이용자는 아래의 조건을 따르는 경우에 한하여 자유롭게

- 이 저작물을 복제, 배포, 전송, 전시, 공연 및 방송할 수 있습니다.

다음과 같은 조건을 따라야 합니다:

저작자표시. 귀하는 원저작자를 표시하여야 합니다.

비영리. 귀하는 이 저작물을 영리 목적으로 이용할 수 없습니다.

변경금지. 귀하는 이 저작물을 개작, 변형 또는 가공할 수 없습니다.

- 귀하는, 이 저작물의 재이용이나 배포의 경우, 이 저작물에 적용된 이용허락조건을 명확하게 나타내어야 합니다.
- 저작권자로부터 별도의 허가를 받으면 이러한 조건들은 적용되지 않습니다.

저작권법에 따른 이용자의 권리의 내용에 의하여 영향을 받지 않습니다.

이것은 이용허락규약(Legal Code)을 이해하기 쉽게 요약한 것입니다.

Disclaimer
Preparation, Structural Characterization, and Application of Reduced Graphene Oxide-Based Hybrid Materials

Jieun Yang

Department of Energy Engineering
Graduate school of UNIST
2015
Preparation, Structural Characterization, and Application of Reduced Graphene Oxide-Based Hybrid Materials

A thesis submitted to the Graduate School of UNIST in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Jieun Yang

12. 19. 2014

Approved by

Advisor

Hyeon Suk Shin
Preparation, Structural Characterization, and Application of Reduced Graphene Oxide-Based Hybrid Materials

Jieun Yang

This certifies that the thesis of Jieun Yang is approved.

12. 19. 2014

Thesis of Advisor: Hyeon Suk Shin
Jin Young Kim
Ji-Hyun Jang
Sang Hoon Joo
Ho-Seok Park
TABLE OF CONTENTS

Table of Contents I

List of Figures V

List of Tables IX

Abstract X

Part 1: Research Background for the Formation of Hybrid Materials Based on Graphene

1.1 Importance of hybrid materials ................................................................. 1

1.2 Development of graphene based hybrid materials ........................................ 2

1.2.1 Methods for functionalization of graphene ............................................. 5

1.2.1.1 Covalent functionalization of graphene ........................................... 6

1.2.1.2 Non-covalent functionalization of graphene ....................................... 7

1.2.1.3 Nanoparticles functionalized graphene ............................................. 10

1.2.1.4 Substitutional doping ......................................................................... 10

1.3 Control of the electrical properties of graphene .............................................. 11

1.3.1 p-type doped graphene ........................................................................... 11

1.3.2 n-type doped graphene ........................................................................... 12

1.4 Application of graphene based hybrid materials .......................................... 15

1.5 Research objectives and approaches ............................................................ 18

1.6 References .................................................................................................... 20

Part 2. Functionalization of Graphene Oxide (GO) and Reduced Graphene Oxide (rGO) and Their Applications

2.1 Introduction ..................................................................................................... 31

2.1.1 References ................................................................................................ 30

2.2 Graphene-C60 hybrid materials by assembly of non-covalent bonding and their electrical property

2.2.1. Abstract .................................................................................................. 31

2.2.2. Introduction ............................................................................................ 31

2.2.3. Experimental section ............................................................................. 32

2.2.3.1. Preparation of graphene oxide (GO) .................................................. 32
2.2.3.2. Synthesis of rGO/C₆₀ wires ................................................................. 33
2.2.3.3. Measurement of UV/Vis spectra and photoluminescence spectra .......... 33
2.2.3.4. Measurement of LUMO and Fermi levels .......................................... 33
2.2.3.5. Fabrication of device ........................................................................ 33

2.2.4 Results and discussions ........................................................................... 34
  2.2.4.1 Liquid-liquid interfacial precipitation for rGO/C₆₀ wires ....................... 34
  2.2.4.2 Energy levels of rGO and C₆₀ wires .................................................... 44
  2.2.4.3 The role of rGO in photovoltaic devices .............................................. 48

2.2.5 Conclusion ............................................................................................... 52

2.2.6 References ............................................................................................... 53

2.3. Field effect transistor of negative and positive charged graphene ............... 56
  2.3.1. Abstract ................................................................................................ 56
  2.3.2. Introduction ......................................................................................... 56
  2.3.3 Experimental section ............................................................................ 58
    2.3.3.1 Preparation of negatively charged and positively charged graphene oxide .... 58
    2.3.3.2 Fabrication of FET device ............................................................... 58
    2.3.3.3 How to prepare devices with GO sheets ......................................... 58
  2.3.4 Results and discussions ........................................................................ 60
    2.3.4.1 Characteristics of negative charged and positive charged graphene ...... 60
    2.3.4.2 Facile methods for fabrication of FET devices through SAMs-treated gold electrode .... 60
    2.3.4.3 Effect of SAMs to the electrical properties of rGO ............................. 68
    2.3.4.4 Electrical property of positive charged graphene ................................ 69
  2.3.5 Conclusion ............................................................................................. 77

2.3.6 References ............................................................................................... 78

Part 3: Hybrid Materials of Graphene and TMD and Their Applications ............ 81
  3.1 Introduction of hybrid materials of rGO/TMD for energy applications .......... 81
    3.1.1 Synthesis of hybrid materials of rGO/TMD ......................................... 82
    3.1.2 Application of rGO/TMD for energy application .................................. 83
3.2. Transition metal dichalcogenide for hydrogen evolution reaction ........................................... 91
   3.2.1 History of hydrogen evolution reaction for TMD ................................................................. 91
   3.2.2 Synthesis of layered TMDs ........................................................................................................ 91
   3.2.3 Factors affecting HER .................................................................................................................. 94
   3.2.4 Comparison of amorphous and crystalline TMD ................................................................. 98
   3.2.5 Hydrogen evolution reaction of 2D TMD .............................................................................. 99
   3.2.6 Conclusion .................................................................................................................................. 105
   3.2.7 References ................................................................................................................................. 106

3.3. Two Dimensional Hybrid Nanosheets of WS₂ and Reduced Graphene Oxide for Hydrogen Evolution Reaction ................................................................. 110
   3.3.1 Abstract ................................................................................................................................... 110
   3.3.2 Introduction .............................................................................................................................. 110
   3.3.3 Experimental section ............................................................................................................... 112
      3.3.3.1. Synthesis of GO and WS₂ .............................................................................................. 112
      3.3.3.2. Synthesis of WS₂/rGO hybrids .................................................................................. 112
      3.3.3.3. Characterization of WS₂/rGO .................................................................................. 112
      3.3.3.4. Electrochemical Measurements .................................................................................. 112
   3.3.4 Results and Discussions .......................................................................................................... 113
      3.3.4.1 Mechanism for synthesis of WS₂/rGO ........................................................................ 113
      3.3.4.2 Application of WS₂/rGO hybrids for hydrogen evolution reaction .......................... 123
   3.3.5 Conclusion ............................................................................................................................... 125
   3.3.6 References ............................................................................................................................... 126

3.4. Synthesis of Cobalt Disulfide on Reduced Graphene Oxide for Hydrogen Evolution Reaction ................................................................................................. 129
   3.4.1 Abstract .................................................................................................................................... 129
   3.4.2 Introduction ............................................................................................................................. 129
   3.4.3 Experimental Section .............................................................................................................. 130
      3.4.3.1 Synthesis of GO ............................................................................................................ 130
      3.4.3.2 CoS₂/rGO hybrid .......................................................................................................... 130

III
List of Figures

Figure 1.1. Images of hybrid materials. (a) Ag@Au, (b) Ag@Pt nanoparticles, (c) Au/Ag alloy, (d) CNT-Nanoparticles nanohybrids, (e) Heterostructure of CdS and CdSe, (f) Au nanoparticles with block-copolymer shell, and (g) C60-CNT nanotubes.................................................................3

Figure 1.2. (a) Energy level diagram of a CdS/PPy nanowire, UV-Vis absorption spectra of CdS/PPy p-n junction wires and Dark/light current density versus applied voltage (J-V) data of hybrid materials. (b) Energy level diagram of CdS/TiO2 heterojunction and (c) The electrical properties of polymer semiconductor and CNT hybrid.................................................................................4

Figure 1.3. (a) Functionalization of GO with P3OT through amidation. (b) The reaction between GO and CH2OH-terminated P3HT chains through an esterification reaction. (c) Schematic illustration and images of aqueous dispersions of graphene sheets and composites via π-π interactions.........................9

Figure 1.4. Electronic dispersion in the honeycomb lattice.................................................................13

Figure 1.5. Control of electrical properties of graphene..............................................................................14

Figure 1.6. (a) Graphene encapsulated Sulfur particles for LIBs, (b) MnCo2O4 and graphene hybrid materials as oxygen reduction electrocatalysts, and (c) photovoltaic devices based on graphene as a novel acceptor material........................................................................................................17

Figure 1.7. Schematic overview of this study.............................................................................................19

Figure 2.2.1. Schematic illustration and SEM images (a-c) showing steps of formation of rGO-wrapped C60 wires.................................................................................................................................35

Figure 2.2.2. SEM images of C60 particles (a), C60 wires after dropping IPA for 2 min (b), and C60 wires left at 4 °C for 1 h (c).........................................................................................................................37

Figure 2.2.3. SEM images of (a) only C60 wires, (b) rGO/C60 wires, and (c) rGO after dissolving C60 wires in m-xylene. (d) TEM images of a rGO/C60 wire. The magnified image in (d) shows rGO layers. The inset in (d) shows Raman spectrum of a rGO/C60 wire in which bands of rGO and C60 were observed.................................................................................................................................38

Figure 2.2.4. TEM images of a C60 wire. (a) The magnified image of the edge area shows crystalline structure from FFT pattern. (b) The magnified image of other edge area shows the amorphous layer.................................................................................................................................39

Figure 2.2.5. SEM images of C60 wires after they were first prepared and then immersed into rGO solution. (a) and (b) most of rGO sheets did not wrap the C60 wires, but were randomly laid on them. (c) In a part of the sample, some small rGO sheets wrapped them.................................................40

Figure 2.2.6. UV/Vis spectra of (a) C60 wires, (b) rGO, and (c) rGO/C60 wires. The spectra were measured after spin-coating the solutions on quartz substrates.................................................................41
Figure 2.2.7. UV-Vis spectra of (a) C$_{60}$ precipitates (by adding the rGO IPA solution), (b) rGO/C$_{60}$ wires left at 4 °C for 1h, (c) C$_{60}$ particles (by adding pure IPA), and (d) C$_{60}$ wires left at 4 °C for 1h.

Figure 2.2.8. CV curve of rGO on glassy carbon electrode.

Figure 2.2.9. Photoelectron spectrum of rGO.

Figure 2.2.10. Photoelectron spectrum of C$_{60}$ wires.

Figure 2.2.11. $I_{ds}$-$V_g$ of (a) rGO in vacuum, (b) C$_{60}$ wires in vacuum, (c) rGO/C$_{60}$ wires in ambient, and (d) rGO/C$_{60}$ wires in vacuum. The bias voltage, $V_{ds}$, was 1 V for (a) and 10 V for (b), 5 V for (c) and (d). Optical images of the corresponding devices are shown in the insets of (a), (b), and (c).

Figure 2.2.12. (a) J-V curves of rGO and rGO/C$_{60}$ wires. (b) IPCE spectrum of rGO/C$_{60}$ wires.

Figure 2.2.13. Photoluminescence spectra of C$_{60}$ wires and rGO/C$_{60}$ wires obtained with excitation at 520 nm.

Figure 2.3.1. Chemical structures of −GO (a) and +GO (b), Zeta potential of −GO (c) and +GO (d), and AFM images of −GO (e) and +GO sheets (f).

Figure 2.3.2. Scheme for the fabrication of +rGO and −rGO FETs. (a) Pre-patterned Au/Cr (30/5 nm) electrode. (b) Fabrication procedure of + rGO FET using MDA SAM. (c) Fabrication procedure of − rGO FET using AUT SAM.

Figure 2.3.3. XPS spectra of −GO (a) and −rGO (b) after reduction: survey and C1s spectra.

Figure 2.3.4. XPS spectra of (a) +GO and (b) +rGO after reduction: survey and C1s spectra.

Figure 2.3.5. Raman spectra of −GO and +rGO (a) and +GO and +rGO (b).

Figure 2.3.6. XPS spectra (S 2p binding energy region) for AUT (a) and MDA (b).

Figure 2.3.7. AFM images of rGO sheets between two electrodes in FET devices.

Figure 2.3.8. SEM images of FET with (a) and without SAM (b). The pre-patterned electrode with MDA was immersed into +GO for 2 h (a). The electrode without MDA was immersed into +GO for 2 h (b).

Figure 2.3.9. $I_{ds}$-$V_g$ curves of −rGO (a) and +rGO (b) in vacuum. The bias voltage, $V_{ds}$, was 0.1 V. The inset shows the SEM images of FET.

Figure 2.3.10. $I_{ds}$-$V_{ds}$ curves of +rGO before (a) and after annealing at 200 °C (b).

Figure 2.3.11. I-V curve of −rGO before (a) and after annealing (b).

Figure 2.3.12. I-V curve of + rGO without SAM in FET device in ambient. The electrode was placed on 80 °C hot plate, and a + GO solution was repeatedly dropped onto it a few times. The inset image shows a SEM image of FET device.

Figure 3.1.1. (a) 2D hybrid- nanosheets can be prepared through vacuum filtration of mixed solution with exfoliated MoS$_2$ and GO sheets. (b) Tri-hybrid materials of Mo$_2$N, Mo$_2$C, and MoS$_2$ catalysts supported on CNT–RGO hybrid.
Figure 3.2.1. (a) Exfoliated WS₂ nanosheets by Li intercalation; (b) 2D WS₂ nanosheet formation through rolling-out shape-transformation processes of 1D W₁₈O₄₉ nanorods; (c) scheme for the formation of WS₂ nanosheets by ball milling; and (d) WS₂ sheets formed through a hydrothermal method.

Figure 3.2.2. (a) Left: ball model of a Mo/WS₂ particle exposing both S-edges and Mo/W-edges, right: differential free energies of H adsorption; (b) upper: synthesis procedure and structural model for mesoporous MoS₂ with a double-gyroid (DG) morphology, lower images: synthesis setup and as-grown films, and TEM images of MoS₂/MoSe₂ film produced by rapid sulfurization, clearly showing exposed edges; (c) upper: schematic solvothermal synthesis with GO sheets to afford the MoS₂/rGO hybrid, and the Tafel plots with several catalysts, lower: illustration of the synthesis procedures of MoS₂/MGF used as an electrocatalyst for the HER.

Figure 3.2.3. Left: HRTEM images of Pt nanoparticles on MoS₂; right: Tafel plots of MoS₂, Pt-C (Pt nanoparticles on glassy C), and Pt-MoS₂. (b) Left: the structure of 2H-MoS₂ and 1T-MoS₂; right: polarization curves of chemically exfoliated and as grown MoS₂ nanosheets, inset: corresponding Tafel plots.

Figure 3.2.4. (a) Typical AFM image of individual chemically exfoliated WS₂ nanosheets, (b) high-resolution STEM images of an as-exfoliated WS₂ monolayer showing regions exhibiting the 1T superlattice, and (c) 2H structures. The inset in (b) shows the strain tensor map generated from the STEM-HAADF image using peak pair analysis. Light (yellow) and dark (black) colors correspond to regions where the strain is in tension and compression, respectively. (d) Polarization curves of bulk and as-exfoliated WS₂ (as-deposited film of 1T phase, sub-monolayer as-exfoliated film, and 2H phase after annealing at 300 °C) along with those corresponding to Pt nanoparticles and bulk WS₂ powder for comparison. (e) TEM images of WS₂/rGO hybrid nanosheets. The inset shows a magnified image of some folded edges of WS₂ sheets. (f) Tafel plots of WS₂ sheets and WS₂/rGO hybrid sheets.

Figure 3.2.5. Potential required to reach 10 mA/cm² for HER catalysts.

Figure 3.3.1. Scheme for synthesis of WS₂/rGO hybrid sheets by the hydrothermal reaction.

Figure 3.3.2. SEM images of as-prepared WS₂ a), freeze-dried WS₂ b), freeze-dried WS₂ after annealing c), as prepared WS₂/rGO d), freeze-dried WS₂/rGO e), and freeze-dried WS₂/rGO after annealing f).

Figure 3.3.3. TEM images of WS₂/rGO hybrid nanosheets. a) As-prepared WS₂/rGO hybrid nanosheets and b) the magnified image of the marked area in a). The inset in b) indicates the diffraction pattern of 2H-WS₂. c) Folded edges of WS₂ sheets on rGO and d) the high-resolution image of c). The inset shows a magnified image of some folded edges of WS₂ sheets.

Figure 3.3.4. TEM image corresponding to EDAX of as-prepared WS₂/rGO hybrid sheets. (a) High-
resolution TEM image of freeze dried WS$_2$/rGO hybrid sheets after annealing. The inset shows the diffraction pattern of 2H-WS$_2$. (b) EDAX spectrum and mapping images of the hybrid sheets after annealing.

Figure 3.3.5. TEM images of only WS$_2$ after annealing and the diffraction pattern with 2H-WS$_2$...

Figure 3.3.6. $N_2$ adsorption-desorption isotherms for freeze dried WS$_2$ after annealing, freeze dried WS$_2$/rGO and freeze dried WS$_2$/rGO after annealing.

Figure 3.3.7. (a) XRD patterns of freeze dried WS$_2$ after annealing, freeze dried WS$_2$/rGO hybrid nanosheets after annealing and freeze dried WS$_2$/rGO hybrid nanosheets. The asterisk (*) indicates WO$_2$. (b) Raman spectrum of the hybrid. XPS analysis of (c) W 4f$_{7/2}$-5f$_{5/2}$ peaks and (d) S 2p$_{3/2}$-1/2 for the WS$_2$ sheets and WS$_2$/rGO hybrid sheets.

Figure 3.3.8. (a) Polarization curves and corresponding (b) Tafel plots recorded on glassy carbon electrodes with a catalyst loading of 400 $\mu$g/cm$^2$. (c) AC impedance spectra of WS$_2$/rGO and WS$_2$.

Figure 3.4.1. SEM images of (a) the CoS$_2$/Co$_3$S$_4$ (the result of reaction without GO), (b) CoS$_2$/rGO (rGO contents of 3 wt%), and CoS$_2$/rGO (7 wt%).

Figure 3.4.2. TEM image of (a) CoS$_2$/rGO hybrid materials, (b) rGO covered with CoS$_2$, and (c) enlarged HRTEM image of the CoS$_2$ nanoparticle. Inset image shows the diffraction pattern of CoS$_2$. (d) EDX elemental mapping of Co and V, EDX spectrum and table showing elemental composition. The atomic ratio of S and Co is 2, confirming the stoichiometry of CoS$_2$.

Figure 3.4.3. XRD patterns of CoS$_2$/Co$_3$S$_4$, CoS$_2$/rGO (3 wt%) and CoS$_2$/rGO (7 wt%).

Figure 3.4.4. The XRD patterns of CoS$_2$/rGO depending on the rGO contents. The asterisk (*) means the diffraction of CoS.

Figure 3.4.5. (a) Polarization curves of CoS$_2$/rGO and CoS$_2$/Co$_3$S$_4$, corresponding (b) Tafel plots recorded on glassy carbon electrodes with a catalyst loading 285 $\mu$g/cm$^2$. 
List of Tables

Table 2.2.1. Element analysis of graphene oxide and reduced graphene oxide…………………48
Table 2.2.2. Solar cell characteristics of rGO and rGO/C_{60} wires…………………………49
Table 2.3.1. Elemental analysis for +GO and –GO sheets……………………………………58
Table 2.3.2. Average values of Dirac point and mobility……………………………………74
Table 2.3.3. Comparison of mobility values for –rGO FETs in other reports………………75
Table 3.1.1. Recent trend of two-dimensional hybrid materials based on graphene…………85
Table 3.2.1. Catalyst structures, onset overpotentials, and Tafel slopes for different MoS_{2}, WS_{2}, and hybrid materials…………………………………………………………………………………102
Abstract

Hybrid nanomaterials have the advantages of their individual components while also exhibiting new properties for practical applications. Many approaches have been studied for the synthesis of hybrid materials composed of metals, metal oxides, metal chalcogenides, polymers, and carbon materials. To apply these to practical applications such as field-effect transistors (FET), photovoltaic devices, and sensors, the synthesis of hybrid materials and fundamental study to understand their unexpected properties are very important. In addition, comprehension of the interaction at the interface between the two materials is needed. This paper discussed our approaches to develop new hybrid materials by means of functionalization.

This thesis can be divided into two major parts for graphene-based hybrid materials: the functionalization of reduced graphene oxide (rGO) and rGO/TMD hybrid materials. The first part describes functionalization related to graphene oxide (GO) and rGO. Although these are the major applications of graphene, it is worth noting that graphene itself has a zero band-gap as well as chemical inertness, which weaken its competitive strength in the field of semiconductors and sensors. Therefore, tuning the electrical properties of graphene is important. Here, to control the electrical properties, the assembly of rGO and fullerene (C_{60}) into hybrid (rGO/C_{60}) wires was performed by π-π interaction between rGO and C_{60}. Structural characterization and possible applications of the interaction between rGO and C_{60} will be discussed. In addition, amine-functionalized rGO, which has an n-doping effect in FET, is introduced. The mechanism of the doping effect and a facile method for the fabrication of rGO FET with self-assembled monolayers (SAMs) will also be discussed.

The second part focuses on the synthesis of transition-metal dichalcogenide (TMD)-functionalized rGO and its electrocatalytic activity in the hydrogen evolution reaction (HER). Relatively, little is known about the synthesis of hybrid materials with TMD and rGO. In addition, the application of bulk TMDs for hydrogen evolution has been ignored for a long time owing to their poor activity. However, these materials, in particular 2D MoS_{2} and WS_{2} nanosheets, are starting to gain attention for use as catalysts in HER, alongside the explosive interest in graphene and other 2D materials. Therefore, synthesis of WS_{2}/rGO hybrid sheets and their electrocatalytic activity levels have been demonstrated. Furthermore, we report the synthesis of a hybrid of CoS_{2}/rGO, which has not been reported, and its electrocatalytic activity in HER.
Part 1: Research Background for the Formation of Hybrid Materials Based on Graphene

The main topic of my Ph.D. research is the synthesis of hybrid materials based on graphene. Before presenting a detailed explanation of the research results, a brief background is presented in this part, which will be helpful to understand my research purpose and strategy. In section 1.1, the current focus on the study of hybrid materials is discussed, and the research trends pertaining to hybrid materials with graphene is introduced in section 1.2, as my research is based on graphene. Section 1.3 presents more detailed functionalization methods to prepare graphene hybrid materials according to their classification, and methods by which their electrical properties depending on functionalization can be tuned are reviewed. Trends of hybrid materials based on graphene toward applications are briefly introduced in section 1.4. Finally, the objective of the research is introduced in section 1.5.

In particular, the background of hybrid of graphene and transition metal dichalcogenide (TMD) will be discussed in part 3 due to the wide range of graphene hybrid materials.
1.1 Importance of hybrid materials

Hybrids materials, i.e., composites consisting of different materials, have emerged in materials science. Strong interactions at the interface between two different materials in a hybrid material can produce unexpected novel properties and can have synergetic effects. Therefore, they can be regarded as new materials due to the emergence of these new properties. Many hybrid materials have been studied such as metal-metal hybrids, metal-organic hybrids, inorganic semiconductors, inorganic-organic hybrids, and carbon materials. (Figure 1.1) The synthesis of hybrid materials has been demonstrated using several methods, including chemical vapor deposition (CVD), template-assisted synthesis, and self-assembly methods.

Among the advantages of hybrid materials, the most important point is the understanding of the energy-level diagram at the hybrid interface. New or improved chemical and physical properties can evolve via control of the energy level. The tuned energy level in hybrid materials facilitates more practical applications. For example, an improved photovoltaic effect can be observed when two different materials accomplish a p-n junction. Figure 1.2a shows that the electrons and holes generated at the interface (PPy/CdS; organic/inorganic) are transported through the CdS and PPy, respectively, thereby efficiently generating photocurrent in the p-n junction of PPy/CdS. The wide light absorption range of the PPy/CdS hybrid materials should be helpful to improve the conversion efficiency of solar energy power. As another application, the heterojunction in hybrid materials can represent effective architecture for improving the photocatalytic activity. First, the built-in potential at the interface of hybrid materials can promote the separation and transportation of photogenerated electron–hole pairs. As a typical example, a CdS/TiO$_2$ heterojunction was used for the investigation of charge separation. The band diagram shows that both the conduction band and the valence band of TiO$_2$ are more negative than those of CdS, in which electron injection from the conduction band of CdS to the conduction band of TiO$_2$ during the trapping of photogenerated holes in the CdS is facilitated. This band offset can effectively drive the charge separations, and prevent charge recombinations, for improved photocatalytic activity. In addition, the electrical property in a hybrid system can be enhanced compared to that of an individual material. For example, polymer semiconductor/CNT provides a high level of mobility. Understanding the electron transport at the interface facilitates various applications. Therefore, we will demonstrate graphene-based hybrid materials with regard to the control of the energy level at the interface in section 1.2.
Figure 1.1. Images of hybrid materials. (a) Ag@Au, (b) Ag@Pt nanoparticles, (c) Au/Ag alloy, (d) CNT-Nanoparticles nanohybrids, (e) Heterostructure of CdS and CdSe, (f) Au nanoparticles with block-copolymer shell, and (g) C_{60}-CNT nanotubes.
Figure 1.2. (a) Energy level diagram of a CDs/PPy nanowire, UV-Vis absorption spectra of CdS/PPy p-n junction wires and Dark/light current density versus applied voltage (J-V) data of hybrid materials.\textsuperscript{10} (b) Energy level diagram of CdS/TiO\textsubscript{2} heterojunction \textsuperscript{11}, and (c) the electrical properties of polymer semiconductor and CNT hybrid.\textsuperscript{12}
1.2 Development of graphene based hybrid materials

There is no doubt that 2D material is considered more, in terms of applications, than other nanostructured carbon allotropes such as 1D nanotubes and 0D fullerenes. 2D graphene consists of monolayers of carbon atoms arranged in a honeycombed network with six-membered rings. The development of graphene includes unique properties such as the half-integer quantum Hall effect for electrons and holes even at room temperature and high carrier mobility. Graphene shows an ambipolar field effect and has a large specific surface area, high transparency, and high thermal conductivity. Due to these properties, graphene can show other excellent characteristics of electronic, mechanical, optical, and transport properties. Due to these extraordinary features, it is possible to apply graphene to a great number of potential applications, such as touch screens, transparent conductive films, high-frequency circuits, and flexible electronics. Therefore, during the last decade, graphene has emerged as a rapidly rising star given the study of its properties, and its diverse fundamental and technological applications.

Although there are many applications of graphene, graphene has a zero band-gap as well as chemical inertness. The application of graphene is therefore limited in the field of semiconductors and sensors. This is one of the main reasons for the explosive increase in the amount of research aimed at the functionalization of graphene, including studies on reactions of graphene with organic and inorganic molecules. Through this functionalization, the electrical properties of graphene were changed. A change of the electrical properties or the opening of the band gap of graphene by doping, intercalation, and striping would be useful for nanoelectronic devices.

Therefore, this chapter describes the synthesis of graphene functionalization, with classifications, and how this functionalization affects the electrical properties of graphene. In particular, functionalization related to graphene oxide (GO) or reduced graphene oxide will be discussed.

1.2.1 Methods for functionalization of graphene

There are general methods to prepare graphene including mechanical exfoliation, chemical exfoliation of graphite, and chemical vapor deposition (CVD) growth. To prepare functionalized graphene, we focus on graphene oxide (GO) and reduced graphene oxide (rGO) with oxygen functional groups because those types of graphene can be dispersed into common organic solvents. Therefore, functionalization of GO or rGO can be easily achieved. This chapter is divided into four sections. First, graphene can be functionalized covalently through the chemistry of oxygen groups of GO (Ch. 1.2.1). Second, chapter 1.2.2 reports non-covalent functionalization and interactions. In chapter 1.2.3, nanoparticles functionalized graphene is introduced briefly. Finally, the specific methods for substitutional doping are discussed. (Ch. 1.2.4)Methods to control the electrical properties of graphene
and electronic devices of doped graphene will be discussed in chapter 1.3.

1.2.1.1 Covalent functionalization of graphene

The functionalized graphene with organic functional groups has been explored for several reasons. The main reason is the dispersion of graphene in common organic solvents. The dispersibility of graphene in organic solvents is an essential to form hybrid materials with graphene. Furthermore, organic functional groups can give new properties by combining with the properties of graphene. When organic functional groups are covalently bound on the graphene surface, this enables control of its electronic properties. In particular, the control of a band gap through chemical doping is a powerful method for the use of graphene in nanoelectronic devices. (In this thesis, functionalization of organic molecules on graphene is also regarded as doping.) The chemistry of functionalized GO with oxygen-functional groups has been widely explored because covalent bonds between organic functional groups and the oxygen groups of GO can be formed. Therefore, GO has often been regarded as the starting material for the graphene hybrids through the covalent attachment of organic groups on its surface. Although there are a lot of molecules for functional groups, we can divide them largely into two methods for functionalization: (a) amidation, and (b) esterification. Amidation can occur by the reaction between carboxyl groups in GO and the amine group in added molecules. For examples, amine-terminated oligothiophenes can be bound on GO through covalent amide bonds. Well-known conjugated polymeric materials such as polythiophene are used for optoelectronic application due to high charge mobility arising from the large number of π electrons delocalized along their molecular chains. The strong interaction between GO and oligothiophene could be observed by the complete fluorescence quenching in comparison with pure oligothiophene. (Figure 1.2a) In addition, simple organic molecules such as porphyrins, phthalocyanines, and azobenzene have been covalently functionalized on GO. Because of the large visible light extinction coefficients, these molecules are usually used as antennas for harvesting energy from photons.

The functionalization of GO with poly(2-hexylthiophene) (P3HT) happens through the formation of ester bonds with the carboxyl groups of GO nanoplates. P3HT/GO which is soluble in organic solvents, facilitates photovoltaic fabrication by solution processing. The result showed enhanced power conversion efficiency in comparison with a pure P3HT/C$_{60}$ material. This remarkable result is attributed to an extended electron delocalization that occurs after the covalent attachment of P3HT with GO in comparison to pure P3HT. Similarly, GO can be grafted to polymeric chains that have reactive species like hydroxyls and amines, for example, poly(ethylene glycol), polyllysine, polyallyamine, and poly(vinyl alcohol). Polymer grafted on graphene can give dispersibility in solvents, mechanical strengthening, and several control of morphologies while graphene contributes to the electrical
conductivity, and chemical reactivity. Another interesting modification of GO, a hybrid material formed by covalent linking of C\textsubscript{60} with GO, has been reported. The C\textsubscript{60}/GO hybrids could be useful in many optoelectronic applications due to their remarkable electronic and optical properties. The functionalization of GO by imidazolium derivatives has also been reported. Through this, composite materials with new properties can be formed. Basically, dispersion and interfacial interaction are important for chemical functionalization of hybrid materials based on graphene.

Modification of graphene, not GO, will be discussed briefly. Covalently modified graphene can be formed by attachment of atoms or molecular to sp\textsuperscript{2} carbon atoms. Such modification maintains the graphene 2D lattice. However, due to the break of the delocalized electron cloud in graphene, there are dramatic changes to its properties. Sofo \textit{et al.}\textsuperscript{[25]} have theoretically predicted the existence of fully hydrogenated graphene, as well as its fluorinated graphene. Hydrogenated graphene was synthesized by the exposure of graphene to cold hydrogen plasma.\textsuperscript{[25-26]} The binding of hydrogen atoms to sp\textsuperscript{2} carbons have changed their hybridization state to sp\textsuperscript{3}, thus altering the electronic properties and local structure while maintaining the graphene hexagonal symmetry. The graphene conduction band formed by π-conjugated p\text{\textsubscript{z}} orbitals is missing in hydrogenated graphene, and consequently, the graphene zero band gap opens. The electronic properties of graphene can be tuned by the degree of hydrogenation. Well-structured partially hydrogenated graphene represent very interesting materials with magnetic, metallic, and semiconducting properties.\textsuperscript{[27]} As another approach, fluorographene was synthesized by fluorination of graphene using XeF\textsubscript{2} at room temperature.\textsuperscript{[28]} Fluorination of graphene dramatically changes its structures and electronic and optical properties. The zero band gap of pristine graphene opens, and fluorographene behaves like an insulator with a resistivity higher than 10\textsuperscript{12} Ω. Also, a high third-order nonlinear optical response of fluorographene dispersion has been observed.\textsuperscript{[29]}

\textbf{1.2.1.2 Non-covalent functionalization of graphene}

The interaction of graphene with functional groups has been studied due to the π-electron system of graphene. It is possible for there to be π–π interactions between graphene and functional groups. Non-covalent functionalization by π–π interactions is an attractive synthesis method. These interactions are most important for the design of devices, because changes in the structure and properties of graphene through π–π interactions can lead to dramatic effects in the electronic properties. Therefore, extensive investigations with π–π interactions have been explored for in device applications.\textsuperscript{[30]}

As a typical example, pyrene with π electron systems has been reported to have a strong interaction toward the basal plane of graphene via π–π stacking.\textsuperscript{[31]} Xu \textit{et al.} prepared stable aqueous dispersions of graphene using a water-soluble pyrene derivative, 1-pyrenebutyrate (PB\textsuperscript{-}), as a stabilizer.\textsuperscript{[32]} These
graphene films with pyrene molecules showed conductivity 7 orders of magnitude larger than that of the GO precursor. In addition, Su et al. presented a unique approach to functionalize graphene sheets with pyrene and perlenediimide as electronic donor and acceptor molecules, respectively. The resulting aqueous graphene dispersion yields single and double layer graphene sheets. A solar cell based on these functionalized graphene nanoplates showed an increase in conductivity. Wu et al. showed polystyrene (PS)/graphene nanoplates. The graphene is homogeneously dispersed in the PS matrix, thereby creating electrically conductive graphene/PS nanocomposites. The skeletons of PS were stacked onto the basal plane of graphene nanoplates by strong π–π interactions with a graft ratio up to 85 wt. %. Non-covalent functionalization of rGO with chitosan by chemical reduction of GO has been demonstrated by Fang et al. The graphene captures the amino and hydroxyl groups of chitosan via zwitterionic interactions and hydrogen bonding, resulting in dispersibility of the composite in water. The graphene suspension is highly biocompatible, which makes the system highly desirable for potential biological and medicinal applications.

For non-covalent functionalized graphene not GO, Hersam et al. showed a self-assembled perylene 3,4,9,10-tetracarboxylic dianhydride (PTCDA) monolayer on epitaxial graphene using STM. The PTCDA molecular structure has a planar molecule based on a perylene backbone with a conjugated π-electron system and carboxylic acid anhydride side groups. After gas-phase deposition in ultrahigh vacuum (UHV), the well-ordered, stable, robust, defect-free monolayer presents opportunities to explore self-assembly chemistry on graphene. This template has a potential toward realizing graphene-based molecular electronic and sensing devices. The site-dependent and spontaneous functionalization of 4-bromobenzene diazonium tetrafluoroborate (4-BBDT) and its doping effect on mechanically exfoliated graphene has also been investigated.
Figure 1.3. (a) Functionalization of GO with P3OT through amidation.\textsuperscript{15} (b) The reaction between GO and CH\textsubscript{2}OH-terminated P3HT chains through an esterification reaction.\textsuperscript{18} (c) Schematic illustration and images of aqueous dispersions of graphene sheets and composites via $\pi - \pi$ interactions.\textsuperscript{31}
1.2.1.3 Nanoparticles functionalized graphene

Carbon nanomaterials with metallic nanoparticles or oxides have been investigated for long time and applied to optoelectronic, catalytic, fuel cells, and batteries.\(^3^8\) The functionalization of metallic and other nanoparticles on graphene sheets has become interested.\(^3^9\) Graphene sheets can be regarded as an ideal substrate for the dispersion of nanoparticles due to its large active surface area, in comparison with carbon nanotubes, amorphous carbon, or graphite, which have a lower active surface area because only the external surface is active.\(^4^0\) The directly chemical reduction method is the most popular strategy used for synthesis of graphene-metal hybrid nanostructures. The direct reduction of metal precursors (HAuCl\(_4\), AgNO\(_3\), K\(_2\)PtCl\(_4\), H\(_2\)PdCl\(_6\), or CuCl\(_2\)) in the presence of graphene oxide (GO) or reduced graphene oxide (rGO) sheets by using reducing agent like amines, NaBH\(_4\), and ascorbic acid in solution has been applied for synthesis of various nanostructures on graphene.

1.2.1.4 Substitutional doping

In particular, carbon atoms in graphene can be substituted by nitrogen or boron atoms. The doped graphene sheets depending on substituted atoms show n- or p-type behavior. In addition, by controlling the degree of this doping modification, the electrical properties of graphene could be potentially tailored, thereby remarkably expanding the application of graphene in nanoelectronics. The incorporation of nitrogen atoms is done sp\(^3\) orbitals; lone pair of electrons on nitrogen atoms can make change the electrical property. n – type semiconducting behavior is expected through lone-pair electron on nitrogen. In general, N-doped graphene sheets are formed by the substitution of O or C atoms with N during reduction or annealing or in situ during graphene growth using CVD,\(^4^1\) arc discharge,\(^4^2\) or solvothermal methods.\(^4^3\) Oxygen or sp\(^3\) carbon atoms that are situated at the defect sites of GO can be substituted by nitrogen during the reduction step using a nitrogen-rich reductive source like ammonia or hydrazine, at high temperature.
1.3 Control of the electrical properties of graphene

Graphene consists of sp² hybrid carbon atoms with the s, pₓ, and pᵧ atomic orbitals on each carbon atom forming three strong σ bonds with three surrounding atoms. An overlap of the remaining pₓ orbital on each carbon atom with neighboring carbon atoms produces a filled band of p orbitals, called the valence band, and an empty band of π* orbitals known as the conduction band. The valence and conduction bands touch at the Brillouin zone corners, thus making graphene a zero-bandgap semiconductor. Figure 1.4 shows the energy spectrum of graphene and a zoomed-in view of the energy bands at one of the Dirac points (at the K or K’ points in the Brillouin zone or the intersection of the valence band and the conduction band). As mentioned above, the opening of the band-gap and investigations of electrical properties in graphene through functionalization are crucial because graphene with a zero band-gap is limited in terms of substantive applications as a sensor or transistor. Its electrical properties can be tuned by chemical doping through chemical species, as noted in sections 1.3.1 and 1.3.2. In this chapter, we focus on the chemical doping (Figure 1.5), including the covalent and non-covalent bonding, of graphene and the related electrical properties. This will be discussed in terms of p-type doped graphene and n-type doped graphene.

1.3.1 p-type doped graphene

In general, molecules with electron-withdrawing groups adsorbed on the surface of graphene will lead to p-type doping of graphene, and molecules with donating groups will lead to n-type doping. First, doping through non-covalent bonding is reviewed. The resistance of graphene decreases rapidly when the device is exposed to NO₂ gas. NO₂ dopes holes into graphene and the minimum conductivity point shifts toward positive gate voltage without limiting carrier mobility and changing the shape of the transfer characteristic of graphene-based FET. The Fermi level of NO₂, exactly at the partially occupied molecular orbital (POMO), is about 0.4 eV below the Dirac point of graphene independent of adsorption configuration. Therefore, the NO₂ molecule is a strong electron acceptor and accepts one electron from graphene. Therefore, p-type doping occurs. Adsorbed Br₂ and I₂ on a layer of graphene inject a high density of holes in graphene through charge transfer leading to p-type doping. Surface adsorbed molecules with electron-withdrawing groups can induce the p-type doping effect of graphene. Due to the fact that Tetrafluoro-tetra-cyanoquinodimethane (F₄-TCNQ) is a strong electron acceptor, F₄-TCNQ adsorbed graphene shows p-type doped properties. Synchrotron-based high-resolution photoemission spectroscopy (PES) reveals that electrons transfer from graphene to F₄-TCNQ and this only occurs at the F₄-TCNQ/graphene interface. Therefore, an electron accumulation layer in F₄-TCNQ and a depletion layer in graphene form at the interface and a p-type doping of graphene is obtained. Other organic molecules with electron-withdrawing groups can also lead to p-type doping of graphene, such
as tetracyanoethylene (TCNE), and tetrasodium 1,3,6,8-pyrenetetrasulfonic acid (TPA). Besides organic molecules, metal atoms with high electron affinity like bismuth, antimony and gold, adsorbed on the surface of graphene also lead to a similar shift of the Dirac point of graphene.

In another approach, a self-assembled monolayer (SAM) of fluoroalkyl trichlorosilane (FTS) on graphene introduces ultra high level hole doping with hole density \(>10^{13} \text{cm}^2\). As the SAMs are growing, the Dirac point of pristine graphene moves towards more positive gate voltage and the mobility \(\mu\) decreases. Because the SAM of FTS extracts electrons from graphene and the SAM serves as negative charged scatters, the mobility inversely depends on the density of charged impurities. This is why the mobility decreases with SAM growth.

In chapter 1.2.1.4, we introduced substitutional doping. It is worth noting that the electronic properties in graphene are modified by the addition of electron donors or acceptors. Nitrogen has one additional electron and boron lacks one compared to carbon. As expected, when boron atoms are incorporated into the basal plane of graphene, the graphene exhibits p-type behavior. Boron doped graphene has been reported by panchokarla et al. through arc discharge of graphite electrodes in the presence of \(\text{H}_2\), \(\text{He}\) and diborane (\(\text{B}_2\text{H}_6\)). XPS demonstrated that B is bonded to the sp\(^2\) carbon. The boron doped graphene shows higher conductivity and the Fermi level shifts 0.65 eV below the Dirac point by calculations indication the p-type doping of graphene.

### 1.3.2 n-type doped graphene

Electron donating groups usually make graphene n-type doping. Ammonia adsorbed graphene and potassium doped graphene also shows n-doping behavior. Furthermore, electron-donating polymer like poly(ethyleneimine) (PEI) results in n-type doped graphene. The electron-doped graphene can be simply distinguished by Raman spectroscopy based on downshifting of the 2D and G bands. For n-type doped graphene, nitrogen atoms are incorporated into the basal plane of graphene as the most commonly used method. The nitrogen doped graphene sheets have been synthesized by a chemical vapor deposition (CVD) method with ammonia gas. In general, N-doped graphene sheets are formed by the substitution of O or C atoms with N during reduction, annealing or in situ during graphene growth using CVD, or arcdischarge. The N-doped graphene sheets are electron-rich so that n-type semiconducting behavior is expected.
Figure 1.4. Electronic dispersion in the honeycomb lattice.
Control of Electrical Properties for Graphene

Chemical doping

- Electron withdrawing groups: Halogens, nitrile (CN), carbonyl (CO) and nitro groups (NO$_2$)
- Electron donating groups: alkyl groups, alcohol groups and amine groups
- Substitutional or surface charge transfer doping:
  - p-type: adding atoms with fewer valence electrons than carbon like boron
  - n-type: adding atoms with more valence electrons than carbon like nitrogen

**Figure 1.5.** Control of electrical properties of graphene.
1.4 Application of graphene based hybrid materials

Graphene which has excellent conductivity, high specific surface area and flexibility has been employed as a supporting materials for LIBs. Metal oxides or metals such as SnO$_2$, Co$_3$O$_4$, Mn$_3$O$_4$, MoO$_2$, TiO$_2$, Fe$_3$O$_4$, V$_2$O$_5$, Sn, and Ge have been synthesized on graphene sheets for preparation of graphene-based hybrid electrodes. The graphene layer can protect the inorganic nanostructures from aggregation during the charge/discharge process and the conductivity can be enhanced after hybridization with graphene. Mn$_3$O$_4$ is a promising anode material with a high theoretical capacity of ca. 936 mAh$^{-1}$. But, its practical capacity only reaches about 400 mA h$^{-1}$ because of its poor conductivity. However, Mn$_3$O$_4$ NPs on graphene anode achieved the capacity of ca. 900 mA h$^{-1}$. It is suggested that the significantly enhanced performance could be mostly attributed to the excellent conductivity of graphene, facilitating efficient conduction of charges carriers. In addition, graphene encapsulated Sulfur NPs, (Figure 1.6a) Fe$_3$O$_4$ nanosphere, Si nanowires, and LiFePO$_4$ particles have shown improved performances. Fe$_3$O$_4$ nanospheres wrapped by graphene nanosheets and further embedded in a 3D graphene foam (GF) to form a 3D hybrid electrode (Fe$_3$O$_4$@GS/GF). The GS/GF hybrid matrix served as a double protection against the volume changes of the Fe$_3$O$_4$ spheres during charge/discharges processes. In addition, the 3D porous graphene framework improved the conductivity and greatly increased the specific surface area of the electrode. The resultant Fe$_3$O$_4$@GS/GF was capable of delivering a high reversible capacity of 1059 mAh$^{-1}$ at 93 mA h$^{-1}$ over 150 cycles. Hybrid materials of rGO/transition metal dichalcogenide will be represented in chapter 3.1.2.1.

Graphene also possesses good electrocatalytic activities for various redox reactions. To date, metals such as Pt, Pd, Au, FePt, and Pt/CuPd, metal oxides such as Co$_3$O$_4$, Fe$_3$O$_4$, MnCo$_2$O$_4$ (Figure 1.6b) and Co/CoO, and other inorganic materials such as MoS$_2$ have been combined with graphene for preparation of electrocatalysts. For example, the Pt-graphene hybrid catalysts has exhibited higher catalytic activity and better stability compared to commercial Pt-C in catalytic reactions like methanol oxidation and the oxygen reduction reaction (ORR). Pd NPs/rGO showed superior performance toward both formic acid and ethanol oxidation compared to the Pd-C catalyst. It is worth mentioning that the Pd NPs were synthesized by directly mixing K$_2$PdCl$_4$ and GO sheets via electrosless deposition. Therefore, the obtained Pd NP-rGO hybrid was free from surface ligands, leading to the much enhanced catalytic activity. However, novel metals with high cost restricts wide application. Interestingly, N-doped graphene showed a stable methanol crossover effect, high current density and good durability when it catalyzed ORR in alkaline solution. A further enhanced methanol crossover effect and higher current density was achieved by loading 5 wt% Fe NPs on n-doped graphene, and the
resultant hybrid showed faster electron transfer and higher stability in both alkaline and acidic solutions than that of Pt or n-doped graphene alone. rGO/metal oxide hybrids are also promising electrocatalysts. Dai et al. reported that Co$_3$O$_4$ NPs hybridized with N-doped-rGO could be used as a bi-functional catalyst for ORR and OER in alkaline solutions, and the ORR catalytic activity is comparable with the commercial 20 wt% Pt on Vulcan XC-72. The high catalytic activity of this composite might be attributed to the synergistic coupling between Co$_3$O$_4$ NPs and graphene. Moreover, Fe$_3$O$_4$ NPs loaded in a 3D N-doped graphene aelogel were demonstrated by Mullen for ORR, which exhibited a better durability than does the commercial Pt-C catalyst.

Graphene with its unique properties, i.e., high optical transparence, high electrical conduction, and mechanical flexibility, has been investigated in the field of solar cells. A lot of results have been reported, where graphene was used as the electrodes, i.e., transparent anodes, non-transparent anodes, transparent cathodes, and catalytic counter electrodes, as well as cases where graphene was used as the active layer for light harvesting materials. (Figure 1.6c) The most important reason for graphene-based materials being used as electrode materials in organic photovoltaic devices is the high electron mobility of graphene, which increases the charge separation and hole transportation. For example, graphene was incorporated into the TiO$_2$ nanostructure anode in dye-sensitized solar cells (DSSCs). In the hybrid anode, graphene could be considered as a bridge for the photoelectrons, and thus enhances the charge transport rate and prevents charge recombination. Functionlized graphene materials have been investigated as electron-acceptor materials in bulk heterojunction photovoltaic devices with P3OT and P3HT as donor material. The interaction between graphene and P3OT/P3HT makes this composite work well as the active layer in bulk heterojunction-organic photovoltaic devices.
Figure 1.6. (a) Graphene encapsulated Sulfur particles for LIBs, (b) MnCo$_2$O$_4$ and graphene hybrid materials as oxygen reduction electrocatalysts, and (c) photovoltaic devices based on graphene as a novel acceptor material.
1.5 Research objectives and approaches

In order to explore unexpected properties through new assemblies of hybrid materials, our strategies of research objectives can be achieved through rGO. Initially, rGO is used as a functional material. As mentioned above, hybrid materials based on graphene have been demonstrated by the functionalization of organic molecules, inorganic molecules, and metal particles on a graphene or rGO surface. However, we have approached rGO functionalized organic wires through an opposite concept. Because rGO and GO have oxygen-functional groups which can disperse into an organic solvent and given that as-prepared GO is negatively charged, rGO and GO can be easily functionalized on organic or inorganic nanostructures via electrostatic interaction in a solution-process. Second, it is well known that rGO can act as a substrate for the nucleation and growth of TMDs. rGO/TMD hybrid materials with a new structure or new chemical composition can be synthesized by means of rGO. The advantages and importance of rGO in rGO/TMD hybrid materials are discussed in section 3.1 in detail. Furthermore, it is important to characterize how the hybrid materials obtained by these approaches are configured systematically and to determine what interactions can exist between hybrid materials obtained by these approaches.
<table>
<thead>
<tr>
<th>Role of rGO</th>
<th>Method</th>
<th>Materials</th>
<th>Electrical property</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tuning electrical property</td>
<td>Non-covalent</td>
<td>rGO/C$_{60}$</td>
<td>p doping effect</td>
<td>FET, Photovoltaic</td>
</tr>
<tr>
<td></td>
<td>Covalent</td>
<td>NH$_2$-rGO</td>
<td>n doping effect</td>
<td>FET</td>
</tr>
<tr>
<td>Template</td>
<td>Non-covalent</td>
<td>WS$_2$/rGO</td>
<td>-</td>
<td>HER</td>
</tr>
<tr>
<td></td>
<td>Non-covalent</td>
<td>CoS$_2$/rGO</td>
<td>-</td>
<td>HER</td>
</tr>
</tbody>
</table>

**Figure 1.7.** Schematic overview of this study.
1.6 References


33. Su, Q.; Pang, S.; Alijani, V.; Li, C.; Feng, X.; Müllen, K. Composites of graphene with large


55. Lherbier, A.; Blase, X.; Niquet, Y.-M.; Triozon, F.; Roche, S., Charge transport in chemically


64. (a) Zou, Y. Q.; Kan, J.; Wang, Y. Fe$_3$O$_4$-graphene rice-on-sheet nanocomposite for high and fast lithium ion storage. J. Phys. Chem. C 2011, 115, 20747-20753; (b) Zhu, X. J.; Lu, Z. Y.;
Oo, M. O.; Hng, H. H.; Ma, J.; Zhang, H.; Yan, Q. Y. Synergetic approach to achieve enhanced lithium ion storage performance in ternary phased SnO$_2$-Fe$_2$O$_3$/rGO composite nanostructures. *J. Mater. Chem.* 2011, **21**, 12770-12776; (c) Zhu, X. J.; Zhu, Y. W.; Murali, S.; Stollers, M. D.; Ruoff, R. S. Nanostructured reduced graphene oxide/Fe$_2$O$_3$ composite as a high-performance anode material for lithium ion batteries. *ACS Nano* 2011, **5**, 3333-3338.


66. Zho, Y. Q.; Wang, Y. Sn@CNT nanostructures rooted in graphene with high and fast Li-storage capacities. *ACS Nano* 2011, **5**, 8108-8114.


75. Guo, S.; Sun, S. FePt nanoparticles assembled on graphene as enhanced catalyst for oxygen


Part 2. Functionalization of Graphene Oxide (GO) and Reduced Graphene Oxide (rGO) and Their Applications

2.1 Introduction

Part 2 has demonstrated the functionalization related to graphene oxide (GO) and reduced graphene oxide (rGO). As we mentioned above, tuning the electrical properties of graphene and investigating new properties through graphene based hybrid materials are important. In previous, C$_{60}$/CNT hybrid materials have reported due to their remarkable electronic and optical properties.\(^1\) Similarly, covalent linking of C$_{60}$ with GO have demonstrated.\(^2\) Chen et al. tried to control the electrical properties between graphene and C$_{60}$. However, they couldn't observe any change because of weak interaction occurred at deposited C$_{60}$ film on graphene.\(^3\) In here, to observe the electron transport, the assembly of reduced graphene oxide (rGO) and fullerene (C$_{60}$) into hybrid (rGO/C$_{60}$) wires was performed by π-π interaction between rGO and C$_{60}$. Structural characterization and possible application by the interaction rGO and C$_{60}$ will be discussed.\(^4\)

In addition, amine-functionalized rGO which have n-doping effect in FET is introduced (chapter 2.3 in part 2). The mechanism of doping effect and a facile method for the fabrication of rGO FET with self-assembled monolayers (SAMs) will be discussed.\(^5\)
2.1.1 References


2.2 Graphene-\(C_{60}\) hybrid materials by assembly of non-covalent bonding and their electrical property

2.2.1. Abstract

The assembly of reduced graphene oxide (rGO) and fullerene (\(C_{60}\)) into hybrid (rGO/\(C_{60}\)) wires was successfully performed by employing the liquid-liquid interfacial precipitation (LLIP) method. The rGO sheets spontaneously wrapped \(C_{60}\) wires through the \(\pi-\pi\) interaction between rGO and \(C_{60}\). Structural characterization of the rGO/\(C_{60}\) wires was carried out by using UV/visible spectroscopy, scanning electron microscopy, and transmission electron microscopy. FET devices with rGO/\(C_{60}\) wires were fabricated to investigate their electrical properties. The \(I_{ds}-V_g\) curves of the hybrid wires exhibited p-type semiconducting behavior both in vacuum and in air, indicating hole transport through rGO as a shell layer, whereas pure \(C_{60}\) wires and rGO sheets showed n-type and ambipolar behaviors, respectively, in vacuum. Possible application of the fabricated wires, such a photovoltaic device, was also demonstrated.

2.2.2. Introduction

Organic and inorganic hybrid materials with carbon allotropes such as fullerene and carbon nanotubes (CNTs) have attracted much attention. The charge transfer at interface of these hybrid materials can show a synergistic effect to induce interesting properties that are different from those of each component. For example, CNTs functionalized with light sensitive materials such as CdSe and TiO\(_2\) nanoparticles showed variation of conductance at a specific wavelength in FET devices due to photo-induced charge transfer from the nanoparticles to CNTs.\(^{1,2,3}\) Wavelength-selective silencing of photoconductivity in Au nanoparticles-coated fullerene wires due to electron transfer by the surface plasmon resonance (SPR) of Au nanoparticles was also reported.\(^4\) These approaches have opened possibilities for application with photo-detectors and sensors.

On the other hand, the charge transfer can be a driving force for the formation of hybrid materials. Wakahara et al. speculated that the strong charge transfer between \(C_{60}\) and ferrocene (Fc) at 782 nm enabled the interaction of the nearest \(C_{60}\)-Fc pair, which is possibly a driving force for the formation of \(C_{60}/Fc\) nanosheets.\(^5\) Besides, hybrid materials consisting of only carbon nanomaterials, such as CNTs coated with \(C_{60}\) molecules, could be prepared by non-covalent functionalization.\(^6,7\) An interesting result was that hybrid materials of higher fullerene (\(C_{70}\)) with an ellipsoidal shape and single-walled carbon nanotubes (SWNTs) showed efficient electron transfer due to improved interaction between \(C_{70}\) and the sidewalls of the SWNTs. A photo-electrochemical device fabricated with the hybrid materials exhibited the highest IPCE value (26 %) among analogous SWNT-based photo-electrochemical devices.\(^8\)
Graphene enables interactions with other organic and inorganic components for hybrid materials through π-π interaction which is efficient due to its large surface area.\textsuperscript{9,10,11} Non-covalent bonding such as hydrogen bonding, Van der Waals interaction, and π-π interaction provides a simpler process for preparation of hybrid materials than covalent bonding. In particular, it is anticipated that reduced graphene oxide (rGO) with functional groups can be exploited to develop many hybrid structures, because it is soluble in various solvents.\textsuperscript{12,13} Indeed, some recent efforts have been made to prepare graphene hybrid materials. For instance, N,N'-dioctyl-3,4,9,10-perylenedicarboximide (PDI) wire with aromatic structures has been coated by rGO via the π-π interaction.\textsuperscript{14} The charge transfer between n-type PDI and rGO in the hybrid wires could be applicable to organic photovoltaic devices. In addition, electrostatic interaction between an aromatic peptide wire with positive charges and rGO with negative charges enabled peptide/rGO core/shell wires. Application of biomolecules is limited due to their poor electrical property and low thermal stability, whereas the rGO-coated peptide wire became conductive and could be used for super-capacitor electrodes.\textsuperscript{12}

Herein, we report the assembly of rGO and C\textsubscript{60} into hybrid wires by employing the liquid-liquid interfacial precipitation (LLIP) method. The process of the assembly was carefully investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and finally the formation of rGO-wrapped C\textsubscript{60} wires was observed. It was identified from UV/Vis spectroscopy that the driving force of the assembly is the π-π interaction between rGO and C\textsubscript{60}. Interestingly, rGO/C\textsubscript{60} hybrid wires showed a p-type semiconducting behavior in field effect transistor (FET) devices both in vacuum and in air, whereas rGO and C\textsubscript{60} displayed ambipolar and n-type semiconducting behaviors in vacuum, respectively. These results indicate electron transfer from rGO to C\textsubscript{60}. Furthermore, we explored some applications such as photoluminescence and a solar cell based on charge transfer.

2.2.3. Experimental section

2.2.3.1. Preparation of graphene oxide (GO)

Graphite oxide was synthesized by modified Hummers method and exfoliated to give a brown dispersion of graphene oxide under ultrasonication.\textsuperscript{29,30,31} The resulting graphene oxide (GO) is negatively charged over a wide pH range since the GO sheet has chemical functional groups such as carboxylic acids. GO suspensions were reduced by hydrazine solution (35 wt\% in water, Aldrich) to convert into reduced graphene oxide (rGO). The as-prepared negatively charged GO suspension (5.0 mL) was mixed with 5.0 mL of hydrazine solution and 35.0 mL of ammonia solution (28–30 \%, Samchun) in a 20 mL glass vial. After stirring for a few minutes, the vial was put in a water bath at 95 °C for 1 h.
2.2.3.2. Synthesis of rGO/C\textsubscript{60} wires

Fullerene (C\textsubscript{60}) powder (sigma Aldrich, 99 %) was dissolved in m-xylene to make a solution of 2 mg/mL and the C\textsubscript{60} solution is kept in a glass vial. The rGO aqueous solution (50 µL) was added into 2 mL isopropyl alcohol (IPA). The rGO IPA solution was then gently added into the glass vial containing the C\textsubscript{60} solution to form a liquid-liquid interface where the upper phase is IPA and the lower phase is the m-xylene solution of C\textsubscript{60}. The vial was loosely capped and kept at 4 °C over 1 day. To remove free rGO sheets, the solution was centrifuged at 500 rpm. The centrifugation with IPA was repeated a few times to wash the hybrid rGO/C\textsubscript{60} wires. The wires obtained were characterized by HR-TEM (JEOL, JEM-2100F, 200 KV). The exposure time was 0.5 s and the current density was 55 pA/cm\textsuperscript{2} in magnified images.

2.2.3.3. Measurement of UV/Vis spectra and photoluminescence spectra

rGO/C\textsubscript{60} wires were spin-coated at 1000 rpm on a quartz plate. The rGO/C\textsubscript{60} wires coated on the quartz plate were dried at 130 °C in vacuum for 1h. Then, absorption and photoluminescence spectra were measured by a UV/Vis spectrometer (cary 5000 model, Varian) and a fluorometer (Cary Eclipse model, Varian), respectively.

2.2.3.4. Measurement of LUMO and Fermi levels

To investigate LUMO energy level of rGO, cyclic voltammogram of rGO was measured by using a standard three-electrode system which consists of a glassy carbon as the working electrode, a platinum mesh as the counter electrode, and a silver wire as the reference electrode. Acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF\textsubscript{6}) was used as the supporting electrolyte. The LUMO energy level of rGO was calculated according to the following equations.

\[
\text{Fc/Fc}^+: 0.595 \text{ V vs. Ag wire} \\
\text{LUMO (eV)} = -4.8 - (E_{\text{onset}} - E_{\text{Fc/Fc}^+})
\]

Photoelectron spectroscopy (surface analyzer model AC-2, RIKEN KEIKI) was used to determine the Fermi energy level of rGO. This is an analyzer for detecting low energy electrons emitted from a solid surface in air by irradiating UV light. The threshold energy of photoelectron emission is called the Fermi level, HOMO level or ionization potential, or work function.

2.2.3.5. Fabrication of device

The FET devices were fabricated by dropping solutions of C\textsubscript{60} wires, rGO, and rGO-wrapped C\textsubscript{60}
wires on pre-patterned source and drain electrodes. The pre-patterned electrodes were defined on SiO2/Si (300 nm thick SiO2 layer on a highly-doped p-type Si(100)) substrates by addressing Cr (5 nm)/Au (20 nm) electrodes by using a conventional photolithography process (photoresist: AZ5214). The channel length between source and drain electrodes was 4 m. Electrical transport properties were measured by using a semiconductor analyzer (KEITHLEY 4200).

The photovoltaic solar cells with the configuration of indium thin oxide (ITO)/rGO-C60 wires/electrolyte/Pt electrode were fabricated. Before the device fabrication, the ITO-coated glass substrate was cleaned by ultrasonic treatment using detergent, deionized water, acetone, and isopropyl alcohol in sequence and dried in an oven for 24 h. The rGO-wrapped C60 wires were spin-coated at 1000 rpm for 30 s onto the cleaned ITO substrate repeatedly. The Pt-coated FTO, used as a counter electrode, was prepared by sputtering on an FTO glass followed by heating at 450 °C in air for 1h. The rGO-wrapped C60 wires coated on ITO and Pt counter electrodes were assembled into a sealed sandwich-type cell by heating with a hot melt of 50 μm thick sealing tapes which served as a spacer between the electrodes. A drop of the electrolyte solution was placed on a drilled hole in the counter electrode of the cell and was driven into the cell by means of vacuum backfilling. The hole was sealed using additional sealant and a cover glass (0.1 mm thick). The redox electrolyte consisted of 0.04 M LiI, 0.02 M I2, 0.5 M 1-hexyl-2,3-dimethylimidazolium iodine, and 0.5 M 4-tert-butylpyridine in acetonitrile. Photovoltaic measurements were recorded by employing a Keithley 2400 digital source meter. Solar cell performance was measured by utilizing an Air Mass 1.5 G (AM 1.5 G) solar simulator with an irradiation intensity of 100 mWcm−2 under ambient condition. External quantum efficiency (EQE) measurements were obtained using the PV measurements OE system with monochromatic light from a xenon lamp. The monochromatic light intensity was calibrated with a Si photodiode and chopped at 4 Hz.

2.2.4 Results and discussions

2.2.4.1 Liquid-liquid interfacial precipitation for rGO/C60 wires

The rGO-wrapped C60 wires (rGO/C60) were prepared by liquid-liquid interfacial precipitation (LLIP).15,16,17 This method is suitable for obtaining a large quantity of C60 wires. It is noted that C60 wires prepared by LLIP have higher strength and better electrical conductivity than C60 wires prepared by solvent evaporation, because the C60 molecules in LLIP are confined within the very narrow space of the interface of two solvents and thus they have the smaller intermolecular distance between the C60 molecules.17
An rGO aqueous solution with a concentration of 0.5 wt% was dispersed in isopropyl alcohol (IPA). The size distribution of the rGO sheets was between a few hundred nm and 2 µm by atomic force microscopy (AFM). Meanwhile, C\textsubscript{60} powder was dissolved in m-xylene to prepare a saturated solution. The rGO IPA solution was gently added into a vial including the C\textsubscript{60} m-xylene solution to form a precipitate at the liquid-liquid interface, wherein the upper phase is the rGO in the IPA and the lower phase is the C\textsubscript{60} m-xylene solution. Once nucleation of the C\textsubscript{60} wires starts to occur at the liquid-liquid interface, green precipitates were observed at the interface along the vial surface. (Figure 2.2.1(a)) By continuously adding the rGO solution into the C\textsubscript{60} solution, the C\textsubscript{60} solution was gradually covered with nanorods with length in a range of 30 and 200 nm. Figure 2.2.1(b) is a SEM image in 2 min since rGO solution was added into the C\textsubscript{60} solution) Note that the C\textsubscript{60} particles and nanorods are attached to rGO sheets as shown in Figures 2.2.1(a) and (b). After dropping all of the rGO solution, the apparent interface of IPA and m-xylene disappeared and C\textsubscript{60} wires were observed. The C\textsubscript{60} wires were partially wrapped with rGO sheets and their lengths were less than a few micrometers. (Figure 2.2.1(c)) To promote the growth of C\textsubscript{60} wires wrapped with rGO, the vial was capped and left at 4 °C in a refrigerator. The color of the precipitates changed to dark green after being held at 4 °C for a certain amount of time. Although the C\textsubscript{60} wires are not fully wrapped with rGO sheets after 1 h, the length of the C\textsubscript{60} wires was more than 10 micrometers. (Figure 2.2.1(d)) It was observed that the C\textsubscript{60} wires were fully wrapped with rGO sheets after 1 day. (Figure 2.2.1(e)) Free rGO sheets were removed by centrifugation at 500 rpm. As a control experiment, C\textsubscript{60} wires were prepared by LLIP using pure IPA without rGO. As soon as IPA was added to the C\textsubscript{60} solution, green precipitates of only C\textsubscript{60} particles were also observed at the interface of the C\textsubscript{60} solution and IPA. (Figure 2.2.2(a)) After dropping IPA for 2 min, long C\textsubscript{60} wires more than a few micrometers were observed (Figure 2.2.2(b)), whereas short C\textsubscript{60} nanorods on rGO sheets were observed in case of adding the rGO IPA solution in Figure 2.2.1(b). It means that the growth of C\textsubscript{60} wires gets slow in the presence of rGO, possibly due to the interaction between rGO and C\textsubscript{60}. After dropping all of the IPA, the mixed solution was capped and left at 4 °C. After 1 h, the C\textsubscript{60} wires with the length of more than 10 micrometers were formed. (Figure 2.2.2(c)) Figure 2.2.3(a) shows a SEM image of pure C\textsubscript{60} wires with a diameter range of 200 - 800 nm. Figure 2.2.3 (b) shows the rGO/C\textsubscript{60} wires left at 4 °C for 1 day. C\textsubscript{60} in the rGO/C\textsubscript{60} wires can be selectively dissolved in m-xylene to confirm the presence of the rGO attached to the C\textsubscript{60} wires. Figure 2.2.3(c) shows the rGO shells that remained after selective dissolution of the C\textsubscript{60} wires in m-xylene. The wrapping of rGO was also confirmed by TEM images in Figure 2.2.3(d).
Figure 2.2.1. Schematic illustration and SEM images (a-e) showing steps of formation of rGO-wrapped C₆₀ wires.

(i) dropping slowly rGO solution into C₆₀ solution
(ii) keeping the mixed solution at 4 °C
The magnified image in Figure 2.2.3(d) obviously shows C_{60} core and rGO shell with layered structure. As a control experiment, we measured HR-TEM images of C_{60} wires only before wrapping rGO sheets and confirmed that there are no layered structures similar to Figure 2.2.3(d). (Figure 2.2.4)

Also, the Raman spectrum of a rGO/C_{60} wire in the inset of Figure 2(d) confirms existence of rGO and C_{60}: D and G bands around 1350 and 1600 cm^{-1} for rGO and A_{g}(2) mode at 1469 cm^{-1} for C_{60}. As a control experiment, C_{60} wires were first prepared by LLIP and then immersed into the rGO solution. Most of the rGO sheets did not wrap the C_{60} wires, but were randomly laid on them. (Figure 2.2.5) In parts of the sample, some small rGO sheets wrapped the wires.

Figures 2.2.6(a)-(c) show UV-Vis spectra of C_{60} wires, rGO, and rGO/C_{60} wires, respectively. The spectrum of the C_{60} wires in Figure 2.2.6(a) shows two bands at 270 nm and 340 nm. These two bands correspond to the strongly allowed electronic transitions, 6^{1}T_{1u}−1^{1}A_{g} and 3^{1}T_{1u}−1^{1}A_{g}, respectively. Since the red shift of the band at 340 nm is correlated with interactions between C_{60} and different molecules, the band is an important indicator for the interaction of fullerene and aromatic rings or fullerene and a polymer. Note that the band at 340 nm in the C_{60} wires shifted to 380 nm in the rGO/C_{60} wires. (Figure 2.2.6(c)) The large shift of 40 nm is correlated to the strong delocalization of π electron system of rGO sheets in the vicinity of the C_{60} wires. This result means that the π-π interaction is the main driving force for the formation of the rGO/C_{60} wires. The π-π stacking reduces the surface energy of the molecules. Furthermore, the π-π interaction was observed even in green precipitates formed as soon as the rGO IPA solution was dropped into the C_{60} solution as presented in Figure 2.2.1(a). Figure 2.2.7(a), the UV/Vis spectrum shows an absorption band at 390 nm which is identical to the result by the π-π interaction provided in Figure 3(c). This means that the C_{60} precipitates (particles) were attached to the rGO sheets. The absorption band at 390 nm remains after the solution was left at 4 °C for 1 h. (Figure 2.2.7(b)) As a control experiment, the growth of C_{60} wires by adding pure IPA into the C_{60} solution was investigated and the results are given in Figures 2.2.7(c) and (d). The C_{60} precipitates (particles) and wires showed an absorption band around 340 nm in the UV/Vis spectra. Therefore, the π-π interaction between C_{60} and rGO sheets occurs from the initial step where the IPA solution with rGO sheets is added to the C_{60} solution.
Figure 2.2.2. SEM images of C$_{60}$ particles (a), C$_{60}$ wires after dropping IPA for 2 min (b), and C$_{60}$ wires left at 4 °C for 1 h (c).
Figure 2.2.3. SEM images of (a) only C\textsubscript{60} wires, (b) rGO/C\textsubscript{60} wires, and (c) rGO after dissolving C\textsubscript{60} wires in m-xylene. (d) TEM images of a rGO/C\textsubscript{60} wire. The magnified image in (d) shows rGO layers. The inset in (d) shows Raman spectrum of a rGO/C\textsubscript{60} wire in which bands of rGO and C\textsubscript{60} were observed.
Figure 2.2.4. TEM images of a C$_{60}$ wire. (a) The magnified image of the edge area shows crystalline structure from FFT pattern. (b) The magnified image of other edge area shows the amorphous layer.
Figure 2.2.5. SEM images of C$_{60}$ wires after they were first prepared and then immersed into rGO solution. (a) and (b) most of rGO sheets did not wrap the C$_{60}$ wires, but were randomly laid on them. (c) In a part of the sample, some small rGO sheets wrapped them.
Figure 2.2.6. UV/Vis spectra of (a) C$_{60}$ wires, (b) rGO, and (c) rGO/C$_{60}$ wires. The spectra were measured after spin-coating the solutions on quartz substrates.
Figure 2.2.7. UV-Vis spectra of (a) C_{60} precipitates (by adding the rGO IPA solution), (b) rGO/C_{60} wires left at 4 °C for 1h, (c) C_{60} particles (by adding pure IPA), and (d) C_{60} wires left at 4 °C for 1h.
2.2.4.2 Energy levels of rGO and C\textsubscript{60} wires

To understand charge transfer in the rGO/C\textsubscript{60} wires, the energy levels of rGO and C\textsubscript{60} were investigated. It is known that GO has a band gap of \(~2.2\) eV and the bandgap of a few-layer rGO sheets can be controlled between \(0.5\) and \(1.4\) eV depending on the extent of reduction by the applied thermal reduction process.\(^{20}\)

In this study, cyclic voltammetry (CV) and photoelectron spectroscopy were employed to measure LUMO and Fermi levels of rGO. The LUMO energy level of rGO was calculated to be \(3.65\) eV using a well-defined reduction peak in the cyclic voltammogram. (Figure 2.2.8) The Fermi level of rGO was \(4.8\) eV from the photoelectron spectrum. (Figures 2.2.9) Above LUMO and Fermi levels are very similar to the results of previous reports: the LUMO level of imidazole-modified GO was \(3.6\) eV by CV and the Fermi level of rGO was \(4.88\) eV by photoelectron spectroscopy or \(4.7\) eV by Kelvin Probe Force Microscopy (KPFM).\(^{21,22,23}\) Therefore, the bandgap of rGO in this study appears to be slightly larger than \(1.15\) eV. This indicates that rGO can be used as an absorber of visible light. (See the example application of a photovoltaic device later in this paper) In case of C\textsubscript{60}, it is known that the LUMO is \(4.3\) eV and the HOMO is \(6.6\) eV.\(^{24}\) Actually, the Fermi level of C\textsubscript{60} wires was \(5.1\) eV by photoelectron spectroscopy. (Figure 2.2.10) Consequently, electrons can transfer from rGO to C\textsubscript{60} in rGO/C\textsubscript{60} wires because the Fermi level of rGO is higher than that of C\textsubscript{60}.

3.3.3 Electrical properties of rGO/C\textsubscript{60} wires

To investigate the electrical properties, we fabricated field effect transistor (FET) devices of rGO/C\textsubscript{60} wires, rGO sheets and C\textsubscript{60} wires. Figure 3.11 shows optical images and I-V\textsubscript{g} curves of the FET devices. Most of the measurements were performed in vacuum to remove the influence of oxygen. Also, an annealing process at \(325\) K for \(8\) hours in vacuum before electrical measurements was carried out to remove adsorbed O\textsubscript{2} and H\textsubscript{2}O on the samples. The rGO sheets exhibited ambipolar characteristics in vacuum, which is identical to previous results.\(^{25,26}\) (Figure 2.2.11(a)) However, the Dirac point appeared near \(V\textsubscript{g} = -20\) V. It is considered that the reduction process using ammonia solution and hydrazine induced the shift of a Dirac point to negative gate voltage, \textit{i.e.} a n-doping effect, due to remaining N atoms.
Figure 2.2.8. CV curve of rGO on glassy carbon electrode.

Working Electrode: Glassy carbon

Counter Electrode: Pt mesh

Reference: Ag wire

Electrolyte: 0.1 M TBAPF₆ in DMF

Preparation of GO or RGO on glassy carbon electrode: dropping and drying

Fe/Fe⁺: 0.595 V vs. Ag wire

LUMO(eV) = -4.8 – (E_{onset} (vs Ag/AgCl)- E_{Fe/Fe⁺}(vs Ag/AgCl))

E_{red} as -0.55 V, E_{LUMO} = -3.65 V
Figure 2.2.9. Photoelectron spectrum of rGO.

Figure 2.2.10. Photoelectron spectrum of C$_{60}$ wires.
Figure 2.2.11. $I_{ds}$-$V_g$ of (a) rGO in vacuum, (b) C$_{60}$ wires in vacuum, (c) rGO/C$_{60}$ wires in ambient, and (d) rGO/C$_{60}$ wires in vacuum. The bias voltage, $V_{ds}$, was 1 V for (a) and 10 V for (b), 5 V for (c) and (d). Optical images of the corresponding devices are shown in the insets of (a), (b), and (c).
It was confirmed from an elemental analysis of rGO which included N atoms of 2.81 wt%. (Table 2.2.1) The FET of the C_{60} wires showed a typical n-type behavior in vacuum. (Figure 2.2.11(b)) This result is consistent with a previous report.\textsuperscript{15} On the other hand, the rGO/C_{60} wires showed p-type behaviors in air as well as in vacuum as shown in Figures 2.2.11(c) and (d), indicating hole transport through rGO. These electrical properties reveal that the p-type behaviors of the rGO/C_{60} wires reveal that rGO sheets are heavily p-doped due to electron transfer from rGO to C_{60} as indicated in the inset of Figure 4(c). The hole mobility (0.04 cm\textsuperscript{2}/Vs) for rGO/C_{60} wire in Figure 2.2.11(c) is lower than that (0.6 cm\textsuperscript{2}/Vs) for rGO sheets in Figure 2.2.11(a). The lower mobility in rGO/C_{60} wires might be due to many junctions between rGO sheets on C_{60} wires. Further, this study indicates that rGO/C_{60} wires are not sensitive to O\textsubscript{2} and H\textsubscript{2}O molecules and are stable even in air.

2.2.4.3 The role of rGO in photovoltaic devices

To further understand interesting optoelectronic behaviors of the rGO/C_{60} wires, such as the photocurrent generation and PL quenching, photovoltaic devices were fabricated. To our best knowledge, rGO has so far been used as an electron acceptor instead of C_{60} in organic photovoltaic devices.\textsuperscript{27,28} However, our results clearly indicate that rGO can act as a sensitizer since the photo-excited electron from rGO is injected into the LUMO energy level of C_{60} as shown in the inset of Figure 2.2.12(a). The rGO/C_{60} wires are regenerated by the redox system (I\textsubscript{3}/I\textsubscript{2}) at the counter electrode via electron migration through the external load. The J-V characteristics of the devices using rGO and rGO/C_{60} wires under simulated AM 1.5 G illumination are shown in Figure 2.2.12(a), while the corresponding numerical results are summarized in Table 2.2.2. To replace rGO with rGO/C_{60} wires caused a significant enhancement of short circuit current (J_{sc}) from 0.07 to 0.19 mAcm\textsuperscript{-2}. The observed current increase can be interpreted that the photo-induced electrons are efficiently transferred from the rGO to C_{60} under light irradiation. (Photo-induced charge transfer was observed in photoluminescence measurements in Figure 2.2.13)

The incident photon to current efficiency (IPCE) was obtained to confirm the photocurrent generation in the solar cell with the rGO/C_{60} wires. As shown in Figure 2.2.12(b), the photocurrent generation of the rGO/C_{60} wires is obvious. It is noted that both rGO and C_{60} in the rGO/C_{60} wires contribute to the photocurrent generation since the IPCE spectral feature from 400 nm to 700 nm is attributable to the contribution of electrons generated from the photo-excitation of both rGO and C_{60}. As a result, this enables significant enhancement of J_{sc} in the solar cell with rGO/C_{60} wires. Even though the performance of the rGO/C_{60} wires still appears relatively low, we highlight that this study is the first report on rGO as a sensitizer for the photovoltaic devices, which should open up new strategies for the development of this field.
### Table 2.2.1. Element analysis of graphene oxide and reduced graphene oxide

<table>
<thead>
<tr>
<th></th>
<th>Graphene oxide</th>
<th>Reduced graphene oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (wt%)</td>
<td>41.27</td>
<td>63.59</td>
</tr>
<tr>
<td>Hydrogen (wt%)</td>
<td>2.78</td>
<td>1.31</td>
</tr>
<tr>
<td>Oxygen (wt%)</td>
<td>28.61</td>
<td>13.70</td>
</tr>
<tr>
<td>Nitrogen (wt%)</td>
<td>0.00</td>
<td>2.81</td>
</tr>
</tbody>
</table>
Figure 2.2.12. (a) J-V curves of rGO and rGO/C₆₀ wires. (b) IPCE spectrum of rGO/C₆₀ wires.

Table 2.2.2. Solar cell characteristics of rGO and rGO/C₆₀ wires

<table>
<thead>
<tr>
<th></th>
<th>Jₛₑ (mA/cm²)</th>
<th>Vₜ (V)</th>
<th>FF (%)</th>
<th>Eₑf (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rGO</td>
<td>0.07</td>
<td>0.18</td>
<td>0.45</td>
<td>0.006</td>
</tr>
<tr>
<td>rGO/C₆₀ wire</td>
<td>0.19</td>
<td>0.33</td>
<td>0.50</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Figure 2.2.13. Photoluminescence spectra of $C_{60}$ wires and rGO/$C_{60}$ wires obtained with excitation at 520 nm.
2.2.5 Conclusion

In conclusion, rGO-wrapped $C_{60}$ wires were successfully prepared via the LLIP method. The main driving force for the assembly of rGO sheets and $C_{60}$ wires is the $\pi-\pi$ interaction. The rGO-wrapped $C_{60}$ wires exhibited p-type semiconducting behaviors in air and in vacuum, indicating charge transfer between rGO and $C_{60}$ and hole transport through rGO. Furthermore, we presented interesting applications such as a photovoltaic device albeit a relatively low efficiency. The assembly of carbon nanomaterials and the electron transfer at interfaces induced interesting and unprecedented properties. Therefore, future efforts will focus not only on new graphene-based nanostructures or hybrid materials with functionalized graphene, but also on charge transfer at interfaces in newly designed hybrids.
2.2.6 References


14. Wang, W.; Goh, E. M.; Manga, K. K.; Bao, Q.; Yang, P.; Loh, K. P. Graphene as atomic
template and structural scaffold in the synthesis of graphene-organic hybrid wire with photovoltaic properties. ACS Nano 2010, 4, 6180–6187.


2.3. Field effect transistor of negative and positive charged graphene

2.3.1. Abstract

A facile method for fabrication of negatively and positively charged reduced graphene oxide (rGO) field effect transistor (FETs) is proposed, which utilizes electrostatic attraction between electrodes and rGO sheets. The pre-patterned gold electrode on SiO₂(300 nm)/Si wafer is prepared, followed by forming self-assembled monolayers (SAMs) with negative or positive charges on the electrode. Negatively and positively charged rGO sheets are functionalized with carboxylic acid and amine groups, respectively. The electrode with SAMs is immersed in a solution with negatively or positively charged graphene oxide (GO) sheets. Then, the GO sheets are selectively adsorbed on the gold electrode via electrostatic attraction. The FET of amine-functionalized rGO exhibits n-doping effect. Furthermore, FET devices fabricated by this method exhibited high mobility of carriers: maximum 82.5 and 27.5 cm²/Vs for hole and electron, respectively, in –rGO devices and maximum 6.7 and 1.8 cm²/Vs for hole and electron, respectively, in +rGO devices.

2.3.2. Introduction

The application of graphene to electronic devices is eagerly anticipated because of its unique physical properties such as high conductance, high mobility of charge carriers, and the quantum Hall effect.\(^1\)–\(^6\) Graphene has an unusual electronic band structure that has a linear energy-momentum relation near the Dirac point where the valence and conduction bands meet, giving ambipolar character with both electron and hole carriers.\(^2\),\(^6\)–\(^8\)

Chemically exfoliated graphene oxide (GO) is an insulator since it has structural defects and many functional groups containing oxygen such as carboxylic acid, hydroxyl, and epoxy groups.\(^9\) However, GO is reduced by reductant or thermal annealing which converts the insulating GO into conductive reduced graphene oxide (rGO). Unlike GO, rGO exhibits ambipolar character\(^10\),\(^11\) or p-type behavior.\(^10\)–\(^14\) The p-type behavior of rGO is due to the fact that hydroxyl groups and physisorbed oxygen serve as electron traps and, therefore, prohibit transport of carriers. Thus, electrical measurement was carried out in vacuum in some reports to remove such effect in ambient condition.\(^13\),\(^14\) Since the oxygen–doping effect is dramatically reduced in vacuum, rGO shows ambipolar behavior. On the other hand, rGO affords the advantage of easy chemical functionalization. The functionalization of rGO enables a change in the electronic band structure of graphene. Therefore, it is very interesting to tune the electrical properties of rGO by functionalization. It has already been reported that the electrical characteristics and band gap could be controlled by the degree of thermal reduction of GO.\(^10\) rGO could show ambipolar characteristics depending on the degree of reduction, inducing the recovery of sp\(^2\)
conjugation.

Very recently, nitrogen-doped graphene has become a hot issue in this field because it changes the electrical properties of graphene. Nitrogen-doped graphene could be synthesized by chemical vapor deposition (CVD) method with NH$_3$ gas at high temperature. Nitrogen could be doped in graphene nanoribbon and rGO by thermal annealing with NH$_3$ gas. A recent STM study of nitrogen-doped CVD-grown graphene showed that nitrogen and carbon at the atomic level have a specific pattern, generally a triangular symmetry. In addition to the direct substitution of carbon by nitrogen in graphene, pyridinic and pyrrolic nitrogen atoms have been also identified. Moreover, the doping of graphene using self-assembled monolayers (SAMs) with amine groups as an electron donor has been studied. The CVD graphene on the SAMs with amine showed n-doping effect which is supposed to be due to the lone pair electrons of amine. So far, the introduction of nitrogen by chemical covalent bonding has not been attempted in research on the doping of graphene. The chemical method provides some advantages such as a solution process and treatment of a large amount of graphene. To investigate electrical properties of graphene like doping, field-effect transistor (FET) device should be fabricated. The fabrication process of rGO FET devices includes the deposition of rGO on a SiO$_2$ wafer and then photolithography or e-beam lithography. However, the process is complicated and, therefore, requires exquisite skill.

In here, an easy and systematic approach to fabricate rGO FET devices is proposed. First, pre-patterned gold electrode on SiO$_2$(300 nm)/Si wafer is prepared, followed by forming SAMs with negative or positive charges on the electrode. The electrode with SAMs is immersed in a solution with negatively or positively charged GO sheets. Then, the GO sheets are selectively adsorbed on the gold electrode via electrostatic attraction. Finally, reduction of GO sheets by hydrazine vapor provides an FET of the negatively or positively charged rGO. Negatively and positively charged GO sheets are functionalized with carboxylic acid and amine groups, respectively. The amine-functionalized rGO FET exhibited the shift of the Dirac point to negative gate voltage, indicating n-doping effect. To the best of our knowledge, this is the first report on n-doping effect by functionalization of rGO. Furthermore, FET devices fabricated by this method exhibited high mobility of carriers: maximum 82.5 and 27.5 cm$^2$/Vs for hole and electron, respectively, in −rGO devices and maximum 6.7 and 1.8 cm$^2$/Vs for hole and electron, respectively, in +rGO devices. Details on the fabrication of rGO FETs and their electrical characteristics are presented.
2.3.3 Experimental section

2.3.3.1 Preparation of negatively charged and positively charged graphene oxide

Graphite oxide was synthesized by modified Hummers method and exfoliated to yield a brown dispersion of graphene oxide under ultrasonication. The resulting graphite oxide (GO) is negatively charged over a wide pH range since the GO sheet has chemical functional groups such as carboxylic acids. Positively charged GO was synthesized by using N-ethyl-N’-(3-dimethylaminopropyl)carbodiimide methiodide (EDC, 98%, Alfa Aesar) and ethylenediamine (99%, Sigma-Aldrich). Negatively charged GO suspension (50 mL) was combined with EDC (600 mg) and ethylenediamine (4 mL) and stirred for 4 h, and afterwards the mixture solution was dialyzed for 24 h to remove EDC and ethylenediamine. Then a positively charged GO suspension of dark brown color was obtained. Negatively and positively charged GO suspensions were reduced by hydrazine monohydrate vapor (98%, Aldrich) at 80 °C for 24 h.

2.3.3.2 Fabrication of FET device

The pre-patterned electrodes were defined on SiO₂/Si (300 nm thick SiO₂ layer on a highly-doped p-type Si(100)) substrates by addressing Cr (5 nm)/Au (30 nm) electrodes by using a conventional photolithography process (photoresist: AZ 5214). The channel length between source and drain electrodes was 4 μm. Electrical transport properties were measured by using a semiconductor analyzer (KEITHLEY 4200). The mobility was calculated using \( \mu = \frac{L/W}{C_{ox} V_{sd}} \frac{\Delta I_{sd}}{\Delta V_{g}} \), where L and W are the channel length and width, \( C_{ox} \) the gate oxide capacitance, \( V_{sd} \) the source-drain voltage, \( I_{sd} \) the source-drain current, and \( V_{g} \) the gate voltage. The linear regime of the transfer characteristic was used to obtain the mobility.

2.3.3.3 How to prepare devices with GO sheets

An amine-functionalized GO (+GO) solution (0.05 mg/mL) was adjusted to pH 4.5 with HCl. +GO solution (2 mL) was transferred into a vial. Then, the device with negative charged electrodes by MDA SAM was immersed into the +GO solution for 1–2 h. The +GO sheets were spontaneously deposited on the electrodes by electrostatic attraction. Finally, DI water was used to wash the electrodes. An –GO solution (0.5 mg/mL) was adjusted to pH 10 with NaOH. –GO (2 mL) solution was transferred in a vial. The positive charged electrodes with AUT SAM were immersed into the vial with –GO solution for 1–2 h. The –GO sheets were coated on the electrodes by electrostatic attraction. Finally, the electrodes were washed gently by DI water.
Figure 2.3.1. Chemical structures of –GO (a) and +GO (b), Zeta potential of –GO (c) and +GO (d), and AFM images of –GO (e) and +GO sheets (f).

<table>
<thead>
<tr>
<th>Table 2.3.1. Elemental analysis for +GO and –GO sheets</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>C/N ratio</td>
</tr>
</tbody>
</table>
2.3.4 Results and discussions

2.3.4.1 Characteristics of negative charged and positive charged graphene

Graphene oxide was prepared by modified Hummers method.\(^\text{20}\) As-prepared GO has negative charge due to the deprotonation of the carboxylic acid at the edge and this is called negatively charged graphene oxide \((-\text{GO})\). (Figure 2.3.1(a)) Positively charged GO \((+\text{GO})\) sheets were prepared by introducing the amine groups (NH\(_2\)) of negatively charged GO sheets through the N-ethyl-N'-(3-dimethyl aminopropyl)carbodiimide methiodide (EDC) mediated reaction between carboxylic acids and excess ethylenediamine and their protonation.\(^\text{21}\) (Figure 2.3.1(b)) The zeta potential measurement identified that negatively and positively charged GO sheets are stable in aqueous solution (Figure 2.3.1(c) and (d)). Element analysis (EA) was performed to analyze elements in \(-\text{GO}\) and \(+\text{GO}\) sheets. Since nitrogen was detected in \(+\text{GO}\) solution but not in \(-\text{GO}\) solution, it was confirmed that \(+\text{GO}\) was functionalized with ethylenediamine (Table 2.3.1). Atomic force microscopy (AFM) showed the size distribution of the \(-\text{GO}\) and \(+\text{GO}\) sheets between a few hundred nm and 10 \(\mu\)m (Figure 2.3.1(e) and (f)).

2.3.4.2 Facile methods for fabrication of FET devices through SAMs-treated gold electrode

Next, GO FET devices were fabricated. In the previous conventional fabrication method for FET, rGO solution is dropped onto a SiO\(_2\) substrate. Before the deposition of metal electrodes on rGO sheets, photolitography or e-beam lithography has to be utilized to design a metal electrode.\(^\text{22}\) It is difficult, however, to find the location of rGO due to coated photoresists, so this method requires a great deal of effort to design electrodes. To simplify the complicated fabrication process of FETs, we first make gold electrodes and then SAMs on the electrode. Alkanthiol has usually been used for SAM on gold electrodes due to the strong affinity between sulfur and gold.\(^\text{23}\) In this study, we use carboxylic acid and amine-terminated SAMs, which have a negative and positive charge, respectively. Finally, a thin layer of GO sheets can be easily deposited on the Au electrode through the electrostatic attractions between the charged SAMs and the charged GO sheets.

The pre-patterned electrodes are defined on SiO\(_2\)/Si (300 nm thick SiO\(_2\) layer on a highly-doped p-type Si(100)) substrates by addressing Cr (5 nm)/Au (30 nm) electrodes by using a conventional photolithography process (Figure 2.3.2(a)). The channel length between the source and drain electrodes was 4 \(\mu\)m. Negatively charged SAMs were formed on the Au electrodes to attach \(+\text{GO}\). 12-Mercaptododecanoic acid (MDA) was used for negatively charged SAMs due to the desorption of carboxylic acid. Pre-patterned electrode was immersed into 1 mM MDA ethanol solution for 24 h (Figure 2.3.2(b)). When the electrode was in the MDA solution, the MDA molecules were diffused and attached to the Au electrode due to the strong affinity between sulfur and gold. As time passed, tail
groups became straight-ordered.\textsuperscript{23,24} Then, the electrode with SAMs was immersed into 0.1 M NaOH solution (pH 12.3) for 30 min to make the SAMs negatively charged. The resulting SAM-treated electrodes were repeatedly rinsed in ethanol and water and were dried under N\textsubscript{2} gas. The SAM-treated electrode was immersed into amine-functionalized GO (+GO) solution for 1 h. +GO was spontaneously deposited on the electrode by electrostatic attraction with negatively charged electrodes.\textsuperscript{25} Finally, +GO was reduced by hydrazine vapor at 80 °C to be converted into +rGO.\textsuperscript{14} (See XPS and Raman data for GO and rGO sheets before and after reduction in Figure 2.3.3 ~ 2.3.6.) In the last step, annealing in vacuum at 200 °C for 1 h was performed to remove SAMs on the electrode. For negatively charged rGO FET, 1-aminoo11-undecathiol (AUT) was used as a NH\textsubscript{2}-terminated thiol (Figure 2.3.2(c)). The pre-patterned electrode was immersed in a 1 mM AUT ethanol solution for 24 h. The AUT-treated electrode was then soaked in 0.1 HCl (pH 1.3) solution for 30 min to form positively charged SAMs. Then the resulting substrates were repeatedly rinsed in ethanol and water and were dried under N\textsubscript{2} gas. The following steps for rGO-FET are the same as the above procedures for +rGO FET. 88 devices out of total 96 devices showed adsorption of –GO sheets connecting two Au electrodes by using the electrostatic attraction in this paper. This result indicates that successful rate in the device fabrication with –GO by using this method is 91 %. In case of device fabrication with +GO sheets, the successful devices out of total 64 devices were 52 (81 %). We employed X-ray photoelectron spectroscopy (XPS) to identify SAMs. The XPS results of the AUT-treated and MDA-treated Au substrates are shown in Figure 2.3.6. The important determinant is the existence of sulfur. The spectrum of S 2p binding energy for 11-AUT SAM showed two major components at 162.5 eV and 168.5 eV. These peaks indicate the formation of a thiolate intermediate. This indicates that the primary interaction in the monolayer is via a Au-S bond with the loss of the thiolic hydrogen.\textsuperscript{26,27}
Figure 2.3.2. Scheme for the fabrication of +rGO and −rGO FETs. (a) Pre-patterned Au/Cr (30/5 nm) electrode. (b) Fabrication procedure of + rGO FET using MDA SAM. (c) Fabrication procedure of − rGO FET using AUT SAM.
Figure 2.3.3. XPS spectra of –GO (a) and –rGO (b) after reduction: survey and C1s spectra.
Figure 2.3.4. XPS spectra of (a) +GO and (b) +rGO after reduction: survey and C1s spectra.
Figure 2.3.5. Raman spectra of −GO and +rGO (a) and +GO and +rGO (b).
Figure 2.3.6. XPS spectra (S 2p binding energy region) for AUT (a) and MDA (b).
Figure 2.3.7. AFM images of rGO sheets between two electrodes in FET devices.
2.3.4.3 Effect of SAMs to the electrical properties of rGO

Figure 2.3.8 shows SEM images with and without MDA SAMs. +GO sheets were adsorbed on the MDA-treated electrode, as shown in Figure 2.3.8a. Some +GO sheets form a channel between two electrodes. However, +GO sheets were not observed on the electrode without MDA. (Figure 2.3.8(b)) We could observe the difference between SAM-treated electrodes and the bare electrodes. The height of rGO sheets between electrodes in FET devices was analyzed by AFM which revealed that the height of the rGO sheets was in the range of 0.3 ~ 10 nm. (Figure 2.3.7) Although the layer number of +rGO in each FET is not same, their electrical properties show n-doped effect, with Dirac point at negative voltage, independent of the number of layers of rGO sheets. (See the electrical properties data in Figure 2.3.9)

As mentioned earlier, the SAMs should be removed for the electrical measurement of rGO in the fabricated FET. SAMs may induce contact resistance between the electrode and rGO. The effect of the SAMs on the electrical characteristics was actually observed in the I-V curve. The I-V curve for +rGO FET with MDA SAMs before annealing shows a behavior like Schottky contact (Figure 2.3.10(a)). The I-V curve like Schottky contact is supposed to be due to the formation of a barrier by SAM between the gold electrode and +rGO. On the other hand, thermal annealing in vacuum was performed at 200 °C for 1 h to remove SAMs. Schlenoff et al. reported the thermal stability for desorption of formed SAMs on metal. Complete desorption of sulfur from gold was achieved at 200 ~ 210 °C. Therefore, the I-V curve was measured after thermal annealing to prove the removal of SAMs from the electrode. Surprisingly, the I-V curve was like ohmic contact (Figure 2.3.10(b)). This result indicates that SAMs can be effectively removed via thermal treatment in vacuum. In addition, the current level is significantly increased after the annealing. The SAMs increased the contact resistance between the electrode and +rGO and reduced the current level. However, the current level is increased by removing SAMs through thermal treatment. For –rGO FETs, the same trend was observed (Figure 2.3.11).

To determine if the change in the I-V curve (Schottky or ohmic contact and current increase after annealing) was caused by the presence of SAMs, a +rGO FET without SAMs was fabricated as a control experiment. As described above, an electrode was placed on an 80 °C hot plate, and a +GO solution was dropped onto it a few times because it is difficult to make the device without SAMs by immersing the pre-patterned electrode in +GO solution. The device was reduced by hydrazine vapor, as above method. Figure 2.3.12 shows the SEM image of the device and the I-V curves before and after annealing. The current level before thermal annealing was slightly higher than that after annealing. The p-doping effect was induced because the water and oxygen molecules were adsorbed on +rGO before annealing. However, the p-doping effect was reduced when the adsorbed species were removed by annealing,
which caused the decrease of the current level. Unlike the device with SAMs, both I-V curves before and after annealing showed ohmic contact. These results demonstrate that I-V curves are changed by the presence of SAMs, and prove that SAMs influence the electrical properties.

2.3.4.4 Electrical property of positive charged graphene

The +rGO FET was placed in vacuum to remove the influence of oxygen and water molecules before electrical characterization. Figure 2.3.9 shows I-V_g curves of +rGO and −rGO with SEM images of devices. The Dirac point (the gate dependence of minimum conductivity) of −rGO appeared near V_g = 0 V (Figure 2.3.9(a)). However, the Dirac point of amine-functionalized +rGO appeared at V_g = −40 V. This result shows a large negative shift compared to −rGO, indicating n-doping effect in +rGO. The shift of Dirac point is related to molecules with electron donating groups. The n-type doping drives the Dirac points below the Fermi level. The amine groups functionalized at the end of the graphene oxide served as an electron donor and transformed rGO into n-doped rGO. (See Table 2.3.2 for average values of the Dirac points of −rGO and +rGO FET devices) In addition to the shift of the Dirac point, FET devices fabricated by the present method exhibited high mobility of charge carriers. The maximum value in mobility of −rGO was 27.5 cm²/Vs for electron and 82.5 cm²/Vs for hole. Furthermore, the average mobility of −rGO FET was estimated to be 14.9 cm²/Vs for electron and 43.6 cm²/Vs for hole for five FET devices. (See Table 2.3.2) Note that transistors with rGO sheets with regular shape and suitable size were used for convenient mobility calculation. It has been reported that typical values of mobility of −rGO ranged between 0.001 and 10 cm²/Vs, depending largely on film thickness and reduction conditions. However, some reports showed relatively high mobilities: hole mobilities of 10 – 30 cm²/Vs in FETs with solvothermal reduction treatment and hole mobility of maximum 95 cm²/Vs in FETs with films made of large rGO sheets. We compared mobility values in this study with those in other studies in Table 2.3.3. It should be noted that the mobility value is dependent on the reduction method and film thickness (sheets or film). The comparison in Table 4.3 indicated that the mobility in our study is very high. Furthermore, we for the first time presented results of FET devices with amine-functionalized rGO (+rGO) by covalent boning. The mobility of electrons and holes in +rGO devices was lower by about 1–2 orders of magnitude than that in −rGO devices. The maximum mobilities of electron and hole were 1.8 and 6.7 cm²/Vs, respectively. The average mobility for +rGO devices was 0.6 cm²/Vs for electron and 2.1 cm²/Vs for hole, respectively. The electrical phenomena of n-type doped behavior in +rGO FETs are reproducible (six FET devices were made and characterized) with the average Dirac point shift of −21.6 V in Table 2.3.3. The reduction of carrier mobility in +rGO is believed to be due to amine groups as scattering centers. Another possible reason for the mobility decrease of +rGO is more functional groups and defects through complicated steps.
when we synthesize +rGO.
Figure 2.3.8. SEM images of FET with (a) and without SAM (b). The pre-patterned electrode with MDA was immersed into +GO for 2 h (a). The electrode without MDA was immersed into +GO for 2 h (b).
Figure 2.3.9. $I_{ds}$-$V_g$ curves of -rGO (a) and +rGO (b) in vacuum. The bias voltage, $V_{ds}$, was 0.1 V. The inset shows the SEM images of FET.
Figure 2.3.10. $I_d$-$V_d$ curves of +rGO before (a) and after annealing at 200 °C (b).
Figure 2.3.11. I-V curve of -rGO before (a) and after annealing at 200 °C (b).
Figure 2.3.12. I-V curve of + rGO without SAM in FET device in ambient. The electrode was placed on 80 °C hot plate, and a + GO solution was repeatedly dropped onto it a few times. The inset image shows a SEM image of FET device.

<table>
<thead>
<tr>
<th></th>
<th>Electron (cm²/Vs)</th>
<th>Hole (cm²/Vs)</th>
<th>Dirac point (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-rGO</td>
<td>14.9ᵃ</td>
<td>43.6ᵃ</td>
<td>2.5ᵃ</td>
</tr>
<tr>
<td>+rGO</td>
<td>0.6ᵇ</td>
<td>2.1ᵇ</td>
<td>-21.6ᵇ</td>
</tr>
</tbody>
</table>

ᵃaverage values for five -rGO devices.
baverage values for six +rGO devices.
### Table 2.3.3. Comparison of mobility values for –rGO FETs in other reports

<table>
<thead>
<tr>
<th>Reference</th>
<th>Hole mobility (cm²/ V·s)</th>
<th>Electron mobility (cm²/ V·s)</th>
<th>Reduction method</th>
<th>Scheme of device</th>
<th>Measurement</th>
<th>Sample type</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Nat. Nanotech</em> 2008, 3, 270</td>
<td>1 (average)</td>
<td>0.2 (average)</td>
<td>Hydrazine vapor reduction at 80 °C for 24h and thermal annealing at 200 °C</td>
<td>Vacuum</td>
<td>Film</td>
<td></td>
</tr>
<tr>
<td><em>Adv. mat.</em> 2010, 22, 4872</td>
<td>0.06 (average)</td>
<td>0.015 (average)</td>
<td>Thermal annealing</td>
<td>Ambient</td>
<td>Film</td>
<td></td>
</tr>
<tr>
<td><em>Nanotechnology</em> 2010, 21, 165205</td>
<td>0.25 (average)</td>
<td>0.07 (average)</td>
<td>Hydrazine solution</td>
<td>Ambient</td>
<td>Film</td>
<td>sheets</td>
</tr>
<tr>
<td><em>Nano Lett.</em> 2010, 10, 92</td>
<td>5.4 (maximum for single layer)</td>
<td>1.1 (maximum for single layer)</td>
<td>Thermal annealing at 1000 °C</td>
<td>Ambient</td>
<td>Film</td>
<td></td>
</tr>
<tr>
<td><em>Phys. Chem. Chem. Phys.</em> 2010, 12, 2164</td>
<td>1.5 ~ 3.5</td>
<td>-</td>
<td>Thermal annealing at 1000 °C</td>
<td>Ambient</td>
<td>sheets</td>
<td></td>
</tr>
<tr>
<td><em>ACS nano</em> 2011, 5, 870</td>
<td>95 (max)</td>
<td>-</td>
<td>Hydrazine solution</td>
<td>Ambient</td>
<td>film</td>
<td></td>
</tr>
<tr>
<td>This study (–rGO)</td>
<td>43.55 (average)</td>
<td>14.91 (average)</td>
<td>Hydrazine vapor reduction at 80 °C for 24h</td>
<td>Vacuum</td>
<td>sheets</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82.5 (max)</td>
<td>27.54 (max)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This study (+rGO)</td>
<td>2.07 (average)</td>
<td>0.63 (average)</td>
<td>Hydrazine vapor reduction at 80 °C for 24h</td>
<td>Vacuum</td>
<td>sheets</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.69 (max)</td>
<td>1.82 (max)</td>
<td>The first report on the mobility of n-doped rGO</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.3.5 Conclusion

In summary, we proposed a facile method for the fabrication of rGO FET with self-assembled monolayers (SAMs). The device fabrication was simplified through the electrostatic attraction between an electrode with charged SAMs and a negative or positive GO. Finally, a reduction of GO sheets by hydrazine vapor provided a FET of the negatively or positively charged rGO. The amine groups functionalized at the end of the GO served as an electron donor and transformed rGO into n-doped rGO. Our approach for rGO FET, which provided high mobility of charge carriers, will enable various applications in electronic devices because of the solution process.
2.3.6 References


Part 3: Hybrid Materials of Graphene and TMD and Their Applications

3.1 Introduction of hybrid materials of rGO/TMD for energy applications

2D materials such as hexagonal BN (h-BN) and transition-metal dichalcogenide (TMDs) derived from their bulk crystals have also been developed in recent years due to their promising properties and broad range of applications in, for example, electronics, optoelectronics, catalysis and energy storage devices. Here, we describe various types of hybrid nanomaterials based on rGO/TMD, particularly focusing on their preparation methods and applications in catalysis, energy storage, and electronic/optoelectronic devices.
3.1.1 Synthesis of hybrid materials of rGO/TMD

2D nanomaterials consisting of rGO and TMD have received a considerable amount of attention recently owing to their enhanced performance capabilities. There are a number of advantages of hybrid nanostructures based on rGO/TMD. First, rGO can act as a substrate for the nucleation and growth of TMDs. In addition, the rGO conducting network in rGO/TMD affords rapid electron transport from less conductive TMDs to the electrode during the HER, and strong interaction between GO and TMD can offer an abundance of active adsorption sites on hybrid materials. As a result, high performance can occur in the HER. Furthermore, GO can induce changes in the chemical composition and morphology according to the composition.

To date, rGO/TMD nanomaterials including CdS, CdSe, CdTe, MoS$_2$, WS$_2$, PbS, and ZnS have been synthesized. Generally, the hydrothermal method is most commonly used to synthesize rGO/TMD hybrid materials. For example, MoS$_2$/rGO, which is best known for rGO/TMD can be easily synthesized by a solvothermal method with (NH$_4$)$_2$MoS$_4$ and hydrazine in a N,N-dimethylformamide (DMF) solution of GO. Similarly, a hydrothermal reaction is almost always used to synthesize MoS$_2$/rGO through Na$_2$MoO$_4$·2H$_2$O for metal precursor and NH$_2$CSNH$_2$ or L-cysteine for the S precursor.

As another approach, the stacking of different 2D nanosheets, with unusual properties and new phenomena to be explored, has drawn much attention. 2D hybrid-nanosheets can be prepared through the vacuum filtration of a mixed solution with exfoliated MoS$_2$ and GO sheets. In addition, tri-hybrid materials have also been demonstrated for diverse applications. For example, MoS$_2$/rGO composites were synthesized for further deposition of TiO$_2$ nanoparticles to prepare the TiO$_2$/MoS$_2$/rGO hybrids were prepared by a hydrothermal method. They show good photocatalytic activities under visible light due to a broadened optical window for effective light harvesting and a short diffusion optical window for excellent charge transport. Recently, Mo$_2$N, Mo$_2$C, and MoS$_2$ catalysts supported on CNT–RGO hybrids were prepared by a modified urea glass route for counter electrodes in QDSSCs.

The preparation of other types of TMD on rGO has recently been realized. For example, MoSe$_2$/rGO could be obtained by the hydrothermal reaction of Na$_2$MoO$_4$ and hydrazine hydrate-Se in distilled water. Hydrazine was used as a reductant for Se. We also demonstrated for the first time a WS$_2$/rGO via hydrothermal reaction. We showed that WS$_2$ nanosheets can be selectively fabricated using tungsten chloride and thioacetamide precursors. This will be discussed in section 3.3 in detail.
Wang et al. also demonstrated WS$_2$/rGO composites prepared by the hydrothermal reaction of tungsten chloride and cysteine for sodium ion batteries. Lee et al. demonstrated n-doped graphene and few-layer WS$_2$ via surfactant-assisted synthesis under hydrothermal conditions. The effects of the surfactant amount on the number of WS$_2$ layers were investigated and the performance of layered composites as high-energy density lithium-ion battery anodes was evaluated. As a similar strategy, ZnSe NPs on n-doped graphene sheets were demonstrated by a one-pot hydrothermal process, where [ZnSe](diethylenetriamine)$_{0.5}$ nanobelts acted as not only the precursor for the preparation of ZnSe NPs but also the nitrogen source for doping GO.

3.1.2 Application of rGO/TMD for energy application

Lithium-ion batteries are one of the most promising rechargeable battery systems. The main issue is the aggregation and structural deterioration of nanostructured electrodes during the charge/discharge process at the lithium-insertion reaction. Graphene hybrids with the excellent conductivity and high surface areas have been employed as supporting materials to overcome these problems. Recently, the application of TMDs, especially MoS$_2$, in LIBs has gained attention, and improved energy storage performance has been realized using hybrid nanostructured electrodes. MoS$_2$ sheets have been combined with graphene nanosheets for improved conductivity and stability. Such hybrid materials can be obtained by the methods mentioned above. For example, the electrochemical performances of the MoS$_2$/rGO composites to their robust composite structure as well as the synergistic effects between layered MoS$_2$ and graphene have been demonstrated. Layered MoS$_2$/rGO composites were synthesized by a hydrothermal method with subsequent annealing applied in a H$_2$/N$_2$ atmosphere at 800 °C for 2 h. The layered MoS$_2$ is supported on the graphene surface, which then form MoS$_2$/rGO composites. The MoS$_2$/rGO materials exhibit a 3D architecture morphology consisting of curved nanosheets, which are attributed to the self-assembly of graphene hydrogel during the hydrothermal process. This structure, with a large exposed surface area possesses a short diffusion distance for the Li$^+$ ions and a large electrode-electrolyte contact area for the flux of Li$^+$ ions across the interface leading to an enhanced rate capability. In addition to the high specific capacity, the composites showed excellent cyclic stabilities.

A layered WS$_2$/rGO composites prepared by a hydrothermal methods with an appropriated amount of CTAB surfactant showed a high specific capacity of 905 mAhg$^{-1}$ at 100 mAg$^{-1}$, excellent cycleability (average of 0.08 % capacity fading per cycle for 100 cycles), and rate performance (20% capacity reduction with a 50-fold increase in the current density from 100 mAg$^{-1}$ to 5000 mAg$^{-1}$). The efficient transport of electrons and Li through the composite can occur due to the curvature in the porous structure. In addition, sodium ion batteries can be constructed using TMD/rGO hybrid materials. Layered
MoS₂/rGO prepared by the vacuum filtration of a mixed solution of MoS₂ and GO was evaluated as a counter electrode in a Na-ion battery. The electrode showed good Na cycling ability with a stable charge capacity of approximately 230 mAhg⁻¹. Static uniaxial tensile tests performed on crumpled composite papers showed a high average strain to failure rate which reached approximately 2%. When applied as anodes in Na-ion batteries, WS₂/rGO exhibited a high reversible sodium storage capacity of about 590 mAhg⁻¹. Some examples of TMD-based hybrid electrodes for alkali metal batteries are listed in Table 3.1.1.

To date, Pt-group metals have been utilized as the most effective electrocatalysts for hydrogen evolution reactions in an acidic medium. However, their low abundance and high cost considerably limit the large-scale application of Pt-based catalysts. Recently, great efforts have been made to explore efficient non-noble catalysts. A few successful examples were shown, including MoS₂, MoSe₂, WS₂, Mo₂C, Ni₂P, and Co₀.₆Mo₁.₄N₂. Some layered TMDs, such as MoS₂ and WS₂ are well-known electrocatalysts and have drawn much attention due to their good catalytic properties for HER. The excellent conductivity and large specific surface area of graphene make it an attractive matrix for the synthesis for hybrid materials for electrocatalytic reactions. Therefore, improved performance can be observed when using composites of rGO/TMD. The electrocatalyst for rGO/TMD will be discussed in section 3.2. Due to their low cost and good photostability, chalcogenide materials have been considered the suitable photocatalysts for environmental applications. Hybrid materials are important in photocatalysis, as a single-component catalyst may not be able simultaneously to meet the numerous requirements of high-performance photocatalysis (i.e., broad visible light adsorption, a large specific surface area, effective electron-hole pair generation and minimized charge carrier recombinations). Therefore, hybrid materials have been explored for photocatalysts. As examples, CdS functionalized graphene for visible-light-driven photocatalytic H₂ production has been demonstrated. A high H₂-production rate (1.12 mmol h⁻¹) which is about 4.87 times that of pure CdS NPs, has been achieved. Yu et al. reported that a ZnSe NP-decorated N-doped graphene composite showed superior activity for the decomposition of methyl orange (MO) under visible-light irradiation. Hou et al. demonstrated a 2D porous g-C₃N₄ nanosheet/nitrogen-doped graphene/layered MoS₂ (CNNS/NRGO/MoS₂) ternary nanojunction. CNNS with a large surface area can absorb visible light, together with the layered MoS₂, to enhance light absorption and generate more photoelectrons. The charge separation and transfer were improved at the CNNS/MoS₂ interface, where the NRGO worked as an the electron mediator for shuttling electron-holes between CNNS and MoS₂ sheets. Some of the recent trends are summarized in Table 3.1.1.
Figure 3.1.1. (a) 2D hybrid nanosheets can be prepared through vacuum filtration of mixed solution with exfoliated MoS$_2$ and GO sheets.\textsuperscript{11} (b) Tri-hybrid materials of Mo$_2$N, Mo$_2$C, and MoS$_2$ catalysts supported on CNT–RGO hybrid.\textsuperscript{13}
Table 3.1.1. Recent trend of two-dimensional hybrid materials based on graphene

<table>
<thead>
<tr>
<th>Reference</th>
<th>Materials</th>
<th>Structure</th>
<th>Method</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACS Nano</td>
<td>MoS$_2$/rGO</td>
<td>2D</td>
<td>Vacuum filtration with acid-treated MoS$_2$ flakes and GO</td>
<td>Sodium-ion battery</td>
</tr>
<tr>
<td>2014, 8, 1759</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2013, 3, 839</td>
<td>graphene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J. Solid State Sci. Technol.</td>
<td>MoS$_2$/rGO</td>
<td>2D</td>
<td>Vacuum filtration with MoS$_2$ and GO sheets</td>
<td>Li-ion battery</td>
</tr>
<tr>
<td>2013, 2, M3034</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Int. J. Hydrogen. Energ.</td>
<td>MoS$_2$/rGO</td>
<td>2D</td>
<td>Hydrothermal method</td>
<td>Supercapacitor</td>
</tr>
<tr>
<td>2013, 38, 14027</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J. Phys. Chem. C</td>
<td>MoS$_2$/rGO</td>
<td>2D</td>
<td>Hydrothermal method</td>
<td>Photocatalyst</td>
</tr>
<tr>
<td>2012, 116, 25415</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J. Am. Chem. Soc.</td>
<td>MoS$_2$/rGO</td>
<td>0D-2D</td>
<td>Solvothermal method</td>
<td>Electrocatalyst</td>
</tr>
<tr>
<td>2011, 133, 7296</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanoscale</td>
<td>MoS$_2$/rGO</td>
<td>2D</td>
<td>Hydrothermal method</td>
<td>Mg battery</td>
</tr>
<tr>
<td>2013, 5, 9562</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2014, DOI:10.1002/aenm.201300775</td>
<td>CNT-graphene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J. Mater. Chem. A</td>
<td>MoSe$_2$/rGO</td>
<td>2D</td>
<td>Hydrothermal method</td>
<td>Electrocatalyst</td>
</tr>
<tr>
<td>2014, 2, 360</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2014, 49, 204</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Journal</td>
<td>Material</td>
<td>Dimension</td>
<td>Synthesis Method</td>
<td>Application</td>
</tr>
<tr>
<td>-----------------------</td>
<td>------------</td>
<td>-----------</td>
<td>------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td><em>Chem. Comm.</em> 2014, DOI:10.1039/C4CC00840E</td>
<td>WS$_2$/rGO</td>
<td>2D</td>
<td>Hydrothermal method</td>
<td>Sodium-ion battery</td>
</tr>
<tr>
<td>Nanoscale 2013, 5, 7890</td>
<td>WS$_2$/rGO</td>
<td>2D</td>
<td>Hydrothermal method</td>
<td>Li+ storage</td>
</tr>
</tbody>
</table>
3.1.3 References


3.2. Transition metal dichalcogenide for hydrogen evolution reaction

3.2.1 History of hydrogen evolution reaction for TMD

The development of new catalysts for use in renewable H\textsubscript{2} production has attracted much interest because H\textsubscript{2} is regarded as an important energy carrier for the future.\textsuperscript{1,2} An efficient H\textsubscript{2} evolution catalyst needs to have a high current density and be low cost, in addition to requiring excellent stability.\textsuperscript{3} Although the most effective catalyst is well known to be Pt, which has zero overpotential, this precious metal is prohibitively expensive to use commercially. Therefore, the synthesis of new catalysts that are high in abundance and are low cost remains a significant challenge.\textsuperscript{4}

The application of bulk transition metal dichalcogenides (TMDs) for H\textsubscript{2} evolution has been ignored for a long time owing to their poor activity (Tafel slope of 692 mV/dec and onset potential of around −0.09 V vs. RHE for bulk MoS\textsubscript{2}).\textsuperscript{5} However, these materials, in particular 2D MoS\textsubscript{2} and WS\textsubscript{2} nanosheets, are starting to gain attention for use as catalysts for the HER, alongside the explosive interest in graphene and other 2D materials.\textsuperscript{6,7,9} TMDs exhibit a variety of polymorphs.\textsuperscript{6} Their band-gap can be tunable, and the exfoliated sheets can gain metallic properties on a change in phase.\textsuperscript{10} MoS\textsubscript{2} and WS\textsubscript{2} with a 2H phase are mainly semiconducting, but can change to a metallic 1T phase by exfoliation with Li intercalation. Consequently, research regarding the diverse properties of TMDs with variable structures and morphologies is highly important, and the catalytic activity of these materials for the HER needs to be explored further. This chapter deals with the progress that has been made concerning the synthetic methods used to prepare 2D MoS\textsubscript{2} and WS\textsubscript{2} nanosheets, and their resulting catalytic activity. Furthermore, we summarize the key factors that affect the HER activity of TMDs, and afterwards discuss the reasons behind the high catalytic activity of 2D MoS\textsubscript{2} and WS\textsubscript{2} nanosheets.

3.2.2 Synthesis of layered TMDs

2D layered TMDs are attractive for use in next generation nanoelectronic devices, energy storage devices, and as catalysts.\textsuperscript{6,11} MoS\textsubscript{2} and WS\textsubscript{2} are typical examples of layered TMDs, forming vertically stacked, weakly interacting layers held together by van der Waals interactions, similar to graphite. 2D thin layers can be extracted using the same methods as are used to produce graphene sheets, namely, mechanical exfoliation with scotch tape and chemical exfoliation.\textsuperscript{10-13} In addition, MoS\textsubscript{2} films can be grown by CVD, using precursors such as MoO\textsubscript{3} and S powder.\textsuperscript{14-17} Another method used to prepare 2D MoS\textsubscript{2} sheets is via a hydrothermal reaction involving Na\textsubscript{2}MoO\textsubscript{4} and SC(NH\textsubscript{2})\textsubscript{2}.\textsuperscript{18,19} In the chemical exfoliation method, 2D MoS\textsubscript{2} sheets can be prepared via liquid exfoliation in a solvent by direct sonication, Li intercalation with n-BuLi, or lithiation by electrochemical reaction.\textsuperscript{12,13} An interesting feature of Li intercalation is the change from semiconducting 2H phase MoS\textsubscript{2} to the metallic 1T phase.
Electron transfer from Li to the transition metal during intercalation leads to destabilization of the original crystal structure. Li-intercalated MoS$_2$ tends to adopt a more stable octahedral coordination.$^{20}$ The transformation from 2H to 1T significantly affects the catalytic activity for the HER, which will be discussed further in chapter 3.2.3.

Similar to MoS$_2$, 2D WS$_2$ sheets can be prepared by mechanical or chemical exfoliation of bulk WS$_2$, and CVD, whereby the WS$_2$ thin films are synthesized from precursors such as WOCl$_4$ and H$_2$S(CH$_2$)$_2$SH at 200–600 °C.$^{8,21}$ WS$_2$ sheets also exhibit metallic properties by interaction with Li (Fig. 3.2.1(a)).$^8$ In addition, WS$_2$ sheets can be synthesized from 1D W$_{18}$O$_{49}$ with the assistance of a surfactant via the rolling-out method (Fig. 3.2.1(b)).$^{22}$ Wang’s group mixed WO$_3$ and S by ball milling, placed the ball-milled mixture into a tube furnace, and heated it at 600 °C in an Ar atmosphere, resulting in the formation of sheet-structured WS$_2$ powder (Fig. 3.2.1(c)).$^{23}$ WS$_2$ sheets were also synthesized using a solid state reaction with WO$_3$·H$_2$O and SC(NH$_2$)$_2$ at 773 K in a N$_2$ atmosphere.$^{24}$ On the other hand, the use of a hydrothermal reaction to form WS$_2$ sheets was recently reported by our group.$^{25}$ This synthetic procedure has generally been difficult to achieve, although the specific reasons for this are not completely clear. One possible reason is that, because the synthesis involves sulfurization of an intermediate, the structure of the final WS$_2$ product may follow the structure of this intermediate. In general, the hydrothermal reaction first gives the intermediate, WO$_3$, with a 0D or 1D structure, and this is then sulfurized to produce the WS$_2$ product.$^{17,26}$ The structure of WO$_3$ therefore appears to remain in the form that it is in during the sulfurization. Recently, our group reported the preparation of WS$_2$ and WS$_2$/reduced graphene oxide (rGO) hybrid sheets via a one-pot process using a hydrothermal reaction at low temperature.$^{25}$ WS$_2$ sheets were selectively synthesized using WCl$_6$ and CH$_3$C(S)NH$_2$ as starting materials, and the WS$_2$/rGO hybrid sheets were then produced simply by adding GO sheets (Fig. 3.2.1(d)).
Figure 3.2.1. (a) Exfoliated WS$_2$ nanosheets by Li intercalation$^6$; (b) 2D WS$_2$ nanosheet formation through rolling-out shape-transformation processes of 1D W$_{18}$O$_{49}$ nanorods$^{22}$; (c) scheme for the formation of WS$_2$ nanosheets by ball milling$^{23}$; and (d) WS$_2$ sheets formed through a hydrothermal method.$^{25}$
3.2.3 Factors affecting HER

The first report on HER activity of bulk MoS\(_2\) was published in 1977.\(^5\) This material exhibited an onset potential at approximately \(-0.09\) V vs. RHE, and a Tafel slope of 692 mV/dec, but was considered to be an inefficient catalyst because of the large internal resistance in the bulk structure of the semiconductor.\(^5,27\) However, advancement in the HER catalyzed by TMDs has recently been achieved. Hinnemann \textit{et al.} calculated the free energy of H adsorption on MoS\(_2\) edge sites by density function theory (DFT), and found that it was close to the free energy of H adsorption on both hydrogenase and Pt,\(^28\) thus, the edges of MoS\(_2\) were considered as active sites in catalysis for H\(_2\) evolution. This was experimentally verified by Chorkendorff’s group in 2007, where MoS\(_2\) nanoparticles were produced on Au (111) through physical vapor deposition of Mo in H\(_2\)S under UHV conditions, and were estimated to show an onset potential of around \(-0.15\) V vs. RHE and a Tafel slope of 55–60 mV/dec.\(^29\) They also exhibited an exchange current density proportional to the length of edge sites, demonstrating that the edges of the MoS\(_2\) were highly catalytically active, while no correlation with the surface area of MoS\(_2\) was seen. This result was totally different from that observed for the HER in bulk MoS\(_2\). As the catalytic activity was found to be greatest at the edges of the MoS\(_2\), three approaches to improve the performance of the HER have been primarily explored. The first of these involves enhancement of the intrinsic catalytic activity of TMDs. This has been carried out by doping MoS\(_2\) with Co.\(^30\) This metal is often used to promote MoS\(_2\) in catalyzing the hydrosulfurization reaction.\(^31\) DFT calculations showed that Co-doped MoS\(_2\) had a lower binding energy for H at the S-edges (\(\Delta G_H\) decreased to 0.10 eV from 0.18 eV for undoped MoS\(_2\)), showing that the S-edges could contribute to the HER and are therefore additional active sites (Fig. 3.2.2(a)).\(^30\) The edges of MoS\(_2\) are composed of S-edges (S-terminated, (- 1010)) and Mo-edges (Mo-terminated, (10-10)). Mo-edges with adsorbed S dimers are the dominant structure of MoS\(_2\) nanoparticles given in Refs. 32 and 33. In general, Mo-edges (\(\Delta G_H = 0.08\) eV) are more effective for the HER than the S-edges (\(\Delta G_H = 0.18\) eV).\(^34\) In case of WS\(_2\), the Co promotion induced the creation of active sites with higher activity that that prior to the promotion.\(^30\)

The second approach is to increase the number of active sites of the catalyst. The research groups of Jaramillo and Cui demonstrated excellent HER activity by controlling the surface properties of MoS\(_2\) (Fig. 3.2.2(b)). In 2012, Jaramillo and co-workers engineered the surface structure of MoS\(_2\) to preferentially expose edge sites.\(^35\) They synthesized a highly ordered double-gyroid MoS\(_2\) bicontinuous network with nanoscale pores. The double-gyroid MoS\(_2\) structure was synthesized by electrodeposition of Mo into a porous silica template, followed by sulphidization with H\(_2\)S. The basal plane of MoS\(_2\) has a limited number of active sites at the surface; however, this can be overcome by changing the surface structure. The high surface curvature of this catalyst exposed a large fraction of edge sites, leading to
excellent activity with an onset potential of −0.2 to −0.15 V vs. RHE and a Tafel slope of 50 mV/dec for the HER. In addition, Cui’s group produced MoS\textsubscript{2} and MoSe\textsubscript{2} films with vertically aligned layers that maximally exposed the edges on the film surface. The MoS\textsubscript{2} films were synthesized from e-beam evaporated, ultrathin Mo films using a rapid sulfurization/selenization process in a horizontal tube furnace, with elemental S/Se powders used as the precursors. The edge terminated films were expected to maximize catalytic activity for the HER; however, Tafel slopes measured from the films were in the range of 105–120 mV/dec, which were larger than expected. Although it is true that edges of MoS\textsubscript{2} work as active sites, only a quarter of the edge sites were found to be active. Therefore, it is not beneficial to unconditionally increase the number of edges. Chorkendorff and co-workers investigated the activity of MoS\textsubscript{2} on porous C paper. They attempted to increase the quantity of active sites by using an aqueous (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24} solution on C paper; however, the obtained Tafel slope of 120 mV/dec was not adequate. They attributed this poor performance for the HER to transport limitations through the porous network of the C paper.
Figure 3.2.2. (a) Left: ball model of a Mo/WS$_2$ particle exposing both S-edges and Mo/W-edges, right: differential free energies of H adsorption; (b) upper: synthesis procedure and structural model for mesoporous MoS$_2$ with a double-gyroid (DG) morphology; lower images: synthesis setup and as-grown films, and TEM images of MoS$_2$/MoSe$_2$ film produced by rapid sulfurization, clearly showing exposed edges; (c) upper: schematic solvothermal synthesis with GO sheets to afford the MoS$_2$/rGO hybrid, and the Tafel plots with several catalysts; lower: illustration of the synthesis procedures of MoS$_2$/MGF used as an electrocatalyst for the HER.
The third approach to improving the catalytic activity of the HER is to increase electron transport from the active sites to the electrodes. This should overcome the issue of the poor electrical transport of MoS$_2$. One potential strategy for achieving this was developed by Chorkendorff’s group, who synthesized 1D multi-walled MoS$_2$ nanotubes coated on multi-walled carbon nanotubes (MWMoS$_2$@MWCNT). The core/shell structures were expected to have excellent properties due to the high surface area of the conductive MWCNTs in combination with the catalytic activity of the MoS$_2$. However, the obtained Tafel slope (109 mV/dec) was still quite large. This was attributed to limited conduction through the inner layers of the MoS$_2$. To overcome this problem, a graphene-based hybrid was considered as it was speculated that the chemical and electrical coupling effects, the high surface area, and the electrical conductivity of graphene would afford an increase in the activity of the HER. In 2011, Dai and co-workers reported the synthesis of MoS$_2$ on rGO sheets, and demonstrated high HER electrocatalytic activity of the resulting MoS$_2$/rGO material (Fig. 3.2.2(c)). The MoS$_2$/rGO hybrid was synthesized via a solvothermal reaction between (NH$_4$)$_2$MoS$_4$ and N$_2$H$_4$ in GO. During this process, the interaction between MoS$_2$ and graphene resulted in selective growth of highly dispersed MoS$_2$ nanoparticles on the GO, without any aggregation occurring. The uniform dispersion of MoS$_2$ on GO produced an abundance of accessible edges that could serve as active catalytic sites for the HER. The underlying graphene sheets formed an interconnected conducting network that afforded rapid electron transport from the less-conducting MoS$_2$ to the electrodes. With highly exposed edges and excellent electrical coupling to the underlying graphene sheets, the MoS$_2$/rGO hybrid catalyst exhibited excellent HER activity with a small overpotential of ~−0.1 V, large cathodic currents, and a Tafel slope as small as 41 mV/dec. Similarly, Liu’s group synthesized MoS$_2$ nanoparticles on mesoporous graphene foams (MoS$_2$/MGF) that had a high specific surface area and an interconnected conductive graphene skeleton (Fig. 3.2.2(c)). As this structure could allow rapid electron transfer, the MoS$_2$/MGF hybrid exhibited excellent electrocatalytic activity for the HER, with a Tafel slope of 42 mV/dec.
3.2.4 Comparison of amorphous and crystalline TMD

The edges of MoS$_2$ are classed as active sites for the HER in DFT studies because the S atoms at the edges are unsaturated.$^{28}$ As a result, H atoms can adsorb onto these atoms with a small free energy of adsorption. Merki et al. therefore hypothesized that the activity was related to the unsaturated S atom.$^{39}$ Amorphous MoS$_2$ has many defect sites and many coordinately and structurally unsaturated S atoms. This eventually leads to the evolution of H$_2$. Amorphous MoS$_2$ thin films (which can be regarded as MoS$_3$ as the Mo/S ratio as calculated to be 1:2.9 by X-ray photoelectron spectroscopy (XPS)) were obtained by electrodeposition, and an onset potential of $-0.15$ V vs. RHE and a Tafel slope of 40 mV/dec were observed. The HER catalyzed by amorphous MoS$_2$ might be similar to that by the incomplete cubane-type [Mo$_5$S$_4$]$^{4+}$ catalysts reported by Chorkendorff’s group in 2008.$^{40}$ This was considered to be a very efficient catalyst for HER at that time; however, poor stability was a problem. Similarly, MoS$_3$ and MoS$_2$ particles for HER catalysis were reported by Hu and co-workers in 2012.$^{41}$

The acidification of (NH$_4$)$_2$MoS$_4$ was used to prepare amorphous MoS$_3$ particles. These exhibited a highly electrocatalytic HER, with a Tafel slope of 41 mV/dec. More unsaturated S atoms exist in amorphous MoS$_3$ in comparison to highly crystalline MoS$_2$. The unsaturated S atoms in amorphous MoS$_3$ can form S–H bonds, which induce H$_2$ evolution. The same reasoning as above can be applied, where the highly crystalline MoS$_2$ particles have lower HER activity than MoS$_3$ because the number of unsaturated S atoms is diminished. Recently, the importance of effectively increasing the surface area for catalyst loading has been identified as essential for improving electrocatalytic HER efficiency. Hence, Li and co-workers grew graphene sheets on a 3D Ni foam, and then synthesized MoS$_2$ on the surface through thermolysis of (NH$_4$)$_2$MoS$_4$ at 100–300 °C.$^{42}$ Interestingly, the amorphous MoS$_x$ (stoichiometrically close to Mo$_2$S$_3$) obtained at lower temperatures such as 120 °C showed the best electrocatalytic activity, with an onset potential of $-0.141$ to $-0.109$ V vs. RHE and a Tafel slope of 42.8 mV/dec. Using XPS, they estimated that the amorphous state was more active than crystalline MoS$_2$. They also speculated that the higher HER activity was related to the presence of bridging S$_2^2$ or apical S$_2$ in the amorphous state.

Li and co-workers investigated the HER activity of MoS$_2$ and WS$_2$ on carbon cloth according to the crystallinity of the TMD.$^{50}$ Interestingly, amorphous MoS$_2$ exhibited more activity than its crystalline analog, whereas, WS$_2$ gave the opposite result. In case of WS$_2$, the highly crystalline material showed good activity, with a Tafel slope of 68 mV/dec; however, the exact reason for this has not yet been reported.$^{43}$
3.2.5 Hydrogen evolution reaction of 2D TMD

In order to achieve improved electrochemical performance, 2D TMD sheets are expected to be the most advantageous electrode materials due to their large surface areas. Furthermore, ultrathin structures have become important when attempting to improve electrical contact with the electrode. Therefore, the exfoliation of layered TMDs has received much attention. Zhang and colleagues have become pioneers in the field of TMD exfoliation by lithiation for electrochemical reactions. They reported the catalytic activity of 2D MoS$_2$ nanosheets and metal nanoparticle (Pt, Pd, and Ag) decorated MoS$_2$ sheets (Fig. 3.2.3(a)), and found that the metal nanoparticles had mainly (111) and (101) orientations on the MoS$_2$ surface. In addition, The MoS$_2$ sheets gave a Tafel slope of 94 mV/dec, and Pt-MoS$_2$ hybrid sheets showed much higher electrocatalytic activity (Tafel slope of 40 mV/dec) towards the HER. They explained that the exposed facets of the Pt nanoparticles on MoS$_2$ could provide effective adsorption of H intermediate species, which is thought to be important for activation of the HER. The exfoliated MoS$_2$ sheets used consisted of co-existing 2H and 1T phases, and thus the HER performance was not dramatically enhanced. Recently, Jin’s group reported the activity of 1T-MoS$_2$ nanosheets by intercalation of n-BuLi for HER (Fig. 3.2.3(b)). They synthesized flower-like MoS$_2$ nanosheets with a high density of exposed edges directly on graphite substrates via CVD. The MoS$_2$ nanosheets were exfoliated in n-BuLi solution to convert the as-grown semiconducting 2H-MoS$_2$ into the metallic 1T-MoS$_2$ nanosheets. Interestingly, 1T-MoS$_2$ nanosheets after exfoliation with Li intercalation had dramatically improved HER activity. The structure of the flower-like MoS$_2$ nanosheets provided a high density of exposed edges, and the 1T-MoS$_2$ sheets exhibited a decreased charge transfer resistance relative to the as-grown MoS$_2$ nanostructures. This system demonstrated improved electrode kinetics and better electrical transport, providing a Tafel slope of 43 mV/dec. Xie’s group reported defect engineering of the MoS$_2$ basal plane to expose active edge sites. They successfully employed a scalable method for MoS$_2$ ultrathin nanosheets via a hydrothermal reaction that involved a high concentration of precursors and different amounts of SC(NH$_2$)$_2$, obtaining controllable defect modulation in the MoS$_2$ nanosheets. Although the basal plane of MoS$_2$ is more stable than the edges, the abundant defects on the MoS$_2$ basal plane could lead to an increase in surface area and active edge sites by forming cracks on the sheets. The defect-rich MoS$_2$ nanosheets exhibited HER activity with a small onset overpotential of 120 mV and a Tafel slope of 50 mV/dec. WS$_2$, unlike MoS$_2$, exhibits poor performance for the HER, and so has not been intensively studied. However, recent results concerning the HER are turning attention back to this material. Some reports have demonstrated greatly improved catalytic performance, with an overpotential of $-0.06$ V and a Tafel slope of 72 mV/dec for WS$_2$ sheets synthesized via the ball milling method. Chemical exfoliation is likely to be more suitable for catalyst applications where large quantities of materials are required. Chhowalla’s group reported the performance of exfoliated 1T-
WS₂ sheets (Figure 3.2.4(a)),⁸ and found that when the transformation from the 2H to 1T occurred, the structure became highly distorted. Therefore, the as-exfoliated WS₂ nanosheets included a high proportion of strained metallic 1T phase (Figure 3.2.4(b)). They studied the influence of strain on catalytic activity. Along with increased strain on the 1T phase, the exchange current density increased and the free energy of atomic H adsorption on the surface of distorted 1T-WS₂, calculated through DFT, was close to zero, with a strain value of 2.7%. However, there was no improvement in 2H-WS₂ without strain (Figure 3.2.4(c)). As a result, the exfoliated 1T-WS₂ sheets with metallic phase exhibited an overpotential and Tafel slope of −0.2 to −0.15 V and 60 mV/dec, respectively (Figure 3.2.4(d)). Recently, we were able to synthesize WS₂ and WS₂/rGO hybrid sheets via a hydrothermal method (Figure 3.2.4(e)). The 2H-WS₂ grown on the rGO interconnected conducting network was able to afford rapid electron transport and improved crystallinity after annealing, inducing increased catalytic activity. Therefore, the hybrid material showed excellent HER activity with a small overpotential, and a Tafel slope of 58 mV/dec (Figure 3.2.4(f)). Table 1 and Figure 3.2.5 summarizes the HER performance of a variety of MoS₂ and WS₂ structures.
Figure 3.2.3. Left: HRTEM images of Pt nanoparticles on MoS$_2$; right: Tafel plots of MoS$_2$, Pt-C (Pt nanoparticles on glassy C), and Pt-MoS$_2$.$^{45}$ (b) Left: the structure of 2H-MoS$_2$ and 1T-MoS$_2$; right: polarization curves of chemically exfoliated and as grown MoS$_2$ nanosheets, inset: corresponding Tafel plots.$^7$
Figure 3.2.4. (a) Typical AFM image of individual chemically exfoliated WS\textsubscript{2} nanosheets,\textsuperscript{8} (b) high-resolution STEM images of an as-exfoliated WS\textsubscript{2} monolayer showing regions exhibiting the 1T superlattice, and (c) 2H structures.\textsuperscript{8} The inset in (b) shows the strain tensor map generated from the STEM-HAADF image using peak pair analysis. Light (yellow) and dark (black) colors correspond to regions where the strain is in tension and compression, respectively.\textsuperscript{8} (d) Polarization curves of bulk and as-exfoliated WS\textsubscript{2} (as-deposited film of 1T phase, sub-monolayer as-exfoliated film, and 2H phase after annealing at 300 °C) along with those corresponding to Pt nanoparticles and bulk WS\textsubscript{2} powder for comparison.\textsuperscript{8} (e) TEM images of WS\textsubscript{2}/rGO hybrid nanosheets. The inset shows a magnified image of some folded edges of WS\textsubscript{2} sheets.\textsuperscript{25} (f) Tafel plots of WS\textsubscript{2} sheets and WS\textsubscript{2}/rGO hybrid sheets.\textsuperscript{25}
Table 3.2.1. Catalyst structures, onset overpotentials, and Tafel slopes for different MoS$_2$, WS$_2$, and hybrid materials

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Structure</th>
<th>Onset overpotential (V)</th>
<th>Tafel slope (mV/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$ nanoparticles, ref 29</td>
<td>0D</td>
<td>-0.15</td>
<td>55~60</td>
</tr>
<tr>
<td>Co-promoted MoS$_2$, ref 30</td>
<td>3D structure</td>
<td>-</td>
<td>101</td>
</tr>
<tr>
<td>Mesoporous MoS$_2$, ref 35</td>
<td>3D structure</td>
<td>-0.2~0.15</td>
<td>50</td>
</tr>
<tr>
<td>MWMoS$_2$@MWCNT, ref 4</td>
<td>1D nanotube</td>
<td>-0.2~0.15</td>
<td>109</td>
</tr>
<tr>
<td>1T-MoS$_2$, ref 7</td>
<td>2D nanosheets</td>
<td>-0.187</td>
<td>43</td>
</tr>
<tr>
<td>Defect-rich MoS$_2$ sheets, ref 9</td>
<td>2D sheets</td>
<td>-0.12</td>
<td>50</td>
</tr>
<tr>
<td>MoS$_2$/rGO, ref 37</td>
<td>0D-2D</td>
<td>-0.1</td>
<td>41</td>
</tr>
<tr>
<td>Pt nanoparticle/MoS$_2$, ref 45</td>
<td>0D-2D</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>MoS$_2$ on mesoporous graphene, ref 38</td>
<td>0D-3D</td>
<td>-0.1</td>
<td>42</td>
</tr>
<tr>
<td>Amorphous MoS$_2$ film, ref 39</td>
<td>2D thick film</td>
<td>-0.15</td>
<td>40</td>
</tr>
<tr>
<td>MoS$_x$ on graphene/Ni foam, ref 42</td>
<td>3D structure</td>
<td>-0.15</td>
<td>42.8</td>
</tr>
<tr>
<td>Amorphous MoS$_3$ particles, ref 41</td>
<td>0D nanoparticles</td>
<td>-0.2</td>
<td>41</td>
</tr>
<tr>
<td>WS$_2$ nanosheets, ref 23</td>
<td>2D sheets</td>
<td>-0.06</td>
<td>70</td>
</tr>
<tr>
<td>WS$_2$ nanoparticles on carbon cloth, ref 43</td>
<td>0D nanoparticles</td>
<td>-0.15</td>
<td>68</td>
</tr>
<tr>
<td>1T-WS$_2$ nanosheets, ref 8</td>
<td>2D sheets</td>
<td>-0.1</td>
<td>60</td>
</tr>
<tr>
<td>WS$_2$/rGO sheets, ref 25</td>
<td>2D sheets</td>
<td>-0.2~0.15</td>
<td>58</td>
</tr>
</tbody>
</table>
Figure 3.2.5. Potential required to reach 10 mA/cm$^2$ for HER catalysts.
3.2.6 Conclusion

This highlight has focused on the recent developments concerning the synthesis of layered TMDs, in addition to their application to catalysis of the HER. Based on the discussed approaches to enhancing the HER performance of MoS$_2$ and WS$_2$, 2D MoS$_2$/WS$_2$ sheets and their hybrids are identified as being highly promising candidates to replace conventional Pt catalysts. However, many challenging issues associated with the use of these materials remain, and will form the basis of future research themes. The most important issue that requires elucidation is the exact mechanisms by which the HER proceeds on WS$_2$ and MoS$_2$, as it is known that they vary between materials. Further details on the mechanism need to include crystallinity and identification of active sites, and the effect of strain in the 1T phase on HER performance should be clarified. The knowledge gained then needs to be successfully transferred to the development of new TMD structures or engineered surfaces for maximizing HER performance. In addition, hybrid materials such as WS$_2$/rGO hybrid sheets have demonstrated great promise for overcoming some of the limitations of TMDs, and for affording new functions for efficient H$_2$ evolution.
3.2.7 References


31. Shiva, K.; Ramakrishna Matte, H. S. S.; Rajendra, H. B.; Bhattacharyya, A. J.; Rao, C. N. R. Employing synergetic interactions between few-layer WS₂ and reduced graphene oxide to improve lithium storage, cyclability and rate capability of Li-ion batteries. *Nano Energy 2013*, 2, 787-793.


3.3. Two Dimensional Hybrid Nanosheets of WS$_2$ and Reduced Graphene Oxide for Hydrogen Evolution Reaction

3.3.1 Abstract

A hydrothermal reaction is known to be a facile method for synthesis of large amounts of transition metal dichalcogenide (TMD) sheets. However, the synthesis of WS$_2$ sheets and the hybrid based on WS$_2$ sheets have not been studied because it is complicate to synthesize. Therefore, we developed an efficient method to synthesize WS$_2$ Sheets by hydrothermal method, in which tungsten chloride, thioacetamide were used as starting materials and graphene oxide (GO) was added to form WS$_2$/reduced graphene oxide (WS$_2$/rGO) hybrid sheets. They were systematically investigated by field emission scanning electron microscopy, high-resolution transmission electron microscopy, X-ray diffraction, raman spectrometer and X-ray photoelectron spectroscopy. We could observe that 2H-WS$_2$ sheets with high crystalline were successfully synthesized. In addition, the WS$_2$/rGO hybrid sheets exhibited excellent electrocatalytic activity in the hydrogen evolution reaction (HER) relative to only WS$_2$ sheets. A Tafel slope of ~58 mV/decade was measured for WS$_2$/rGO hybrid sheets in the HER. The hybrid sheets are attributed to the synergistic effects between WS$_2$ sheets and rGO sheets.

3.3.2 Introduction

Monolayers of transition metal dichalcogenides (TMDs) have been recently receiving interest for both fundamental and technological investigations. One key to the realization of the potential of TMDs is the synthesis of high quality materials. One interesting TMD compound is WS$_2$ in which the electrical properties can be varied from metallic and semiconducting by tuning the crystal structure and the number of layers.$^1$ Conventionally mono- or few-layered WS$_2$ can be obtained by mechanical exfoliation or grown by chemical vapor deposition (CVD), using precursors such as WOCl$_4$ and HS(CH$_2$)$_2$SH.$^{1a,2}$ In addition, chemical methods for large scale synthesis of layered WS$_2$ have been reported. For example, WS$_2$ nanosheets with lateral dimensions of 100 nm have been synthesized from one-dimensional (1D) W$_{18}$O$_{49}$ with assistance of surfactants via a rolling-out method.$^3$ Recently, powder of WS$_2$ nanosheets was obtained by a two-step process that involves mixing WO$_3$ and S by ball milling and heating the mixture and S powder to 600 °C in Ar.$^4$ A solid state reaction with tungstic acid and thiourea in N$_2$ atmosphere at 773 K has also produced layered WS$_2$.$^5$ Hydrothermal reaction is known to be a facile method for large scale manufacturing of TMD nanosheets at relatively low temperature. The synthesis of MoS$_2$ sheets has been well studied using precursors such as sodium molybdate and thioacetamide or thiourea as the S source.$^6$ Although inorganic fullerene-like (IF) WS$_2$ nanoparticles,
1D nanotubes, or 1D rods have been obtained by the hydrothermal method,\textsuperscript{7,8} synthesis of WS\textsubscript{2} sheets by the hydrothermal reaction has yet to be realized. The primary reason for this is due to the fact that the WO\textsubscript{x} precursor required for the formation of WS\textsubscript{2} nanosheets does not occur in 2D form. Instead WO\textsubscript{x} prefers to form 1D or 0D nanostructures. Thus sulfurization of the WO\textsubscript{x} favors the formation of 0D fullerene-like or 1D nanotube/nanorod like WS\textsubscript{2} nanostructures. This is in contrast to MoS\textsubscript{2} nanosheets in which the MoO\textsubscript{3} precursor is a layered compound.\textsuperscript{9,10} The absence of a facile WS\textsubscript{2} nanosheet synthesis method has also prevented the study of WS\textsubscript{2}/graphene hybrid structures, despite their potentially useful applications. We therefore develop a hydrothermal method for synthesis of WS\textsubscript{2} nanosheets and then we integrate rGO nanosheets into the reactor to fabricate novel WS\textsubscript{2}/rGO hybrids.

We report detailed structural analyses of the synthesized products and investigate their potential catalysts for hydrogen evolution reaction (HER). The primary uniqueness of our work is the synthesis of WS\textsubscript{2} and rGO/WS\textsubscript{2} nanosheets using a scalable hydrothermal method and their implementation as efficient catalysts for HER. It has been shown that MoS\textsubscript{2} nanostructures are promising electrocatalysts for H\textsubscript{2} production.\textsuperscript{11} The overpotential of MoS\textsubscript{2} catalysts is -200 \textasciitilde -150 mV and Tafel slopes are in a range of 55\textasciitilde40 mV/dec.\textsuperscript{11-13} Recent results have suggested that WS\textsubscript{2} nanosheets could be interesting as HER electrocatalysts. Overpotential of -60 mV and a Tafel slope of \textasciitilde70 mV/dec have been measured for WS\textsubscript{2} sheets synthesized by the ball milling method\textsuperscript{4} while values of -150 mV and \textasciitilde70 mV/dec have been obtained for WS\textsubscript{2} particles on carbon cloth.\textsuperscript{12} Voiry \textit{et al.} showed that both the overpotential (-100 mV) and Tafel slopes (60 mV/dec) can be lowered by utilized WS\textsubscript{2} nanosheet catalysts that contain a high concentration of the metallic 1T phase.\textsuperscript{14}

Herein, we report the synthesis of WS\textsubscript{2} and WS\textsubscript{2}/rGO nanosheets using one-pot hydrothermal reaction process at low temperature. We show that WS\textsubscript{2} nanosheets are selectively fabricated using tungsten chloride and thioacetamide precursors. We also show that WS\textsubscript{2} nanosheets readily hybridize with rGO nanosheets when GO is added in the reaction vessel. This is one of the first reports on selective synthesis of WS\textsubscript{2} and WS\textsubscript{2}/rGO hybrid nanosheets by the hydrothermal reaction. We further demonstrate that WS\textsubscript{2}/rGO nanosheets exhibit good catalytic activity for hydrogen evolution. Based on impedance measurements, the better catalytic performance is attributed to enhanced charge transfer kinetics due to the intimate contact between the catalytic WS\textsubscript{2} nanosheets and the rGO support.
3.3.3 Experimental section

3.3.3.1. Synthesis of GO and WS$_2$

GO was made by the modified Hummers method, and exfoliated using a high pressure homogenizer. WS$_2$ sheets were synthesized by a one-step hydrothermal reaction. In a typical experiment, 11.897 g of tungsten chloride (WCl$_6$, sigma Aldrich, ≥99.9%) and 22.767 g of thioacetamide (CH$_3$CSNH$_2$, Sigma Aldrich, ≥99.0%) were dissolved in 400 mL of DI water and stirred 1 h at room temperature. The solution was transferred to a 500 mL Teflon-lined stainless steel autoclave, heated up to 265 °C, and kept for 24 h. After cooling naturally, the product was filtered, washed with DI water, and freeze dried for 24 h.

3.3.3.2. Synthesis of WS$_2$/rGO hybrids

WS$_2$/rGO hybrid sheets were synthesized by the same hydrothermal reaction condition as that for WS$_2$ sheets. A GO solution of 5 mg/mL was added to the mixture of tungsten chloride and thioacetamide, and a total volume of the solution was adjusted to 400 mL. The solution was transferred to a 500 mL Teflon-lined stainless steel autoclave, heated up to 265 °C and kept for 24 h. After that, the product was cooled naturally, filtered, and washed with DI water. The black product was freeze dried for 24 h to prepare freeze dried WS$_2$/rGO hybrid sheets. The annealing process was performed at 300 °C in vacuum for 10 h.

3.3.3.3. Characterization of WS$_2$/rGO

The samples were characterized with field emission scanning electron microscopy (Hitachi, S4800), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100 F with probe-Cs corrector, 200 kV), X-ray diffraction ((Rikagaku RU-200 diffractometer) equipped with Ni-filtered Cu Kα radiation (40 kV, 100 mA, λ=0.15418 nm), micro Raman spectrometer (Alpha 300s, WITec GmbH) with a laser excitation wavelength of 532 nm, and X-ray photoelectron spectroscopy (K-alpha, Thermo Fisher) with monochromatic Al Kα radiation as the X-ray source.

3.3.4. Electrochemical Measurements

Electrocatalytic measurements were carried out using a 3-electrode cell and a 0.5 M sulfuric acid (H$_2$SO$_4$) electrolyte solution. Graphite rod (Sigma Aldrich) and saturated calomel electrode (Pine Research Instrument) have been used as counter electrode and reference respectively. The reference electrode was calibrated with respect to reversible hydrogen electrode (RHE) using platinum wires as working and counter electrode. In 0.5 M H$_2$SO$_4$: $E_{RHE} = E_{SCE} + 0.256$ V. Materials were dispersed in deionized water at 1mg/ml and sonicated between 15min and 1h. The ink was then drop-casted onto
glassy carbon electrodes of alternately 3mm and 5mm diameters (loading 400 µg/cm²) and capped by Nafion (0.5%, 3µL, Sigma Aldrich). Linear sweep voltammetry was performed with 5 mV/s scan rate using a Pine bipotentiostat from Pine Research Instrumentation and electrodes were cycled at least 40 cycles prior any measurements.

3.3.4 Results and Discussions

3.3.4.1 Mechanism for synthesis of WS₂/rGO

The hydrothermal synthesis of WS₂ is known to be sensitive to temperature. 1D WS₂ structures have been synthesized at 265 °C through WO₃ intermediates, whereas no WS₂ has been synthesized below 240 °C. In a typical process, tungstate precursors such as Na₂WO₄ or (NH₄)₁₀W₁₂O₄₁ react with acid to condense WOₓ nanoparticles or 1D nanostructures that are sulfurized to give WS₂. The WOₓ nanoparticles or 1D structures act as templates for the formation of WS₂. The conversion of WOₓ to WS₂ is not fully explained yet. In this study, we employ WCl₆ as a precursor for W which has been used for vapor phase reaction in CVD and not induced WOₓ. The hydrothermal method was carried out at 265 °C for 24 hrs using WCl₆, thioacetamide (TAA), and graphene oxide (GO) to produce WS₂/rGO hybrid sheets. In the absence of GO, only WS₂ sheets are synthesized. During the hydrothermal reaction, WCl₆ and TAA produces WS₂ on GO sheets and GO is reduced to rGO. As-prepared WS₂/rGO hybrid sheets are then freeze dried and annealed at 300 °C to improve the crystallinity of the nanosheets. The reaction process is supposed to be as follows:

\[
\begin{align*}
C₂H₅NS + 2H₂O & → H₂S + NH₃ + CH₃COOH \quad (eq. 1) \\
WCl₆ + 3H₂S & → WS₂ + 6HCl + S \quad (eq. 2)
\end{align*}
\]

Here, H₂S is released from TAA and reduce WCl₆ to form WS₂ by sulfurization. The scanning electron microscopy (SEM) images of WS₂ and WS₂/rGO hybrid nanosheets are shown in Figure 3.3.2. As-prepared WS₂ and WS₂/rGO hybrid nanosheets are shown in Figures 3.3.2(a) and 3.3.2(d), respectively. Images of freeze-dried samples are shown in Figures 3.3.2(b) and (e). The WS₂ nanosheets maintain their structure without any noticeable change after freeze-drying. However, the as-prepared WS₂/rGO hybrid nanosheets were found to shrink after freeze drying, possibly due to removal of water adsorbed on rGO (Figure 3.3.2(e)). The microstructure shown in Figure 1e is very similar to rGO hydrogels formed by hydrothermal reaction and freeze-drying of GO. The rGO hydrogels consist of flexible rGO nanosheets that are physically cross-linked. Further annealing of both types of nanosheets at 300 °C did not affect the morphology of the samples as shown in Figures 3.3.2(c) and (f). The WS₂ sheets on rGO were characterized by high-resolution transmission electron microscopy (HR-TEM). Image of the as-prepared WS₂/rGO hybrid sample in Figure 3.3.3(a) shows overlapping
nanosheets. Bilayer WS$_2$ nanosheets could be identified in some areas in Figure 3.3.3(a). Moire pattern and a selected-area electron diffraction (SAED) pattern from the indicated position are shown in Figure 3.3.3(b). The diffraction pattern unambiguously suggests that the WS$_2$ is configured in the 2H phase. Closer examination of the diffraction pattern shows two sets of hexagonal reflections from two overlapping layers, which can be attributed to rotation angle of 25.1 degree from bilayers. The low and high magnification TEM images of WS$_2$/rGO hybrid sheets after annealing are shown in Figures 3.3.3(c) and (d). The folded region in Figure 3.3.3(c) was selected for high magnification observation of the edges (Figure 3.3.3(d)). The inset in figure 3.3.3(d) clearly indicates the interlayer spacing of WS$_2$ is 0.62 nm, which corresponds to the d-spacing of WS$_2$. The WS$_2$ nanosheets on rGO consist of 4 to 12 layers as indicated in Figure 3.3.3(d). We could not observe any edges of rGO sheets consistent with their atomically thin nature. To confirm the existence of rGO, we carried out EDAX mapping of the WS$_2$/rGO hybrid sheets at the location indicated in Figure 3.3.3(a) and Figure 3.3.4. Considerable carbon and oxygen elements were detected, indicating existence of rGO. We also determined the stoichiometry of WS$_2$ from EDAX mapping and the W:S ratio was found to be 1:2. The presence of pure WS$_2$ nanosheets after annealing was also confirmed by HR-TEM imaging of the hexagonal phase (see Figure 3.3.5). We have also measured the Braun-Emmet-Teller (BET) surface of the pure and hybrid nanosheets and found them to range from 10 – 20 m$^2$/g. (See Figure 3.3.6)
Figure 3.3.1. Scheme for synthesis of WS\textsubscript{2}/rGO hybrid sheets by the hydrothermal reaction.
Figure 3.3.2. SEM images of as-prepared WS$_2$ a), freeze-dried WS$_2$ b), freeze-dried WS$_2$ after annealing c), as prepared WS$_2$/rGO d), freeze-dried WS$_2$/rGO e), and freeze-dried WS$_2$/rGO after annealing f).
Figure 3.3.3. TEM images of WS₂/rGO hybrid nanosheets. a) As-prepared WS₂/rGO hybrid nanosheets and b) the magnified image of the marked area in a). The inset in b) indicates the diffraction pattern of 2H-WS₂. c) Folded edges of WS₂ sheets on rGO and d) the high-resolution image of c). The inset shows a magnified image of some folded edges of WS₂ sheets.
Figure 3.3.4. TEM image corresponding to EDAX of as-prepared WS$_2$/rGO hybrid sheets. (a) High-resolution TEM image of freeze dried WS$_2$/rGO hybrid sheets after annealing. The inset shows the diffraction pattern of 2H-WS$_2$. (b) EDAX spectrum and mapping images of the hybrid sheets after annealing.
Figure 3.3.5. TEM images of only WS$_2$ after annealing and the diffraction pattern with 2H-WS$_2$. 
<table>
<thead>
<tr>
<th>Samples</th>
<th>BET (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freeze dried WS₂ after annealing</td>
<td>20</td>
</tr>
<tr>
<td>Freeze dried WS₂/rGO after annealing</td>
<td>13</td>
</tr>
<tr>
<td>Freeze dried WS₂/rGO</td>
<td>8</td>
</tr>
</tbody>
</table>

**Figure 3.3.6.** N₂ adsorption-desorption isotherms for freeze dried WS₂ after annealing, freeze dried WS₂/rGO and freeze dried WS₂/rGO after annealing.
X-ray diffraction (XRD) spectra of WS$_2$ and WS$_2$/rGO hybrid nanosheets are shown in Figure 3.3.7. The reflections at 14.1°, 33°, 58.2° for as-prepared WS$_2$ and freeze-dried WS$_2$ nanosheets, corresponding to (002), (100), and (110) planes, indicate the presence of the hexagonal phase.$^{3,5}$ Although some impurity peaks including those of WO$_2$ were observed, they disappeared after annealing.$^{[18]}$ The impurities may be from oxidation of WS$_2$. The peaks for WS$_2$ nanosheets after annealing appeared at 14.2°, 33.3°, and 58.4° and were sharper, suggesting improved crystallinity. The XRD pattern is also consistent with JPCDS card No.084-1398 for pure hexagonal WS$_2$. The d-spacing of 0.62 nm, consistent with the TEM result, was calculated from the primary (002) diffraction peak. In case of as-prepared WS$_2$/rGO hybrid nanosheets, some impurity peaks were present along with slight shifts of peak positions and broadening. The crystallinity of WS$_2$ in the hybrid nanosheets also improved after annealing. However, the peaks in the hybrid samples are slightly less sharp, suggesting that the presence of rGO induces small disorder in the WS$_2$ structure. The (002) peak of rGO was absent from the XRD samples, consisting with lack of substantial stacking of these layers.$^{5,6,19}$

Our results suggest that GO acts to facilitate the growth of WS$_2$ nanosheets, which may be attributed to the strong interactions between the functional groups on GO and precursors. The representative Raman spectrum of WS$_2$/rGO hybrid nanosheets is shown in Figure 3.3.7(b). Characteristic peaks for WS$_2$ at 350 cm$^{-1}$ and 415 cm$^{-1}$ corresponding to the E$_{2g}$ and A$_{1g}$ modes, respectively, and D and G bands of rGO can be clearly seen.$^{13b,20}$

W 4f$_{7/2,5/2}$ and S 2p$_{3/2,1/2}$ binding energies obtained from X-ray photoelectron spectroscopy (XPS) are shown in Figures 3.3.7(c) and (d). For the WS$_2$/rGO sheets after annealing, doublet peaks for binding energy of W 4f$_{7/2,5/2}$ appeared at 32.5 and 34.6 eV, indicating an oxidation state of W$^{4+}$ (Figure 3.3.7(c)), and the doublet peaks for S 2p$_{3/2,1/2}$ appeared at 162.2 and 163.3 eV, indicating S$^{2-}$ (Figure 3.3.7(d)).$^{12}$ These peaks in the hybrid nanosheets were identical to those of pure WS$_2$ with high crystallinity. For the freeze-dried WS$_2$/rGO, the doublet peaks for the binding energy of W 4f$_{7/2,5/2}$ and S 2p$_{3/2,1/2}$ appear at 31.67 and 33.85 eV and at 161.4 and 162.4 eV, respectively. These peaks were broader than those of WS$_2$/rGO after annealing. There was a shift of ~ 1 eV which can be attributed to adsorption of oxygen and water molecules.$^{21}$ Furthermore, the peak at 35.7 eV was observed only in the freeze-dried WS$_2$/rGO sheets, which may be due to WO$_2$.$^{22}$
Figure 3.3.7. (a) XRD patterns of WS$_2$ sheets and WS$_2$/rGO hybrid sheets. The asterisk (*) indicates WO$_2$. (b) Raman spectrum of the hybrid. XPS analysis of (c) W 4f$_{7/2}$-$5/2$ peaks and (d) S 2p$_{3/2,1/2}$ for the WS$_2$ sheets and WS$_2$/rGO hybrid sheets.
3.3.4.2 Application of WS$_2$/rGO hybrids for hydrogen evolution reaction

Our analyses suggest that it is possible to fabricate high quality WS$_2$ and WS$_2$/rGO hybrids by hydrothermal synthesis. To demonstrate their feasibility in technologically important applications, we investigated the electrocatalytic HER properties of WS$_2$/rGO hybrid nanosheets deposited on a glassy carbon electrode. The polarization curves (I-V plot) from electrodes made from freeze dried WS$_2$/rGO and freeze dried WS$_2$/rGO after annealing yielded overpotentials ranging from -150 ~ -200 mV vs. reversible hydrogen electrode (RHE). (Figure 3.3.8(a)) The overpotential of pure W$_S$ nanosheets was measured to be -350 mV vs. RHE. At -300 mV, the cathode current density was 23 mA/cm$^2$, which is much higher than that observed for freeze dried WS$_2$/rGO (7 mA/cm$^2$) and WS$_2$ (5 mA/cm$^2$). The Tafel plots derived from these data are shown in Figure 3.3.8(b) where the linear portions were fitted to the Tafel equation to determine the slopes. The Tafel plots reveal a slope of 140 mV/dec for annealed WS$_2$, 100 mV/dec for freeze dried WS$_2$/rGO, and 58 mV/dec for freeze dried WS$_2$/rGO after annealing. The much lower Tafel slope value for freeze dried WS$_2$/rGO after annealing is due to the formation of an interconnected conducting network by the underlying rGO so that rapid electron transport from the electrode to the less-conducting WS$_2$ can occur.$^{13b}$ HER performance of TMDs is currently limited by poor electrical transport and inefficient electrical contact between the catalyst and the electrode substrate.$^{23}$ Measurements shown in Figure 3.3.8(c) confirm that the impedance system is substantially lower in the WS$_2$/rGO nanosheets electrodes. In addition to better charge transfer, improved crystallinity of WS$_2$ after annealing along with the removal of oxidized impurities may improve the catalytic performance.
Figure 3.3.8. (a) Polarization curves and corresponding (b) Tafel plots recorded on glassy carbon electrodes with a catalyst loading of 400 μg/cm². (c) AC impedance spectra of WS$_2$/rGO and WS$_2$. 
3.3.5 Conclusion

In conclusion, we have successfully fabricated WS$_2$ and WS$_2$/rGO hybrid nanosheets via hydrothermal synthesis. The WS$_2$/rGO hybrid nanosheets exhibit promising catalytic properties for HER. We attribute the better performance to the formation of an interconnected conducting rGO network that facilitates rapid electron transfer from the electrode to the catalyst and improvement of WS$_2$ crystallinity after annealing. Specifically the WS$_2$/rGO catalysts exhibit overpotential ranging from -150 ~ -200 mV with Tafel slope of 58 mV/dec. Synthesis of WS$_2$ by hydrothermal method has been challenging but here we demonstrate that high quality WS$_2$ nanosheets can be fabricated. Since the hydrothermal method is reasonably scalable, it may be useful for production of large quantities of TMD nanosheets for applications where large quantities are required.
3.3.6 References


5. Shiva, K.; Ramakrishna Matte, H. S. S.; Rajendra, H. B.; Bhattacharyya, A. J.; Rao, C. N. R. Employing synergistic interactions between few-layer WS2 and reduced graphene oxide to improve lithium storage, cyclability and rate capability of Li-ion batteries *Nano Energy* 2013, 2, 787-793.


3.4. Synthesis of Cobalt Disulfide on Reduced Graphene Oxide for Hydrogen Evolution Reaction

3.4.1 Abstract

The synthesis of the pure phase of cobalt sulfide is quite difficult because of the complex stoichiometric compositions of cobalt chalcogenides. Therefore, we developed a facile method to synthesize CoS$_2$/reduced graphene oxide (CoS$_2$/rGO) by the hydrothermal method, in which cobalt acetate, and thioacetamide were used as starting materials and graphene oxide (GO) was added to form hybrid structure. We demonstrate that rGO is essential to produce CoS$_2$ with single phase. Pure CoS$_2$ can’t be synthesized without rGO. The products were systematically investigated by field emission scanning electron microscopy, high-resolution transmission electron microscopy, and X-ray diffraction. We could observe that CoS$_2$ on rGO with high crystallinity and a single phase were successfully synthesized. In addition, the CoS$_2$/rGO hybrids exhibited electrocatalytic activity in the hydrogen evolution reaction (HER) relative only to the product of reaction without rGO. Tafel slope of ~58 mV/decade was measured for CoS$_2$/rGO hybrid sheets in the HER. The properties of hybrid sheets are attributed to the synergistic effects between the CoS$_2$ sheets and rGO sheets.

3.4.2 Introduction

Enormous efforts have been applied to synthesizing TMD nanomaterials due to their excellent electronic, optical, and mechanical properties. Among the interesting TMD compounds, MoS$_2$ and WS$_2$, in which the electrical properties can be changed from metallic to semiconducting by controlling the crystal structure and the number of layers, have been extensively explored. In addition, first-low transition metal dichalcogenide (Fe, Ni, and Co) as well as MoS$_2$ and WS$_2$ have been investigated for their structure and properties. For example, the sulfide minerals that include S$_2^{2-}$ dimer, such as FeS$_2$, CoS$_2$, and NiS$_2$, have been successfully synthesized. These have received interest owing to their potential applications; for example, FeS$_2$, with its band gap of 0.95 eV, has promise as an active layer in photovoltaic devices, and NiS$_2$, with its band gap of 0.3 eV could be used as a Li storage material. In particular, diverse cobalt sulfide compounds with different stoichiometric compositions, such as CoS$_2$, CoS, Co$_9$S$_8$ and Co$_{1-x}$S, have attracted great attention due to their excellent physical, chemical, electronic, and optical properties and their wide potential applications in catalysts. However, the synthesis of the pure phase of cobalt sulfide is quite difficult because of the complex stoichiometric compositions of cobalt chalcogenides. Wang et al. found that the flower-like cobalt sulfides prepared by a solvothermal method were a mixed phase of CoS and Co$_9$S$_8$ (9%). Yin et al. found that when using CoCl$_2$ solution in mixed solution of DMSO and ethanol (volume ration of 7:3), the as-obtained cobalt sulfides consisted of CoS$_2$, CoS and Co$_9$S$_8$. There are few synthetic methods to prepare cobalt sulfides
with pure phase. Thus, more research is required in the synthesis and characterization of using cobalt sulfides with $S_2^{2-}$ dimer as functional materials. In recent, CoS$_2$ film with single phase has synthesized by sulfurization of Co film. The substrate which is deposited Co through e-beam evaporator is located in tube furnace and sulfur powder is vaporized by flowing Ar gas at 550 °C. However, gas phase reaction is occurred at high temperature relatively and the limitation can be existed in terms of mass production. Therefore, it is worth exploring the synthetic method of large scale which has pure phase of CoS$_2$. The absence of a CoS$_2$ synthetic method has also prevented the study of CoS$_2$/graphene hybrid structures, despite their potentially useful applications. Therefore, we report the synthesis of CoS$_2$/rGO hybrid which has not been reported and its electrocatalytic activity for HER.

3.4.3 Experimental Section

3.4.3.1 Synthesis of GO

GO was prepared from graphite powder by the modified Hummers’ method.$^{10}$

3.4.3.2 CoS$_2$/rGO hybrid

GO solution was added to the mixture of cobalt acetate and thioacetamide and the total volume of the solution was adjusted to 400 mL for all reactions. The solution was transferred to a 500 mL Teflon-lined stainless steel autoclave, heated up to 240 °C, and kept for 24 h. After cooling naturally, the product was filtered, washed with DI water, and dried in vacuum at 60 °C for 12 h. During the hydrothermal process, GO was converted to rGO and CoS$_2$/rGO was formed.

3.4.3.3 Characterization

The samples were characterized with field emission scanning electron microscopy (Hitachi, S4800), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100 F with probe-Cs corrector, 200 kV), X-ray diffraction (Rikagaku RU-200 diffractometer equipped with Ni-filtered Cu Kα radiation (40 kV, 100 mA, $\lambda=0.15418$ nm)), and X-ray photoelectron spectroscopy (K-alpha, Thermo Fisher with monochromatic Al Kα radiation as the X-ray source).

3.4.3.4 Electrochemical measurements

Electrocatalytic measurements were carried out using a 3-electrode cell and a 0.5 M sulfuric acid ($H_2SO_4$) electrolyte solution. A graphite rod (Sigma Aldrich) and Ag/AgCl electrode (Wonatech) were used as counter electrode and reference respectively. The reference electrode was calibrated with respect to reversible hydrogen electrode (RHE) using platinum wires as working and counter electrodes. Materials were dispersed in deionized water at 4mg/mL and sonicated for 1h. The ink was then drop-casted onto glassy carbon electrodes of 3 mm diameters (loading 285 µg/cm$^2$) and capped by Nafion
(0.5%, 3 µL, Sigma Aldrich). Linear sweep voltammetry was performed with a 5 mV/s scan rate using a Zive SP2 potentiostat from Wonatech and the electrodes were cycled at least 40 cycles prior to any measurement.

3.4.4 Results and Discussion

The hydrothermal synthesis of CoS$_2$ with single phase is known to be difficult. In a typical process, cobalt precursor such as CoCl$_2$·6H$_2$O reacts with L-cysteine or thioacetamide to prepare CoS$_2$. However, the problem is the inclusion of the impurities such as CoS or Co$_9$S$_8$ in the synthesized CoS$_2$ even if the portion is partial. In this study, the hydrothermal reaction was carried out at 240 °C for 24 h using (CH$_3$COO)$_2$Co·4H$_2$O as a precursor for Co ions, thioacetamide (TAA), and GO to prepare CoS$_2$/rGO. In the absence of GO, mixtures of Co$_3$S$_4$ and CoS$_2$ are synthesized. During the reaction, (CH$_3$COO)$_2$Co·4H$_2$O and TAA produced CoS$_2$ on GO sheets and the GO was reduced to rGO. As-prepared CoS$_2$/rGO hybrid sheets were dried in vacuum at 60 °C. The scanning electron microscopy (SEM) images of CoS$_2$/rGO with different weight percent of rGO and the results without GO are shown in Figures 3.4.1. In the absence of GO, the aggregation of particles with microstructures were obtained. (Figure 3.4.1 (a)) In strong contrast, CoS$_2$ nanoparticles of ~100 nm were decorated uniformly on the rGO sheets. (Figure 3.4.2 (b) and (c)). The transmission electron microscopy (TEM) images also demonstrate the growth of single-crystalline CoS$_2$ nanoparticles on the rGO matrix. (Figure 3.4.2 (a)-(c)) Figure 3.4.2.(b) shows the rGO sheets with approximate interlayer d-spacing of 0.34 nm, which corresponds to the d-spacing of graphite, and the stacked rGO layers were very thin sheets with 3-12 layers. CoS$_2$ nanoparticles with a d-spacing of 0.27 nm were observed in Figure 3.4.2.(c). The measured d-spacing corresponds to the inter-planar spacing of the (200) plane of the cubic phase of CoS$_2$. In addition, the SAED patterns show the single crystal feature of the individual CoS$_2$ particles. (Figure 3.4.2 (c)) To demonstrate the stoichiometry of Co and S, energy dispersive X-ray spectroscopy (EDX) elemental mapping of the CoS$_2$/rGO hybrids was performed (Figure 3.4.2.(d)), and the images indicate the ratio of S to Co is approximately 2. The C and O in the EDX spectrum are attributed to the rGO.

The hybrid structure of CoS$_2$/rGO was characterized by X-ray diffraction (XRD) in Figure 3.4.3. The XRD pattern of the CoS$_2$/rGO (7 wt%) confirms the formation of a cubic CoS$_2$ phase with reflections at 28.2 °, 32.5 °, and 55.4 ° for CoS$_2$/rGO (3 wt% and 7 wt%), corresponding to (111), (200), and (220) planes, indicating the presence of the cubic phase. The XRD pattern is also consistent with JPCDS card No.89-1492 for pure cubic CoS$_2$. The d-spacing of 0.27 nm is consistent with the TEM result, and was calculated from the (002) diffraction peak. However, the diffraction peaks of the produced results without GO can be indexed to CoS$_2$ (JPCDS card No.89-1492) and Co$_3$S$_4$ (JPCDS No. 42-1448). This result indicates that CoS$_2$ with single phase can grow on the GO support. It was also
Part 3

found that the GO content is crucial to synthesize pure CoS$_2$. At lower GO concentration (3 wt% $\leq$ concentration $\leq$ 6 wt%), some impurities of CoS were observed. However, when the GO concentration was increased (> 6 wt%), pure CoS$_2$ could be synthesized. (See XRD spectra in Figure 3.4.4) This result demonstrates that rGO is essential to produce CoS$_2$ with single phase. Also, the (002) peak of rGO was absent from the XRD samples, which is consistent with a lack of substantial stacking of these layers. Our results suggest that GO acts to facilitate the growth of CoS$_2$ nanoparticles, which may be attributed to the strong interactions between the functional groups on GO and the precursors. Because of the higher population of oxygen functional groups, including carboxylic, hydroxyl, and epoxy groups, the GO surface interacts strongly with the coated species, providing pinning forces to the small particles to hinder diffusion and recrystallization. Indeed, rGO has been regarded as a template for the morphology-controlled synthesis of various nanomaterials, including metals, metal oxides, and transition-metal chalcogenides. It appears that rGO sheets contribute to the controlled nucleation and growth, affording optimal chemical interactions and bonding between the nanomaterial and the rGO. For example, Wang et al. reported the synthesis of small Ni(OH)$_2$ nanoparticles decorating GO at a high concentration of oxygen by using a hydrothermal method, whereas Ni(OH)$_2$ plates larger than the particles anchored on graphene sheets with few oxygen functional groups were observed. In addition, Wang et al. demonstrated the synthesis of LiMn$_{0.75}$Fe$_{0.25}$PO$_4$ nanorods decorated on rGO but they observed the formation of irregularly shaped LiMn$_{0.75}$Fe$_{0.25}$PO$_4$ particles in the absence of the rGO. In our group, VS$_4$/rGO hybrids materials with dianion S$_2^{2-}$ have been reported through the hydrothermal method with a GO template. In the absence of GO, VS$_2$ with S$_2^{2-}$ was synthesized instead of VS$_4$. In this case, GO was used for a change of chemical composition, which is different from the above morphology control. Therefore, GO in our result can serve as the promoter to facilitate development of dimer S$_2^{2-}$ as well as the template for growth.

Our results suggest that it is possible to fabricate high quality CoS$_2$/rGO hybrids by the hydrothermal method. To demonstrate their practical applications, we investigated the electrocatalytic HER properties of CoS$_2$/rGO hybrid materials deposited on a glassy carbon electrode. The polarization curves (I-V plot) from CoS$_2$/rGO and CoS$_2$/Co$_3$S$_4$ were measured. The overpotential of CoS$_2$/rGO was measured to be ~ -150 mV vs. RHE and the overpotential required to drive current densities of 10 mA/cm$^2$ is 209 mV. In contrast, CoS$_2$/Co$_3$S$_4$ exhibited little HER activity with an overpotential of 300 mV. The Tafel plots derived from these data are shown in Figure 3.4.5 (a) where the linear portions were fitted to the Tafel equation to determine the slopes. The Tafel plots reveal a slope of 138 mV/dec for CoS$_2$/Co$_3$S$_4$, and 55 mA/dec for CoS$_2$/rGO. (Figure 3.4.5 (b)) The much lower Tafel slope value for CoS$_2$/rGO is due to the formation of a conducting network by the underlying rGO so that rapid electron transport from the electrode to the CoS$_2$ can occur. Furthermore, the metallic property of CoS$_2$ permits
efficient transport of charge from the electrode to the surface of the catalysts, which is desired for high-performance electrocatalysts.\textsuperscript{4b} This result is meaningful in that it is the first report on an application of CoS\textsubscript{2}/rGO for HER, even though performance is not the best. More importantly, as expected, the performance of the CoS\textsubscript{2}/rGO hybrid sheets is much better than CoS\textsubscript{2}/Co\textsubscript{3}S\textsubscript{4} itself. More studies are needed to improve the HER performance. First-low transition metal dichalcogenides have been extensively studied as a family of active catalysts for oxygen reduction reaction (ORR) in acidic electrolyte. Recently, their catalytic activity for HER has been directly identified in experiments.\textsuperscript{2a} The outstanding performance of HER for CoS\textsubscript{2} film has reported (overpotential of 180 mV and Tafel slope of 44.6 mV/dec). Similarly, CoSe\textsubscript{2} nanoparticles on carbon fibers through a two-step reaction showed the overpotential of 137 mV and Tafel slope of 40 mV/dec in same group.\textsuperscript{2b}
Figure 3.4.1. SEM images of (a) the CoS$_2$/Co$_3$S$_4$ (the result of reaction without GO), (b) CoS$_2$/rGO (rGO contents of 3 wt%), and CoS$_2$/rGO (7 wt%).
**Figure 3.4.2.** TEM image of (a) CoS$_2$/rGO hybrid materials, (b) rGO covered with CoS$_2$, and (c) enlarged HRTEM image of the CoS$_2$ nanoparticle. Inset image shows the diffraction pattern of CoS$_2$. (d) EDX elemental mapping of Co and V, EDX spectrum and table showing elemental composition. The atomic ration of S and Co is 2, confirming the stoichiometry of CoS$_2$. 
Figure 3.4.3. XRD patterns of Co$_2$S$_4$/Co$_3$S$_4$, Co$_2$S$_2$/rGO (3 wt%) and Co$_2$S$_2$/rGO (7 wt%).
**Figure 3.4.4.** The XRD patterns of CoS$_2$/rGO depending on the rGO contents. The asterisk (*) means the diffraction of CoS.
Figure 3.4.5. (a) Polarization curves of CoS$_2$/rGO and CoS$_2$/Co$_3$S$_4$, corresponding (b) Tafel plots recorded on glassy carbon electrodes with a catalyst loading 285 μg/cm$^2$. 
3.4.5 Conclusion

In conclusion, we have successfully synthesized CoS$_2$/rGO with single phase of CoS$_2$ via hydrothermal synthesis. The CoS$_2$/rGO hybrid materials exhibit promising catalytic properties for HER. We attribute the better performance to the formation of an interconnected conducting rGO network that facilitates rapid electron transfer from the electrode to the catalyst. Specifically the CoS$_2$/rGO catalysts exhibit overpotential ranging from $\sim$150 mV with Tafel slope of 58 mV/dec. Synthesis of CoS$_2$ with a single phase by the hydrothermal method has been challenging but here we demonstrate that high quality CoS$_2$ by means of rGO can be fabricated. Since the hydrothermal method is reasonably scalable, it may be useful for production of large quantities of TMD for applications where large quantities are required.
3.4.6 Reference


12. (a) Shiva, K.; Ramakrishna Matte, H. S. S.; Rajendra, H. B.; Bhattacharrya, A. J.; Rao, C. N. R.; Employing synergistic interactions between few-layer WS2 and reduced graphene oxide to improve lithium storage, cyclability and rate capability of Li-ion batteries. Nano Energy 2013, 2, 787-793. (b) Chang, K.; Chen, W.; L-cysteine-assisted synthesis of layered MoS2/graphene composites with excellent electrochemical performances for lithium ion batteries. ACS Nano 2011, 5, 4720-4728.


Publication list


