adsorbed on single-layered GO, single-layered r-GO and SLG. Using SLG, GO and r-GO as substrates resulted in the observation of strong Raman peaks in the Raman spectra of dye R6G (shown in Figures 5.1a, c and e, respectively), while the fluorescence background was very low. Due to the large number of Raman peaks for R6G,^{139,238} we only select three representative peaks for detailed discussion. The band observed at approximately 612 cm^{-1} (labelled as P1) was assigned to an in-plane bending motion of the carbon atoms of the xanthenes skeleton. The band observed at approximately 774 cm^{-1} (labelled as P2) was attributed to an out-of-plane bending motion of the hydrogen atoms of the xanthenes skeleton. The band observed at approximately 1648 cm^{-1} (labelled as P3) was attributed to an aromatic stretching vibration mode. Figures 5.1b, d and f show Raman images of the intensity of the three selected Raman peaks of R6G: I_{P1} (top), I_{P2} (middle), and I_{P3} (bottom). The intensity differences of the Raman images are obvious. The intensity of P1 and P2 on a GO substrate are equal, and both are higher than P3 (Figure 5.1b). In the case of r-GO, P1 and P3 are the strongest and weakest Raman signals, respectively (Figure 5.1d). In contrast to the GO and r-GO substrates, the signals with the highest intensity for SLG are P3, and P1 and P2 having the same enhancement (Figure 5.1f). Images based on the relative intensities are also shown in Figures 5.2a, b and c.

Figure 5.1 Typical Raman spectra and Raman images of R6G on GO (a and b), r-GO (c and d) and SLG (e and f). Raman images of I_{P1} (b, d and f-top), I_{P2} (b, d and f-middle), and I_{P3} (b, d and f-bottom) are plotted by the R6G peaks. The inset images are the corresponding optical images of GO, RGO and SLG sheets. All Raman spectra are normalized to the Si peak.

Figure 5.2 Relative intensities of Raman images of R6G on GO (a), r-GO (b) and SLG (c) I_{P1}/I_{P3} (a, b and c-top) and I_{P2}/I_{P3} (a, b and c-bottom).

The intensity ratio of the R6G Raman peaks on GO, r-GO and SLG sheets, I_{P1}/I_{Si} , I_{P2}/I_{Si} , I_{P3}/I_{Si} , I_{P1}/I_{P3} , and I_{P2}/I_{P3} , are plotted in Figure 5.3. Figure 5.1 and 5.3 indicate that SLG, GO and r-GO have different relative Raman intensities of P1/P3 and P2/P3, which was also shown in table 5.1

Figure 5.3 The intensity ratio of the R6G Raman peaks on GO, r-GO and SLG sheets.

(a) I_{P1}/I_{Si} (black), I_{P2}/I_{Si} (red) and I_{P3}/I_{Si} (blue) and (b) I_{P1}/I_{P3} (black) and I_{P2}/I_{P3} (red).

Table 5.1 The intensity ratio of the R6G Raman peaks on GO, r-GO and SLG sheets.

		GO	r-GO	SLG
I_{P1}/I_{Si}	average	0.44745	0.62106	0.12986
	$\pm\Delta$	0.03162	0.02909	0.03699
I_{P2}/I_{Si}	average	0.31153	0.34732	0.14399
	$\pm\Delta$	0.03087	0.03087	0.02123
I_{P3}/I_{Si}	average	0.23507	0.23507	0.93563
	$\pm\Delta$	0.03325	0.03325	0.03805
I_{P1}/I_{P3}	average	1.82051	1.75676	0.20731
	$\pm\Delta$	0.03807	0.02412	0.03498
I_{P2}/I_{P3}	average	1.47499	0.98302	0.17783
	$\pm\Delta$	0.03639	0.02112	0.02789

The large spectral difference between the three substrates originates from the varied orientations of R6G on the substrates. Most of the aromatic dye molecules most likely lie parallel to the surface of graphene.^{153,154,239} For the SLG substrate, the long axis of the R6G molecules should be approximately parallel to the layer of graphene due to strong π - π stacking. The π - π stacking-induced charge transfer between the R6G and graphene is responsible for the Raman signal enhancement and the quenching of fluorescence.^{153,154} This phenomenon is supported by the results shown in Figure 5.1e. The strongest peak is associated with the aromatic C-C bonds (P3), which implies that the R6G molecules interact with the SLG through the aromatic rings. The intensity of the P3 peak of GO is much lower than the P1 and P2 peaks (Figure 5.1a), which indicates that the aromatic rings of R6G are not parallel to the surface of GO or the R6G aromatic rings and the aromatic rings of GO are separated by the chemical groups. As r-GO is prepared, the P3 peak is greatly enhanced due to the recovery of the graphene structure (Figure 5.1c). The SLG and GO substrates have the strongest and weakest π - π stacking interaction with the R6G molecule, respectively. For GO

and r-GO substrates, the P1 and P2 peaks of the R6G molecule are more enhanced relative to the enhancement of the peaks for the SLG substrate. Therefore, an additional enhancement mechanism is most likely present for the GO and r-GO substrates besides the π - π stacking interaction. Yu *et. al.*¹⁵⁷ reported that mildly reduced graphene oxide (MR-GO) nano-sheets significantly increased the Raman signal of rhodamine B (RhB) molecules due to the presence of highly electronegative oxygen species. The species can introduce a strong local electric field around the adsorbed molecules, which are possibly responsible for the additional enhancement. To determine the species and concentrations of oxygen functional groups on GO and r-GO, XPS measurements were performed.

5.2.2 XPS spectra of GO and r-GO

Recently, Zhang *et. al.*²⁴⁰ utilized the first principles theoretical method to study the XPS spectrum of GO. The spectral positions of various oxygen-containing compounds were successfully assigned. Based on the previous theoretical and experimental studies,^{157,241} the C1s spectrum was fitted with four components (shown in Figures 5.4a and b), a peak representing an sp^2 carbon centered at approximately 285 eV (labelled as P_a), a P_b peak at approximately 286 eV representing an sp^3 hybridized carbon (labelled as P_b), a P_c peak at approximately 287.2 eV (labelled as P_c), and a P_d peak at approximately 288.8 eV (labelled as P_d). The low intensity of the sp^2 peak (shown in Figure 5.4a) implies that the as-prepared GO was heavily oxidized. The C/O atomic ratio was approximately 1.8:1 for the as-prepared GO. After reduction, the C/O atomic ratio was approximately 15.8:1, which indicates that most of the chemical groups on the GO were removed and the graphene-like framework was nearly recovered. Calculations indicate²⁴⁰ that the main contributors that compose the P_c peak are epoxy, ether, hydroxyl, carbonyl, and carbonyl-edge groups, whereas

the P_d peak originates from epoxy pairs, epoxy-hydroxy pairs, and carboxyl groups. As shown in Figures 5.4a and b, the P_a and the P_d peaks were nearly unchanged after the reduction; however, the P_c peak greatly decreased and the P_b peak greatly increased. Similar to observations reported by Yu *et. al.*,¹⁵⁷ the latter two components had significant changes with opposite trends. Yu *et. al.* also proposed that this phenomenon could be responsible for the change in Raman signals. The functional groups that compose the P_c peak are favourable for the Raman enhancement, which is in contrast to the structures that contribute to the P_b peak. In our study, as the number of groups that contributed to the P_c peak decreased, the r-GO substrate produced higher Raman enhancement and more highly quenched the R6G fluorescence than the GO substrate. It is worth mentioning that the removal of the groups that contribute to the P_c peak will most likely result in the formation of carbon domains consisting with defect (i.e., C-C single bonds and topological defects). This change will contribute to an increase in the P_b peak. The total area of the P_a peak of the r-GO was slightly greater than the P_a peak observed for GO. The conductivity and fluorescence quenching of the r-GO substrate increased and were stronger than those of the GO.

Due to the heavy oxidation of the as-prepared GO substrate, oxygen functional groups are present on the basal planar of GO and some carbon atoms are removed from the basal planar of the GO, which slightly disrupts the π -conjugation. The oxygen-containing groups related to the P_c peak can generate a strong local dipole moment (μ_{loc}), which can induce a significant local electric field (E_{loc}) under laser excitation (E_o). Furthermore, due to the large polarizability (R) induced by the large π -conjugated domains, GO has an additional local electric field. The interaction between the local electric field and the molecules can be explained by the formula: $E_{loc} = E_o + f(\mu_{loc} + \alpha E_o)$, where f is a geometry-related parameter.^{157,242} The enhanced

electric field can spontaneously lead to an orientation change in the R6G molecules on the GO surface, which would result in higher Raman signals for P1 and P2 than that of P3. Simultaneously, the Raman bands of R6G can be enhanced by a highly polarized electric field through coupling with the Raman polarizability tensors. Nevertheless, after the reduction the local dipole moment and the polarizability of the r-GO will decrease due to the increased P_b component and broken π -conjugation, respectively. The global polarized electric field of r-GO can still affect the orientation of the R6G on r-GO and cause the Raman signal of P1 to be higher than that of P2 and P3. Therefore, the overall Raman enhancement of GO and r-GO result from the dominant π - π stacking interaction and the weak local electric field from the substrate.^{157,243}

Figure 5.4 Typical XPS spectra of (a) GO and (b) r-GO.

5.2.3 Raman spectra of GO and r-GO

Due to the heavy oxidation of the as-prepared GO substrate, oxygen functional groups are present on the basal planar of the GO and some of the carbon atoms in the basal planar of GO are removed, which slightly disrupts the π -conjugation. According to the increase in the D/G Raman ratio (1.8 for GO to 2.4 for r-GO), the reduction

process causes serious damage to the π -conjugation of the r-GO network and results in a more highly defective structure (Figure 5.5).

Figure 5.5 Typical Raman spectra of GO (black) and r-GO (red).

5.2.5 The typical R6G Raman spectra on NaOH and HCl treated GO

To further investigate the effect of the local electronegative oxygen species, a contrast experiment was performed, as shown in Figure 5.6. The ζ potentials of GO dispersed in water were determined to be -50.2 mV at pH 10 and -22.7 mV at pH 2.³⁶ The structure of GO changes according to the pH of the solution: more electronegative oxygen species are present in basic solutions, while fewer electronegative oxygen species are present in acidic solutions.^{244,245} The GO films were treated in solutions with various pH values prior to deposition of R6G on the substrate. The GO substrates treated with NaOH and HCl show the highest and lowest enhancements respectively, which supports the hypothesis that the local electronegative oxygen species of GO provided a large contribution to Raman enhancement.

Figure 5.6 (a) Typical Raman spectra and (b) corresponding intensity ratios of the R6G on untreated (red), NaOH-treated (black) and HCl-treated (blue) GO.

5.2.6 The typical R6G Raman spectra and mapping on different layers GO, r-GO and Graphene

The Raman signals of the R6G molecules on the surface of the three substrates were compared with a varied numbers of layers (≤ 4 layers) (Figure 5.7). The number of layers for each substrate was determined using contrast spectroscopy.^{167,246} The Raman spectra and images of R6G on the three substrates had different thickness dependencies: for GO, monolayer ($I_{P1, P2 \text{ and } P3/1L} < \text{bilayer } (I_{P1, P2 \text{ and } P3/2L}) < \text{trilayer } (I_{P1, P2 \text{ and } P3/3L}) < \text{tetralayer } (I_{P1, P2 \text{ and } P3/4L})$); for r-GO and graphene, monolayer ($I_{P1, P2 \text{ and } P3/1L} > \text{bilayer } (I_{P1, P2 \text{ and } P3/2L}) > \text{trilayer } (I_{P1, P2 \text{ and } P3/3L}) > \text{tetralayer } (I_{P1, P2 \text{ and } P3/4L})$).

Figure 5.7 Typical Raman spectra and images of the R6G on (a and d) 1-4 layered GO, (b and e) r-GO and (c and d) graphene. The inset images are the corresponding optical images of GO, r-GO and graphene sheets. The images are plotted by the three previously selected R6G Raman bands. (The number of layers of the GO, r-GO and graphene are labeled in the images of the P1 Raman bands (top of d-f). The blue dotted lines show the borders between the regions of different numbers of layers)

5.2.7 The G-band Raman intensity of GO sheets and P3 peak of R6G as a function of number of layers

In our previous work,^{236,246} by considering the interference between the incident laser and scattered Raman signal in the graphene/GO layers, the G band intensity dependence on the number of graphene/GO layers was successfully explained using Fresnel's equations. Our results indicated that the intensity of the Raman G band increased almost linearly with the number of layers (≤ 9). Figure 5.8 shows that the G band intensity of GO linearly increased with the number of layers. The R6G peak (P3)

was determined to also linearly increase with the number of layers. Moreover, the slope of the R6G peak (P3) and the G band intensity of GO resulted in an extreme equation. The trend for the enhancement effect of GO with the number of layers could be explained by the interference effect. However, Ling¹⁵³ reported that the interference effect induced by different numbers of graphene layers did not significantly contribute to the Raman intensity observed for the deposited molecules. The electrical conductivity of r-GO is recovered due to the restoration of the π -network, which results in a material similar to graphene. Thus, r-GO shows a similar trend as graphene, and the interference effect induced by the different numbers of layers for r-GO does not result in a major contribution to the observed Raman intensity for the deposited molecules.

There are two possible explanations for the different Raman signals of molecules on GO, r-GO and graphene. First, Raman spectra reveals that the interactions between the molecules and the substrates (i.e., graphene, GO, r-GO) are different,¹⁵⁵ which indicates that the orientation of R6G on the three types of substrate are not the same. Graphene and r-GO may have similar interaction strength with the R6G molecules. However, GO has a strong local dipole and a low degree of π - π stacking, so the interaction between the R6G molecule and GO substrate is less than the interaction between the molecules and the r-GO and graphene substrates. Second, the differences may be caused by the surface potential induced by oxygen-containing functional groups or substrate-induced effects.^{153,247} Due to the doping effect from the SiO₂/Si substrate, the work function of GO, r-GO and graphene sheets will lead to an increase in the thickness, which may affect the efficiency of the chemical enhancement. Further work is required to investigate the origin of this effect.

Figure 5.8 The G-band Raman intensity of GO sheets (blue) and P3 peak (red) of R6G as a function of the number of layers.

5.3 Conclusion

In this chapter, the SERS of R6G molecules on GO, r-GO and graphene were systematically examined. The Raman signals of the molecules on SLG, GO and r-GO substrates were all enhanced but showed completely different results. According to the XPS results, both the oxygenated groups and the local defects on r-GO and GO substrates can significantly affect the Raman signals of molecules. The relative intensities of the Raman signals for the molecules on the three substrates were different, which was due to different adsorption orientations of the adsorption R6G on the three types of substrates. Finally, the enhancement effects on different numbers of layers for graphene, r-GO and GO were studied. The intensities of the Raman signals of the molecules generally decreased as the number of graphene and r-GO layers increased. In contrast, the Raman signals of the molecules generally increased as the number of the GO layers increased. This is the first report of a systematic comparison

regarding the Raman enhancement of molecules on the surface of graphene, r-GO and GO. As SERS substrates, GO and r-GO have many advantages over graphene such as easier preparation, lower cost, and better biocompatibility. Moreover, compared to r-GO and graphene, thicker (≤ 4 layers) GO sheets result in a larger Raman enhancement. This study provide a general understanding of the substrates effect on the orientations of the adsorption molecules, which will be beneficial to study the chemical enhancement mechanism regarding the interaction between the molecule and the substrates.

Chapter 6

Uniform Decoration of Reduced Graphene Oxide Sheets with Gold Nanoparticles

6.1 Introduction

Graphene is a single layer of carbon atoms that are densely packed into a hexagonal structure. Graphene exhibits extraordinary electronic, thermal, and mechanical properties, which have led scientists to believe that it is a promising candidate for a variety of applications.¹⁹⁶ Graphene oxide (GO) originated from the oxidative exfoliation of graphite, GO is a graphene derivatives that is solution-dispersible due to the oxygen-containing functional groups on the basal planar and edges. From a chemical point of view, the presence of oxygen functionalities on the surface of GO is interesting because they can serve as active sites for chemical modification. Therefore, GO is considered to be a promising nano-scale building block with an ultrahigh surface area that can generate new nano-composites.

Recently, accompanying the emergence of various graphene oxide/reduced graphene oxide (GO/r-GO)-based composites or hybrid materials, different methods have been developed to integrate GO/r-GO with other materials such as polymers, quantum dots, metal/metal oxide nano-particles (NPs), and so on.^{54,65,70,79,203,215,248-251} For example, Fu et al. reported an in situ synthesis method was used to synthesize graphene-metal nano-particle-based derivatives, which resulted in surface-enhanced Raman scattering properties (SERS).²⁵¹ Zhu et al. constructed a hybrid three-dimensional (3D) nano-composite film by alternatively assembling a graphene nano-sheet composite with an ionic liquid (IL) and Pt nano-particles (PtNPs).²⁵²

However, room-temperature ionic liquids (RTILs), an efficient system with all the advantages of homogeneous and heterogeneous catalysis, are rarely used for preparing GO/r-GO-NP composites.²⁵² In this chapter, a simple method to fabricate r-GO-Au nano-composites using ionic liquid as a linker is presented.²⁵³ After GO was functionalized with the ionic liquid (i.e., 1-(3-Aminopropyl) imidazole), a uniform distribution of gold NPs were readily adsorbed on the surface of the r-GO sheets by reducing both the GO and the AuCl_4^- anions that were pre-attached to the GO via anion exchange. Similar to other work,^{202,254-258} the use of ionic liquids enabled the selective functionalization of the carboxyl groups on GO with the ionic liquids. Simultaneously, the Au nano-particles will uniformly covalently bond with GO. Finally, the water-soluble r-GO-Au nano-composites can be obtained, which can be used as SERS substrates. This facile approach to synthesize nano-composites will contribute to the synthesis of GO/r-GO-based nano-composites.

6.2 Results and Discussions

6.2.1 Synthesis and morphology of the r-GO-Au nanocomposites

Based on our experimental procedure, a mechanism to interpret the formation of the as-obtained r-GO-Au nano-composites is proposed, as shown in Scheme 6.1. As reported previously,¹⁶⁴ GO sheets have carbonyl groups on the basal planars and edges. These functional groups act as anchor sites that covalently bind with the ionic liquids (ILGO), which enable the subsequent anion exchange to occur. The AuCl_4^- ions attach on the surfaces and edges of the GO sheets (GO-AuCl_4^-).²⁵⁹ The r-GO-Au nano-composites are synthesized, through a one-step reduction.

Scheme 6.1 The formation mechanism for r-GO-Au nanocomposites.

Figure 6.1 (a) TEM image of bare GO. (b) TEM and HRTEM (inset) images of r-GO-Au.

The morphology of the as-prepared r-GO-Au nano-composites were studied by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). Figure 6.1a reveals that the GO sheets were a few layers thick (i.e., a few micrometers). Figure 6.1b is a representative TEM image of the as-synthesized r-GO-Au nano-composites. Uniformly dispersed Au NPs on the r-GO surface can be clearly observed. The integrity of the carbon skeleton was maintained

after the chemical process. The inset image shows the HRTEM of the Au nanoparticles. The lattice spacing is determined to be 0.24 nm, which is close to the lattice spacing for (111) bulk metal face-centred cubic (fcc) Au crystals (0.236 nm).²⁶⁰

6.2.2 FTIR of the r-GO-Au nanocomposites

Figure 6.2 FTIR of GO (black) and ILGO (red)

Fourier transform infrared spectroscopy (FTIR) was performed to characterize the GO and IL functional GO nano-sheets (Figure 6.2). Similar to previous results,^{53,253,261} the stretch at 1288 cm⁻¹ is attributed to a C-N stretching mode in the amido bond. Simultaneously, the band at 1633cm⁻¹ observed in the spectrum for ILGO is assigned to the amide carbonyl stretching mode. Moreover, the doublet²⁵³ at 2849 cm⁻¹ and 2944 cm⁻¹ corresponds to a symmetric ν_{as} (CH₂) and asymmetric ν_{as} (CH₂) of the IL units, respectively. The doublet and the C-H bending modes observed in the ILGO spectrum demonstrate that the IL units were grafted on the basal planar of the GO sheets. All of these observations indicate that the IL is chemically attached to the GO sheets.

6.2.3 XPS of the GO and r-GO-Au nanocomposites

The C1s XPS spectra of the GO and r-GO-Au are shown in Figures 6.3a and b. Both spectra show a peak broader than that of graphite,²⁶² indicating that there are some higher binding energy signals corresponding to C-O species.^{25,26} Therefore, three prominent peaks were used to fit the C1s spectra: sp^2 -C (~ 285 eV), C-O (hydroxyl and epoxy, ~ 287 eV), and C=O (carboxyl, ~ 289 eV).^{160,164,165} The C1s spectrum of the GO indicates that the carbon species are highly oxidized. However, the smaller contribution from the C=O and C-OH peaks (~ 285 - 288 eV) in the r-GO-Au nano-composite spectrum suggests the successful removal of exogenous functional groups by the chemical reduction process. XPS measurements were performed to further investigate the formation of Au NPs on the IL-modified GO sheets. Figure 6.3c shows the XPS peaks for the Au^{3+} species manifested in the form of a doublet at 87.3 ($4f_{7/2}$) and 90.3 eV ($4f_{5/2}$),²⁶³ indicating that Au^{3+} species exist in the GO composites. Figure 6.3d shows the doublet peak, $Au4f_{7/2}$ and $Au4f_{5/2}$, with binding energies of 84.3 and 88.0 eV, respectively. These binding energies are typical for Au^{0264} , which suggest the formation of gold NPs on the r-GO sheets. After reduction, the disappearance of the two peaks at 87.3 and 90.3 eV (Figure 6.3d) indicates that no Au^{3+} species is present in the r-GO composites. From the above analysis of the XPS data, Au NPs were determined to be in-situ loaded onto the functionalized r-GO.

Figure 6.4 shows the N1s XPS spectra for the r-GO-Au nano-composites. This r-GO-Au nano-composite spectrum clearly shows two prominent peaks, which are typical of amide bonding and pyrrole-type nitrogen-containing functional groups,^{265,266} thus enabling the ionic liquid molecules to be successfully grafted on the GO sheets.

Figure 6.3 C1s XPS spectra of GO (a) and r-GO-Au (b). The black solid lines are original spectra; the dash line, dot line and dash and dot line are assigned to sp^2 -C, C-O (hydroxyl and epoxy groups), and C=O (carboxyl groups), respectively. XPS spectra for the GO-AuCl₄⁻ and r-GO-Au nano-composites: (c) GO-AuCl₄⁻, (d) r-GO-Au

Figure 6.4 N1s XPS spectra for the r-GO-Au nano-composites

6.2.4 EDXA of the r-GO-Au nanocomposites

Figure 6.5 (a) SEM image and (b) results of the EDX element analysis of the r-GO-Au. (c) EDXA-C and (d) EDXA-Au mapping images of the sample r-GO-Au. The bright spots show the distribution of C and Au elements on the r-GO-Au surface.

The energy dispersive X-ray analysis (EDXA) data of the r-GO-Au clearly show that the r-GO sheets are decorated with Au nano-particles. Figures 6.5a and b show the SEM image and quantitative analysis of the r-GO-Au, performed with the Au (M) lines in the EDX spectrum. The Au content is estimated to be 10-20% in all areas. Figures 6.5c and d show the EDXA planar distributions of the typical elements on the surface of the r-GO-Au, which further confirm the presence of the elements C and Au.

6.2.5 Raman spectra of the GO and r-GO-Au nanocomposites

Figure 6.6 Raman spectra of the (a) GO, (b) ILGO, (c) GO-AuCl₄⁻ and (d) r-GO-Au.

Figure 6.6 reveals two prominent peaks, a D band (1346 cm⁻¹) and G band (1597 cm⁻¹), in the Raman spectra of the GO, ILGO, GO-AuCl₄⁻ and r-GO-Au. The G and D peaks are clearly broader than that of graphite.²⁶⁷ As is known, a higher disorder in graphite leads to both broader G and D band, and a higher relative intensity of the D band compared to the G band.²⁶⁷ The D band originates from a double resonance (DR) Raman process involving iTO phonon and defects, while the G band originates from the in-plane vibration of sp² carbon atoms, which is a doubly degenerate (iTO and LO) phonon mode (E_{2g} symmetry) at the Brillouin zone center (Γ point). As shown in Figure 6.6, anion exchange and reduction occur after functionalization of the GO with an ionic liquid, as demonstrated by the increase in the intensity ratio of the D to G band (I_D/I_G) of the GO (Table 6.1). The G band position of the r-GO-Au is red shifted compared to that of the GO, indicating compressive strain relaxation in the pristine GO sheet. Moreover, the prominence of the G band of the r-GO presents is due to the restoration of the sp² carbon regions after the chemical reduction treatment.²⁶⁸ The

I_D/I_G ratio increase is believed to be caused by the decrease in the mean crystallite size of the GO. After removal of the exogenous functional groups in the GO sheets by chemical reduction, the re-established GO network is decreased in size, which leads to an increase in the I_D/I_G ratio.¹⁶⁴⁻¹⁶⁶

Table 6.1 The position of the G band and values of I_D/I_G obtained from the Raman spectra.

samples	G band position(cm^{-1})	I_D/I_G
GO	1597.2	1.6
ILGO	1592.5	1.9
GO-AuCl ₄ ⁻	1590.4	2.0
r-GO-Au	1587.6	2.2

6.2.6 The r-GO-Au nanocomposites as SERS substrate

The r-GO-supported Au NPs can be used as a substrate for SERS. R6G molecules, which are commonly probe molecules in SERS experiments, are used to test the efficiency of this kind of substrate. The r-GO with Au NPs was first soaked in a 10^{-6} M R6G solution for about 1h, washed with distilled water to remove those unabsorbed molecules, and dried in air. For the R6G on SiO₂/Si substrate, we dropped 10^{-6} M R6G on SiO₂/Si substrate and let it dry overnight. Figure 6.7 shows the Raman spectra of the R6G on SiO₂/Si and r-GO-supported Au NPs substrate. No Raman signal of the R6G molecules is detected on the SiO₂/Si, due to the low concentration of R6G (10^{-6} M). However, for the same concentration of R6G, the Raman signals on

r-GO-supported Au NPs substrate are much stronger. In our previous work,²⁴⁹ we reported that Au/SLG is a much better substrate than Au film alone: the former gives SERS enhancement of the molecules and can efficiently quench the PL background from both the Au and the molecules. Yu *et. al.* also reported that GO could notably enhance the graphene-metal/molecule binding, which will be studied the impacts of local chemical groups and global Π -conjugation network on the SERS of molecules.¹⁵⁷ So we can say that our r-GO-supported Au NPs is a promising SERS substrate. The assignment of Raman bands of R6G can be found in Ref.¹³⁹ Several spectra which are taken from different positions on r-GO-supported Au NPs substrate present similar behaviour.

Figure 6.7 Raman spectra of the R6G on (a) r-GO-Au and (b) SiO₂/Si substrate. The peaks marked by the stars (*) and the circle dots (•) are the peaks of R6G and Si respectively.

From the Figure 6.7 it also can be seen that the fluorescence backgrounds of R6G on SiO₂/Si and r-GO-supported Au NPs substrate are significantly different. The relative

weak fluorescence background of R6G on r-GO-supported Au NPs substrate is due to the resonance energy transfer from R6G to GO¹⁵³. The relative strong Raman signal and weak molecule fluorescence background make r-GO-supported Au NPs a promising SERS substrate.

6.3 Conclusions

In this chapter, by using the pre-functionalizing the GO with imidazolium cation-based ionic liquids, the r-GO sheets with uniformly distributed Au NPs less than 10 nm in size were successfully synthesized. The addition of Au NPs on the r-GO sheet was characterized by TEM, XPS, Raman spectroscopy and EDXA. The reduction product, the r-GO-supported Au NPs substrate, showed a good SERS effect, as confirmed using R6G as a probe molecule. This method provides a simple way for preparing r-GO-noble metal or r-GO-metal oxide nano-composite materials, such as r-GO-Pt, r-GO-Ag, r-GO-ZnO₂, and GO-MnO₂, these materials can be used for biosensor, catalysis, and SERS applications.

Chapter 7

Influence of graphene oxide support on the electrochemical performance of graphene oxide-MnO₂ nanocomposites

7.1 Introduction

As a green supercapacitor electrode material, MnO₂ shows potential to replace RuO₂ as a result of its high specific capacitance, environmental compatibility, low cost, and abundance in nature. In general, the fabrication of MnO₂ can be readily realized on a large scale using traditional chemical coprecipitation methods.^{269,270} However, MnO₂ powders produced by these methods suffer some disadvantages, such as a lower specific surface area and a lower specific capacitance in most cases. To improve its electrochemical performance, the direct deposition of MnO₂ onto large surface area materials, such as carbon blacks, carbon nano-tubes, and activated or mesoporous carbons,^{178,188,189,191,192,271,272} has shown promise. Recently, graphene oxide (GO), a shining-star material, has been widely investigated as a suitable support for MnO₂ loading.^{79,203} Due to the large accessible surface area provided by the GO, more ions can be transported onto the material surface, which allows the material to achieve a high electric-double-layer capacitance in aqueous electrolytes. Furthermore, nano-structured MnO₂ modified on a GO support can effectively prevent the aggregation of GO nano-sheets caused by van der Waals interactions, which greatly enhance the available electrochemical active surface area for energy storage.

Structurally, a single-layer of graphite oxide also denoted as GO consists of a honeycomb lattice of carbon atoms with oxygen-containing functional groups: carboxyl, hydroxyl, and epoxy groups have been proposed.^{6,273} These functional

groups can enlarge the gap between adjacent GO sheets. For instance, the (002) diffraction peak of pristine graphite is located at $\sim 26^\circ$, and the inter-planar distance is 0.34 nm. After oxidation of the graphite, the diffraction peak is shifted to a lower angle, which is indicative of a larger inter-planar gap. The functional groups and the larger inter-planar gap enable GO sheets to be easily decorated or intercalated by polymers, quantum dots, metal/metal oxide nano-particles (NPs) and other such material that is advantageous for various applications.^{65,79,203,215,248,249,251,274,275} Nevertheless, until now, few reports have focused on the effects from functional groups and the inter-planar gap of the GO on the loading amount of quantum dots or metal/metal oxide nano-particles.

In this chapter, the influence of GO supports on the electrochemical behaviour of MnO₂-GO nano-composites is studied. As demonstrated, GO fabricated from commercial expanded graphite (denoted as GO1) possesses more functional groups and a larger inter-planar gap compared to GO from commercial graphite powder (denoted as GO2). The surface area and functionalities of GO have significant effects on the morphology and electrochemical activity of MnO₂, such that the loading amount of MnO₂ on GO1 is much higher than that on GO2. Elemental analysis performed using inductively coupled plasma optical emission spectroscopy (IC-OES) confirmed that higher amounts of MnO₂ load onto GO1. As an electrode of a supercapacitor, MnO₂-GO1 nano-composites show a larger capacitance (307.7 F g^{-1}) and a better electrochemical activity than MnO₂-GO2, possibly due to the high loading, good uniformity, and homogeneous distribution of MnO₂ on the GO1 support.

7.2 Characterization and Supercapacitor performances of GO-MnO₂ nanocomposites

7.2.1 XRD of GO-MnO₂ nanocomposites

XRD patterns of the CEG and CGP before and after oxidation are shown in Figure 7.1. The single peak at 2θ of 26.3° indicates a typical graphitic structure. Compared to the CGP, the CEG spectrum shows a broad peak shifted 0.4° to a larger angle, suggesting that the CEG is amorphous and has a larger interlayer spacing. After chemical oxidation treatments, the GO2 (oxidized CGP) presents two XRD peaks corresponding to typical graphitic faces, whereas the pattern of GO1 (oxidized CEG) shows only one XRD peak. The XRD results thus reveal that the CEG can more easily be exfoliated than the CGP. The two diffraction peaks of the GO2 spectrum at approximately 26.3° and 42.5° , as shown in Figure 7.1b, correspond to the (002) and (101) planes of the graphitic framework, respectively.^{276,277} The weakness and broadness of the peaks indicate an amorphous carbon framework, which occurs because the interlayer spacing of the few-layered graphene sheet is similar to that of normal graphite. This result suggests that the CGP has been partially converted into GO. In addition, main peaks exist at 12.1° in GO2 and 10.6° in GO1, corresponding to a d-spacing of 0.73 nm and 0.83 nm, respectively. These peaks are similar to the typical diffraction peak of GO and are possible indications of the presence of defects within the few-layered graphene.²⁷⁸ The larger inter-planar gap than of GO1 compared to that of GO2 reveals the higher oxidation degree of GO1.

Figure 7.1 XRD patterns of (a) commercial expand graphite (CEG) and commercial graphite powder (CGP); (b) GO1 and GO2 sheets. Typical diffraction peaks of graphite and GO are labelled by * and Δ , respectively.

7.2.2 SEM, TEM and HRTEM of GO-MnO₂ nanocomposites

Figures 7.2a and b show the morphology differences between the CEG and CGP. The CEG has a larger graphite piece than the CGP, which leads to larger sheets (Figures 7.2c, d). Figures 7.3a and b show that the MnO₂-GO1 and the MnO₂-GO2 retain the skeleton structure of the GO with diameters of approximately ten micrometers, which is even larger than that of pristine GO (Figures 7.2c, d). This result means that, after a hydrothermal reaction, the nano-composites agglomerate. TEM measurements show the surface morphology of the GO sheets to be uniformly decorated with MnO₂ nano-rods and nano-flakes. Interestingly, both MnO₂ nano-rods and nano-flakes can be found on the GO2, while only MnO₂ nano-flakes can be found on the GO1. Park and Keane have found that the strong epitaxial interaction between the catalytic species and the graphitic planars leads to a homogeneous distribution of the loaded Pd.²⁷⁹ The large interplanar spacing and high specific surface area of GO1 is generally accepted to enhance the epitaxial interaction between nano-MnO₂ and the

GO planars. As a result, MnO₂ nano-flakes can be distributed uniformly on GO1 with a smaller size than the MnO₂ nano-rods and nano-flakes on the GO2.²⁸⁰

Figure 7.2 SEM (a, b) and TEM (c, d) images of the obtained samples: (a) CEG, (b) CGP, (c) GO1 and (d) GO2.

The inset HRTEM images in Figure 7.3 show the lattice fringes of the MnO₂-GO1 and MnO₂-GO2 nano-composites. Three distinct sets of lattice spacing of approximately 0.237 nm, 0.29 nm, and 0.48 nm are shown, corresponding to the (211), (001), and (200) planes of the α -MnO₂, respectively. The inset images in Figure 7.3a and the upper inset image in Figure 7.3b present MnO₂ nano-flakes epitaxially grown on the GO1 and GO2. Both occurrences of epitaxially grown MnO₂ nano-rods on the GO2 are shown in the lower inset image in Figure 7.3b. The presence of clear lattice fringes in the HRTEM images confirm the crystalline nature of the α -MnO₂ nano-rods

and nano-flakes. The following Raman and XPS characterization also prove that the polymorph of the MnO₂ is α -MnO₂.

Figure 7.3 Low- and high-magnification TEM images of (a) MnO₂-GO1 and (b) MnO₂-GO2.

7.2.3 The typical Raman spectra and images of GO-MnO₂ nanocomposites

Typical Raman spectra collected from different regions of the samples are shown in Figure 7.4. The spectra contain one diagnostic Raman scattering band of the α -MnO₂ at $\sim 643\text{ cm}^{-1}$, which belongs to the A_g spectroscopic species originating from breathing vibrations of the MnO₆ octahedral.²⁸¹ Two peaks at ~ 305 and 360 cm^{-1} corresponding to the bending modes of O-Mn-O were observed in the spectra of the nano-composites, stemming from the formation of Mn₂O₃ or Mn₃O₄ induced by the laser heating.²⁸² The appearance of a strong A_g -mode is consistent with the HRTEM result that the crystalline α -MnO₂ was readily formed on the GO support. Two other prominent peaks, the D band (1345 cm^{-1}) and the G band (1597 cm^{-1}), belong to the GO.^{208,283-285} From Figure 7.4, the ratio of α -MnO₂ to G is shown to be very different. The MnO₂-GO1 has a larger α -MnO₂ to G ratio than the MnO₂-GO2, which means

that the content of MnO₂ in the MnO₂-GO1 is higher than that in the MnO₂-GO2. The Raman results are consistent with the ICP and XPS results.

Figure 7.4 Raman Spectra of (a) MnO₂-GO1 and (b) MnO₂-GO2 sheets. (* α -MnO₂)

Figure 7.5 presents Raman images of the MnO₂-GO₁ and MnO₂-GO₂ sheets. From the Raman intensities of A_g α -MnO₂ (530 cm⁻¹ ~ 730 cm⁻¹) (Figures 7.5a, d), the D-peak (1200 cm⁻¹ ~ 1440 cm⁻¹) (Figures 7.5b, c), and G-peak (1460 cm⁻¹ ~ 1680 cm⁻¹) (Figures 7.5e, f), the nano-composite component is observed to be approximately the same (the bright regions indicate the same shape). The Raman images of the D and G modes of the GO are the same, while the bright yellow point is due to the thicker part of the GO sheets. Comparing the Raman images of the A_g mode of the α -MnO₂ to the D and G modes of the GO reveals that the relative contrasts are opposite. The framework of the GO may be partially or totally substituted by MnO₂. After the reaction, the nano-composites become agglomerated layer by layer. The TEM images in Figure 7.3 also show the same results. Moreover, the MnO₂ and GO may be at different planars, which will cause the defocus during Raman mapping.

Figure 7.5 Raman images of (a, d) A_g α-MnO₂ intensity, (b, c) D-peak intensity, (e, f) G-peak intensity of (a, b, c) MnO₂-GO2 (d, e, f) MnO₂-GO1.

7.2.4 The element analysis, XPS and BET of GO-MnO₂ nanocomposites

The element analysis was further conducted using inductively coupled plasma (ICP) to demonstrate that different amounts of Mn are present in the nano-composite materials. The ICP-OES analysis of the Mn concentrations in the nano-composites confirmed that the MnO₂-GO1 (230.3 mg/gr) has a higher Mn content than the MnO₂-GO2 (153.6 mg/gr), which would affect their morphology and electrochemical performance.

The nano-composites obtained using different GO sources were further studied by Nitrogen adsorption-desorption measurements. Figure 7.6 show that all the samples display a type-IV isotherm, indicating a mesoporous structure. Although the MnO₂-GO1 and MnO₂-GO2 share the same adsorption-desorption isotherm type, their surface areas and pore size distributions are quite different. As for the MnO₂-GO1, the specific surface area and the total pore volume was measured to be ~238.1 m²/g and ~0.711 cm³/g, respectively, which are larger values than those measured for the MnO₂-GO2. Remarkably, these values are much higher than those for MnO₂

produced in the previous report using a traditional co-precipitation method of KMnO₄ and Mn²⁺.²⁸⁶ The pore size distribution plots of the MnO₂-GO1 and MnO₂-GO2 were calculated by the Barrett–Joyner–Halenda (BJH) method, using the desorption branch of the N₂ isotherms. Though the MnO₂-GO1 and MnO₂-GO2 have comparable pore volumes, the MnO₂-GO2 shows a narrower pore size distribution than MnO₂-GO1 with a pore diameter range of 20–50 nm. These results clearly demonstrate that the graphite source has a significant effect on the microstructure of the GO. The specific surface area and effective pores (8–50 Å) were reported to be effective in increasing the double-layer capacitance of carbon and multiplying the redox active sites for metal oxide loading; therefore, the pseudo-capacitance will significantly increase. As a result, the unique structure could be useful for enhancing the capacity of the MnO₂-GO1.^{209,287,288}

Figure 7.6 Nitrogen adsorption–desorption isotherms of the (a) MnO₂-GO1 and (b) MnO₂-GO2 obtained using different GO sources. The inset shows BJH pore-size distributions.

The narrow scans XPS further confirm the different oxygen content in the GO1 and GO2 and manganese and carbon contents in the MnO₂-GO1 and MnO₂-GO2. As shown in Figures 7.7a and b, the model curves yield three components: sp²-C (~284.5

eV), C–O (hydroxyl and epoxy, ~286.5 eV), and C=O (carboxyl, ~288 eV).¹⁶⁴⁻¹⁶⁶ The contribution of the C=C band decreases from 50% for the GO2 to 40% for the GO1. An obvious broadening of C=C band is also observed, indicating a more disordered structure for the GO1, which is in good agreement with the XRD results.

The spectra in Figures 7.7c and d illustrate the existence of MnO₂ by the peaks assigned to Mn 2p_{3/2} (642.7 eV) and Mn 2p_{1/2} (653.9 eV), respectively. The peaks have a spin-energy separation of 11.2 eV, which further supports the presence of α -MnO₂ in the nano-composites.^{190,289}

The spectra in Figures 7.7e and f show that in addition to the oxygen signals (O 1s, 532.4 eV) from the graphene sheets, the O 1s peak observed at 530.0 eV is assigned to oxygen bonded to manganese.²⁹⁰ From the quantitative analysis of the XPS data, the corresponding atomic ratios of Mn to C for the MnO₂-GO1 and MnO₂-GO2 in the nano-composite were estimated to be 1:1.61 and 1:1.81, respectively, by integrating the area of each element peak areas, with their relative sensitive factor taken into account. It is worth noting that most carbon atoms in the graphene sheets have not been substituted by Mn. However, the MnO₂-GO1 still has more Mn replacements in the nano-composite than the MnO₂-GO2. These data further confirm the existence of α -MnO₂ and that the loading of MnO₂ is higher in the MnO₂-GO1 than that in the MnO₂-GO2.

Figure 7.7 C 1s spectra of (a) GO1 (b) GO2; Mn 2p spectra of (c) MnO₂-GO1 (d) MnO₂-GO2; O 1s spectra of (e) MnO₂-GO1 and (f) MnO₂-GO2.

7.3.5 Electrochemical performances of GO-MnO₂ nanocomposites

The electrochemical performances of GO obtained from different graphite sources before and after loading of MnO₂ were investigated by cyclic voltammograms (CVs) and galvanostatic charge/discharge measurements in a 1 M Na₂SO₄ solution between -0.3 and 0.8 V (Figure 7.8). The plots in Figure 7.8a show an almost rectangular profile induced by an ideal capacitive behaviour. GO is known to show a lack of

symmetry.²⁸⁹ The poor electrochemical performance of the GO is due to its poor electrical conductivity and low faradic reaction rate. However, the capacitance of the GO2 (21.39 F g⁻¹) is higher than that of the GO1 (0.64 F g⁻¹). Figure 4.8b shows the galvanostatic charge/discharge curves of the GO1, GO2, MnO₂-GO1 and MnO₂-GO2 at a current density 100 mA g⁻¹. After MnO₂ loading, the capacity of the MnO₂-GO1 is twice that of the MnO₂-GO2, which is the result of the higher loading amount of MnO₂ for the GO1 than that for the GO2.

Figure 7.8 (a) CVs of GO1, GO2, MnO₂-GO1 and MnO₂-GO2 at 5 mVs⁻¹ in 3 M KOH electrolyte; (b) Galvanostatic charge/discharge curves of GO1, GO2, MnO₂-GO1 and MnO₂-GO2 at 100 mA g⁻¹ in 3 M KOH electrolyte.

Figures 7.9a and b show the CV curves of the MnO₂-GO1 and MnO₂-GO2 nanocomposites. The MnO₂-GO1 CV curve shows a lack of symmetry at high scan rates (Figure 7.9b), which is likely due to pseudocapacitance from MnO₂.^{79,289} Specific capacitances of the nano-composites calculated at current densities of 100, 250, and 500 mA g⁻¹ from the discharge curves were determined to be 176.0, 165.8, and 140.3 F g⁻¹, respectively, for the MnO₂-GO2 electrode and 307.7, 297.3, and 184.6 F g⁻¹, respectively, for the MnO₂-GO electrode. (Figures 7.9c, d) The specific capacitance of the MnO₂-GO1 electrode was almost twice that of the MnO₂-GO2 electrode. The

enhanced electrochemical performance of MnO₂-GO electrode is due to the high MnO₂ loading by using the GO1 with abundant surface functionalities. High loading and homogeneous distribution of MnO₂ on GO surface are advantageous for GO network to transport ions in the pore system and increase the MnO₂-electrolyte interfacial area. Therefore, the excellent capability of GO1 makes it attractive particularly for energy storage applications. Different GO precursors obviously have significant effect on the electrochemical capacitive performance before or after loading other nano-materials. Thus, it is important to obtain highly porous and surface-functionalized graphene for supercapacitor applications.

Figure 7.9 CV curves of (a) MnO₂-GO1 and (b) MnO₂-GO2 at different scan rates in 3 M KOH electrolyte; Galvanostatic charge/discharge curves of (c) MnO₂-GO1 and (d) MnO₂-GO2 at different current.

The cycling stability of supercapacitor is a crucial parameter for their practical applications. The cyclic performances of GO1, GO2, MnO₂-GO1, and MnO₂-GO2 are investigated as shown in Figure 6.10 GO1 and GO2 have 100% specific capacitance retention after 200 charge and discharge cycles. However, MnO₂-GO1 and MnO₂-GO2 show specific capacitance lost of 40% and 21% after 200 charge and discharge cycles, respectively. Both graphene composites show cycling performance degradation, which is different from pristine CGP and CEG after oxidation. Therefore, the introduction of MnO₂ might be the main cause of cycling instability of the composite. Recent studies also show the decrease in specific capacitance is due to the corrosion behaviour and degradation of the MnO₂ microstructure.^{286,289} In our experiment, the active material detachment from the current collector due to the dissolution during the charging/discharging cycles is also found.

Figure 7.10 Cycle life of GO1, GO2, MnO₂-GO1 and Mn-GO2 in 3 M KOH electrolyte.

7.3 Conclusions

The results from the investigation of the chemical structure, morphology, and electrochemical behaviour of the MnO₂-GO1 and MnO₂-GO2 indicate that the initial properties of GO have notable influences on the morphology and electrochemical activity of the GO-MnO₂ nano-composites. The GO synthesized from the CEG has more functional groups and a larger inter-planar distance. Therefore, a high quantity of MnO₂ nano-particles can be distributed homogeneously on the GO1. Because of the high surface area of the MnO₂-GO1 and the high loading efficiency of the MnO₂, the specific capacitance of the MnO₂-GO1 is almost twice that of the MnO₂-GO2. The surface chemistry and structural properties of the GO is of significant importance as a nano-particle carrier for various applications, such as catalysts, energy storage devices.

The influence of the Surface Chemistry of Graphene on the Performance of a Graphene/Polypyrrole Electrochemical Supercapacitor Electrode

There is a strong interest in electrochemical supercapacitors in advanced power research area as a result of their high power density and high cycling stability.¹⁷⁴ Since the last decade, polypyrrole (PPy) has been investigated as a supercapacitor electrode material.^{119,179,291-294} Composite solutions of PPy with carbon materials have effectively improved the mechanical and electrochemical properties of the electrodes.^{179,292,294} In this regard, the conducting polymer on the surface of the carbon carrier provides a high pseudo-capacitance, while each carbon nano-support acts as the micro-electrode. High conductivity carbon also facilitates the electron transfer from redox reactions in the conducting polymer matrix. Coating MWNTs with a 5 nm-thick PPy film has been reported to improve the capacitance of MWNTs from 50 F g⁻¹ to 163 F g⁻¹,²⁹⁴ an improvement of more than 3 times. A fully reversible and fast faradic reaction can be obtained using a thin PPy layer in the polymer/carbon composite electrode (< 10 nm). Hence, most of the PPy could contribute to the pseudo-capacitive charge storage.^{179,194} Graphene-based materials are of great interest due to their extraordinary properties, such as a large thermal conductivity, superior mechanical properties,²⁹⁵ and unusual electrical properties,²⁹⁶ generated from their extensive π -conjugation. Moreover, their chemical stability, large surface area, and broad electrochemical window render them as an attractive electrode material for

supercapacitor applications.^{3,82,83,197,295,297} Although the surface characteristics of graphene are found to be crucial to improving the graphene/PPy electrochemical performances, there has been no systematic investigations into the graphene surface effect on the high-performance graphene electrode.¹⁹⁹ Most of the graphene-based supercapacitor reports have utilized the less surface functional reduced graphene oxide^{83,298,299} or CVD grown graphene.¹²⁵

The surface chemistry of graphitic carbon has long been regarded as crucial for polymer growth, metal/metal oxide nano-particle nucleation and pseudo-capacitance generation.^{83,300,301} Different surface functionality types are reported to have different capacitance contribution mechanisms. For example, both the electron acceptor character of acidic groups³⁰² and nitrogen heteroatoms in the forms of pyrrolic and pyridinic nitrogens in a carbon network are regarded to have a pronounced effect on the pseudo-capacitance generation.³⁰³ However, the oxygen- and nitrogen-containing functionalities have a diverse effect on the carbon electronic properties, which are also important for a carbon-based supercapacitor, especially when carbon nanostructures are acting as pseudo-capacitive charge collectors or micro-electrodes for Faradic charge transfer reactions. Oxygeneous functionalities with abundant carbon have poor conductivity, which hinders the electron transfer efficiency during Faradic reactions. Opposed to oxygen, the electron-donor character of nitrogen increases the carbon Fermi level and confers advanced electronic properties to the carbon matrix.^{180,183,184,303} The functional groups attached to carbon can act as electron donors^{184,185,303} and/or electron acceptor groups,^{182,302} which provide not only a pseudo-capacitance but also active sites for monomer adsorption. Pristine carbon is not favourable for polymer growth due to the absence of surface functionalities for monomer affiliation. On the other hand, the N or O containing carbon materials

facilitate polymer growth on both sides of the graphene; however, the different synergistic effects induced by their varied conductivity have not been systematically investigated until now.

Because of the importance of carbon surface chemistry to conducting polymer growth and its contribution for capacitance improvement, four types of surface functionalized graphene, amine modified graphene ($\text{NH}_2\text{-G}$), nitrogen-doped graphene (NG), graphite oxide (GTO) and reduced graphite oxide (RGO), were used as carbon carriers to prepare a graphene/10 wt% PPy composite by a chemical method. The electrochemical performance of as-prepared graphene/PPy composite electrodes were evaluated by cyclic voltammetry, a galvanostatic technique and impedance spectroscopy with a sample loading of 10 mg cm^{-2} using nickel foam as the current collector. All of the graphene electrodes showed capacitance improvement after loading of PPy. The surface functionalities of graphene were found to have a close relationship to the magnitude of the graphene capacitance increment and cycling performance.

In this chapter, a series of functionalized graphene derived from GTO were prepared and doped with PPy to systematically investigate the collective effect of surface functionalization and conducting polymer hybridization on supercapacitor performance. The surface chemistry of graphene was found to be of significant importance for PPy growth and PPy/graphene electrochemical performance improvement. A high specific capacitance (393.67 F g^{-1}) was achieved using N-doped graphene/polypyrrole (NG-PPy) electrode, which is larger than those of $-\text{NH}_2$ modified graphene/PPy (225.33 F g^{-1}), GTO/PPY (165.25 F g^{-1}), and RGO/PPy electrodes (150.00 F g^{-1}) under the same measurement conditions. Incorporation of N into the graphene network enhanced the electron transfer efficiency and improved the

graphene surface wettability; therefore, the largest synergistic effect was achieved using NG-PPy. The work herein demonstrates that the doping of the graphitic material with N before the growth of the conducting polymer is essential to prepare graphitic-conducting polymer composites with a high cycling stability and a specific capacitance for supercapacitor application.

8.2 Characterization and Supercapacitor performances of Graphene/PPy nanocomposites

8.2.1 Morphology and structure of Graphene/PPy nanocomposites

The chemical structures of NG, RGO, and NH₂-G prepared from GTO by different methods are shown in Scheme 8.1. The thickness of the GTO sheets was approximately 15 nm, as confirmed by AFM, which indicates that the as-prepared GTO is present in tens of layers. The NG was formed by annealing graphite oxide at 550 °C under inert gas protection with NH₃ gas as the nitrogen source.³⁰⁴ The NH₂-G (primary amine modified graphene) was prepared from a one-step solvothermal reduction of graphite oxide, which was functionalized with primary amine groups. Meanwhile, the graphite oxide was reduced by NaBH₄ as reported previously³⁰⁵ (denoted as RGO).

The surface character of the NG, GTO, RGO, and NH₂-G was identified using XPS (Figure 8.1). Figure 8.1a shows the survey scan of four samples normalized by the intensity of the carbon peak (at 284.5 eV). The survey scan of the graphite oxide shows the oxygen peak at ~ 530 eV with the highest intensity, compared to those of NG, RGO, and NH₂-G. The C1s peak of the GTO and RGO can be fitted with three components at binding energies of 284.5, 285.8, and 286.8 eV, corresponding to sp²

hybridized C atoms, C-OH / C-O, and C=O groups, respectively. The RGO spectrum shows a considerable decrease in the concentration, as indicated by the change in absorption of the C-O and C=O spectral bands (Figure 8.1c). The atomic ratio of C to O as calculated from the XPS spectrum is 10.7:1 for NH₂-G, 1.9:1 for GTO, 9.8:1 for RGO and 13.5:1 for NG. The high C to O ratios of NH₂-G, RGO, and NG indicates the de-oxygenation or reduction of the GTO; therefore, structural and electronic perturbations associated with oxidation will be repaired and the conductivity recovered.²⁷³ As for the nitrogen in the NG, the binding energies at approximately 400.2, 398.1 and 399.7 eV represent pyrrolic, pyridinic and quaternary nitrogen, respectively, with molar ratios of 0.32: 0.43: 0.25 (Figure 8.1d). Unlike NG, NH₂-G has two deconvoluted peaks at 398.2 and 399.5 eV, which are assigned as pyridinic N and primary amine (-NH₂), with an atomic ratio of 0.76: 0.24 (Figure 8.1b). In our previous study, -NH₂ modification of graphene was found to be an effective method to improve the graphene capacitance value as a result of the introduction of pseudo-capacitive interactions and an improvement of the wettability.²¹⁰ Although NH₂-G has a higher nitrogen concentration (8.6 %) than that of NG (4.3 %), NG has abundant quaternary and pyridinic nitrogen, which are proven to be capable of assisting in electron transfer and enhancing pseudo-capacitance generation.^{181,187,303,304}

The SEM images of GTO-PPY, NG-PPY and NH₂-G-PPY show porous structures; however, RGO-PPY is slightly aggregated (Figure 8.2). The BET surface area of the graphite oxide, RGO, NG and NH₂-G are 19, 9.39, 80.98, 52.49 m²/g, respectively. After the loading of polymer, their surface area decreased. For example, the surface area of NH₂-G-PPY was reduced to 30.55 m²/g.

Scheme 8.1 Chemical structure of NG, NH₂-G, RGO and their synthetic methods from GTO.

Figure 8.1 XPS survey scan of GTO, RGO, NG and NH₂-G (a); N1s spectrum of NH₂-G (b), NG (d); C1s spectrum of GTO and RGO (c).

Figure 8.2 The SEM image of GTO-PPy (a), NG-PPY (b) and NH₂-G-PPy (c) and RGO-PPy (d)

8.2.2 Electrochemical performances of Graphene/PPy nanocomposite

However, compared to the N doping in the graphene network from mainly pyrrolic and pyridinic nitrogen, ionizable primary amines are hypothesized to be more advantageous for polymer growth. Therefore, NH₂-G and NG should have different effects on polymer growth and the pseudo-capacitance increment magnitude after polymer loading. To determine the optimum loading of PPy in the graphene matrix to achieve the maximum specific capacitance value of the graphene/PPy composite, NH₂-G was utilized as a model carbon carrier. The weight ratio of PPy to NH₂-G varied from 1 to 80% for the preparation of the NH₂-G/PPy composite. The CVs of the NH₂-G supercapacitors with a PPy weight ratio from 1 to 80% performed at a scan rate of 50 mV s⁻¹ are shown in Figures 8.3 and 8.4. A 10% weight ratio loading of PPy was found to give the highest specific capacitance value, more than that of 1%, 50% and 80% PPy loading. Therefore, a PPy weight ratio of ~9%

was selected to prepare graphene/PPy composite electrodes for the following experiments.

Figure 8.3 Cyclic voltammetry curves of primary amine modified graphene ($\text{NH}_2\text{-G}$) with different polypyrrole doping weight ratio from 1 to 80% PPy at a scan rate of 50 mVs^{-1} in a 6 M KOH electrolyte.

Figure 8.4 Specific capacitance of $\text{NH}_2\text{-G-1\%PPy}$ and $\text{NH}_2\text{-G-10\% PPy}$ with respect to the scan rate from 5 to 250 mV s^{-1} .

Figure 8.5 shows the CVs of GTO (a), NG (b), NH₂-G (c), and RGO (d) at a scan rate of 2 mV s⁻¹ before and after loading of ~9% polypyrrole. All four types of graphene show a current density increment after loading of ~9% polypyrrole, reflecting an increase in the charge storage. GTO-PPy was observed to have a comparable capacitance with that of RGO-PPy (Figures 8.5a and d). CV curves of pristine RGO, NG, and NH₂-G show a large integration area and exhibit a rectangular shape, which is a characteristic feature for an ideal capacitor with good charge propagation (Figures 8.5b, c and d). The specific capacitances of GTO, NG, NH₂-G, and RGO calculated from the CV curves at 2 mV s⁻¹ are 23.75, 115.83, 205.33, and 79.83 F g⁻¹, respectively, with sample loading of 20 mg on nickel foam. NG and NH₂-G show larger capacitance values than that of RGO, though NG, NH₂-G and RGO all have low oxygen content after nitrogen incorporation or reduction. This phenomenon is consistent with previous reports on NH₂-G and N doped carbon,^{185,186,303} which is a result of pseudo-capacitive interactions that are absent in RG. The specific capacitances of GTO-PPy, NG-PPy, NH₂-G-PPy, and RGO-PPy were determined to be 165.25, 393.67, 225.33 and 150.00 Fg⁻¹, respectively. Every graphene electrode showed an enhanced performance after loading of 9 wt% polypyrrole, among which graphite oxide and NG showed a capacitance increment magnitude of 12.19 and 3.55 times, respectively.

Figure 8.6 shows the amplitude of the capacitance increment on NH₂-G, RGO, GTO and NG electrodes before and after loading of 10wt% polypyrrole. After the loading of PPy, the average specific capacitance values of NH₂-G, RGO, GTO and NG increased by 1.15, 2.10, 12.19 and 3.55 times compared with those without PPy loading. The NH₂-G-PPy composite capacitance value of 225.33 F g⁻¹ shows a negligible increment compared with that of NH₂-G (205.33 F g⁻¹). However, there is

no significant difference in the surface morphology or BET surface area of the four electrodes (Figure 8.2). This result further indicates that the surface chemistry of graphene plays an important role in modeling PPy growth and further influences the capacitance increment amplitude.

Figure 8.5 Cyclic voltammetry curves of GTO, NG, NH₂-G, and RGO before (grey) and after (black) doped with ~9% PPy with scanning rate of 2 mVs⁻¹ in 6 M KOH electrolyte.

GTO has long been regarded as a poor electrode material due to its large electronic resistance. However GTO-PPy and RGO-PPy have comparable capacitance values with ~9% PPy. Surface functional groups have long been regarded as advantageous for monomers anchored by electrostatic interaction. Therefore, the existence of oxygeneous groups is favourable to achieve a homogeneous coating of polymer onto graphite oxide surface. Because graphite oxide itself might be partially reduced during the in-situ polymerization process, graphite oxide-PPy has a larger capacitance value (165.25 F g⁻¹), than that of RGO-PPy (150.00 F g⁻¹).

Figure 8.6 Specific capacitance of NH₂-G, RGO, GTO and N-G before (shadow) and after loading of 10 wt % PPy (blank and shadow).

Figure 8.7 shows the electrochemical performance of GTO-PPy, NG-PPy, NH₂-G-PPy, and RGO-PPy electrodes. NG-PPy shows the highest CV integration area (Figure 8.7a), followed by that of NH₂-G-PPy, GTO-PPy and RGO-PPy electrodes. The charge-discharge curves of GTO-PPy and RGO-PPy (Figure 8.7b) are compared with NH₂-G-PPy and NG-PPy (Figure 8.7d) under the current density of 0.26 A g⁻¹. The unsymmetrical shape of the curve and degraded coulomb efficiencies of the GTO-PPy electrode indicate a poor conductivity, resulting from the presence of oxygenous groups on graphite oxide that were not reduced. Hydroxyl, carboxyl, and even the carbonyl functional group were reported to be capable of generating a pseudo-capacitance. However, the oxygen-containing functional groups demonstrate only quasi-reversible capacitance values, which gradually decrease after long cycling in an alkaline electrolyte.³⁰¹

Figure 8.7 Comparison of CVs of graphite oxide, NG, NH₂-G, and RGO at a scan rate of 50 mV s⁻¹; and b) charge-discharge curves of GTO-PPy and RGO-PPy at 0.26 A, c) charge-discharge curves of NG-PPy, NH₂-G-PPy at 0.1 A, and d) NG-PPy, NH₂-G-PPy at 0.26 A.

Most of the oxygenous groups of the RGO are removed, and the electronic properties become similar to that of graphite oxide (Figure 8.7d). However, the poor wetting ability of the RGO might hinder pyrrole monomer adsorption, leading to a non-uniform polypyrrole coating, and reducing the surface area of the polypyrrole in contact with the electrolyte and graphene. Therefore, the pseudo-capacitive charge production from the polypyrrole and the transfer efficiency in the carbon network are decreased accordingly. In this aspect, graphite oxide with oxygenous functionalities can generate a homogeneous coating of polypyrrole on the graphene surface, significantly improving the pseudo-capacitive charge production efficiency. Figure 8.7c shows the charge-discharge curves of the NG-PPy and NH₂-G-PPy electrodes at a current density of 0.1 A g⁻¹. The symmetric triangular shape of the galvanostatic

curves indicates reversible Faradic reactions combined with an improved conductivity compared to that shown in Figure 8.7b. The IR drop read from discharge curves at -0.2 V is much lower than that of GTO-PPy or RGO-PPy. The improved electrical properties from the introduction of nitrogen and higher pseudocapacitive charge generation/transfer efficiency are responsible for the excellent electrochemical performance of NG-PPy. The SEM image of NG-PPy shows that the NG retains a porous and layered structure after annealing at 550 °C and coating with PPy (Figure 8.2). Together with the NG porous structure, the uniform PPy coating on the NG 3D surface accounts for the large specific capacitance increments, compared with that of RGO-PPy. The specific capacitance of NG-PPy and NH₂-G-PPy electrodes calculated from galvanostatic curves under the current density of 0.26 A g⁻¹ are 338.8 and 230.1 F g⁻¹, which are in agreement with the values calculated from CV curves.

Figure 8.8 shows the rate performance of the four electrodes with scan rates from 2 to 50 mV s⁻¹. The introduction of polypyrrole is responsible for the generation of pseudo-capacitance from Faradic reaction of oxidation / reduction of polymer during doping and dedoping of ions which gives improved capacitance value. NG-PPy electrode has highest capacitance value of 393.67 F g⁻¹, as compared with those of NH₂-G-PPy (225.33 F g⁻¹), GTO-PPy (165.25 F g⁻¹) and RGO-PPy (150.00 F g⁻¹) under a scan rate of 2 mV s⁻¹.

Figure 8.8 Specific capacitance of NH₂-G, N-G, RGO, GTO before (a) and after loading of ~9% PPy with respect to the scan rate from 2 to 50 mV s⁻¹.

The capacitance value of NG-PPy can retain 267 F g⁻¹ at a scan rate of 50 mV s⁻¹, which further indicates the potential of NG-PPy for fast energy storage device applications.

The cycling instability is regarded as the main hindrance for currently developed pseudo-capacitors. As shown in Figure 8.9, the capacitance of GTO-PPy lost 59% (from 111.3 to 43.9 F g⁻¹) after 540 charging/discharging cycles at a current density 0.26 A g⁻¹. However, the capacitance of NG-PPy decreased only ~9% (from 296.9 to 267.8 F g⁻¹) under the same conditions. Compared with that of NG-PPy electrode the

deterioration of specific capacitance of GTO-PPy electrode due to the large internal resistance presented can be clearly seen. NG-PPy has superior cycling stability over GTO-PPy electrodes. Highest capacitance value and excellent cycling performance endows NG-PPy superior candidate in application of high capacity, cycling stable and fast energy storage devices.

Figure 8.9 Cycling stability of NG-PPy and GTO-PPy, with specific capacitance calculated from successive charge-discharge cycles at current density 0.26 A g^{-1} , with a voltage window of 0.6 V.

EIS data further shows the electrochemical behaviour of different electrodes. The complex-planar impedance plots for $\text{NH}_2\text{-G-PPy}$ and NG-PPy electrodes with frequency from 0.01 to 100 K Hz at applied potential of 10 mV is shown in Figure 8.10. All the impedance curves of four electrodes show semi-circle in high frequency region and straight line in low frequency region. The impedance plot of NG-PPy is nearly perpendicular to real axis, which indicates fast charge-transfer kinetics and the electric responses resembling a circuit with low resistance and large capacitance

connected in parallel. However, unlike NG-PPy, the as-prepared NH₂-G-PPy, GTO-PPy, RGO-PPy show 45 degree phase angle at low frequency, indicating the retarded ion mobility or charge transfer efficiency in the electrode. For the best two electrodes NG-PPy and NH₂-G-PPy, NH₂-G-PPy shows slightly lower internal resistance than that of NG-PPy. As reported previously, the internal resistance has multiple origins, eg., inter-granular electronic resistance between carbon particles, or contact resistance between electrode material and current collector,³⁰⁶ charge transfer resistance at electrode/electrolyte interface.³⁰⁷ Due to the complexity of internal resistance origin, we ascribe superior performance of NG-PPy as supercapacitors to the improved electronic properties from introduction of nitrogen in NG. High conductivity of NG facilitating charge transfer efficiency from ion doping and dedoping of PPy is responsible for the vertical lined response of Nyquist curve at low frequency. Therefore, NG-PPy has superior electrochemical behaviour among the four electrodes.

Figure 8.10 Impedance Nyquist plots of $\text{NH}_2\text{-G-PPy}$, NG-PPy , GTO-PPy , RGO-PPy electrodes between 100 kHz and 10 mHz at 10 mV signal level.

8.8 Conclusions

Our investigation leads to the understanding of the combined effect of polypyrrole growth and capacitance increment magnitude on a carbon/polypyrrole-based supercapacitor. NG-PPy shows the best capacitive performance (393.67 F g^{-1}), compared with RGO-PPy (150 F g^{-1}), $\text{NH}_2\text{-G-PPy}$ (225.33 F g^{-1}), and GTO-PPy (165 F g^{-1}). Incorporation of a conducting polymer and porous carbon species with a

defined surface chemistry to form hybrid nano-materials represents an opportunity for the design of novel materials with significantly improved performance as an electrochemical supercapacitor. For graphene/polypyrrole composite based supercapacitors, the doping of nitrogen in the graphene network is essential to improve the electrical properties of the graphene and to facilitate the uniform growth of polypyrrole on both sides of the graphene. Therefore, the largest synergistic effect can be achieved from pseudo-capacitance generation in uniform polypyrrole coating layers, and improved charge transfer efficiency can be achieved from nitrogen doping. The capacitance improvement from N doping is also applicable to other graphitic material/conducting polymer composite preparations for promising energy storage applications.

Chapter 9

Conclusions and Future work

9.1 Conclusions

Using the contrast spectroscopy to examine the influence of the functional groups of GO on its properties and applications is a very effective method. Its potential as SERS substrates and the electrochemical performance of the GO derivatives were also studied in this thesis.

(1) Using white light contrast spectroscopy, we successfully determined the number of GO layers (≤ 10 layer) and obtained a refractive index of GO sheets (≤ 10 layer) of $n_{GO}=1.2-0.24i$. Using Fresnel's equations, we calculated the contrast and G band intensity, which agreed well with our experimental data. The results provide further evidence that this refractive index may have broad applications in further studies of GO. The contrast mapping was performed to demonstrate that this method is a convenient and powerful approach for the rapid visualization of the different thicknesses of GO sheets. Because of the increasingly promising properties discovered and proposed for single layer or few layer GO sheets, contrast spectroscopy will be useful as an accurate, facile and efficient method to determine the thickness of GO layers (≤ 10 layer), which will be useful in the future fundamental and practical studies.

(2) A series of experiments were performed to systematically examine the SERS of R6G molecules on GO, r-GO and graphene. Because of the local chemical functional groups on GO and r-GO, we found that the Raman spectra of R6G on the three types of substrate were significantly different. Firstly, the relative intensities of the Raman

signals of R6G on the three kinds of substrates are different because of the different adsorption orientation of R6G on the three types of substrates. Secondly, the interaction between the R6G molecule and the three types of substrates are different; the enhancement effect on different layers of graphene, r-GO and GO also showed the opposite trend: for GO, monolayer < bilayer < trilayer < tetralayer; for r-GO and graphene, monolayer > bilayer > trilayer > tetralayer. Because of easier preparation, lower cost, and better biocompatibility GO and r-GO are good SERS substrates. Furthermore, thicker (≤ 4 layers) GO sheets possess higher Raman enhancement, which can be used to study the chemical enhancement mechanism of the interaction between the molecule and the substrate.

Through selective pre-functionalization of GO with imidazolium cation-based ionic liquids, we have successfully decorated the r-GO sheet with uniformly distributed Au NPS with a size less than 10 nm. Using R6G as a probe molecule, we investigated the ability of r-GO-supported Au NPs to be a SERS substrate. This simple method can be used to prepare other r-GO-noble metals or r-GO-metal oxide nano-composites, which can be used for biosensor, catalysis, and SERS applications.

(3) To study the influence of the initial properties of GO on the morphology and electrochemical behaviour of MnO_2 -GO composites, we use two kinds of graphite to synthesize the GO sheets. Interestingly, we found that the GO synthesized from CEG has more functional groups and a larger inter-planar distance than that from CGP, which causes the high quantity and the homogeneous distribution of MnO_2 nanoparticles on GO1. The specific capacitance of MnO_2 -GO1 is almost twice that of MnO_2 -GO2 because of the high surface area of MnO_2 -GO1 and the high loading efficiency of MnO_2 . Therefore, the surface chemistry and structural properties of GO

are important for the nano-particle carrier in various applications, such as catalyst and energy storage devices.

To understand the combined effect of polypyrrole growth and capacitance properties of the graphene/polypyrrole based supercapacitors, four types of graphene/polypyrrole composites were synthesized and used as the supercapacitor electrode. The NG-PPy composites show better capacitive performance (393.67 Fg^{-1}) than RG-PPy (150 Fg^{-1}), $\text{NH}_2\text{-G-PPy}$ (225.33 Fg^{-1}), and GO-PPy (165 Fg^{-1}). Therefore, the introduction of nitrogen doping into the graphene network can significantly improve the graphene electrical properties and facilitate the uniform growth of polypyrrole on both sides of the graphene. The uniform polypyrrole coating layers can generate the pseudo-capacitance, and the nitrogen can improve the charge transfer efficiency. Moreover, the improved effect that results from the N doping-induced capacitance is also applicable to the preparation of other graphitic material and conducting polymer composites for promising energy storage applications. Therefore, the incorporation of conducting polymer and porous carbon species with a defined surface chemistry to form hybrid nano-materials represents an opportunity for the design of novel materials with significantly improved performance as electrochemical supercapacitors.

9.2 Future works

(1) The contrast spectroscopy of GO and r-GO

As mentioned in Chapter 3, the contrast spectroscopy of GO shows deviation in the range of 420-520 nm between the calculation results and the experimental data. Although we proposed several possible reasons for this deviation, the actual reasons need to be further studied and elucidated. Simultaneously, we found that the contrast

of the r-GO was different from that of GO, but similar to graphene. A detailed contrast experiment should be performed to investigate how do the chemical functional groups on GO and r-GO affect the contrast.

(2) The charge transfer between graphene/GO/r-GO and molecules

We have studied the SERS of R6G on graphene/GO/r-GO and r-GO-Au NPs in Chapters 4 and 5. However, the particular causes of the chemical enhancement between the graphene-based materials and the molecules are still unclear. Our study, demonstrates that the local chemical functional groups on the substrates and the π -network of the graphene-based materials can affect the SERS efficiency. Further study will be performed to investigate the mechanism.

(3) Using graphene based materials in supercapacitors or lithium ion batteries

Because graphene-based materials have a high specific surface area and good electrical conductivity, they can be widely used in supercapacitors and lithium ion batteries. As the work in Chapters 6 and 7 show, the surface chemistry of graphene/GO/r-GO will greatly influence the quantity and morphology of the loaded materials and consequently the electrochemical performance. In particular, the N-doped GO/r-GO shows good electrical conductivity and can be decorated with metal/metal oxide/polymer/CNT/CNW. A series of experiments should be performed to find better graphene based materials, which have a high specific surface area and good electrical conductivity and possess better properties for their applications in supercapacitors or lithium ion batteries.

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