

Electrochemical on-surface synthesis of an oxygen-doped graphene nanoribbon as a catalyst for chemical etching of silicon

Cheng Yingbo

2026

Contents

Contents	I
Chapter 1. General Introduction	1
1.1 Introduction of graphene nanoribbons	1
1.2 Synthesis of graphene nanoribbons.....	3
1.3 Doping of graphene nanoribbons	8
1.4 Matel-assisted chemical etching.....	10
1.5 Carbon-based catalyst for chemical etching of silicon	12
1.6 Motivation and objectives	13
References	18
Chapter 2. Experimental	28
2.1 General information	28
2.1.1 Two-zone chemical vapor deposition	28
2.1.2 Transfer of graphene nanoribbons.....	29
2.2 Characterization	30
2.2.1 Scanning tunneling microscopy (STM)	30
2.2.2 Raman spectroscopy.....	30
2.2.3 Atomic force microscope (AFM).....	31
2.2.4 Mass spectrometry.....	31
2.2.5 Cyclic voltammetry (CV).....	31
2.2.6 Equipment and characterization for organic synthesis	32
2.3 Calculation.....	32
2.3.1 Bandgap simulation.....	32
2.3.2 Local density of states (LDOS) mapping simulation	33
2.3.3 Raman simulation.....	33
2.3.4 Optical absorption spectra simulation.....	33
2.3.5 Spin density, electron density mapping simulation	33
2.3.6 Total energy and energy level simulation	34
References	35

Chapter 3. Electrochemical On-Surface Synthesis of Edge-Functionalized Graphene Nanoribbon at Room Temperature.....	36
3.1 Introduction.....	36
3.2 Experimental	39
3.2.1 Synthesis of 2-butoxynaphthalene.....	39
3.2.2 Preparation of Au (111) substrate and iodine-covered Au (111).....	40
3.2.3 Cell assembling and electrochemical on-surface synthesis	41
3.2.4 Electro-absorption measurement	42
3.3 Results and discussion	43
3.3.1 Structural determination of edge-functionalized GNRs	43
3.3.2 Mechanism of electrochemical on-surface synthesis	57
3.3.3 Electrochemical layer-by-layer growth of GNRs.....	71
3.4 Conclusion	76
References	78
Chapter 4. Oxygen-Doped Graphene Nanoribbons as Superior Catalysts Beyond Noble Metals in Vapor-Phase Chemical Etching of Silicon	83
4.1 Introduction.....	83
4.2 Experimental	86
4.2.1 Sample preparation	86
4.2.2 Vapor-phase chemical etching of silicon	87
4.2.3 Photoconductivity measurement	89
4.3 Results and discussion	91
4.3.1 Electron-donating property of 5A-OGNRs	91
4.3.2 Si etching catalytic performance of the 5A-OGNR, gold, and other carbon-based materials.....	95
4.3.3 Other applications of 5A-OGNR.....	102
4.4 Conclusion	104
References	105
Chapter 5. Theoretical Investigation of the Catalytic Activity of Oxygen-Doped Graphene Nanoribbons	108
5.1 Introduction.....	108
5.2 Experimental	111

5.2.1	Computational methods	111
5.2.2	Scanning tunneling microscopy (STM) characterization	112
5.3	Results and discussion	113
5.3.1	Si etching configuration of 5A-OGNR, 5A-GNR, and 7A-GNR	113
5.3.2	Adsorption, reaction pathway, and Gibbs free energy simulations	118
5.3.3	Transition state and rate-determining step study of GNRs	127
5.3.4	Comparison between graphene and GNRs in silicon etching.....	132
5.4	Conclusion	134
	References	135
Chapter 6.	General Conclusions	139
Appendix		142
List of publications		182
Presentations at conferences		182
Acknowledgement		183

Chapter 1. General Introduction

1.1 Introduction of graphene nanoribbons

Graphene nanoribbons (GNRs), one-dimensional graphene structures, have attracted significant attention for their electronic properties, which can be controlled by varying their width and edges¹⁻⁴. Owing to their remarkable tunability, GNRs are highly promising materials for a wide range of electronic applications, including transistors, sensors, and quantum dots⁵⁻⁹. Depending on the edge geometry, GNRs are typically categorized into three types¹⁰⁻¹²: armchair, zigzag, and chiral, as illustrated in Figure 1.1a. Armchair GNRs possess edges aligned in an armchair configuration, whereas zigzag GNRs feature edges arranged in a zigzag pattern. GNRs exhibiting other edge orientations are collectively referred to as chiral GNRs^{10,11}. These three configurations yield strikingly different boundary conditions for the π -electron wavefunctions, leading to contrasting band structures and electronic behaviors. Armchair-edged GNRs (AGNRs) are generally semiconducting, with a band gap that scales inversely with ribbon width^{10,11}. Tight-binding and density functional theory (DFT) calculations reveal that AGNRs can be categorized into three distinct families according to the number of dimer lines across their width (N): $3p$, $3p+1$, and $3p+2$, where p is a positive integer. Among these, the $3p+2$ family exhibits the smallest band gap, approaching metallic behavior as their width increases. In contrast, the $3p$ and $3p+1$ families display progressively larger band gaps, with a hierarchy of gap size represented by $(3p + 1) > 3p > (3p + 2)$. This systematic dependence of the band gap on both N and the edge geometry provides a clear quantum mechanical basis for electronic tunability in

AGNRs^{13,14}. Unlike AGNRs, early tight-binding calculations predicted that all zigzag graphene nanoribbons (ZGNRs) are metallic¹⁵⁻¹⁷. They feature a flat electronic band with a high density of states at zero energy and localized edge states on both sides of the ribbon, independent of width. By applying external electric fields or chemical modification, ZGNRs can transition between half-metallic and semiconducting states, making them potential candidates for spintronic applications¹⁸⁻²⁰. The relationship between magnetic ordering and electronic confinement in ZGNRs remains a central theme in low-dimensional carbon physics. Apart from edge configuration, the width of the GNR also plays a critical role (Figure 1.1b). This width dependence allows continuous tuning of electronic properties from metallic to semiconducting¹⁰⁻¹². In summary, GNRs represent an exceptional class of carbon nanostructures in which atomic-level geometry directly dictates electronic behavior. Their unique structure-property correlation, defined by width and edge type, allows precise control over band gap, carrier mobility, and spin polarization. The ability to design and synthesize GNRs with atomic precision has thus opened new opportunities for both fundamental studies of quantum-confined carbon systems and the development of next-generation electronic, spintronic, and catalytic devices.

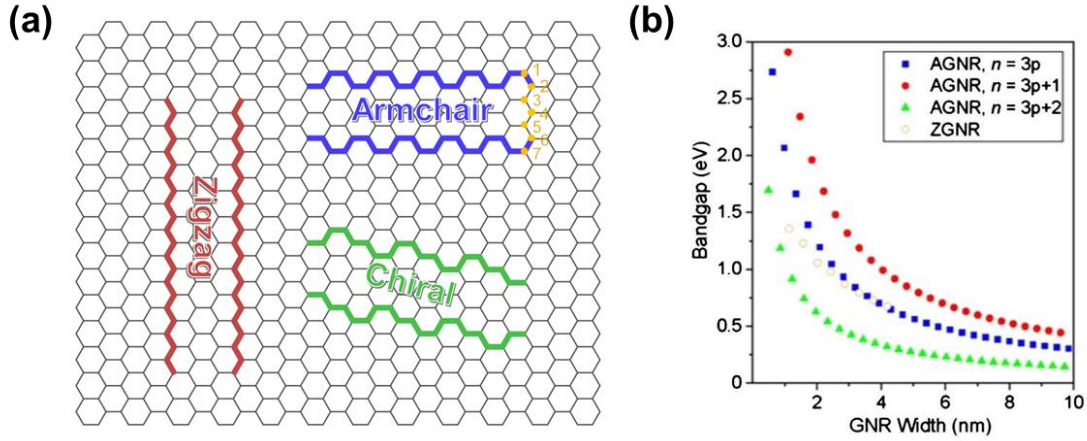


Figure 1.1. (a) Edge structures of three types of GNRs: zigzag, armchair, and chiral. (b) Electric properties of graphene nanoribbons¹¹.

1.2 Synthesis of graphene nanoribbons

The synthesis of graphene GNRs has been deeply studied as their unique electronic and chemical properties are directly related to the atomic structure, particularly the width and edge configuration. To precisely control these characteristics, two kinds of synthetic methods have been developed: top-down and bottom-up approaches. Each method offers distinct advantages and limitations in terms of structural precision, scalability, and tunability.

As shown in Figure 1.2, the top-down approach involves cutting or unzipping GNRs from larger carbon materials, such as graphene, graphite, or carbon nanotubes (CNTs), using physical or chemical methods^{21–28}. This method enables large-scale production of GNRs but generally results in poor control over the edge structure and width uniformity. One of the earliest and most widely used top-down methods is lithographic patterning, in which

graphene films are etched into narrow ribbons using electron-beam lithography or plasma etching²⁴⁻²⁶. While this technique provides control over ribbon dimensions and orientation, it often introduces defects that can significantly affect electronic properties. Another prominent top-down method is the unzipping of CNTs^{21,28}. This process involves longitudinally cutting multi-walled or single-walled CNTs through chemical oxidation, plasma treatment, or mechanical forces to produce nanoribbon structures. The oxidative unzipping method uses strong oxidants such as potassium permanganate (KMnO₄) in acidic media to open CNT sidewalls. This technique yields narrow GNRs with relatively smooth edges, but the harsh reaction conditions lack atomic accuracy, which may lead to edge defects. Alternatively, plasma or mechanical unzipping offers cleaner processes, but they often result in a lower yield and less reproducibility. Overall, while top-down methods are advantageous for scalability, they are hard to produce GNRs with atomically precise edges and uniform widths, which are essential for reliable electronic and catalytic applications.

In contrast, the bottom-up approach offers atomic-level control over the width, edge configuration, and chemical composition of GNRs^{4,10,11,14}. Among these strategies, on-surface polymerization has emerged as a powerful method for constructing GNRs with well-defined edge structures and width²⁹⁻³⁷. As shown in Figure 1.3, in this process, precursors are deposited onto catalytic metal surfaces such as Au(111), Ag(111), or Cu(111) under ultrahigh vacuum conditions (UHV)³⁷. Upon thermal activation, these monomers undergo coupling reactions to form linear polymer chains on the catalytic metal surface. Subsequent cyclodehydrogenation at higher temperature converts these

polymers into fully conjugated GNRs with atomically precise edge structures. By designing precursor molecules, the resulting nanoribbons can be synthesized with predetermined widths and edge configurations (armchair or zigzag), thereby resulting in controlled electronic properties. This bottom-up methodology thus provides good structural control, enabling the systematic synthesis of GNRs for fundamental studies and potential applications in nanoscale electronic and optoelectronic devices.

However, there are still two challenges that hinder the synthesis of edge-functionalized GNRs. Firstly, because fragile substituents tend to degrade at high temperatures (300-500 °C) during polymerization and cyclodehydrogenation³⁸⁻⁴⁰, only exceptionally stable substituents can withstand these harsh conditions⁴¹⁻⁴³. For example, electron-withdrawing groups such as cyanide and fluorine, as well as electron-donating groups such as alkoxy, typically decompose around 300 °C. Secondly, on-surface synthesis is limited to monolayer growth, as the dehydrogenation step requires direct contact between the prepolymer chains and the thermally activated metal surface to facilitate hydrogen atom abstraction⁴⁴⁻⁴⁶. Consequently, achieving multilayered growth, which is essential for large-scale or bulk production of GNRs, remains a significant challenge.

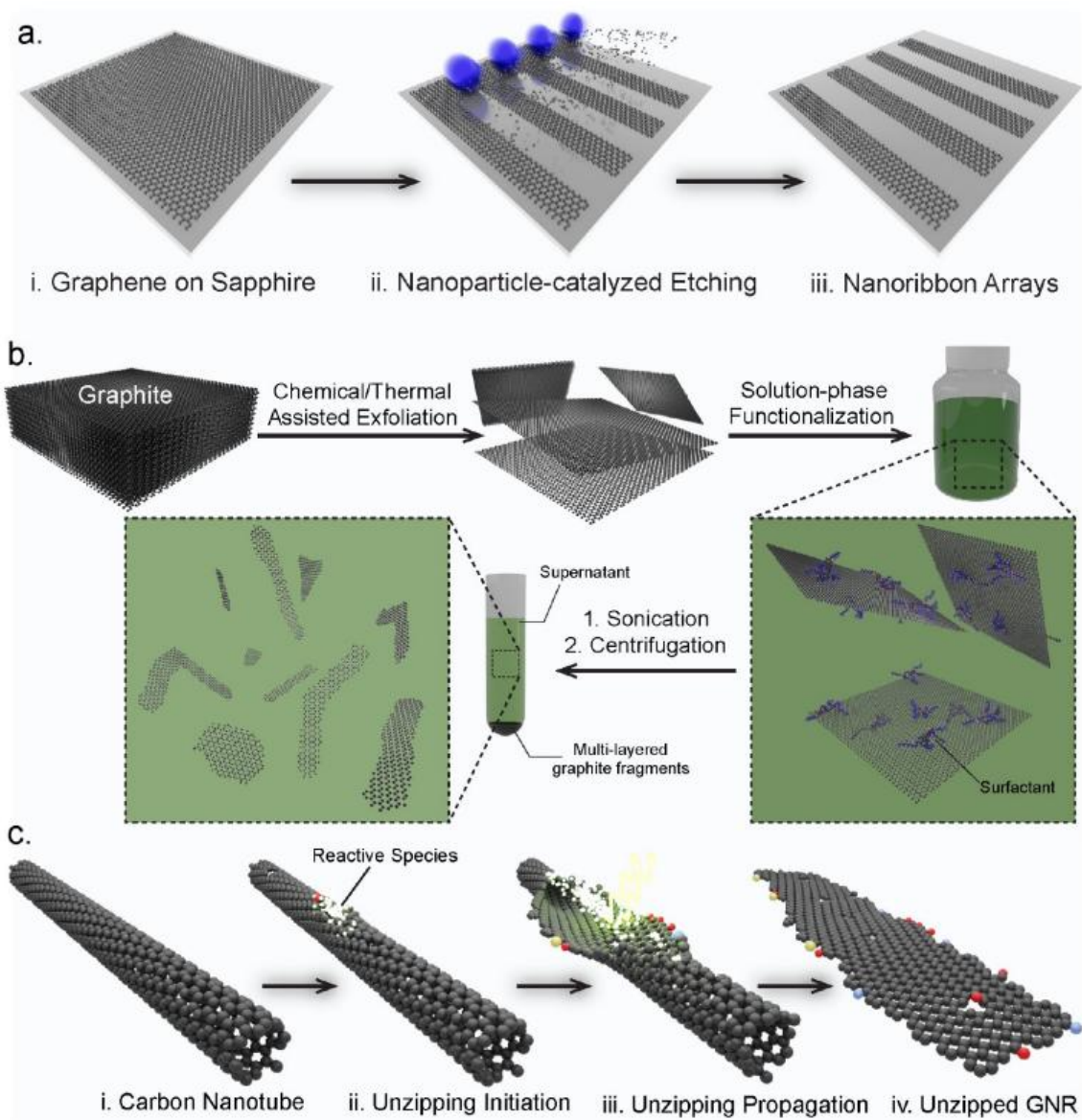


Figure 1.2. Top-down method for GNR fabrication¹¹. (a) Formation of GNR arrays using nanoparticle-catalyzed etching of graphene. (b) Unzipping of graphite to GNRs. (c) Unzipping of CNTs to GNRs.

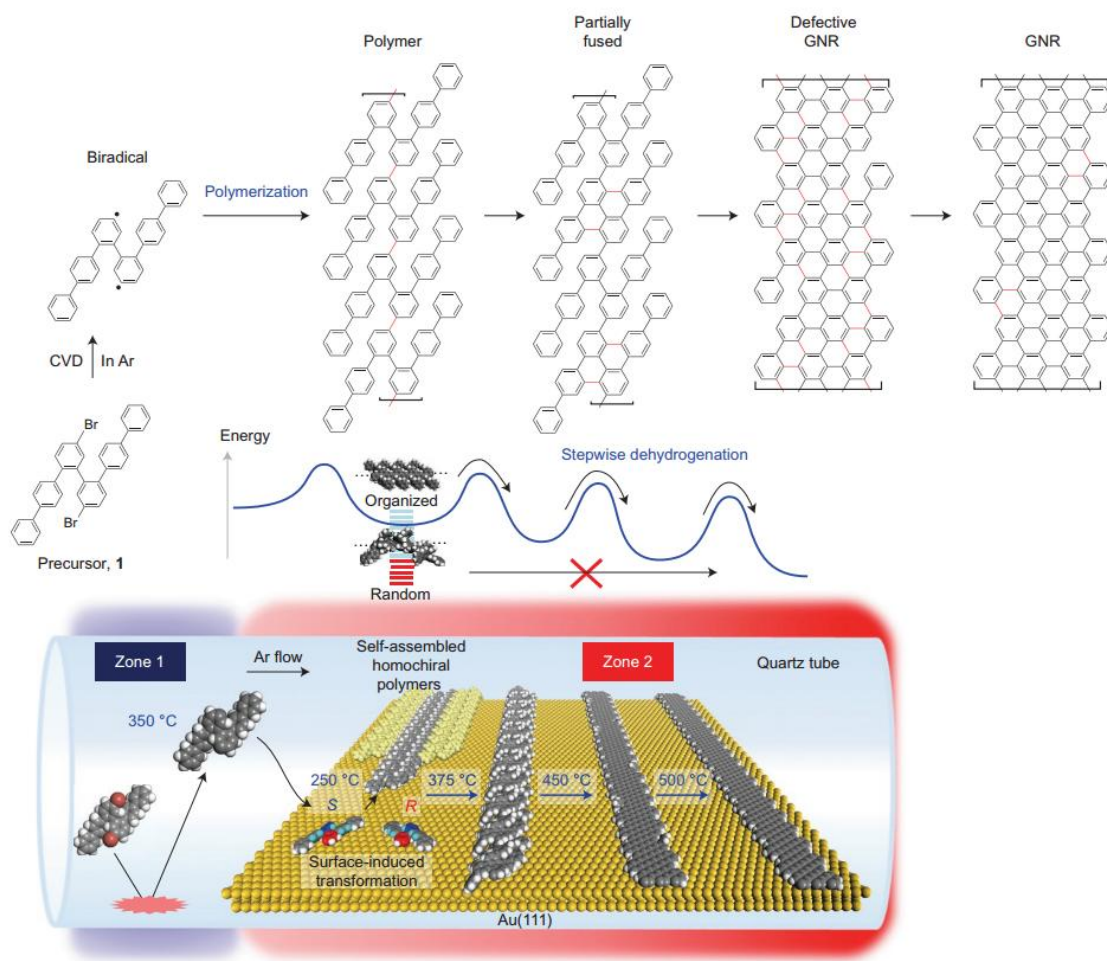


Figure 1.3. On-surface growth of acene-type GNRs from Z-bar-linkage by 2Z-CVD³⁷.

1.3 Doping of graphene nanoribbons

The electronic structures of GNRs are sensitive to heteroatom doping, which can significantly influence their chemical properties. Many researchers have found that doping heteroatoms, such as nitrogen (N) and boron (B), can alter the electronic structure of GNRs, thereby improving their catalytic properties for redox reactions^{47–50}. For example, Shigeki Kawai *et al.* successfully synthesized boron-doped graphene nanoribbons that exhibit strong electron-accepting properties via on-surface chemical reactions with an employed organoboron precursor⁵¹. Then, Youyong Li *et al.* demonstrated that boron-doped GNRs exhibit high catalytic performance in the oxygen reduction reaction via DFT simulations⁴⁹ (Figure 1.4a,b). The charge distribution on the boron-doped GNR will be nonuniform because of the smaller electronegativity of boron (2.04) with respect to carbon (2.55), which induces a positive charge on the boron atom. Boron atoms will act as active sites for O₂ adsorption and reduction. In contrast, nitrogen doping, which introduces nitrogen atoms with higher electronegativity, leads to the adjacent carbon atoms becoming positively charged^{52,53} (Figure 1.4c). Those carbon atoms with a positive effective charge will work as active points for redox reactions. Therefore, heteroatom doping is considered to be an effective way to improve the catalytic performance of carbon materials, including GNRs (Figure 1.4d,e).

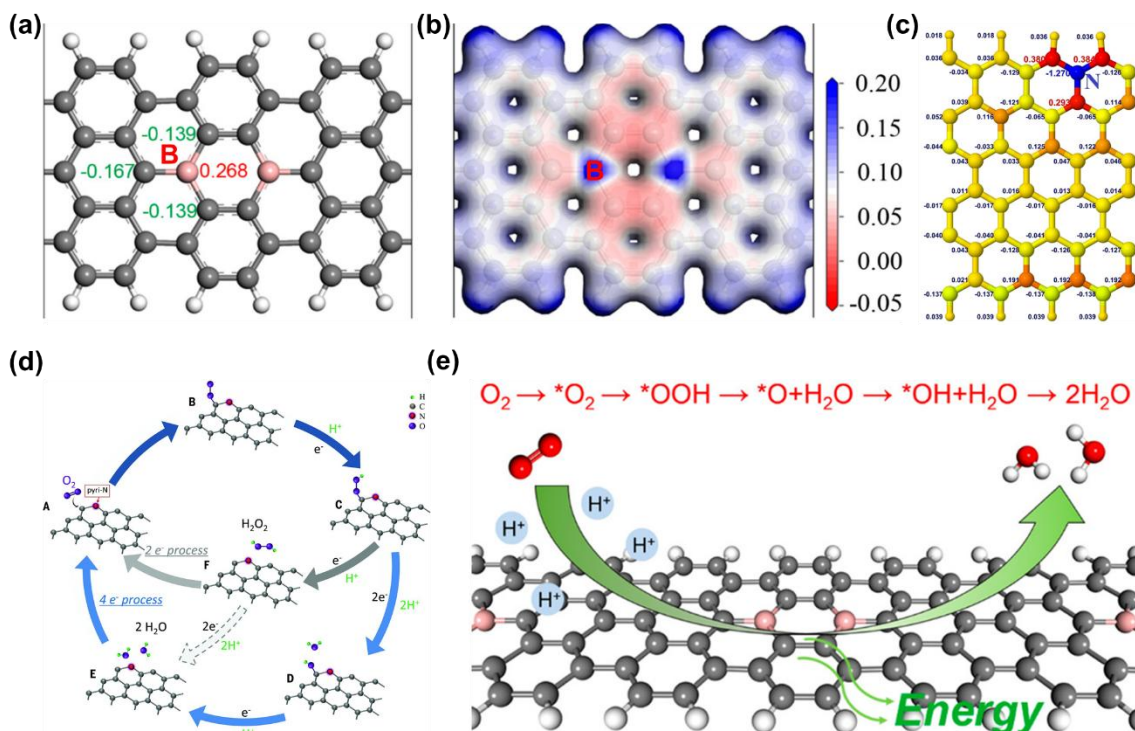


Figure 1.4. (a) Mulliken charge values on boron-doped GNR and carbon atoms neighboring the boron⁴⁹. (b) Electrostatic potential (ESP) isosurface on boron-doped GNR⁴⁹. (c) Mulliken charge values on nitrogen-doped graphene⁵³. (d) Pathway for oxygen reduction reaction (ORR) on nitrogen-doped graphene⁵². (e) Schematic pathway for ORR on boron-doped GNRs⁴⁹.

1.4 Metal-assisted chemical etching

Metal-assisted chemical etching (MaCE) is a widely used wet-chemical technique for fabricating silicon (Si) nanostructures. In this process, noble metal catalysts such as silver (Ag), gold (Au), or platinum (Pt) are first deposited onto the Si surface to induce localized etching^{54–58}. The etching solution generally consists of hydrogen peroxide (H_2O_2) as an oxidizing agent and hydrofluoric acid (HF) as an etchant. When the Si substrate coated with the metal catalyst is immersed in the solution or placed in the vapor⁵⁹, H_2O_2 is reduced on the metal surface, generating holes that are injected into the underlying Si. These holes promote the oxidation of Si at the metal/Si interface, and the resulting SiO_2 is subsequently dissolved by HF, thereby enabling localized etching beneath the metal catalyst⁵⁴ (Figure 1.5a). This catalytic process enables anisotropic etching and the precise formation of Si nanostructures, such as nanowires, nanopores, and microchannels, without complex lithographic steps⁶⁰ (Figure 1.5b).

However, MaCE also presents several challenges arising from the metal catalysts. One major issue is contamination of the Si surface by residual metal nanoparticles after etching^{61,62}. As shown in Figure 1.5c, even a single gold particle could dig deeply into Si⁶³. Such unpredictable contamination may occur during the etching process and act as deep-level traps or recombination centers in Si, severely damaging the electrical properties of wafers. Therefore, developing a new catalyst without contamination could be important.

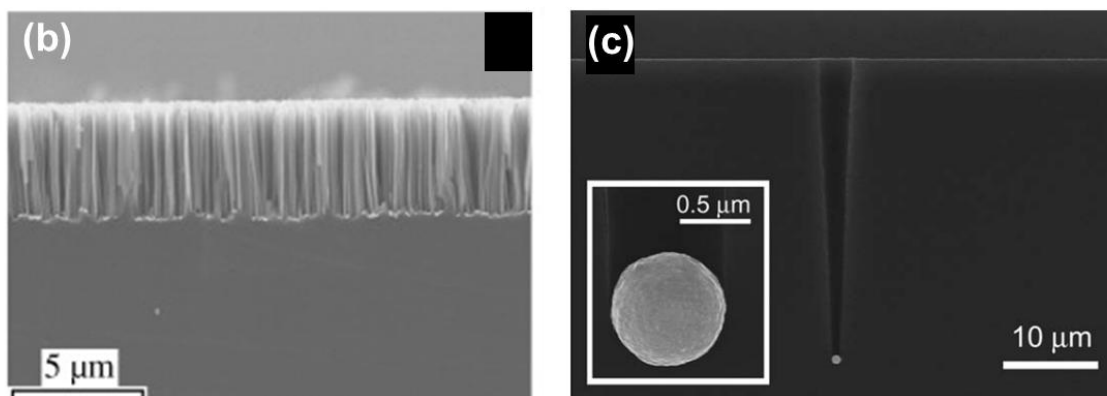
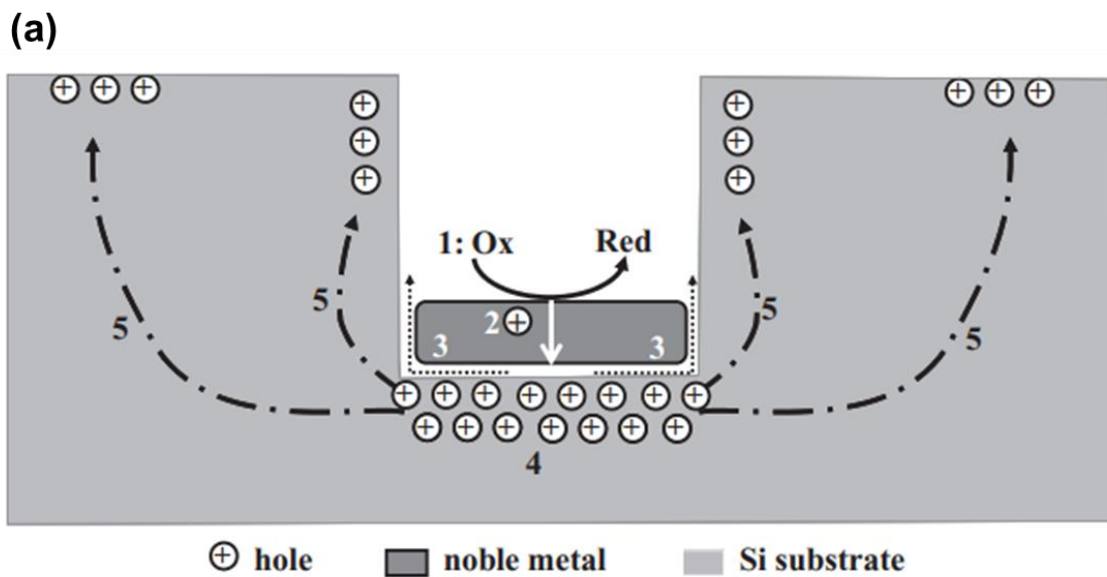


Figure 1.5. (a) Scheme of processes involved in MaCE⁵⁴. (b) SEM cross-sectional image of a typical Si sample after MaCE⁶⁰. (c) MaCE catalyzed by a single spherical Au particle⁶³.

1.5 Carbon-based catalyst for chemical etching of silicon

To address contamination hazards posed by noble-metal catalysts, carbon-based materials have been explored as alternative catalysts for silicon etching (Figure 1.6)^{61,64–66}. Carbon-based materials offer several advantages over noble metals. For example, carbon residues can be more easily removed than metallic contaminants. Moreover, carbon-based materials cost less than noble metals such as gold. Previous studies have demonstrated the catalytic activity of various carbon-based materials, including graphene⁶⁴, carbon nanotubes⁶¹, and graphene oxide^{65,66}, in the chemical etching of silicon. However, the catalytic performance of these carbon-based catalysts remains lower than that obtained with noble metals. Therefore, the development of high-performance carbon-based catalysts is essential for advancing the fabrication of silicon nanostructures.

To improve the catalytic performance of carbon-based materials, many studies have shown that edge structures and dopants in graphene can alter local π -electron density, thereby enhancing catalytic performance in redox reactions^{67–70}. Notably, one-dimensional (1D) carbon materials, such as GNRs, exhibit a higher abundance of edge structures than two-dimensional (2D) materials such as graphene, potentially offering more active sites for etching reactions^{68,69}. Among the various types of GNRs, armchair graphene nanoribbons stand out as promising materials for catalysis due to their tunable electronic properties and high stability. Heteroatom-doping of A-GNRs could be a promising strategy to enhance the catalytic performance of carbon-based catalysts in the Si etching process.

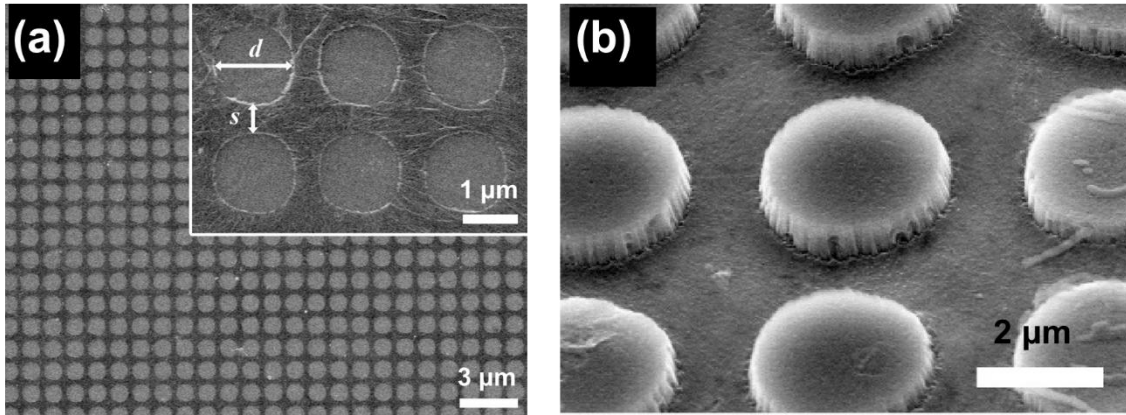


Figure 1.6. (a) Top-view SEM images of CNT-patterned Si before etching⁶¹, (b) Si micropillars etched by using undoped CNTs catalyst in (a)⁶¹.

1.6 Motivation and objectives

GNRs have attracted widespread attention due to their tunable electronic properties, which can be precisely controlled by modifying their widths and edge structures. We think edge functionalization, achieved by introducing electron-donating or electron-withdrawing groups into the conjugated framework, is a powerful strategy for tailoring the electronic energy levels, charge distribution, and interfacial characteristics of GNRs. Such chemical modifications are vital for enhancing device performance and for expanding the potential applications of GNRs in catalysis, optoelectronics, and energy conversion. Consequently, the development of reliable methods for synthesizing edge-functionalized GNRs has become an essential topic in nanocarbon research. Among the various synthetic approaches developed, on-surface synthesis on thermally activated metal substrates under UHV conditions has emerged as one of the most powerful and widely adopted methods. In this

process, molecular precursors are deposited onto a catalytic metal surface, followed by thermally induced polymerization and subsequent cyclodehydrogenation to yield fully conjugated GNRs. This method enables atomic-level control over ribbon width and edge orientation, resulting in highly ordered, defect-free structures.

However, it faces two intrinsic limitations: the thermal instability of functional substituents and the restriction of growth to a single molecular layer. The first limitation arises from the fragility of functional groups in precursor molecules, which often decompose at high temperatures, typically between 300 and 500 °C. Because the on-surface synthesis method required a high temperature over 300 °C to induce the surface-assisted polymerization and dehydrogenation. Consequently, conventional UHV-based methods are generally unsuitable for synthesizing edge-functionalized GNRs. The second challenge is the inherent monolayer growth constraint of thermal on-surface synthesis. Because dehydrogenation requires direct contact between prepolymers and the metal catalyst surface to remove hydrogen atoms, only the bottom molecular layer can be converted into GNRs. As a result, multilayer or bulk growth can still not be achieved in most cases, which is crucial for scalable production. Overcoming these limitations requires a fundamentally different synthetic strategy that enables low-temperature reactions compatible with fragile substituents while permitting controlled, vertical layer-by-layer growth beyond the monolayer limit.

In this thesis, we developed an on-surface electrochemical method for the synthesis of GNRs. It utilizes redox reactions of asymmetric precursors (2-butoxynaphthalene) within the electric double layer, where a strong electric

field is confined to the solid-electrolyte interface. We successfully achieved the layer-by-layer growth of strong electron-donating GNRs on gold electrodes at temperatures below 80°C without decomposing functional groups. Then, we found a previously unknown heterochiral di-cationic polymerization mechanism for GNR synthesis. Besides, electrochemically produced GNRs with butoxy functional groups exhibit strong catalytic activity for silicon, exceeding that of noble metals. Our technique enables the production of various edge-functional GNRs.

In Chapter 1, we introduced the background of graphene nanoribbons, focusing on synthesis methods and edge functionalization. The background of metal-assisted chemical etching was also discussed.

In Chapter 2, we introduce the typical experimental procedures and the characterization method.

In Chapter 3, to address the decomposition of functional groups at high temperatures and the limitation of monolayer growth in the conventional on-surface synthesis method, we developed the electrochemical on-surface synthesis method as a novel approach for the controlled growth of edge-functionalized GNRs. Unlike conventional on-surface thermal synthesis techniques, which require high-temperature activation (300-500 °C) and are unsuitable for thermally fragile substituents, this strategy operates via a fundamentally different reaction mechanism. By integrating electrochemical control with molecular self-assembly at the solid-liquid interface, we achieved low-temperature polymerization and dehydrogenation processes, enabling the synthesis of structurally well-defined, edge-functionalized GNRs. Then, the

mechanism of this method is further studied using an in situ electro-absorption measurement. We demonstrated that electrochemical on-surface synthesis proceeds via a reaction pathway fundamentally distinct from traditional radical polymerization. The key active intermediate is a dicationic species generated by a two-electron oxidation at a high potential. This dication promotes heterochiral dicationic polymerization, in which coupling selectively occurs between the carbon atom at position 1 of the dication and the carbon atom at position 5 of the precursor. The resulting polymer undergoes dehydrogenation, ultimately forming edge-functionalized GNRs. We demonstrate that our electrochemical on-surface synthesis method provides a versatile and scalable platform for constructing atomically precise GNRs with functionalized edges.

In Chapter 4, to study the catalytic performance of the 5A-OGNR in Si etching, we performed a vapor-phase Si etching experiment using H_2O_2 as the oxidant, HF as the etchant, and 5A-OGNR as the catalyst. We also set reference experiments with carbon-based catalysts and the gold catalyst in the same etching conditions. The results show that 5A-OGNRs exhibit the best catalytic performance among other materials, surpassing that of graphene, carbon nanotubes, graphene oxide, and gold. In addition to its catalytic performance, it also exhibits remarkable photoconductive behavior upon FeCl_3 doping. The result shows the potential of electrochemically synthesized 5A-OGNRs as next-generation functional materials for nanoscale electronics, optoelectronics, and semiconductor processing.

In Chapter 5, to study the underlying mechanism of the high catalytic performance of 5A-OGNR in Si etching, we performed density functional theory (DFT) calculations. The H_2O_2 reduction process with 5A-OGNR,

undoped GNRs, and graphene catalyst was compared. This step is essential to the Si etching process because it generates holes and oxidizes the Si. The results indicate that introducing oxygen atoms will alter the charge distribution in 5A-OGNRs, forming active sites at adjacent carbon atoms. The active sites will contribute to both the adsorption of H_2O_2 and its reduction. Therefore, 5A-OGNRs will exhibit higher catalytic performance than undoped ones. The DFT calculation not only successfully explains the mechanism by which 5A-OGNRs can exhibit high catalytic performance, but also provides guidance on designing effective carbon-based catalysts for Si etching.

In chapter 6, a general conclusion and future perspective were given.

References

1. Son, Y.-W., Cohen, M. L. & Louie, S. G. Energy Gaps in Graphene Nanoribbons. *Phys. Rev. Lett.* **97**, 216803 (2006).
2. Yang, L., Park, C.-H., Son, Y.-W., Cohen, M. L. & Louie, S. G. Quasiparticle Energies and Band Gaps in Graphene Nanoribbons. *Phys. Rev. Lett.* **99**, 186801 (2007).
3. Zhou, X. & Yu, G. Modified Engineering of Graphene Nanoribbons Prepared via On-Surface Synthesis. *Advanced Materials* **32**, 1905957 (2020).
4. Cai, J. *et al.* Atomically precise bottom-up fabrication of graphene nanoribbons. *Nature* **466**, 470–473 (2010).
5. Llinas, J. P. *et al.* Short-channel field-effect transistors with 9-atom and 13-atom wide graphene nanoribbons. *Nat Commun.* **8**, 633 (2017).
6. Wang, X. *et al.* Room-Temperature All-Semiconducting Sub-10-nm Graphene Nanoribbon Field-Effect Transistors. *Phys. Rev. Lett.* **100**, 206803 (2008).
7. Li, H. *et al.* Photoluminescent Semiconducting Graphene Nanoribbons via Longitudinally Unzipping Single-Walled Carbon Nanotubes. *ACS Appl. Mater. Interfaces* **13**, 52892–52900 (2021).

8. Lin, M.-W. *et al.* Approaching the intrinsic band gap in suspended high-mobility graphene nanoribbons. *Phys. Rev. B* **84**, 125411 (2011).
9. Schwierz, F. Graphene transistors. *Nature Nanotech* **5**, 487–496 (2010).
10. Lou, S. *et al.* Graphene nanoribbons: current status, challenges and opportunities. *Quantum Front* **3**, 3 (2024).
11. Saraswat, V., Jacobberger, R. M. & Arnold, M. S. Materials Science Challenges to Graphene Nanoribbon Electronics. *ACS Nano* **15**, 3674–3708 (2021).
12. Nakada, K., Fujita, M., Dresselhaus, G. & Dresselhaus, M. S. Edge state in graphene ribbons: Nanometer size effect and edge shape dependence. *Phys. Rev. B* **54**, 17954–17961 (1996).
13. Tian, C., Miao, W., Zhao, L. & Wang, J. Graphene nanoribbons: Current status and challenges as quasi-one-dimensional nanomaterials. *Reviews in Physics* **10**, 100082 (2023).
14. Houtsma, R. S. K., De La Rie, J. & Stöhr, M. Atomically precise graphene nanoribbons: interplay of structural and electronic properties. *Chem. Soc. Rev.* **50**, 6541–6568 (2021).
15. Ezawa, M. Peculiar width dependence of the electronic properties of carbon nanoribbons. *Phys. Rev. B* **73**, 045432 (2006).

16. Fujita, M., Wakabayashi, K., Nakada, K. & Kusakabe, K. Peculiar Localized State at Zigzag Graphite Edge. *J. Phys. Soc. Jpn.* **65**, 1920–1923 (1996).
17. Wakabayashi, K., Fujita, M., Ajiki, H. & Sigrist, M. Electronic and magnetic properties of nanographite ribbons. *Phys. Rev. B* **59**, 8271–8282 (1999).
18. Fernández-Rossier, J. Prediction of hidden multiferroic order in graphene zigzag ribbons. *Phys. Rev. B* **77**, 075430 (2008).
19. Palacios, J. J., Fernández-Rossier, J. & Brey, L. Vacancy-induced magnetism in graphene and graphene ribbons. *Phys. Rev. B* **77**, 195428 (2008).
20. Son, Y.-W., Cohen, M. L. & Louie, S. G. Half-metallic graphene nanoribbons. *Nature* **444**, 347–349 (2006).
21. Chen, C. *et al.* Sub-10-nm graphene nanoribbons with atomically smooth edges from squashed carbon nanotubes. *Nat. Electron* **4**, 653–663 (2021).
22. Jiao, L., Wang, X., Diankov, G., Wang, H. & Dai, H. Facile synthesis of high-quality graphene nanoribbons. *Nature Nanotech* **5**, 321–325 (2010).
23. Jiao, L., Zhang, L., Wang, X., Diankov, G. & Dai, H. Narrow graphene nanoribbons from carbon nanotubes. *Nature* **458**, 877–880 (2009).

24. Liu, L. *et al.* Nanosphere Lithography for the Fabrication of Ultranarrow Graphene Nanoribbons and On-Chip Bandgap Tuning of Graphene. *Advanced Materials* **23**, 1246–1251 (2011).
25. Shi, Z. *et al.* Patterning Graphene with Zigzag Edges by Self-Aligned Anisotropic Etching. *Advanced Materials* **23**, 3061–3065 (2011).
26. Wang, X. & Dai, H. Etching and narrowing of graphene from the edges. *Nature Chem.* **2**, 661–665 (2010).
27. Li, X., Wang, X., Zhang, L., Lee, S. & Dai, H. Chemically Derived, Ultrasooth Graphene Nanoribbon Semiconductors. *Science* **319**, 1229–1232 (2008).
28. Ago, H., Kayo, Y., Solís-Fernández, P., Yoshida, K. & Tsuji, M. Synthesis of high-density arrays of graphene nanoribbons by anisotropic metal-assisted etching. *Carbon* **78**, 339–346 (2014).
29. Cai, J. *et al.* Atomically precise bottom-up fabrication of graphene nanoribbons. *Nature* **466**, 470–473 (2010).
30. Huang, H. *et al.* Spatially Resolved Electronic Structures of Atomically Precise Armchair Graphene Nanoribbons. *Sci. Rep.* **2**, 983 (2012).
31. Kimouche, A. *et al.* Ultra-narrow metallic armchair graphene nanoribbons. *Nat Commun.* **6**, 10177 (2015).

32. Ruffieux, P. *et al.* On-surface synthesis of graphene nanoribbons with zigzag edge topology. *Nature* **531**, 489–492 (2016).
33. Rizzo, D. J. *et al.* Inducing metallicity in graphene nanoribbons via zero-mode superlattices. *Science* **369**, 1597–1603 (2020).
34. De Oteyza, D. G. *et al.* Substrate-Independent Growth of Atomically Precise Chiral Graphene Nanoribbons. *ACS Nano* **10**, 9000–9008 (2016).
35. Wang, X.-Y. *et al.* Bottom-Up Synthesis of Heteroatom-Doped Chiral Graphene Nanoribbons. *J. Am. Chem. Soc.* **140**, 9104–9107 (2018).
36. Rizzo, D. J. *et al.* Topological band engineering of graphene nanoribbons. *Nature* **560**, 204–208 (2018).
37. Sakaguchi, H., Song, S., Kojima, T. & Nakae, T. Homochiral polymerization-driven selective growth of graphene nanoribbons. *Nature Chem.* **9**, 57–63 (2017).
38. Carbonell-Sanromà, E. *et al.* Doping of Graphene Nanoribbons via Functional Group Edge Modification. *ACS Nano* **11**, 7355–7361 (2017).
39. Hayashi, H. *et al.* Experimental and Theoretical Investigations of Surface-Assisted Graphene Nanoribbon Synthesis Featuring Carbon–Fluorine Bond Cleavage. *ACS Nano* **11**, 6204–6210 (2017).

40. Panighel, M. *et al.* Stabilizing Edge Fluorination in Graphene Nanoribbons. *ACS Nano* **14**, 11120–11129 (2020).
41. Nguyen, G. D. *et al.* Atomically precise graphene nanoribbon heterojunctions from a single molecular precursor. *Nature Nanotech.* **12**, 1077–1082 (2017).
42. Blackwell, R. E. *et al.* Spin splitting of dopant edge state in magnetic zigzag graphene nanoribbons. *Nature* **600**, 647–652 (2021).
43. Sun, K. *et al.* On-surface synthesis of disilabenzene-bridged covalent organic frameworks. *Nat. Chem.* **15**, 136–142 (2023).
44. Björk, J., Stafström, S. & Hanke, F. Zipping Up: Cooperativity Drives the Synthesis of Graphene Nanoribbons. *J. Am. Chem. Soc.* **133**, 14884–14887 (2011).
45. Clair, S. & De Oteyza, D. G. Controlling a Chemical Coupling Reaction on a Surface: Tools and Strategies for On-Surface Synthesis. *Chem. Rev.* **119**, 4717–4776 (2019).
46. Grill, L. & Hecht, S. Covalent on-surface polymerization. *Nat. Chem.* **12**, 115–130 (2020).

47. Lherbier, A., Liang, L., Charlier, J.-C. & Meunier, V. Charge carrier transport and separation in pristine and nitrogen-doped graphene nanowiggle heterostructures. *Carbon* **95**, 833–842 (2015).
48. Bronner, C. *et al.* Aligning the Band Gap of Graphene Nanoribbons by Monomer Doping. *Angew. Chem. Int. Ed.* **52**, 4422–4425 (2013).
49. Wang, L. *et al.* Potential Application of Novel Boron-Doped Graphene Nanoribbon as Oxygen Reduction Reaction Catalyst. *J. Phys. Chem. C* **120**, 17427–17434 (2016).
50. Carbonell-Sanromà, E. *et al.* Doping of Graphene Nanoribbons via Functional Group Edge Modification. *ACS Nano* **11**, 7355–7361 (2017).
51. Kawai, S. *et al.* Atomically controlled substitutional boron-doping of graphene nanoribbons. *Nat. Commun.* **6**, 8098 (2015).
52. Guo, D. *et al.* Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts. *Science* **351**, 361–365 (2016).
53. Li, M., Zhang, L., Xu, Q., Niu, J. & Xia, Z. N-doped graphene as catalysts for oxygen reduction and oxygen evolution reactions: Theoretical considerations. *Journal of Catalysis* **314**, 66–72 (2014).

54. Huang, Z., Geyer, N., Werner, P., De Boor, J. & Gösele, U. Metal-Assisted Chemical Etching of Silicon: A Review: In memory of Prof. Ulrich Gösele. *Advanced Materials* **23**, 285–308 (2011).
55. Han, H., Huang, Z. & Lee, W. Metal-assisted chemical etching of silicon and nanotechnology applications. *Nano Today* **9**, 271–304 (2014).
56. Surdo, S. & Barillaro, G. Voltage- and Metal-assisted Chemical Etching of Micro and Nano Structures in Silicon: A Comprehensive Review. *Small* **20**, 2400499 (2024).
57. Srivastava, R. P. & Khang, D. Structuring of Si into Multiple Scales by Metal-Assisted Chemical Etching. *Advanced Materials* **33**, 2005932 (2021).
58. Huo, C. *et al.* Metal-Assisted Chemical Etching of Silicon in Oxidizing HF Solutions: Origin, Mechanism, Development, and Black Silicon Solar Cell Application. *Adv. Funct. Materials* **30**, 2005744 (2020).
59. Hildreth, O. J. & Schmidt, D. R. Vapor Phase Metal-Assisted Chemical Etching of Silicon. *Adv. Funct. Materials* **24**, 3827–3833 (2014).
60. Peng, K. *et al.* Uniform, Axial-Orientation Alignment of One-Dimensional Single-Crystal Silicon Nanostructure Arrays. *Angew. Chem. Int. Ed.* **44**, 2737–2742 (2005).

61. Wilhelm, T. S. *et al.* Ordered Si Micropillar Arrays via Carbon-Nanotube-Assisted Chemical Etching for Applications Requiring Nonreflective Embedded Contacts. *ACS Appl. Nano Mater.* **2**, 7819–7826 (2019).
62. Kubota, W., Utsunomiya, T., Ichii, T. & Sugimura, H. Chemical Etching of Silicon Assisted by Graphene Oxide in an HF–HNO₃ Solution and Its Catalytic Mechanism. *Langmuir* **37**, 9920–9926 (2021).
63. Lee, C.-L., Tsujino, K., Kanda, Y., Ikeda, S. & Matsumura, M. Pore formation in silicon by wet etching using micrometre-sized metal particles as catalysts. *J. Mater. Chem.* **18**, 1015 (2008).
64. Kim, J., Lee, D. H., Kim, J. H. & Choi, S.-H. Graphene-Assisted Chemical Etching of Silicon Using Anodic Aluminum Oxides as Patterning Templates. *ACS Appl. Mater. Interfaces* **7**, 24242–24246 (2015).
65. Xu, Y., Zhao, Q., Chen, J., Zhang, J. & Xu, B. Rapid graphene oxide assisted chemical etching of silicon in HF/H₂O₂ solution. *Phys. Scr.* **99**, 085914 (2024).
66. Hirano, T., Nakade, K., Li, S., Kawai, K. & Arima, K. Chemical etching of a semiconductor surface assisted by single sheets of reduced graphene oxide. *Carbon* **127**, 681–687 (2018).

67. Zhao, H. *et al.* Carbon for the oxygen reduction reaction: a defect mechanism. *J. Mater. Chem. A* **3**, 11736–11739 (2015).
68. Shen, A. *et al.* Oxygen Reduction Reaction in a Droplet on Graphite: Direct Evidence that the Edge Is More Active than the Basal Plane. *Angew. Chem. Int. Ed.* **53**, 10804–10808 (2014).
69. Deng, D. *et al.* Size effect of graphene on electrocatalytic activation of oxygen. *Chem. Commun.* **47**, 10016 (2011).
70. Tang, C. *et al.* Topological Defects in Metal-Free Nanocarbon for Oxygen Electrocatalysis. *Advanced Materials* **28**, 6845–6851 (2016).

Chapter 2. Experimental

2.1 General information

In this chapter, the experimental methodology for the two-zone chemical vapor deposition of 5-armchair graphene nanoribbon (5A-GNR) and 7-armchair graphene nanoribbon (7A-GNR), which will serve as a comparison sample, is described. The GNR transfer method will be described. All general information about the characterization equipment will be provided.

2.1.1 Two-zone chemical vapor deposition

The two-zone chemical vapor deposition system employed a quartz tube reactor (26 mm in diameter and 86 cm in length) connected to a rotary pump that evacuated the chamber to pressures below 7×10^{-4} Torr. The system was equipped with a two-zone electric furnace controlled by a programmable temperature controller, an argon (Ar) gas delivery line with a mass-flow controller, and a mantle heater for precursor evaporation. For the synthesis of GNRs, the molecular precursors (a mixture of 3,9-dibromoperylene and 3,10-dibromoperylene for 5-AGNR and 10,10'-dibromo-9,9'-bianthracene for 7-AGNR) were placed in a quartz boat together with the Au(111)-deposited mica or glass substrate inside the quartz tube. Ar gas was introduced at a flow rate of 500 sccm, maintaining the system pressure at approximately 1 Torr. The GNR synthesis proceeded in two sequential stages. In the first stage, the temperature of zone 2 was set to 250 °C to promote precursor evaporation. In comparison, the precursor pathway in zone 1 was maintained at 350 °C to assist in precursor transport and polymerization on the substrate surface. In the second stage, the

temperature of zone 2 was further elevated to induce dehydrogenation, thereby converting the polymer chains into fully conjugated graphene nanoribbons.

2.1.2 Transfer of graphene nanoribbons

GNRs produced by electrochemical on-surface synthesis or by CVD were transferred from Au(111) to silicon (Si) substrates for other studies. As shown in Figure 2.1, the GNR/Au(111)/glass assembly was first immersed in water to detach the GNR/Au(111) film from the glass substrate. Subsequently, the gold layer would dissolve in an aqueous etchant solution containing 50 mM iodine (I_2) and 1.1 M potassium iodide (KI). After the complete dissolution of the gold film, a silicon substrate was brought into contact with the floating GNR layer. After approximately 20 minutes, the silicon substrate with the transferred GNRs was removed from the etchant, rinsed sequentially with sodium sulfite (Na_2SO_3) solution and deionized water to neutralize residual iodine, and finally dried on a hot plate at 90 °C for 20 minutes.

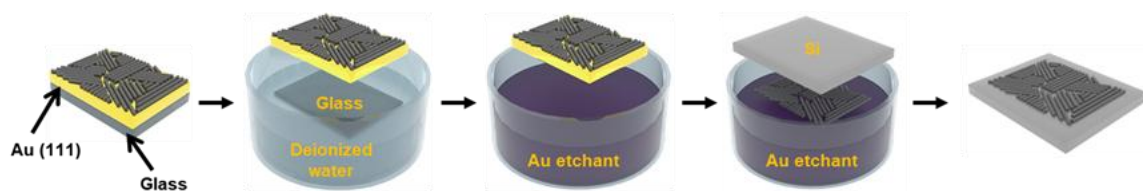


Figure 2.1. Illustration of the transfer process of the GNRs from Au (111) to Si.

2.2 Characterization

2.2.1 Scanning tunneling microscopy (STM)

STM characterization was performed to investigate the molecular and electronic structures of GNRs. All samples for LT-STM measurements were degassed in UHV and annealed at 150°C for 1 h before the measurements. LT-STM measurements were conducted in constant-current mode using a low-temperature scanning tunneling microscopy system (UNISOKU, USM-1100SA-2C) operating at 77 K. The tip was a tungsten wire that had been electrochemically etched. dI/dV spectra were acquired with a reduced feedback loop during voltage sweeps, with V_{sample} set to -0.5 V and I at 200 pA. The differential conductance map was recorded with the V_{sample} set at -0.2 V or 0.6 V and I at 80 pA by a digital lock-in amplifier with a modulation frequency of 350 Hz and an AC voltage of 2 mV. Images obtained were analyzed using SPIP software.

Room-temperature scanning tunneling microscopy (RT-STM) was performed using an instrument (formerly Molecular Imaging, PicoSPM) under Ar at room temperature. STM measurements were performed in constant-current mode, with all STM images taken at a tip bias of 0.2 V and a constant current of 5 pA. The tip used was an electrochemically etched Pt-Ir (80:20) wire.

2.2.2 Raman spectroscopy

Raman spectroscopy was performed using a Raman instrument (Lambda Vision Inc., LVRAM500/532) with a 532-nm excitation laser.

2.2.3 Atomic force microscope (AFM)

The GNRs were transferred to the Si substrate using the transfer method described in chapter 2.1.2 to perform the AFM measurement. AFM measurements were performed (CSI, AFM Galaxy Dual Controller, and Digital Instruments MultiMode AFM-2) to investigate the thickness of GNRs on the Si substrate.

2.2.4 Mass spectrometry

The sample of electrochemically on-surface synthesized GNR was analyzed using high-resolution mass spectrometry (HRMS) in positive ion mode. The instrument used was a Fourier transformation-ion cyclotron resonance mass spectrometer (FT-ICR-MS), equipped with a 7-tesla superconductive magnet and a matrix-assisted laser desorption/ionization (MALDI) ion source. The matrix used was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DTCB).

2.2.5 Cyclic voltammetry (CV)

All CV measurements were conducted using a Solartron Analytical SI 1287 electrochemical workstation with a scan rate of 50 mV s⁻¹. Platinum and silver wires served as the counter and reference electrodes, respectively. The electrolyte solution consisted of 100 mM tetrabutylammonium hexafluorophosphate in o-DCB. All cell fabrication was performed in a nitrogen-filled glove box. An Au(111) substrate was used as the working electrode for CV measurements of the 2-butoxynaphthalene solution (Chapter 3). A 5 mM solution was used for TTF CV measurement (Chapter 4). For the

CV measurement of electrochemically produced GNR, 5-AGNR, and 7-AGNR, all GNRs were formed on Au (111) substrates (Chapter 4).

2.2.6 Equipment and characterization for organic synthesis

A JEOL JNM-ECP300 (300 MHz for ^1H) instrument was used. NMR spectra were measured in parts per million using tetramethylsilane (δ 0.00 ppm for chloroform- d) as the internal standard for ^1H NMR. Thin-layer chromatography (TLC) and column chromatography were performed on Art. 5554 (Merck KGaA) and silica gel 60N (Kanto Chemical Co.), respectively. Gel permeation chromatography (GPC) was performed on an LC-9201 system (Japan Analytical Industry) with JAIGEL 1H and 2H polystyrene columns (eluent: CHCl_3 , flow: 10 mL/min).

2.3 Calculation

2.3.1 Bandgap simulation

Bandgap simulations were conducted through the CASTEP¹ module of the BIOVIA Materials Studio software suite (Dassault Systèmes SE). Molecular mechanics (MM) was utilized to optimize the structure before performing DFT calculations. To perform the MM calculation, the COMPASS II force field, along with the Forcite module, was utilized. For DFT structural optimization and bandgap simulations, the CASTEP module was utilized. The exchange-correlation functional used was the Perdew-Burke-Ernzerhof generalized-gradient approximation (GGA-PBE)², and Ultrasoft pseudopotentials were generated using the On-The-Fly Generated (OTFG) method.

2.3.2 Local density of states (LDOS) mapping simulation

Local density of states (LDOS) calculations were performed at the GGA-PBE² level, as implemented in DMol3³ (BIOVIA Materials Studio software, Dassault Systèmes SE).

2.3.3 Raman simulation

Raman simulations were conducted using the CASTEP module in the BIOVIA Materials Studio software suite (Dassault Systèmes SE). Norm-conserving pseudopotentials were employed with $16 \times 4 \times 1$ k-points. The plane-wave cutoff energy was set to 830 eV. The maximum threshold for force and displacement tolerances during structural optimization was 0.1 eV Å⁻¹ and 0.0005 Å, respectively.

2.3.4 Optical absorption spectra simulation

The purpose was to identify species that participate in the polymerization reaction, such as cation radicals and di-cations of 2-butoxynaphthalene. TD-DFT calculations were conducted at the TD-UB3LYP^{4,5} level using a 6-311G(d,p) basis set. A Gaussian⁶ program was used to simulate absorption spectra of these species.

2.3.5 Spin density, electron density mapping simulation

To identify chemical species that contribute to growth reactions among precursors, cation radicals, and dications of 2-butoxynaphthalene, we carried out spin-density and electron-density mapping calculations using the Gaussian program. The 6-311G(d,p) basis set was used to calculate the spin density of the cation radical species at the UB3LYP level.

2.3.6 Total energy and energy level simulation

To understand the reaction mechanism in terms of thermodynamics and kinetics, we employed the Gaussian program to compute the total energy and the HOMO-1 energy levels of various structures at the RB3LYP level, using the 6-311G(d,p) basis set. All the molecules were optimized by geometrical optimization.

References

1. Clark, S. J. et al. First principles methods using CASTEP. *Zeitschrift für Kristallographie. Crystalline Materials* **220**, 567–570 (2005).
2. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
3. Delley, B. From molecules to solids with the DMol3 approach. *The Journal of Chemical Physics* **113**, 7756–7764 (2000).
4. Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *The Journal of Chemical Physics* **98**, 5648–5652 (1993).
5. Nelsen, S. F., Weaver, M. N., Zink, J. I. & Telo, J. P. Optical Spectra of Delocalized Dinitroaromatic Radical Anions Revisited. *J. Am. Chem. Soc.* **127**, 10611–10622 (2005).
6. Frisch M. J. et al. Gaussian 09, *Revision B.01*, Wallingford CT (2009).

Chapter 3. Electrochemical On-Surface Synthesis of Edge-Functionalized Graphene Nanoribbon at Room Temperature

3.1 Introduction

The on-surface synthesis of edge-functionalized graphene nanoribbons (GNRs) remains a formidable challenge. First, fragile substituents are prone to thermal degradation at 300-500 °C¹⁻⁴. Second, conventional on-surface approaches are typically limited to monolayer formation, as dehydrogenation occurs only when prepolymers are in direct contact with a thermally activated metal surface⁵⁻⁷. There was one exception that successfully synthesized a second-layer GNR by using the UHV method⁸. This method accomplishes the dehydrogenation of prepolymers via a domino-like effect triggered remotely by direct contact between the GNR segment and the gold substrate. Direct contact between the prepolymer and a metal substrate is still necessary for second-layer growth, which remains a limitation of multilayer growth. These limitations hinder the precise incorporation of functional groups and restrict the scalable production of structurally defined GNRs.

To address these problems, we developed an on-surface electrochemical synthesis technique that harnesses redox reactions within the electric double layer (EDL) at the solid-liquid interface. Within the EDL, typically confined to nanometer-scale thickness, the electric field provides a unique reaction environment capable of activating adsorbed molecules at room temperatures⁹⁻¹³. As shown in Figure 3.1a, by applying voltage pulses controlled by a function generator to the working electrode immersed in an electrolyte containing tetrabutylammonium hexafluorophosphate (TBAPF₆) as conductive salts, 1,2-

dichlorobenzene (o-DCB) as solvents, and 2-butoxynaphthalene as precursor monomers, edge-functionalized GNRs will form on the working electrode layer by layer. Different from the polymerization reaction induced by high temperature in the conventional UHV method, this room-temperature electrochemical method prevents the thermal decomposition of functional groups. Moreover, because the EDL can keep forming on top of existing GNRs, the reaction can proceed continuously in the vertical direction, enabling layer-by-layer GNR growth and thus scalable fabrication.

Then, to study the mechanism of electrochemical on-surface synthesis. As shown in Figure 3.1b, we identified a pathway for electrochemical on-surface synthesis. In this pathway, a dication generated by two-electron oxidation at high voltage serves as the active intermediate, driving heterochiral dicationic polymerization followed by oxidation-induced dehydrogenation, ultimately leading to the formation of GNRs. Through a combination of experimental design, characterization, and DFT simulations, we successfully elucidated the mechanism underlying the heterochiral growth of edge-functionalized GNRs.

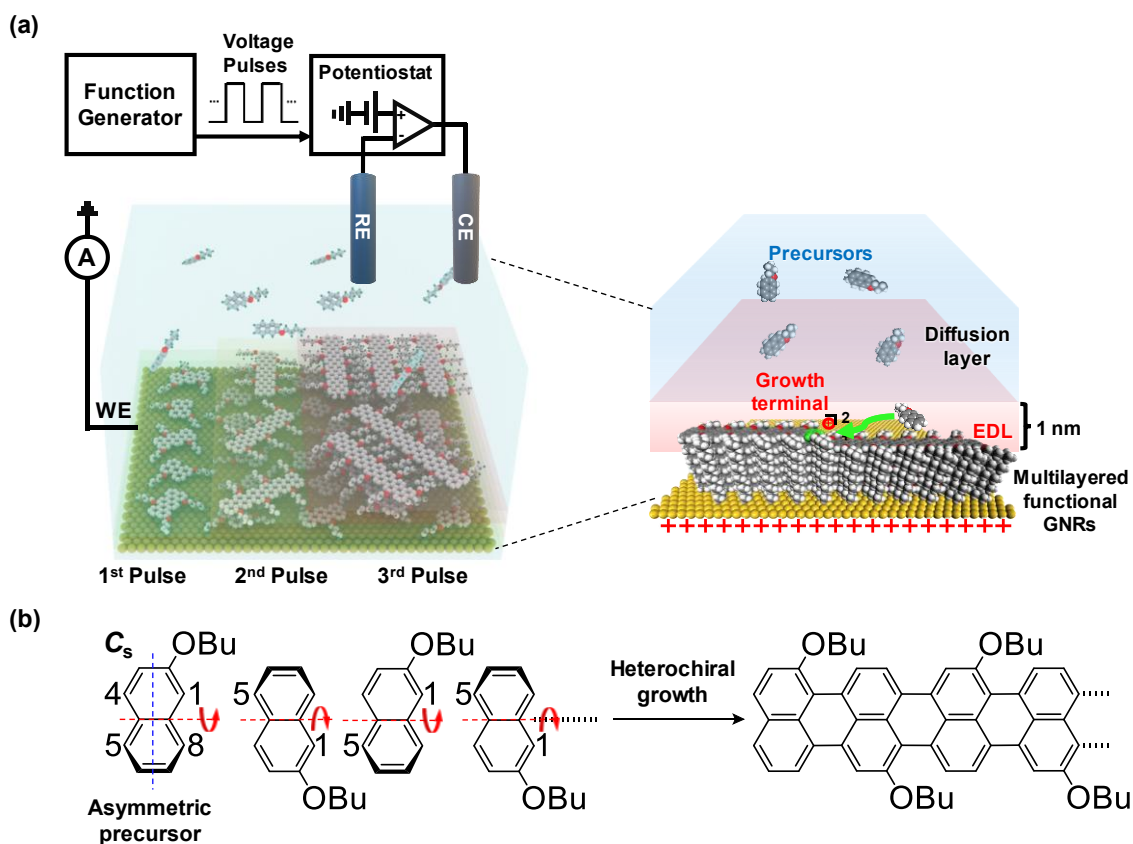
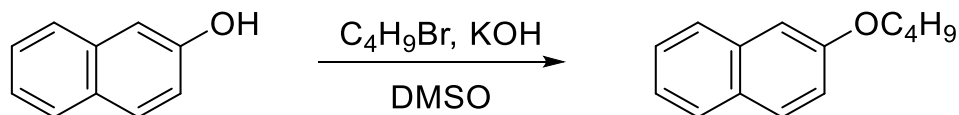


Figure 3.1. Concept of electrochemical on-surface synthesis. Illustration of (a) electrochemical on-surface synthesis and (b) heterochiral growth of functional GNRs from asymmetric precursors of 2-butoxynaphthalene.

3.2 Experimental

3.2.1 Synthesis of 2-butoxynaphthalene

The 2-butoxynaphthalene was synthesized by the following method in Scheme 3.1. A solution of 2-naphthol (2.88 g, 20.0 mmol), 1-bromobutane (3.30 g, 24.1 mmol), and KOH (2.25 g, 40.1 mmol) in DMSO (30 mL) was stirred at 95°C overnight. The reaction mixture was diluted with water and cooled in the refrigerator. The precipitated solid was separated by filtration and purified by chromatography (silica gel, hexanes) followed by GPC (CHCl_3) to afford 2-butoxynaphthalene (2.88 g, 14.4 mmol, 72% yield) as a white solid.



Scheme 3.1. Synthesis of 2-butoxynaphthalene.

Figure 3.2 shows the ^1H NMR spectrum of 2-butoxynaphthalene. ^1H NMR (300 MHz, CDCl_3) δ 7.77-7.70 (m, 3H), 7.42 (ddd, $J = 6.9, 6.9, 1.2$ Hz, 1H), 7.32 (ddd, $J = 6.9, 6.9, 1.2$ Hz, 1H), 7.31 (s, 1H), 7.14 (dd, $J = 6.9, 1.2$ Hz, 1H), 4.08 (t, $J = 6.6$ Hz, 2H), 1.88-1.79 (m, 2H), 1.60-1.48 (m, 2H), 1.00 (t, $J = 7.2$ Hz, 3H).

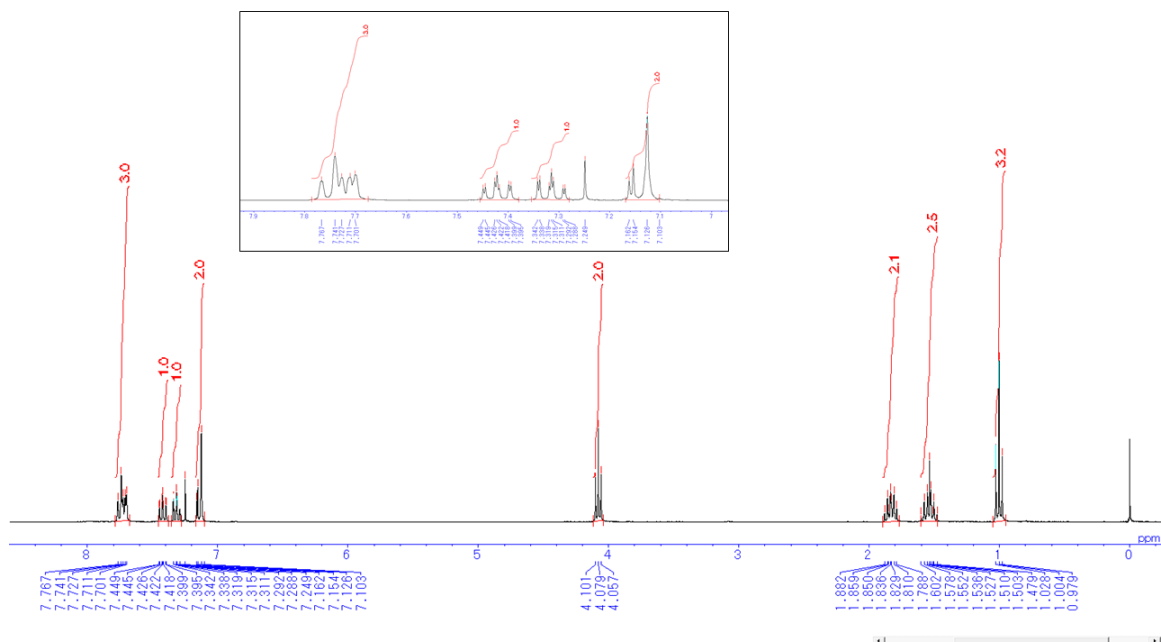


Figure 3.2. ¹H NMR spectrum of 2-butoxynaphthalene. The inset shows the magnification of the chemical shift between 7 and 8 ppm.

3.2.2 Preparation of Au (111) substrate and iodine-covered Au (111)

An Au(111) substrate for electrochemical GNR growth was prepared using a homemade e-beam vacuum deposition system. Evaporated gold was deposited on a $2.8 \times 2.8 \text{ cm}^2$ mica substrate, which was then heated at 350°C under a vacuum of $2.6 \times 10^{-6} \text{ Pa}$. An Au layer with a thickness of 40 nm was deposited at a rate of $0.5 \text{ \AA s}^{-1}$. To prepare the iodine-covered Au (111)^{14,15}, an Au (111)/mica substrate was immersed in a 10 mM iodine/chloroform solution for 2 minutes. The substrate was subsequently washed with chloroform and dried on a hot plate at 70°C for 5 min to remove the remaining solvent.

3.2.3 Cell assembling and electrochemical on-surface synthesis

As shown in Figure 3.3, the electrolyte solution was prepared in a glovebox filled with nitrogen by mixing 5 mM of 2-butoxynaphthalene and 100 mM of TBAPF₆ in o-DCB. Working electrodes, including Au(111), iodine-covered Au(111), and ITO, 0.5 × 1.0 cm² in size, were used. A platinum wire served as the counter electrode, and a silver wire served as the reference electrode. Three substrates were employed as working electrodes for different purposes. The first two substrates, Au(111) and iodine-covered Au(111), were used to examine GNR structures via STM measurements, while the transparent conductive ITO substrate was used for optical measurements. The sample cell was heated at 80 °C on a hot plate with continuous stirring for 10 minutes. Voltage pulses were applied using a potentiostat (Huso Electro Chemical System, HECS 990C) equipped with a function generator (NF, Wave Factory WF1974). After the synthesis, the sample was washed with DCM several times to remove the by-product, which could be caused by the decomposition of the TBAPF₆ or o-DCB at high voltages.

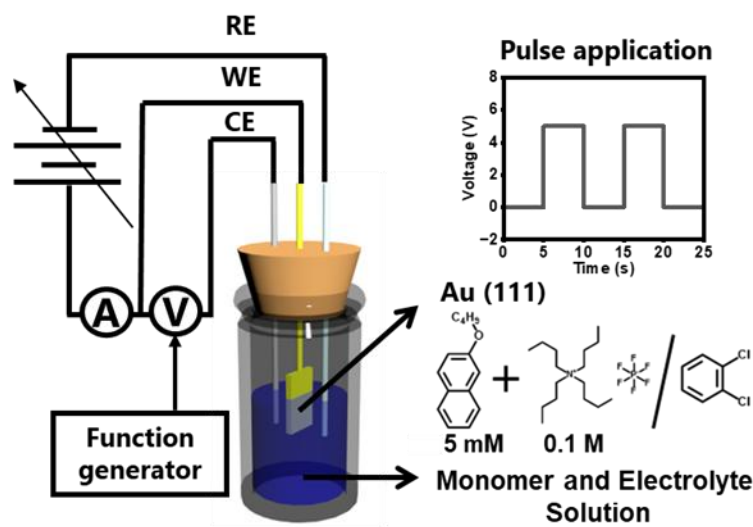


Figure 3.3. Assembly of the electrochemical cell and the electric circuit.

3.2.4 Electro-absorption measurement

As shown in Figure 3.4, in the electro-absorption cell, ITO electrodes were sandwiched with a 250 μm plastic spacer. To perform electro-absorption spectroscopy, 50 μL of electrolyte solution was injected into the cell. An optical absorption spectrometer (Lambda Vision Inc., LVmicro/SUV-100S-NIR) was used to characterize the in situ optical absorption. To measure the potential-dependent electro-absorption spectrum, various voltages ranging from 0.5 V to 3 V (vs. Ag/Ag^+) were applied for 15 s. For the temporal profile of electro-absorption measurements, we applied a voltage of 2.5 V (vs. Ag/Ag^+) for 25 sec and recorded from start to 55 sec.

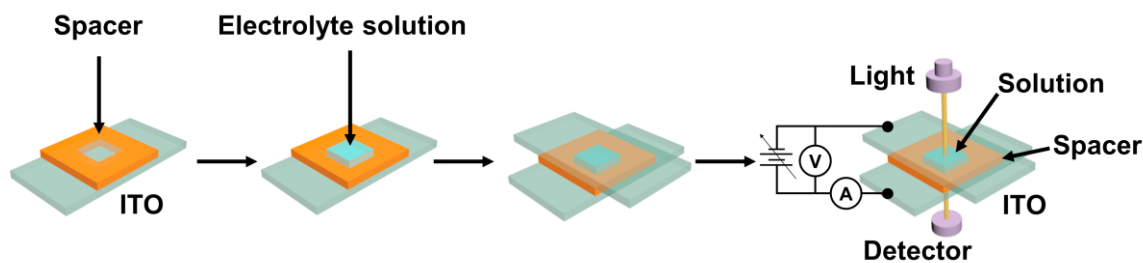


Figure 3.4. Fabrication process of the electro-absorption cell.

3.3 Results and discussion

3.3.1 Structural determination of edge-functionalized GNRs

As shown in Figure 3.5, low-temperature STM (LT-STM) operated at 77 K in a UHV environment was used to identify the products that were electrochemically synthesized on the iodine-covered Au(111). We applied 5 V (vs. Ag/Ag^+) voltage pulses for 0.5 s, 3 times to synthesize the sample. The LT-STM images of the electrochemically on-surface synthesized products reveal strand-like structures with side groups alternately arranged along both edges (Figure 3.5a). The substituents on each edge exhibit a periodicity of 0.85 nm, and the strand width is approximately 1.65 nm (Figure 3.5b and c). These experimental measurements are consistent with the proposed structural model of armchair-edged 5-AGNRs with butoxy substituents, which we name 5A-OGNR for short. Besides, as shown in Figure 3.5d, large-area LT-STM images further confirm that the 5A-OGNRs grow uniformly across the substrate. The STM images directly prove that our electrochemical method can synthesize high-quality edge-functionalized GNRs.

During the synthesis, we also found that the substrate will influence the quality of 5A-OGNRs. As shown in Figure 3.6a-d, the average length of 5A-OGNRs formed on iodine-covered Au(111) is about 10 nm, corresponding to approximately 11.7 precursor units, whereas those grown on bare Au(111) average only 5 nm in length. Despite differences in morphology, both samples exhibit identical Raman spectra (Figure 3.6e and f), confirming that the same type of GNR product was formed under both conditions. The results indicate that iodine-covered Au(111) is more suitable for 5A-OGNRs growth. To better explain the observed results, we evaluated the lattice mismatch between the 5A-OGNR and the iodine-covered Au(111) surface, as well as between the 5A-OGNR and the Au(111) substrate. As shown in Figure 3.7a and b, the iodine-covered Au(111) substrate exhibits a compressed hexagonal lattice with parameters of 4.2, 5.4, and 4.2 Å along the a, b, and c axes, respectively. The bare Au(111) substrate exhibits the same hexagonal lattice of 2.9 Å along all three axes. The GNR periodicity (8.5 Å) mismatches with the lattice spacing of Au(111) and iodine-covered Au(111) by 3.53% and 1.17%, respectively, indicating that the iodine-modified Au(111) surface provides a more favorable template for epitaxial GNR growth. Besides, to achieve a high degree of polymerization, iodine-modified Au(111) also helps control the nucleation rate on the surface, which is critical for producing longer GNRs. If the density of the precursors adsorbed on the substrate is too high, the grown GNRs are likely to collide with each other, leading to a decrease in chain length.

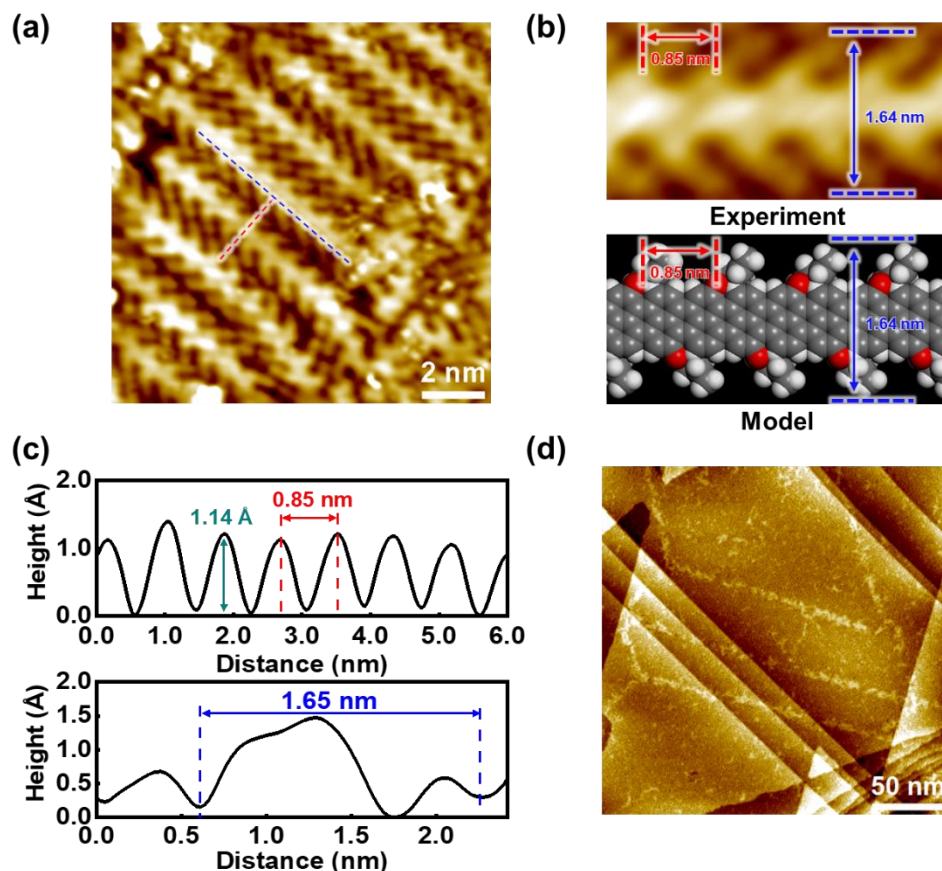


Figure 3.5. STM Characterization of electrochemically produced GNRs. (a) LT-STM image (-0.97 V, 580 pA) of electrochemically produced sample (5 V, 0.5 sec, 3 cycles). Red and blue dotted lines indicate the marks for (b). (b) Magnified LT-STM image of the strand with the structure of a GNR (top) and the theoretical model of 5A-OGNR (bottom). (c) Cross-sectional analysis of strand periodicity (top) and width (bottom). (d) Large-area LT-STM (-0.61 V, 580 pA) image of electrochemically produced GNR (200 × 200 nm).

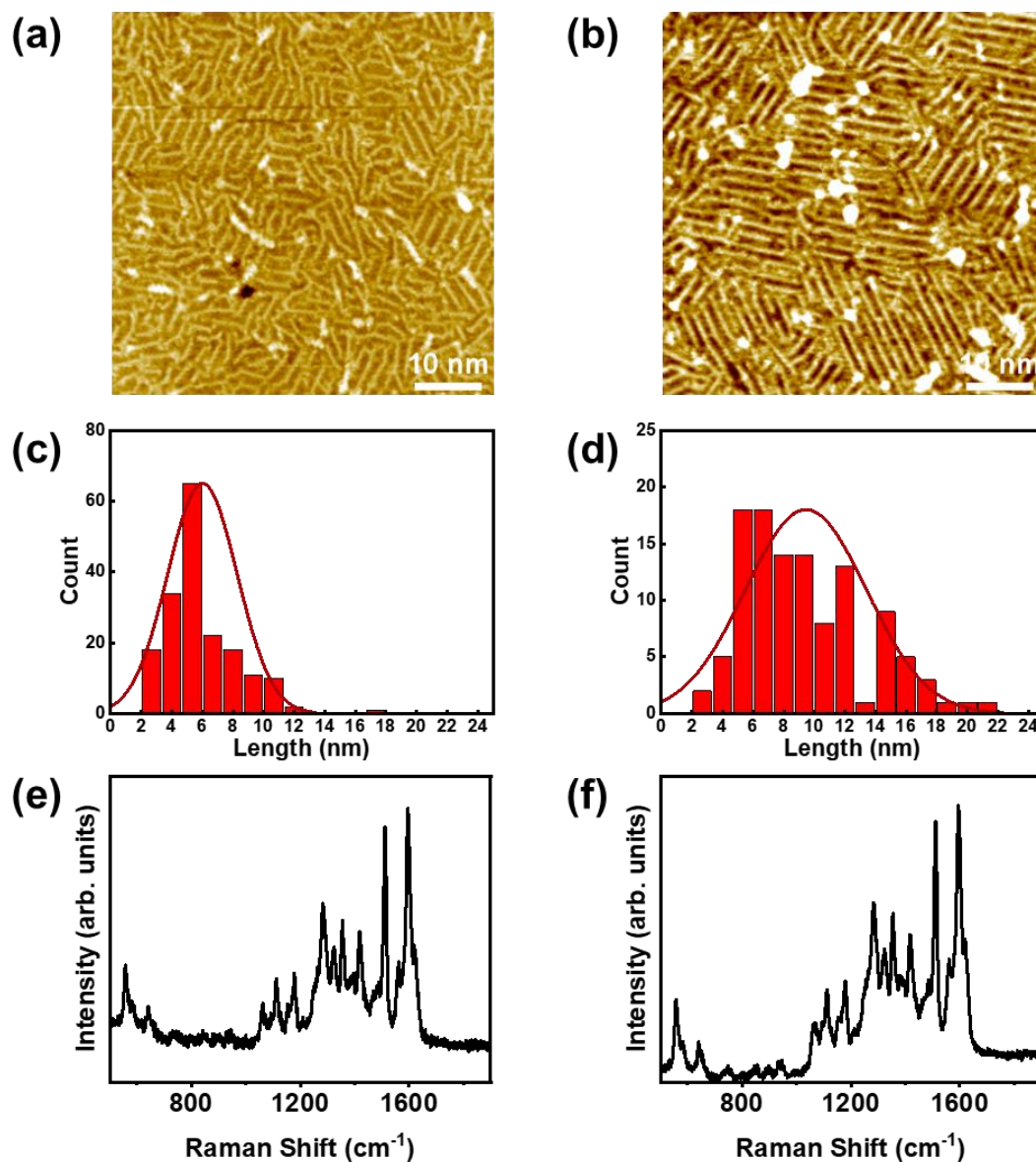


Figure 3.6. Ambient STM images (-0.2 V, 5 pA) of electrochemically produced GNR on (a) Au (111) and (b) iodine-covered Au (111). Histograms of strand lengths of electrochemically produced GNRs on (c) Au (111) and (d) iodine-covered Au (111). Raman spectra of electrochemically produced GNRs on (e) Au (111) and (f) iodine-covered Au (111).

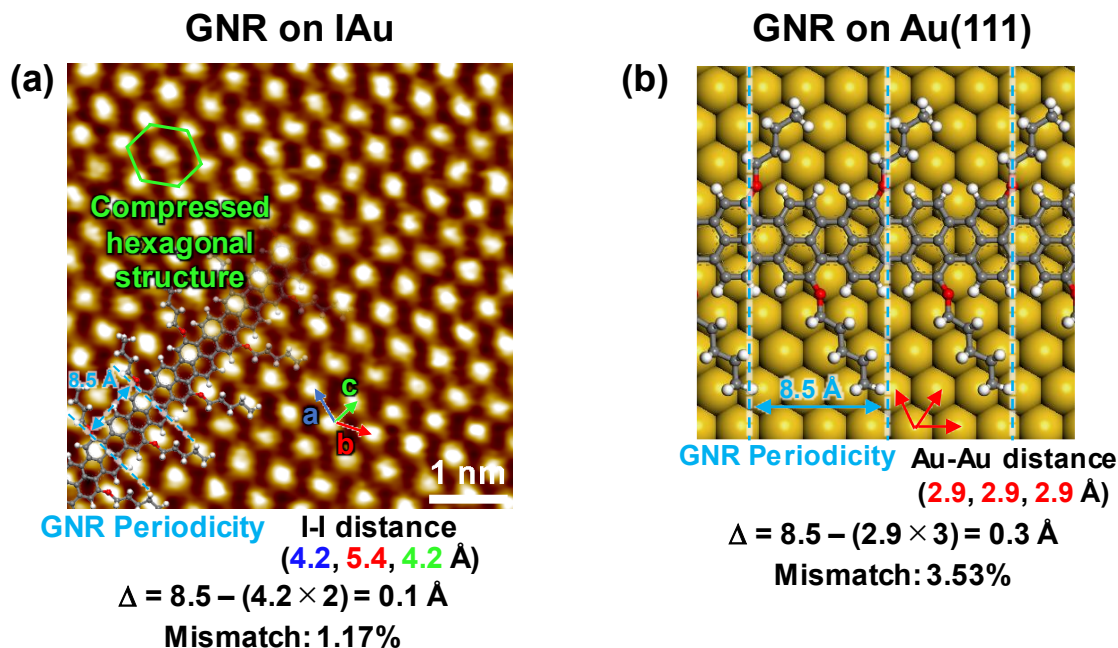


Figure 3.7. (a) LT-STM image of iodine-covered Au (111) with an overlapped chemical structure of 5A-OGNR. The inset shows a, b, and c axes, and a compressed hexagonal lattice structure. Distances between iodine atoms along the a, b, and c axes are 4.2, 5.4, and 4.2 Å, respectively. The mismatch between 5A-OGNR and substrate is 1.17%. (b) Lattice matching between the 5A-OGNR and Au(111). Distances between Au atoms along the a, b, and c axes are 2.9, 2.9, and 2.9 Å, respectively. The mismatch between 5A-OGNR and substrate is 3.53%.

To study the electronic structure of the electrochemically synthesized 5A-OGNR, we performed scanning tunneling spectroscopy (STS) measurements. The 5A-OGNR on iodine-covered Au(111) shows a bandgap of 0.84 eV, in close agreement with the density functional theory (DFT) value of 0.74 eV (Figure 3.8). The slight discrepancy can be attributed to electron screening by the metallic substrate and charge transfer effects between the 5A-OGNR and the surface. The STS-derived bandgap is also consistent with that obtained from optical measurements, as discussed later. Furthermore, dI/dV mapping of the GNRs shows qualitative agreement with the simulated results (Figure 3.9). Then, we performed the optical absorption characterization to determine the bandgap of 5A-OGNR. Instead of using an iodine-covered Au substrate, we chose the conductive ITO substrate due to its transparency. As shown in Figure 3.10a, the optical absorption spectrum shows a peak in the near-infrared region, extending to 1500 nm. The Tauc relation connects the bandgap value and the photon energy $h\nu$ ¹⁶⁻¹⁸:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

α denotes the absorption coefficient, $h\nu$ denotes the photon energy, A is the proportionality constant, E_g denotes the bandgap of the semiconductor material, and n depends on the type of electronic transition, which is 0.5 in the 5A-OGNR. The peak at 1400 nm was due to an equipment artifact, which prevented accurate estimation. Therefore, we removed this peak from the absorption spectrum of the GNR film when calculating the Tauc plot. As shown in Figure 3.10b, the bandgap of 0.85 eV obtained from the Tauc plot in the absorption spectrum fits well with that obtained from STS.

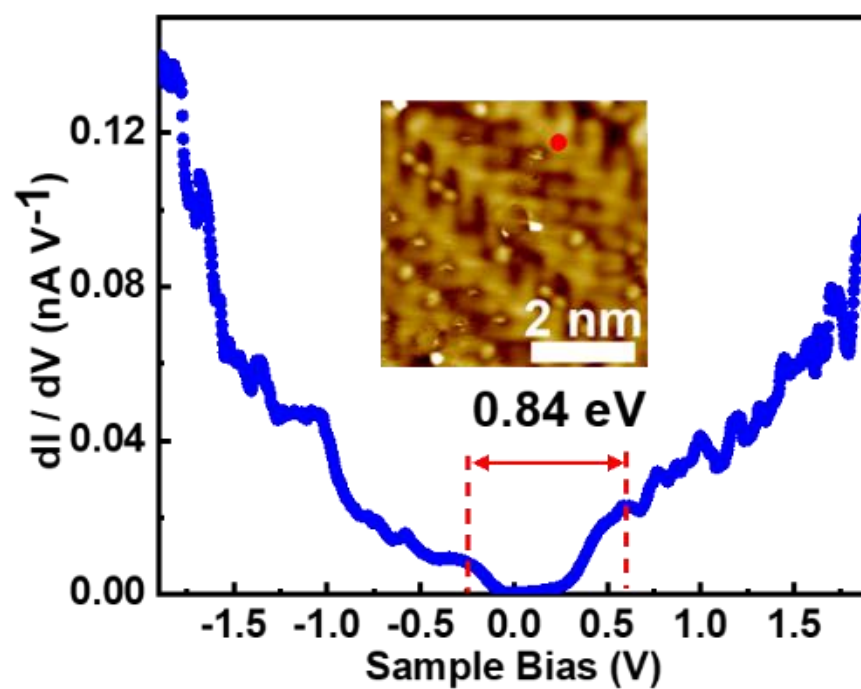


Figure 3.8. STS profile of the bandgap. The inset shows the measured location and the simulated bandgap value.

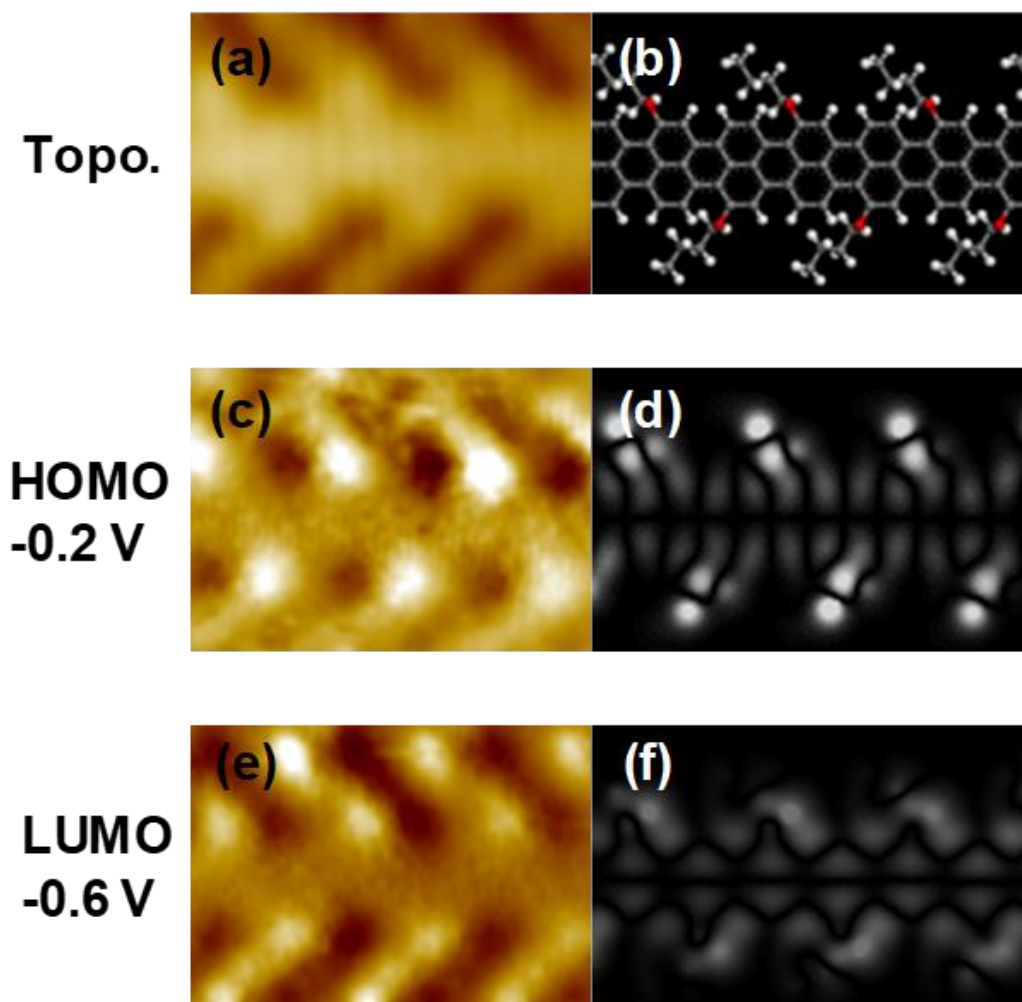


Figure 3.9. Experimental LT-STM topography of electrochemically produced GNR on iodine-covered Au(111) (a) and molecular models (b). Experimental constant-height dI/dV maps (c,e) and simulation of LDOS maps (d,f).

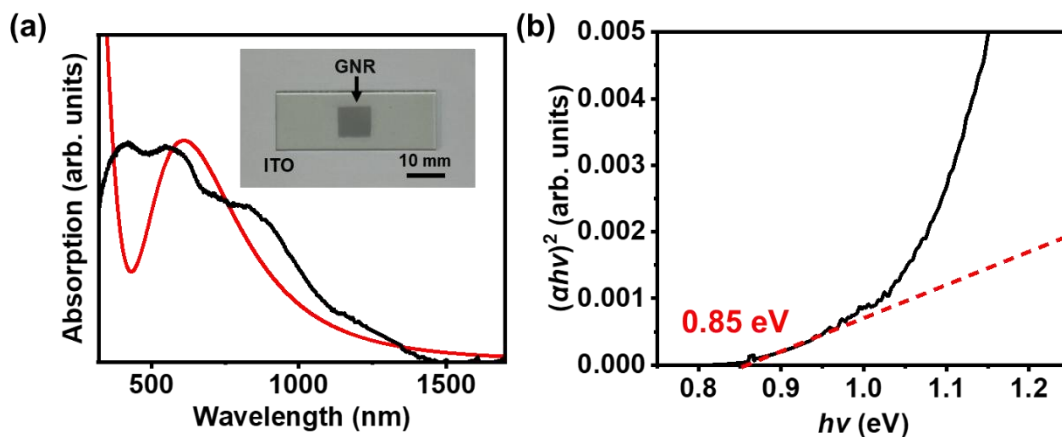


Figure 3.10. (a) Optical absorption spectrum of GNR films on ITO (black) and the simulation (red). The inset displays a photograph of GNR films. (b) Tauc plot obtained from the optical absorption spectrum of electrochemically produced GNR film on an ITO electrode, showing the bandgap value.

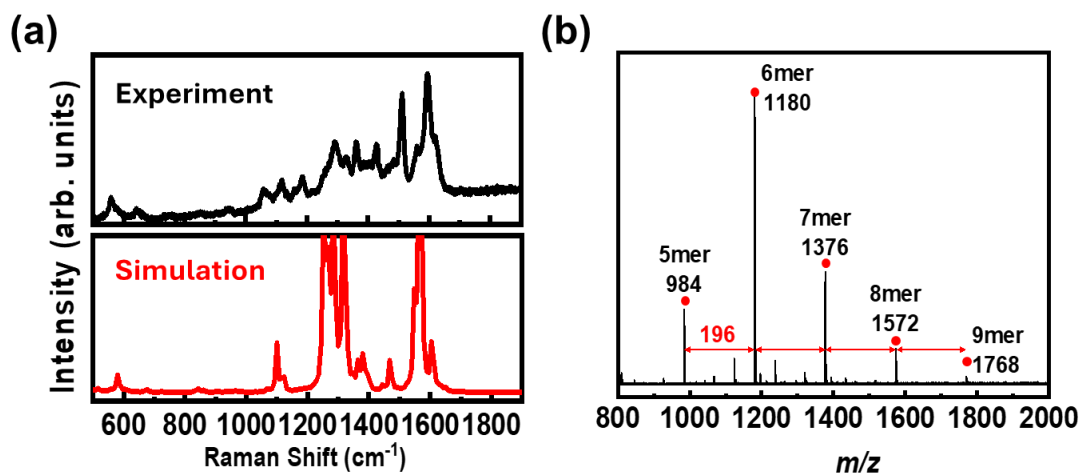


Figure 3.11. (a) Experimental (top) and simulated (bottom) Raman spectra. (b) MALDI-FT-ICR MS spectrum of GNRs showing the number of units.

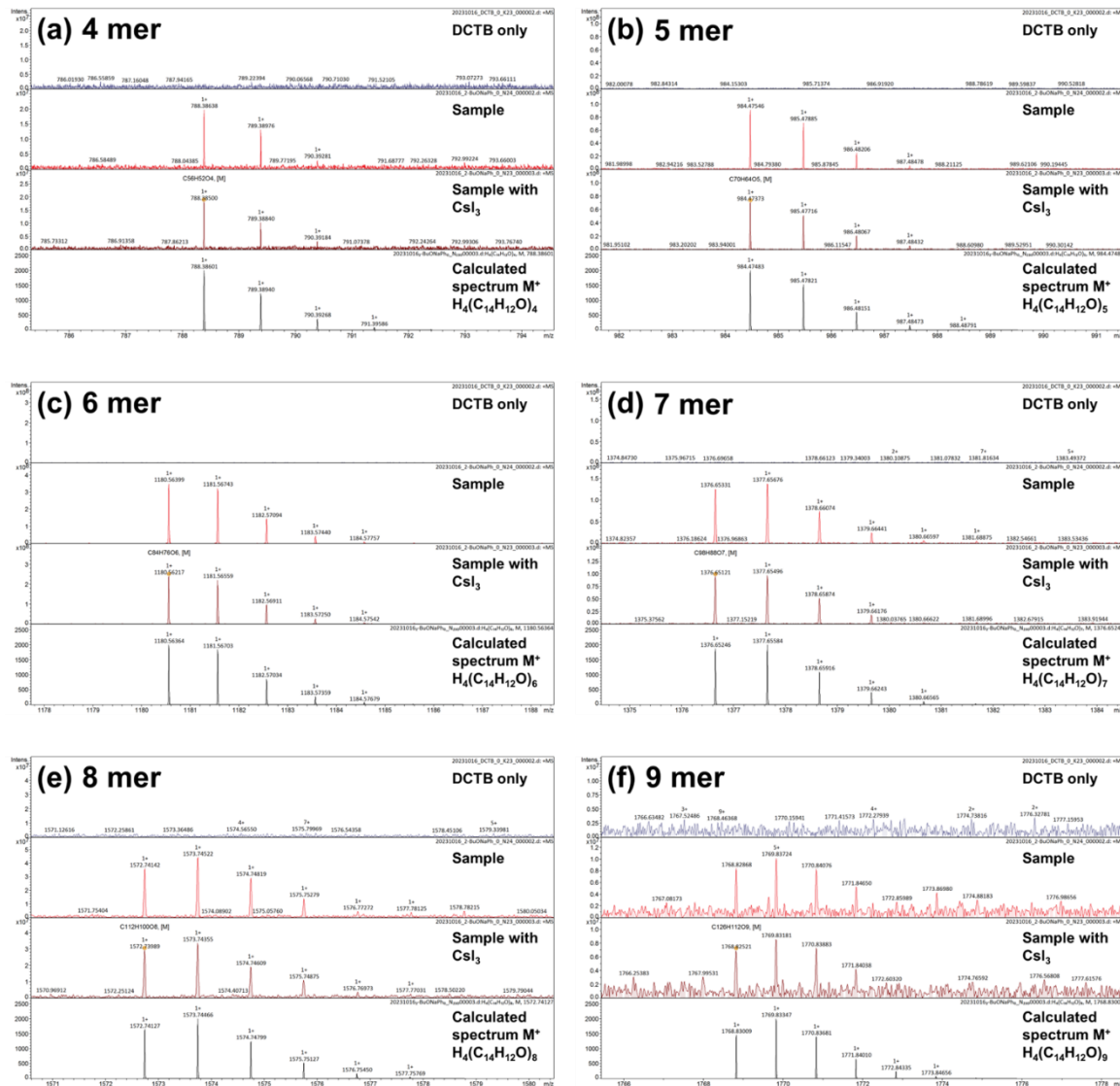


Figure 3.12. (a-f) MALDI-FT-ICR MS analysis of electrochemically produced GNR with unit length of 4, 5, 6, 7, 8, 9 mers, respectively. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malonitrile (DTCB) was used as a matrix.

The Raman spectrum of 5A-OGNR exhibits G-bands^{19,20} at 1600 cm⁻¹, D-bands at 1000 to 1400 cm⁻¹, and radial breathing like mode (RBLM) bands at 544 cm⁻¹ (Figure 3.11a). To compare the experimental results with the simulation, we use the Gaussian program to simulate the Raman spectrum of a 10-mer of 5A-OGNR in the gas phase. Peaks of G-bands and RBLM-bands matched the experimental results. However, compared to experimental data, the D-band simulation includes the experimental peak positions, whereas the intensity in the simulation is different from the experimental. This discrepancy may arise from the various lengths of GNRs in the sample. Furthermore, as shown in Figure 3.11b, the matrix-assisted laser desorption/ionization Fourier transform ion cyclotron resonance mass spectrum (MALDI-FT-ICR-MS) of electrochemically produced 5A-OGNR represents periodic peaks with an interval of 196 m/z. It fits well with the mass of a single unit of the proposed 5A-OGNR structure. The mass spectrum of 5A-OGNR with 4, 5, 6, 7, 8, 9 units is shown in Figure 3.12.

Besides, we also tried to use STM to characterize the 5A-OGNRs synthesized on ITOs, but it failed due to the roughness of the ITO surface being even higher than the thickness of the 5A-OGNRs (Figure 3.13a and b). As shown in Figure 3.13c, because the Raman spectrum of products formed on ITOs is the same as that of the 5A-OGNR produced on Au(111), and the EDL can also be formed on ITOs, we conclude that our electrochemical method can also synthesize 5A-OGNRs on other substrates.

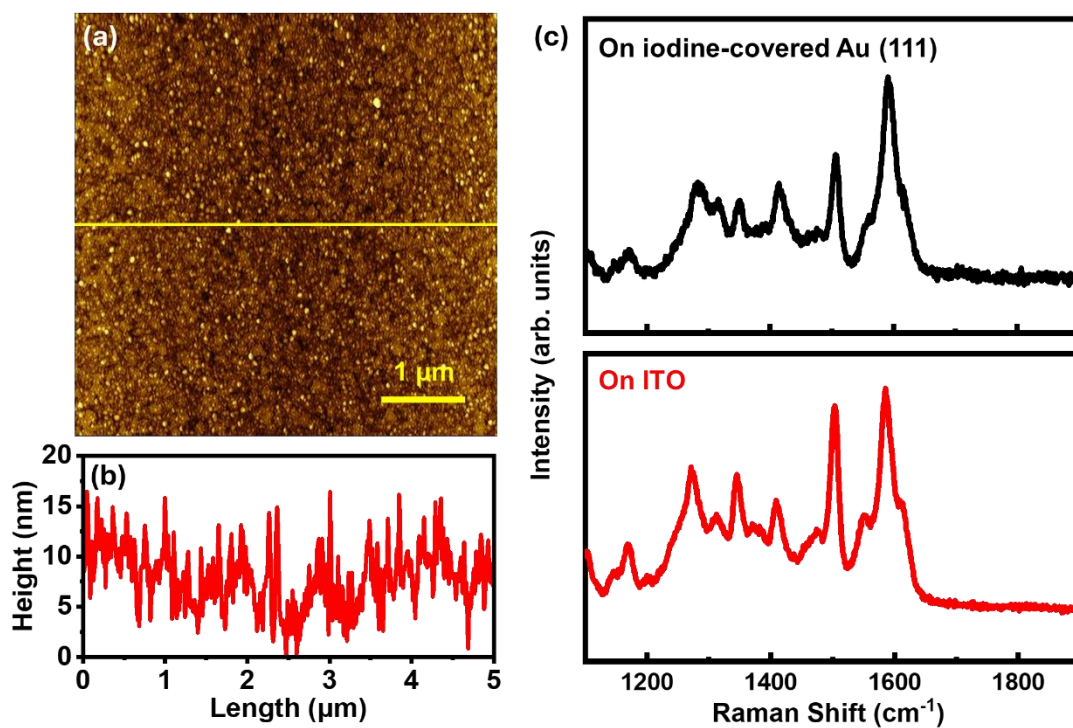


Figure 3.13. (a) AFM image and cross-section of the ITO substrate. (b) Roughness of the ITO substrate. (c) Raman spectra of electrochemically produced GNRs formed on iodine-covered Au(111) and ITO substrates (5 V, 0.5 sec, 30 cycles).

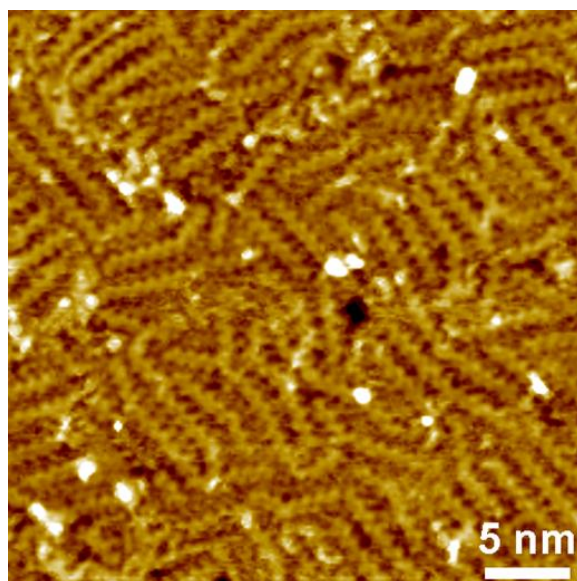


Figure 3.14. Ambient STM image of electrochemically produced GNR on iodine-covered Au(111) at room temperature (5 V, 0.5 sec, 30 cycles).

Then, the influence of temperature on the electrochemical method for GNR synthesis is studied. As shown in Figure 3.14, 5A-OGNRs require at least 30 more cycles of voltage pulses to fully cover the sample at room temperature, whereas the sample grown at 80°C only needs three cycles of voltage pulses. This indicates that higher temperatures enhance GNR growth, making temperature a crucial factor in their electrochemical growth. Higher temperatures improve polymerization by overcoming activation energy, and it is believed that the dehydrogenation reaction is supposed to be the same. An 80°C reaction temperature also enhances diffusion of the precursor, which improves mass transfer in the EDL^{21,22}.

As a result of chapter 3.3.1, based on high consistency between structural characterization results and theoretical simulation, we confirmed that the chemical structure of the product is an armchair-edged 5-AGNR with butoxy substituents, which is named 5A-OGNR. Our electrochemical on-surface synthesis method enables room-temperature edge-functionalization of GNRs while avoiding the decomposition of substituents, providing an advantage over the UHV on-surface synthesis method. The reaction pathway is proposed to involve the heterochiral coupling of 2-butoxynaphthalene units, alternately oriented with their aromatic planes facing upward and downward, followed by dehydrogenation. We further speculate that specific active sites for heterochiral coupling exist within the active species, where coupling reactions preferentially occur (Figure 3.1b).

3.3.2 Mechanism of electrochemical on-surface synthesis

To identify the active species involved in the electrochemical on-surface synthesis of 5A-OGNRs, we performed electro-absorption spectroscopy on the sample solution using a transparent sandwiched ITO cell with a 250- μm spacer filled with an electrolyte solution containing 2-butoxynaphthalene precursors (Figure 3.4). DFT calculations predict that the dication species formed via two-electron oxidation of the precursor exhibits a peak around 750 nm and an infrared absorption above 1500 nm. The radical cation resulting from one-electron oxidation shows a peak around 500 nm and near-infrared absorption around 1000 nm (Figure 3.15a). The electroabsorption spectrum recorded at 3 V (vs. Ag/Ag^+) matches the simulated spectrum well. It indicates that both cation and dication exist in the electrolyte solution after we applied the voltage. As shown in Figure 3.15b, the one-electron oxidation happens at around 1.5 V, and the two-electron oxidation happens when the voltage is over 2 V. To study the relationship between dication formation and the value of voltage, various voltages were applied to the transparent ITO cell. As shown in Figure 3.16, the electroabsorption response shows nonlinear behavior to the applied voltage. When the voltage was lower than 2 V, no dication absorption at 1600 nm was observed. However, when the voltage was higher than 2 V, strong infrared absorption at 1600 nm could be observed. When the voltage reaches 3 V, the absorption of the dication will be saturated. Besides, as shown in Figure 3.17, after removing the applied voltage, the infrared absorption around 1600 nm will decay within 50 seconds, indicating that the optical absorption is caused by the active intermediates. The absorption results are consistent with the cyclic

voltammogram results, indicating that the formation of a dication requires a potential above 2 V.

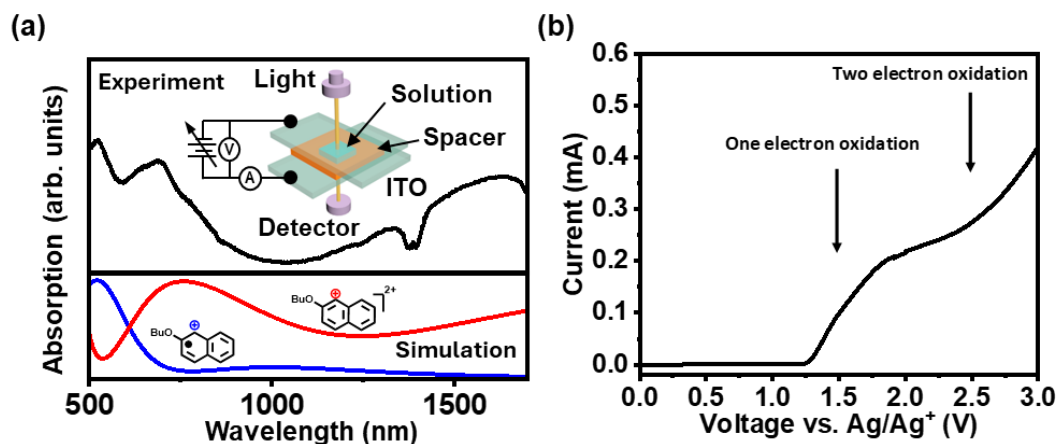


Figure 3.15. (a) Electro-absorption spectrum after voltage application (3 V, 15 sec; top) and simulated spectra of dication and cation radicals (bottom). The inset shows the experimental setup. (b) Cyclic voltammogram of 5 mM 2-butoxynaphthalene with 0.1 M TBAPF₆ in o-DCB. The scan rate was set as 50 mV s⁻¹.

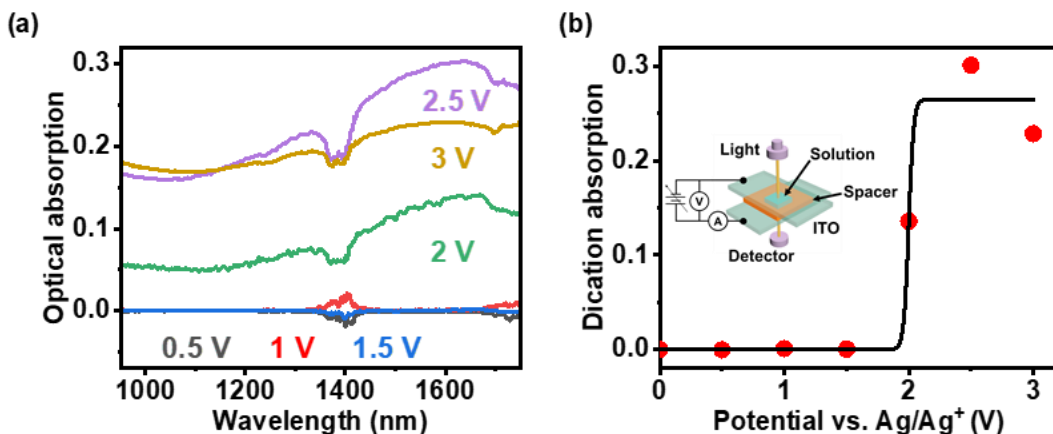


Figure 3.16. (a) Electro-absorption of the sample cell (5 mM 2-butoxynaphthalene in electrolyte solution) after applying voltages for 15 s. (b) Voltage dependence on absorption of dication in the sample cell observed at 1600 nm. The inset shows the experimental setup.

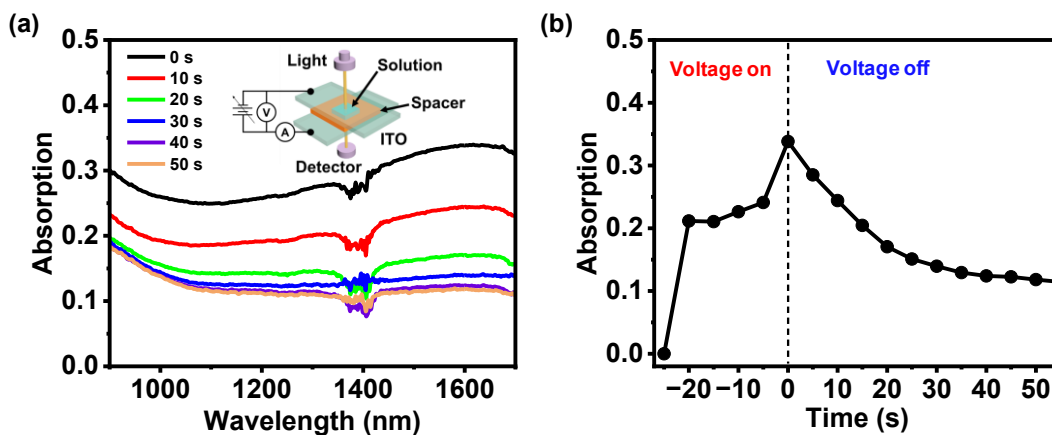
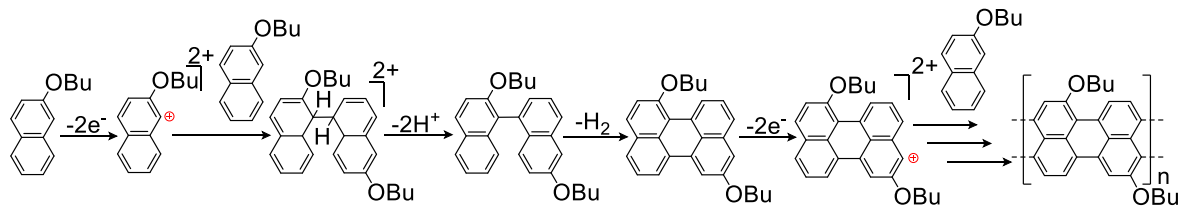


Figure 3.17. (a) Time-dependent electro-absorption spectra of the sample cell after 2.5 V application for 25 s. The inset shows the experimental setup. (b) Temporal profile of electroabsorption at 1600 nm.

Additionally, the voltage dependence of 5A-OGNR growth yield was investigated by analyzing the optical absorption of GNR films formed on ITO electrodes (Figure 3.18a). The results exhibit a nonlinear response similar to that observed in the optical absorption of dication species. Accordingly, the yield of 5A-OGNR increases proportionally with the concentration of electrochemically generated dication species (Figure 3.18b). These findings strongly suggest that the dication serves as the key active intermediate governing 5A-OGNR growth. To study the mechanism underlying the electrochemical growth of 5A-OGNR, we conducted theoretical studies focusing on both thermodynamics and kinetics. We first identified the chemical species participating in the growth reactions among neutral precursors, radical cations, and dications. Two possible mechanisms were considered, including the radical cation mechanism^{23–25} and the dication mechanism. The first one is the radical cation polymerization mechanism. In conventional electropolymerization of conducting polymers such as polythiophenes, coupling occurs among radical cations at positions of high spin density²⁶. However, this mechanism is not suitable for the observed heterochiral coupling, because the radical cation of 2-butoxynaphthalene lacks sufficient spin density at carbons 1 and 5 (Figure 3.19). Then, we considered the dication mechanism, the dication generated by two-electron oxidation of the precursor might serve as an electrophilic agent, driving the coupling reaction by attacking precursor molecules (scheme 3.2).



Scheme 3.2. Reaction mechanism of 5A-OGNR growth.

The DFT-calculated electrostatic potential map shows that the carbon at position 1 of the dication has the highest hole density, suggesting it should be the most reactive site. In contrast, other positions display delocalized charge distributions (Figure 3.19). This differs markedly from the neutral precursor, in which all carbons exhibit nearly uniform electron density.

Then, we performed DFT-based thermodynamic calculations to explore the GNR growth pathway under the dication mechanism. We simulated potential combinations of reactive sites in coupling reactions between the dication and precursor, then compared the Gibbs free energy of the resulting coupled products. As shown in Figure 3.20, we generated products for dimers by coupling the carbon at position 1 of the dication with carbon at positions 1, 4, 5, and 8 of the precursors to explore all possible chemical structures of dimers. The same procedures were applied to form trimer and tetramer models (Figures 3.21 to 3.23). In our model, dehydrogenation reactions are assumed to coincide with polymerization during GNR growth. Due to their lower oxidation potential, oligomers and polymers may undergo one-electron oxidation more readily than their precursors, forming C-C bonds via dehydrogenation. As shown in Figure 3.23, DFT results show that the minimum free energy for trimers and tetramers

corresponds to heterochiral coupling of GNRs formed between the carbon at position 1 of the dication and the carbon at position 5 of the precursor. The free energy of these heterochiral coupling GNRs decreases with increasing chain length, exhibiting a pronounced negative slope (Figure 3.24). These findings indicate that the heterochiral configuration is the most thermodynamically stable. From a kinetic perspective, we analyzed the HOMO-1 energy level of the possible coupled GNR dimers and trimers products to assess their tendency toward two-electron oxidation and dication formation. As shown in Figure 3.25, the dimers and trimers of heterochiral coupling GNRs possess the highest HOMO-1 energy among all candidates, suggesting that they undergo two-electron oxidation most efficiently, which will promote dicationic polymerization.

Our proposed dication-based mechanism thus explains the selective reaction between the carbon at position 1 of the dication and the carbon at position 5 of the precursor, resulting in heterochiral edge-functionalized GNRs, as shown in Scheme 3.2. This model is further supported by precursor-dependence experiments using symmetric molecules such as 2,6-dibutoxy- and 2,7-dibutoxynaphthalene. As shown in Figure 3.26, the LT-STM measurements confirmed that these symmetric precursors failed to produce GNRs under identical electrochemical conditions, and the Raman spectra show no G-band peak, which is a signature in GNRs. The electroabsorption spectroscopy also shows no formation of dicationic species (Figure 3.27a and b). These results suggest the crucial role of precursor asymmetry in the electrochemical on-surface synthesis of GNRs. The asymmetric structure of 2-butoxynaphthalene

stabilizes the hole localized at the carbon in position 1 of the dication, whereas symmetric precursors cannot.

In conclusion, the electrochemical on-surface synthesis of 5A-OGNR is proven to proceed through a heterochiral dicationic polymerization mechanism, in which the carbon at position 1 of the dication attacks the carbon at position 5 of an incoming precursor (scheme 3.2). This pathway is both thermodynamically favorable and kinetically accessible. The 5A-OGNR growth mode is proposed to follow a chain-growth process, since the dicationic active site at the growth front remains immobilized on the surface rather than diffusing freely.

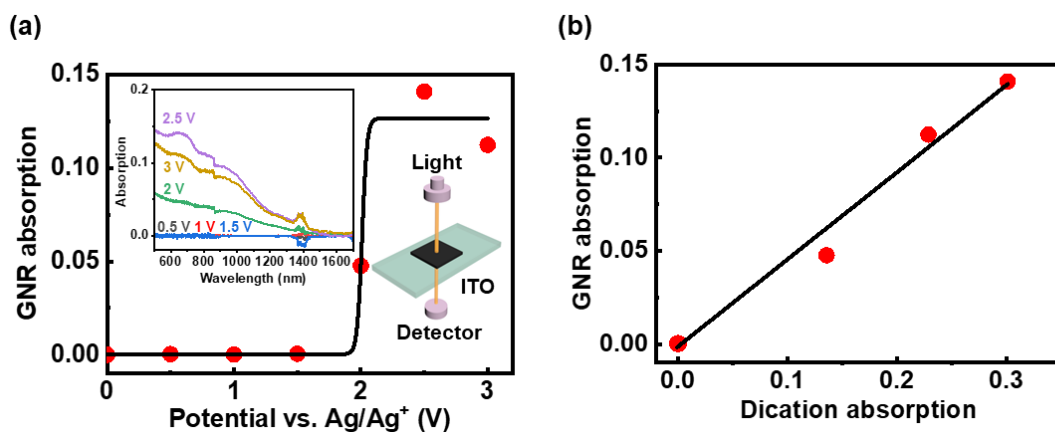


Figure 3.18. (a) The electrochemical voltage dependence on the absorption of a GNR film formed on ITO at 650 nm. The inset shows the setup and voltage-dependent absorption spectra of a GNR film. (b) The correlation between the dication absorption at 1600 nm in the cell and GNR absorption at 650 nm.

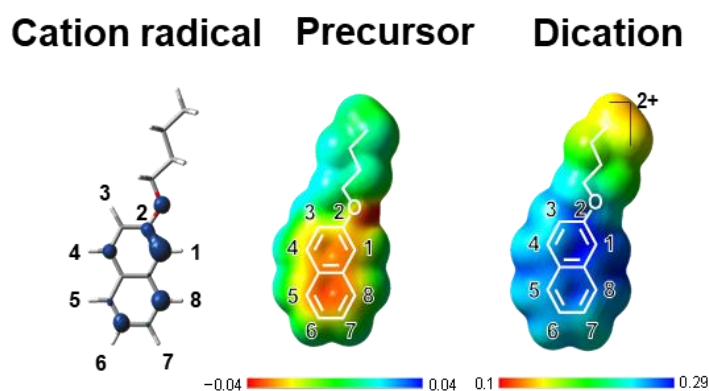


Figure 3.19. Spin density of the cation radical (left), electron density of precursor (center), and dication (right).

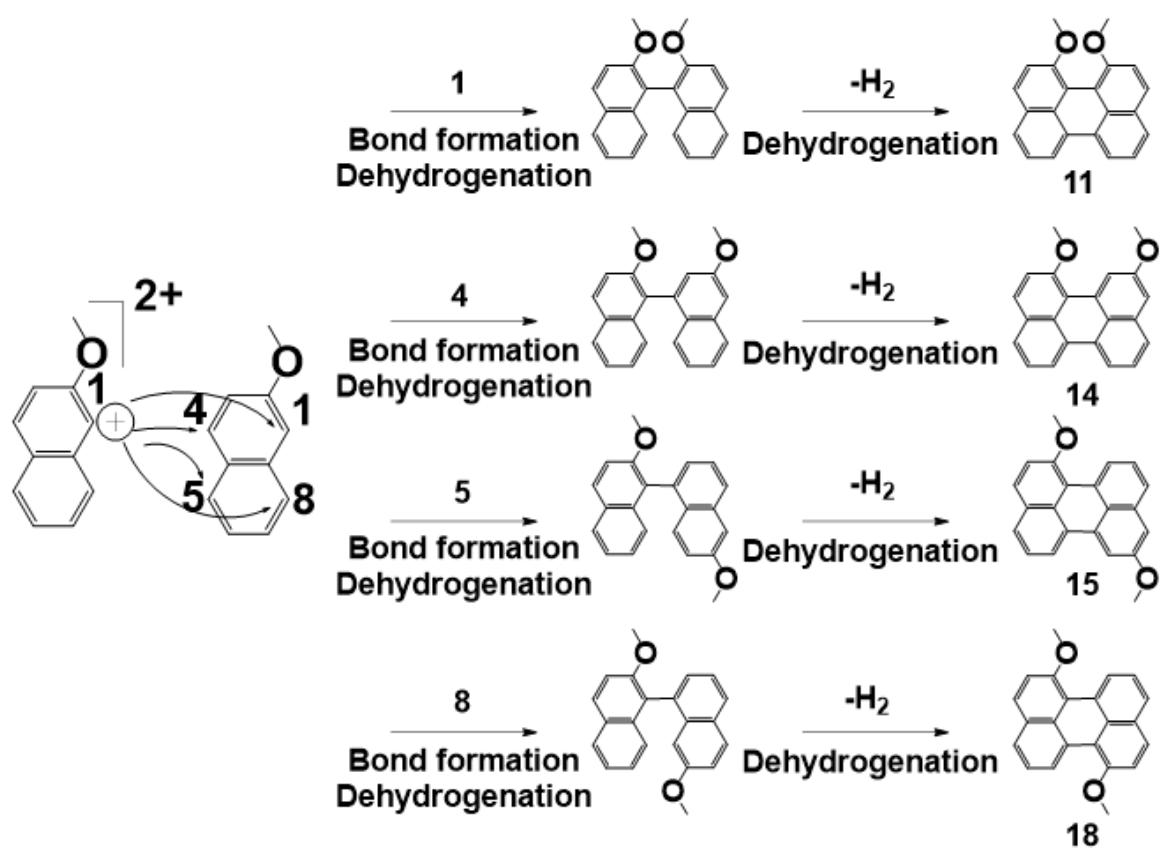


Figure 3.20. Possible reaction pathways and products of the dimer.

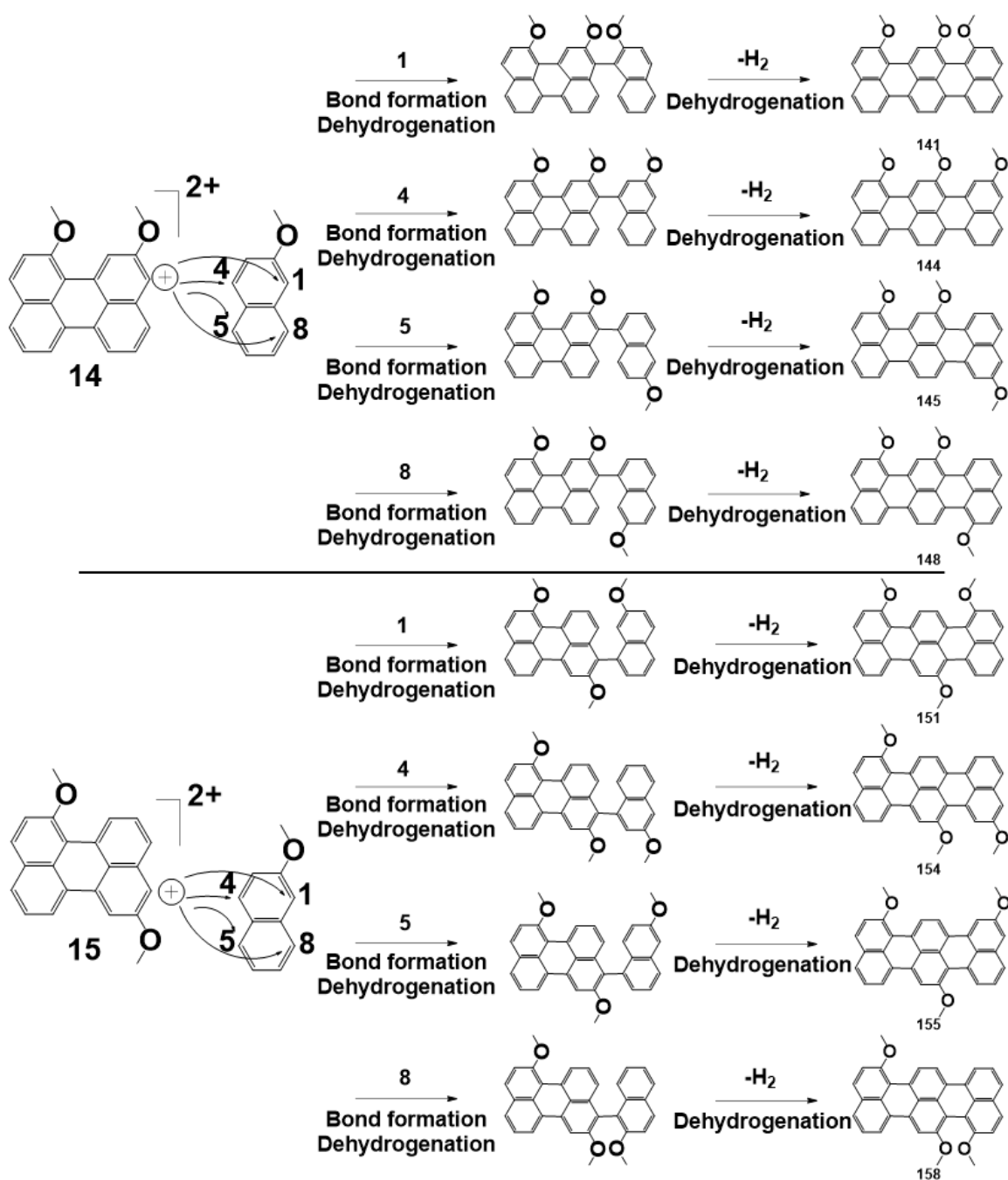


Figure 3.21. Possible reaction pathways and products of the trimer.

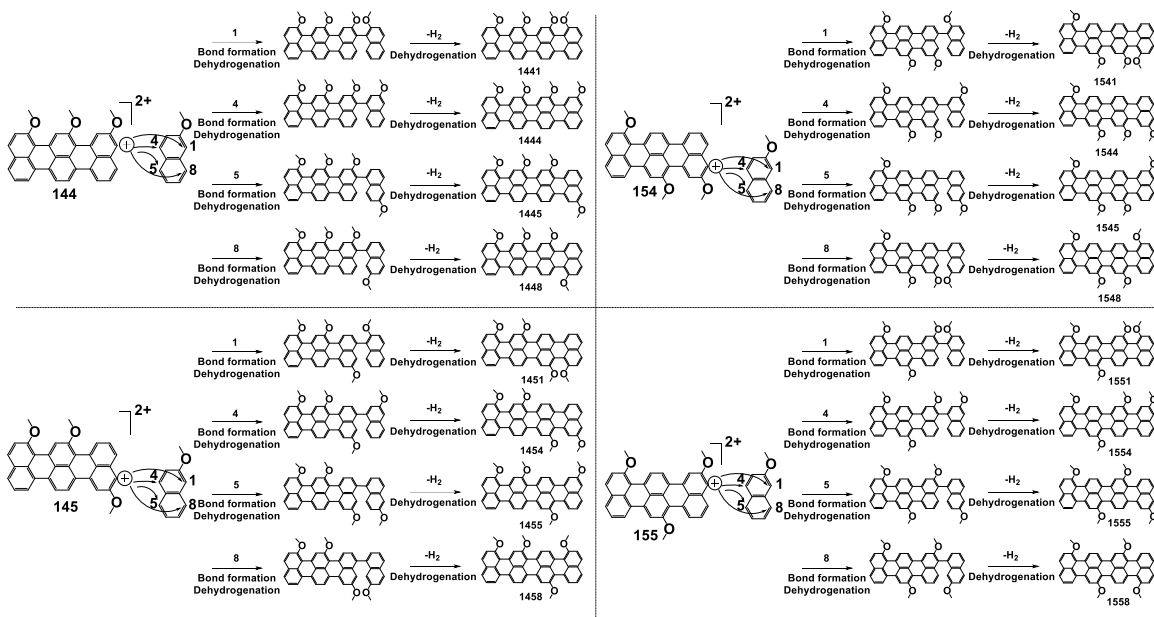


Figure 3.22. Possible reaction pathways and products of the tetramer.

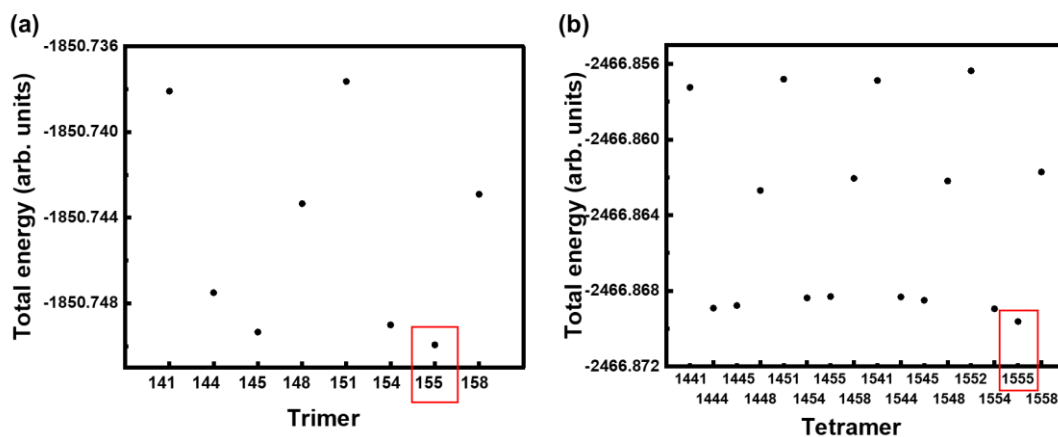


Figure 3.23. (a) Total energies of possible trimer products. (b) Total energies of possible tetramer products. The red square shows the minimum energy in both figures.

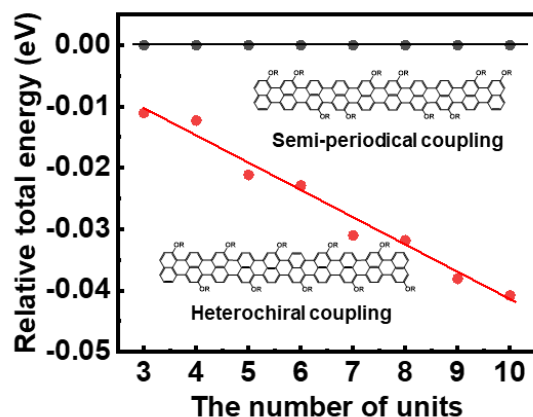


Figure 3.24. The unit number dependence of total energies of the heterochiral-coupled GNR (red) and semi-periodical-coupled GNR (black). The inset shows structures.

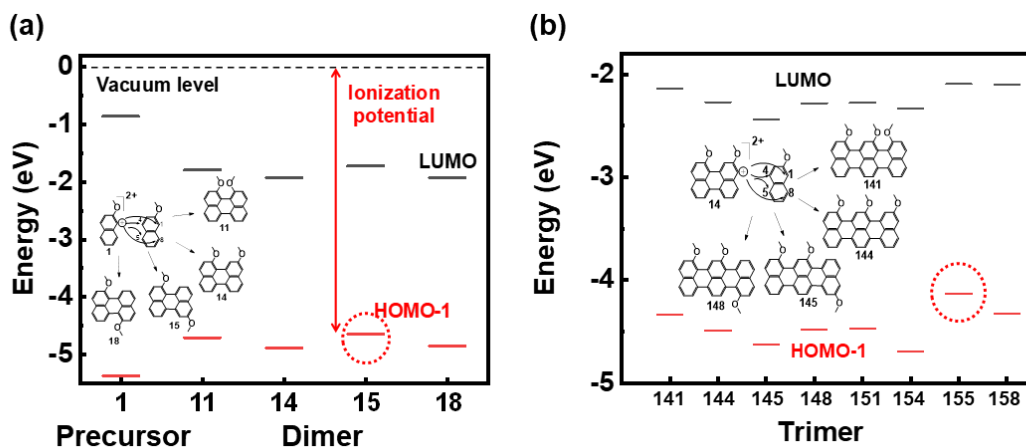


Figure 3.25. (a) Energy levels of HOMO-1 and LUMO for possible dimer products and precursors. (b) Energy levels of HOMO-1 and LUMO for possible trimer products. The inset shows examples of products. The dotted red circle indicates the highest HOMO-1.

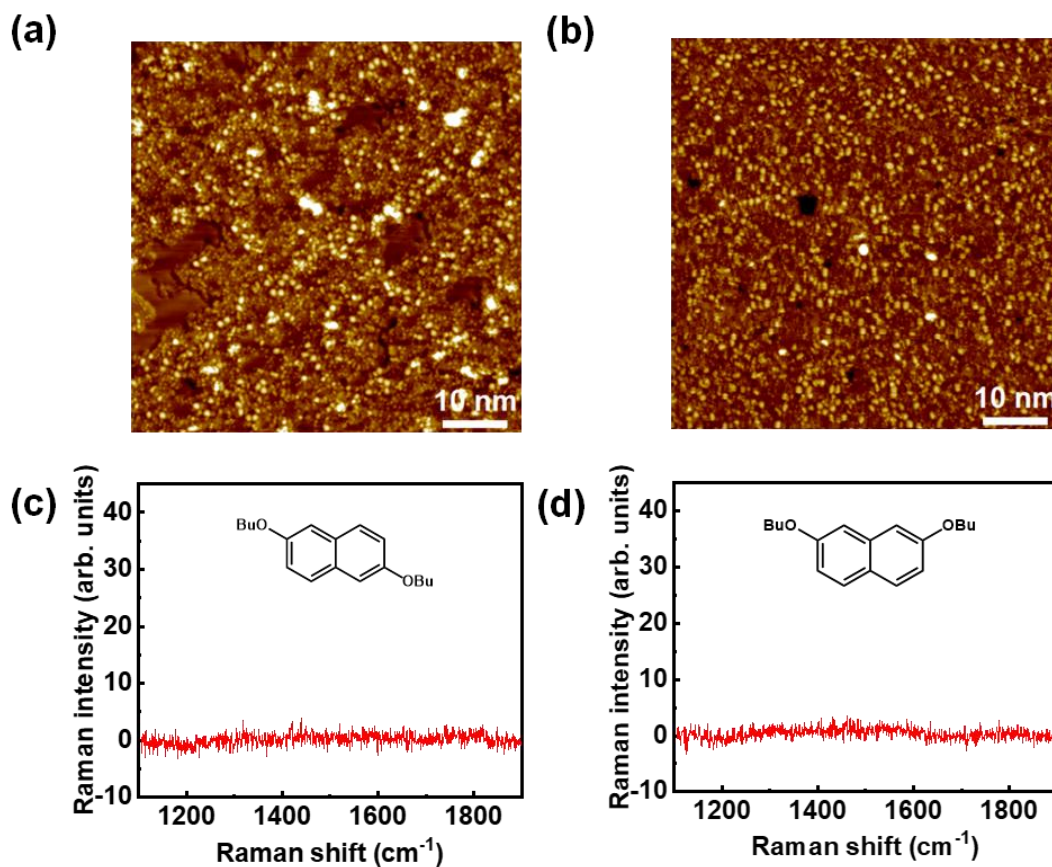


Figure 3.26. LT-STM (0.2 V, 5 pA) images and Raman spectra of electrochemically treated Au (111) in a 5 mM sample solution of (a, c) 2,6-dibutoxynaphthalene, (b, d) 2,7-dibutoxynaphthalene with 0.1 M of TBAPF₆ in o-DCB after voltage application (5 V, 0.5 s, 3 cycles), respectively. The insets in (c) and (d) show chemical structures.

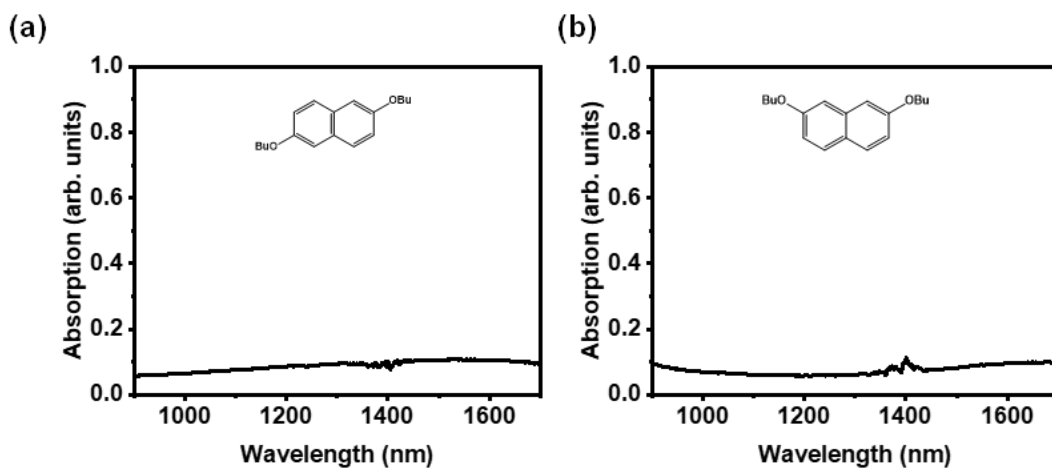


Figure 3.27. Electro-absorption spectra of the sample cell (5 mM in electrolyte solution) of (a) 2,6-dibutoxynaphthalene and (b) 2,7-dibutoxynaphthalene after 2.5 V application for 25 s. The insets in (a) and (b) show chemical structures.

3.3.3 Electrochemical layer-by-layer growth of GNRs

In addition to the advantage of room-temperature synthesis, which prevents the thermal decomposition of functional groups, our electrochemical on-surface method also enables the synthesis of multilayer GNRs. This is because the EDL can continue to form even when the GNR products cover the electrode surface. As shown in Figure 3.28, LT-STM was used to characterize the GNR growth process on iodine-covered Au(111) by increasing the number of applied voltage pulses. When a single voltage pulse of 5 V (vs. Ag/Ag⁺) is applied to the working electrode for 0.5 seconds, the corresponding LT-STM image reveals a random distribution of short 5A-OGNR chains, each with a length of less than 1 nm (Figure 3.28a). The surface coverage ratio of this sample is approximately 82.3%. After a second voltage pulse, several 5A-OGNR strands with extended chain lengths of around 10 nm begin to appear in the LT-STM image (Figure 3.28b). Upon applying a third pulse, the electrode surface becomes fully covered by a highly ordered array of 5A-OGNRs with long, uniform chains. The average chain length is about 10 nm (Figure 3.28c). A fourth pulse yields a high-density 5A-OGNR array similar to that obtained after the third pulse, though with a slightly reduced degree of order (Figure 3.28d). The LT-STM images in Figures 3.28c and 3.28d show that most strands consist of linear chains coupled regioselectively. However, occasional kinks observed at the ends of these straight chains suggest that collisions between neighboring chains occurred during growth, leading to local non-regioselective coupling events. Therefore, controlling the absorption of monomers on the working electrode is essential. It also explains why 5A-OGNR grown on the iodine-covered Au(111) substrate is better than bare Au(111).

To determine the thickness of the multilayered GNRs, AFM measurements were conducted on GNR films transferred from iodine-covered Au(111) to a Si substrate, since STM cannot characterize the film thickness when the substrate surface is entirely covered by GNR (Figure 3.29). The thickness and Raman intensity of the GNR films are found to increase proportionally with the number of applied voltage pulses. Based on STM analysis, the estimated thickness of a monolayer GNR is 0.114 nm (Figure 3.5c). When a voltage pulse of 5 V is applied, AFM characterization reveals the formation of approximately 2.46 layers (Figure 3.30). These results indicate that electrochemical on-surface synthesis enables multilayer GNR growth, unlike conventional UHV on-surface synthesis, which is generally limited to monolayer formation due to its reliance on metal-catalyzed dehydrogenation that requires direct contact between the reactants and the metal surface. An exception was reported for bilayer GNR synthesized under UHV conditions, where dehydrogenation of prepolymers was achieved through a domino-like mechanism remotely triggered by direct contact between a GNR segment and the gold substrate⁸. However, this process still requires direct contact between the prepolymer and the metal surface for the initiation of second-layer growth, thereby remaining a fundamental limit for achieving multilayer GNR synthesis. In contrast, electrochemical on-surface synthesis relies on redox processes that occur within the EDL at the solid-liquid interface. This electrochemical growth mechanism enables layer-by-layer deposition of GNRs on the electrode surface, as the EDL can keep forming above the top layer even when GNRs fully cover the electrode^{27,28}. As shown in LT-STM images (Figure 3.28), it is evident that elongated GNR growth initiates on electrode regions already covered with short-chain GNRs. These

observations suggest that GNRs adhere more effectively to adlayers than to the electrode surface. The improved ordering of strands observed after the third voltage pulse may result from structural matching between the adlayer and the newly formed GNRs. Similar ordering phenomena have been reported for poly-p-phenylene (PPP), where surface-bound bromine atoms drive molecular alignment²⁹. Additionally, previous studies have reported that the orientation of polythiophene is enhanced on iodine-covered Au(111) surfaces¹⁴. These phenomena are attributed to epitaxial growth, in which polymers align along the crystalline lattice of the substrate through interactions between halogen atoms and polymer chains. In this study, the alignment of GNRs is enhanced through epitaxial interactions between top-layer GNRs and short-chain GNRs in the underlying layer. This unique feature of electrochemical on-surface synthesis establishes it as a scalable approach to produce edge-functionalized GNRs.

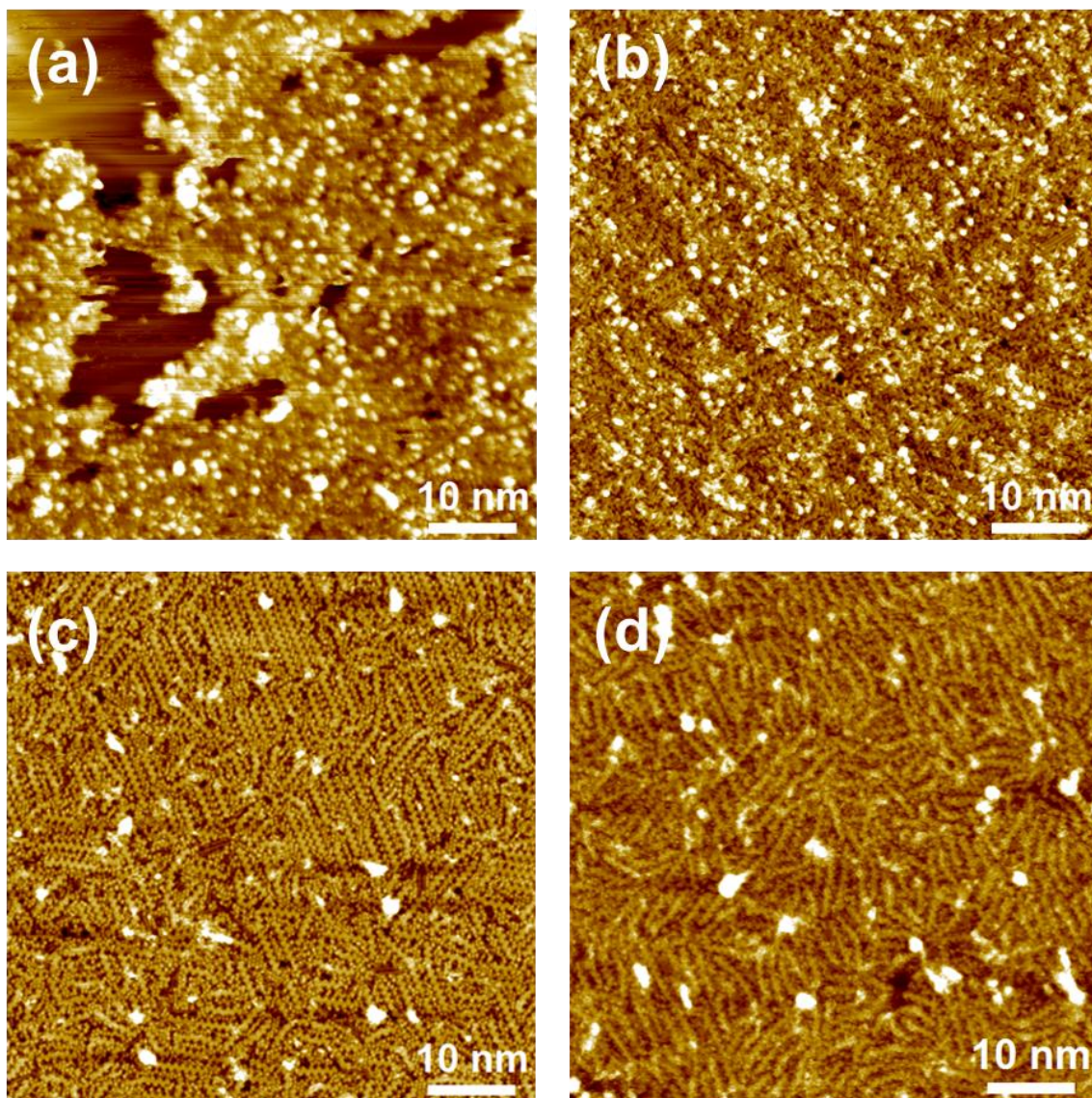


Figure 3.28. Voltage cycle dependence on electrochemical GNR growth. LT-STM images of electrochemically produced samples (5 V, 0.5 s) with (a) one cycle (STM measurement conditions: -1.95 V, 160 pA), (b) two cycles (-0.31 V, 580 pA), (c) three cycles (-0.76 V, 580 pA) and (d) four cycles (-0.81 V, 580 pA), respectively.

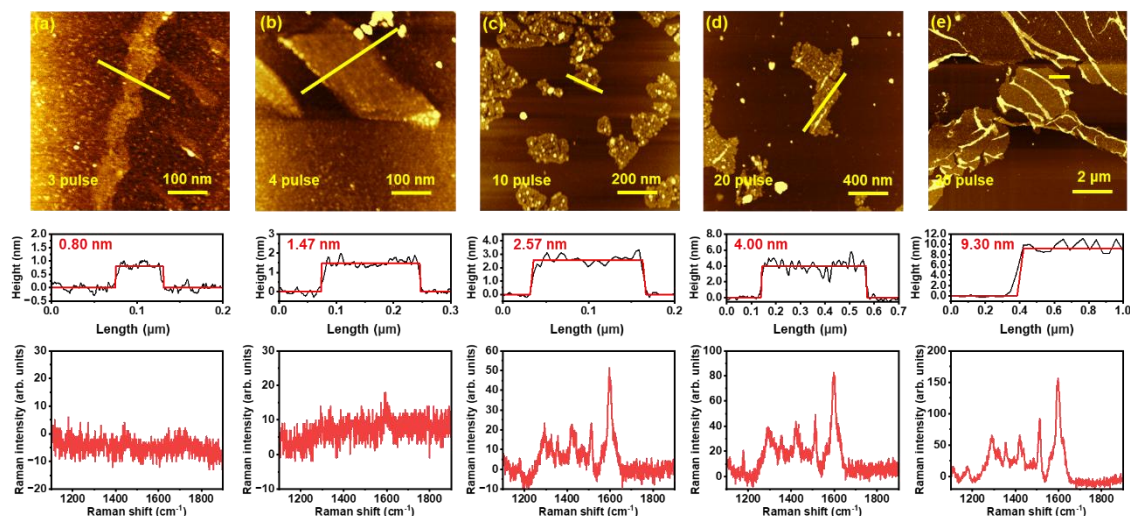


Figure 3.29. (a-e) AFM images, cross sections, and Raman spectra of GNRs obtained after applying various numbers of voltage cycles (3, 4, 10, 20, and 30 cycles) (5 V, 0.5 sec).

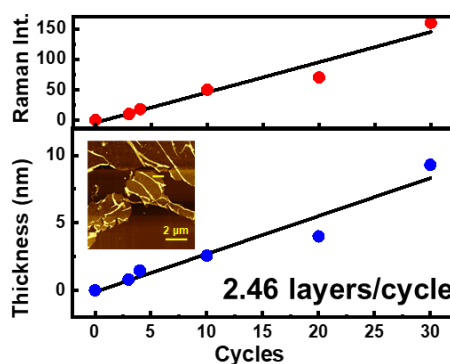


Figure 3.30. Thickness and Raman intensity of electrochemically produced GNR films transferred from iodine-covered Au(111) to Si substrates with different numbers of cycles (5 V, 0.5 sec). The inset shows an AFM image of a GNR film (30 cycles) on Si.

3.4 Conclusion

In this study, we successfully established an electrochemical on-surface synthesis method as a novel approach for the controlled growth of edge-functionalized GNRs. This strategy represents a different reaction mechanism from conventional thermal on-surface synthesis techniques that require high-temperature activation (300-500 °C). By integrating electrochemical control with molecular self-assembly at the solid-liquid interface, we realized low-temperature polymerization and dehydrogenation processes, enabling the synthesis of structurally well-defined, edge-functionalized 5A-OGNRs while preserving their chemical integrity.

LT-STM analysis confirmed the formation of armchair-edged 5A-OGNRs with butoxy substituents arranged alternately along both edges. The measured periodicity of 0.85 nm between substituents and a width of 1.65 nm are in excellent agreement with theoretical models. Notably, when the synthesis was conducted on iodine-covered Au(111) substrates at 80°C, the resulting 5A-OGNRs exhibited a highly aligned structure, attributed to epitaxial growth. This epitaxial alignment is a unique feature of electrochemical on-surface synthesis, enabling large-area ordering of GNRs and offering a promising route toward scalable fabrication.

Through systematic experimentation, we revealed that electrochemical on-surface synthesis proceeds via a different reaction pathway fundamentally distinct from traditional radical polymerization. As demonstrated in Figure 3.1b, the key active intermediate is a dication species generated through two-electron oxidation at high potential. This dication drives heterochiral dicationic

polymerization, in which coupling selectively occurs between the carbon at position 1 of the di-cation and the carbon at position 5 of the precursor. The resulting product then undergoes oxidation-induced dehydrogenation, ultimately leading to the formation of 5A-OGNRs. Furthermore, the electrochemical approach enables multilayer growth, which is an achievement unattainable with conventional on-surface synthesis. The conventional on-surface synthesis will be limited to monolayers due to the dehydrogenation constraints coming from the metal surface.

In conclusion, this work not only provides a detailed mechanistic understanding of electrochemical on-surface synthesis but also establishes a practical and scalable approach for constructing edge-functionalized graphene nanoribbons with atomic precision. The discovery of the heterochiral dicationic polymerization pathway represents a conceptual advancement in on-surface chemistry, expanding the synthetic method for GNRs.

References

1. Carbonell-Sanromà, E. *et al.* Doping of Graphene Nanoribbons *via* Functional Group Edge Modification. *ACS Nano* **11**, 7355–7361 (2017).
2. Hayashi, H. *et al.* Experimental and Theoretical Investigations of Surface-Assisted Graphene Nanoribbon Synthesis Featuring Carbon–Fluorine Bond Cleavage. *ACS Nano* **11**, 6204–6210 (2017).
3. Panighel, M. *et al.* Stabilizing Edge Fluorination in Graphene Nanoribbons. *ACS Nano* **14**, 11120–11129 (2020).
4. Nguyen, G. D. *et al.* Atomically precise graphene nanoribbon heterojunctions from a single molecular precursor. *Nature Nanotech* **12**, 1077–1082 (2017).
5. Björk, J., Stafström, S. & Hanke, F. Zipping Up: Cooperativity Drives the Synthesis of Graphene Nanoribbons. *J. Am. Chem. Soc.* **133**, 14884–14887 (2011).
6. Clair, S. & De Oteyza, D. G. Controlling a Chemical Coupling Reaction on a Surface: Tools and Strategies for On-Surface Synthesis. *Chem. Rev.* **119**, 4717–4776 (2019).
7. Grill, L. & Hecht, S. Covalent on-surface polymerization. *Nat. Chem.* **12**, 115–130 (2020).

8. Ma, C. *et al.* Remote-Triggered Domino-like Cyclodehydrogenation in Second-Layer Topological Graphene Nanoribbons. *J. Am. Chem. Soc.* **145**, 10126–10135 (2023).
9. Stillinger, F. H. & Kirkwood, J. G. Theory of the Diffuse Double Layer. *The Journal of Chemical Physics* **33**, 1282–1290 (1960).
10. Bohinc, K., Kralj-Iglič, V. & Iglič, A. Thickness of electrical double layer. Effect of ion size. *Electrochimica Acta* **46**, 3033–3040 (2001).
11. Wu, J. Understanding the Electric Double-Layer Structure, Capacitance, and Charging Dynamics. *Chem. Rev.* **122**, 10821–10859 (2022).
12. Li, P., Jiao, Y., Huang, J. & Chen, S. Electric Double Layer Effects in Electrocatalysis: Insights from Ab Initio Simulation and Hierarchical Continuum Modeling. *JACS Au* **3**, 2640–2659 (2023).
13. Lück, J. & Latz, A. Modeling of the electrochemical double layer and its impact on intercalation reactions. *Phys. Chem. Chem. Phys.* **20**, 27804–27821 (2018).
14. Sakaguchi, H., Matsumura, H. & Gong, H. Electrochemical epitaxial polymerization of single-molecular wires. *Nature Mater.* **3**, 551–557 (2004).

15. Huang, L., Zeppenfeld, P., Horch, S. & Comsa, G. Determination of iodine adlayer structures on Au(111) by scanning tunneling microscopy. *The Journal of Chemical Physics* **107**, 585–591 (1997).
16. Jubu, P. R. *et al.* Comment about the use of unconventional Tauc plots for bandgap energy determination of semiconductors using UV–Vis spectroscopy. *Results in Optics* **14**, 100606 (2024).
17. Makuła, P., Pacia, M. & Macyk, W. How To Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV–Vis Spectra. *J. Phys. Chem. Lett.* **9**, 6814–6817 (2018).
18. Tauc, J., Grigorovici, R. & Vancu, A. Optical Properties and Electronic Structure of Amorphous Germanium. *Physica Status Solidi (b)* **15**, 627–637 (1966).
19. Sasaki, K. Basic Principles of Raman Spectroscopy for Graphene. *NTT Technical Review* **11**, 10–14 (2013).
20. Wu, J.-B., Lin, M.-L., Cong, X., Liu, H.-N. & Tan, P.-H. Raman spectroscopy of graphene-based materials and its applications in related devices. *Chem. Soc. Rev.* **47**, 1822–1873 (2018).
21. Çiftçi, H., Testereci, H. N. & Öktem, Z. Electrochemical polymerization of 2-aminothiazole. *Polym. Bull.* **66**, 747–760 (2011).

22. Petrowsky, M. & Frech, R. Temperature Dependence of Ion Transport: The Compensated Arrhenius Equation. *J. Phys. Chem. B* **113**, 5996–6000 (2009).
23. Aoshima, S. & Kanaoka, S. A Renaissance in Living Cationic Polymerization. *Chem. Rev.* **109**, 5245–5287 (2009).
24. Kamigaito, M., Ando, T. & Sawamoto, M. Metal-Catalyzed Living Radical Polymerization. *Chem. Rev.* **101**, 3689–3746 (2001).
25. Zhou, Y.-N., Li, J.-J., Wu, Y.-Y. & Luo, Z.-H. Role of External Field in Polymerization: Mechanism and Kinetics. *Chem. Rev.* **120**, 2950–3048 (2020).
26. Khalifa, I. B. *et al.* Correlation structure–properties of poly(3-methylthiophene) (P3MTh) synthesized using TiCl_4 as an oxidant. *Synthetic Metals* **162**, 1724–1730 (2012).
27. Morgado, J. Modulation of the electrical double layer in metals and conducting polymers. *Sci. Rep.* **12**, 307 (2022).
28. Tybrandt, K., Zozoulenko, I. V. & Berggren, M. Chemical potential–electric double layer coupling in conjugated polymer–polyelectrolyte blends. *Sci. Adv.* **3**, eaao3659 (2017).

29. Abyazisani, M., MacLeod, J. M. & Lipton-Duffin, J. Cleaning up after the Party: Removing the Byproducts of On-Surface Ullmann Coupling. *ACS Nano* **13**, 9270–9278 (2019).

Chapter 4. Oxygen-Doped Graphene Nanoribbons as Superior Catalysts Beyond Noble Metals in Vapor-Phase Chemical Etching of Silicon

4.1 Introduction

Graphene nanoribbons (GNRs) have attracted significant attention as promising nanocarbon materials due to their unique electronic, optical, and catalytic properties, which can be tuned by controlling their width, edge structure, and functionalization^{1–4}. Metal-assisted chemical etching (MaCE) is a well-established technique for fabricating silicon nanoarchitectures by employing noble metals such as gold, silver, or platinum as catalysts^{5–7}. Although these metals exhibit high etching rates, their limited availability, high cost, and potential contamination risks pose challenges for semiconductor manufacturing. Carbon-based catalysts such as carbon nanotubes⁸ (CNTs), graphene oxide⁹, and graphene¹⁰ have been proposed as alternatives. However, their catalytic efficiencies remain inferior to those of noble metals.

In this chapter, we demonstrate that electrochemically synthesized 5A-OGNR, which is mentioned in Chapter. 3 exhibits remarkably high catalytic activity for vapor-phase silicon etching, surpassing that of CNTs, graphene, undoped 5A-GNR, 7A-GNR, and even gold. The Si etching experiment was carried out in a vapor-phase etching condition. After we transferred the 5A-OGNR to silicon (Si) substrates and exposed the substrate to a vapor mixture of hydrofluoric acid (HF) and hydrogen peroxide (H₂O₂), the Si regions covered with 5A-OGNR underwent significant etching with a high etching rate of 2.0 $\mu\text{m}\cdot\text{h}^{-1}$, surpassing the etching rate of gold (1.4 $\mu\text{m}\cdot\text{h}^{-1}$).

As illustrated in Figure 4.1, the etching of silicon is an electrochemical process in which the catalyst, either a metal or a carbon-based material, functions as the cathode. The silicon substrate serves as the anode. Based on previously reported mechanisms, the etching reaction occurring at the catalyst/Si interface proceeds through three consecutive steps⁵. (a) H_2O_2 is first adsorbed onto the surface of the catalyst and subsequently reduced to water, accompanied by the generation of holes. (b) The holes generated in this step diffuse through the catalyst and are injected into the underlying silicon. (c) The injected holes oxidize the silicon in direct contact with the catalyst, and the oxidized silicon is then dissolved by HF, producing volatile silicon tetrafluoride (SiF_4) or hexafluorosilicic acid (H_2SiF_6) as a by-product, which diffuses away along the interface. If we only consider the energy, Si will be oxidized by H_2O_2 and etched by HF even without the catalyst. But the actual etching rate without a catalyst could be very low, about 10 nm per hour¹¹. Therefore, the Si regions covered with the catalyst will be etched while the other uncovered areas remain unetched in our vapor-phase etching condition.

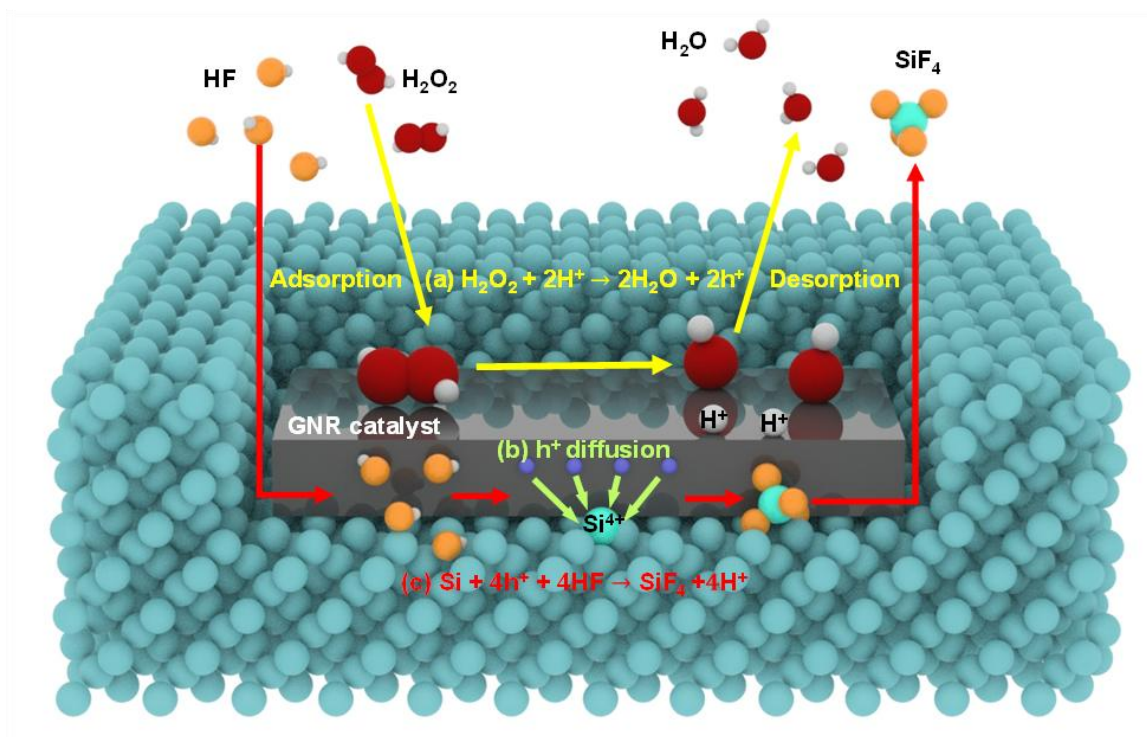


Figure 4.1. Illustration of GNR-assisted chemical etching of Si.

4.2 Experimental

4.2.1 Sample preparation

To prepare the sample of electrochemically produced 5A-OGNR, we applied voltage pulses (3 V vs. Ag/Ag⁺) on the iodine-covered gold working electrode. The pulse duration was set to be 5 seconds; two pulses were applied with an interval of 10 seconds at 80 °C to allow the consumed monomer to be adsorbed again onto the electrode from the electrolyte after the first pulse. After the process, we washed the resulting GNR-covered gold substrate with dichloromethane (DCM) several times. We then transfer the 5A-OGNR to a p-type Si substrate (10-20 Ω cm resistivity, 0.5×1.0 cm²) by using the method in Chapter 2.1.2.

To prepare the sample of CNT and graphene, we dropped 10 μ L of the sample solutions on Si substrates and then dried them at 60°C for 30 min. We used commercially available solutions of metallic CNT dispersed (Meijo nano carbon, EC-DL) and semiconducting CNT dispersed (Meijo nano carbon, RS-1), which were diluted 10 times with deionized water, to create CNT dispersed solutions for our etching experiment. For the graphene solution, we sonicated graphene (FUJIFILM Wako Chemicals) in 1-methyl-2-pyrrolidone (0.1 mg mL⁻¹) for 30 min to create the dispersed solution.

To prepare the Si substrates covered by 5-AGNR and 7-AGNR, we synthesized them by using the 2-Zone CVD method¹². Then, we use the same transfer procedure in Chapter 2.1.2 to prepare the sample for Si etching.

4.2.2 Vapor-phase chemical etching of silicon

The etching experiments were conducted as shown in Figure 4.2. A solution was prepared by mixing 25 mL of 46% HF with 0.5 mL of 30% H_2O_2 , and then it was injected into a sealed Teflon container. Before the vapor-phase etching, we preheated the etching solution in a water bath at 50°C for 30 minutes. After preheating, the Si substrates coated with GNRs or other carbon-based materials were placed flat on a platform inside the container. The Si substrate will not come into direct contact with the etchant solution¹³. The container was subsequently sealed and maintained in a dark water bath at 50°C for 1 hour to prevent light-induced reactions¹⁴. After the etching process, the Si substrate was carefully removed and rinsed thoroughly with deionized water 3 times to remove residual chemicals from its surface. This process ensures a controlled etching environment to examine the catalytic effects of GNRs and other catalysts under vapor-phase etching conditions. Finally, scanning electron microscopy (SEM) is used to check the top view of the etched Si. Then the Si will be cut to check the cross-sectional view.



Figure 4.2. Illustration of the Si vapor-etching process. The etchant solution consisted of 25 mL of 46% HF and 0.5 mL of 30% H₂O₂. Etching proceeded at 50°C for 1 h.

4.2.3 Photoconductivity measurement

To measure photoconductive properties, we prepared 5A-OGNRs electrochemically on an ITO substrate by applying voltage pulses (3 V vs. Ag/Ag⁺) with a 0.5 s period for 3000 cycles. The interval between cycles was set to 2.5 s. The resulting 5A-OGNRs on ITO were then doped by immersing them in a 10 mM iron chloride (FeCl₃) acetonitrile solution for 2 min in a glovebox, followed by several washes with acetonitrile and DCM (Figure 4.3). After doping, FeCl₃-doped 5A-OGNRs on ITO were peeled off the substrate by sonicating it in DCM. Collected flakes of GNRs in DCM solution were then transferred onto glass substrates and dried on a hot plate at 80°C for 10 min. To create a photoconductive cell, gold was deposited on transferred GNRs on a glass substrate, which was covered with a 25-μm grid mesh. Photoconductive cells of 5-AGNR and 7-AGNR were prepared in the same way as electrochemically produced 5A-OGNRs.

The semiconductor analyzer (Keithley 4200-SCS) and a homemade probe station were used to measure photoconductivity properties. Once the sample was connected to the probes (Fig. 5e), the chamber was evacuated to 10⁻⁴ Pa. Current was measured at a constant voltage of 1 V in a dark environment. The sample was exposed to 6 cycles of a green laser at 532 nm with a power of 1 mW for 20 s, with a 30 s interval between cycles.

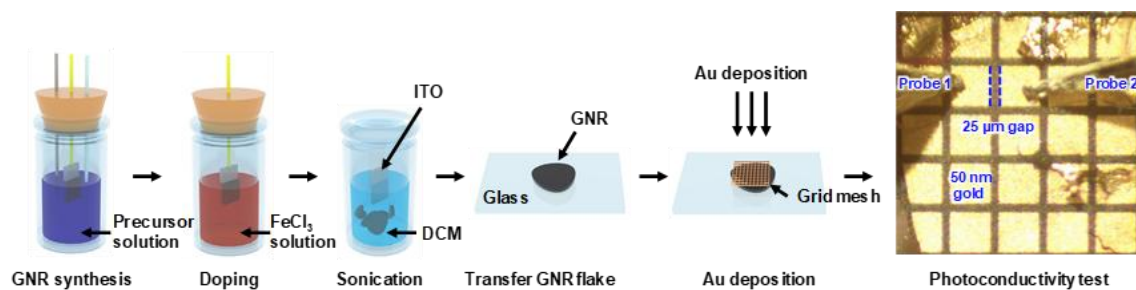


Figure 4.3. Fabrication of the photoconductive cell of electrochemically produced GNRs.

4.3 Results and discussion

4.3.1 Electron-donating property of 5A-OGNRs

The electron-donating property of 5A-OGNR is critical for its catalytic performance in vapor-phase silicon etching. As shown in Figure 4.4, the cyclic voltammogram (CV) of 5A-OGNR on Au(111) exhibits a broad oxidation peak spanning from 0.12 V to over 1.1 V versus SHE. Notably, the first oxidation peak of 5A-OGNR occurs at a lower potential than that of the strong electron-donating molecule tetrathiafulvalene (TTF, 0.62 V), demonstrating that 5A-OGNR possesses a highly electron-donating nature. This enhanced electron-donating ability is attributed to the dense introduction of butoxy substituents along the GNR backbone, which increases the electron density near the oxygen atoms of the 5A-OGNR. The broad oxidation range also implies that multiple sites along the polymer chain can participate in electron donation.

Furthermore, as shown in Figure 4.5, 5A-OGNR exhibits reversible redox peaks in both forward and reverse scans. This behavior indicates that the polymer undergoes repeated oxidation and reduction without significant structural or chemical degradation, indicating its excellent electrochemical stability. In contrast, 5-GNR and 7-AGNR produced via two-zone chemical vapor deposition¹² without butoxy substituents display irreversible features in their CV profiles. Such irreversibility suggests that these GNRs undergo decomposition upon oxidation, which limits their durability and electrochemical performance. The comparison shows the critical role of the butoxy substituents in stabilizing the GNR backbone, ensuring long-term cycling durability. Collectively, these observations confirm that

electrochemically synthesized 5A-OGNR is a robust and reliable material for catalytic applications.

In addition to electron-donating ability, the electrochemical potential requirements for silicon etching are a key consideration⁵. As shown in Figure 4.6, the standard reduction potential of H_2O_2 is 1.76 V versus SHE, whereas that of Si is 0.67 V versus SHE. Therefore, an effective catalyst for Si etching should possess an oxidation potential within this potential window to enable efficient electron transfer at the catalyst/Si interface. Unlike noble metals, which have a specific redox potential, 5A-OGNR exhibits a broad oxidation peak, allowing multiple oxidation states to coexist across a wide potential range. This property enables the GNR to mediate both H_2O_2 reduction and silicon oxidation effectively. Consequently, the combination of a highly electron-donating property and a broad, tunable oxidation potential makes 5A-OGNR a versatile and highly effective catalyst for vapor-phase silicon etching.

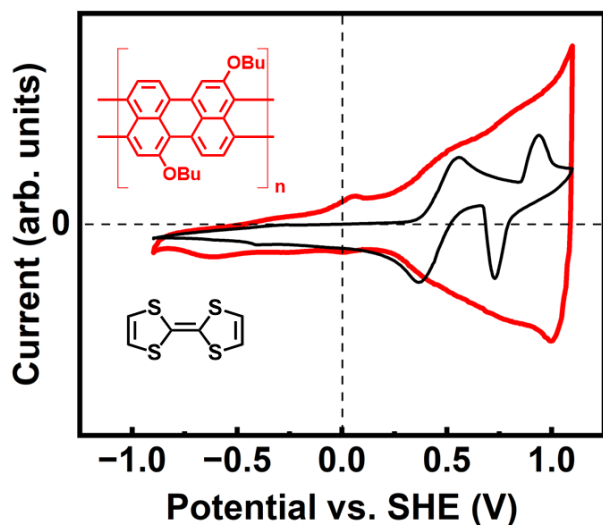


Figure 4.4. Cyclic voltammetry of GNR films on the Au(111) (red) and TTF (black) in o-DCB electrolyte solution. The inset shows chemical structures.

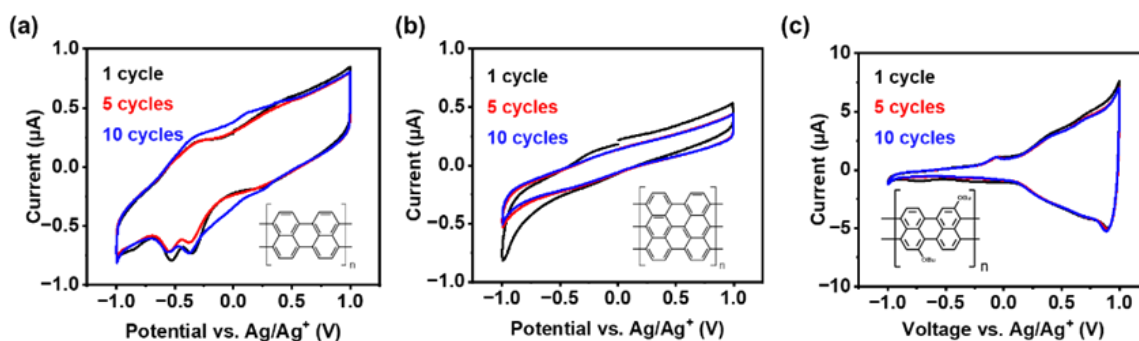


Figure 4.5. CV curves (scan rate of 50 mV s^{-1}) of (a) 5-AGNR, (b) 7-AGNR, and (c) 5A-OGNR, deposited on Au (111), measured in electrolyte solution with 0.1 M TBAPF_6 in o-DCB. Black, red, and blue curves show 1, 5, and 10 cycles, respectively. The inset shows the chemical structures.

Potential vs. SHE

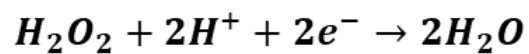
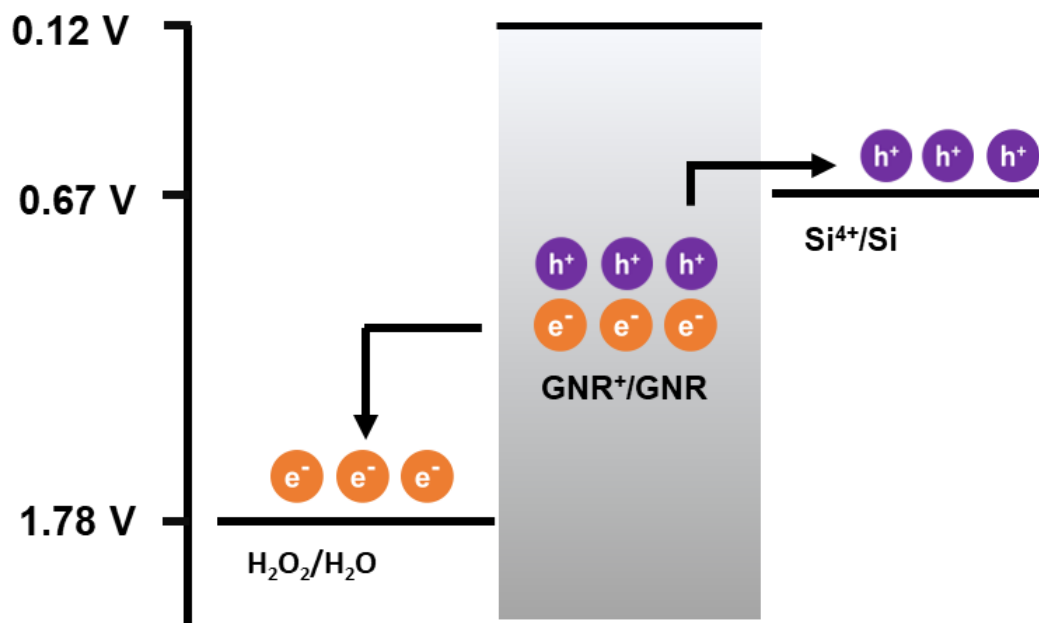


Figure 4.6. Illustration of the standard electrode potential of H_2O_2 , 5A-OGNR, and Si to explain the mechanism of vapor-phase chemical etching of Si.

4.3.2 Si etching catalytic performance of the 5A-OGNR, gold, and other carbon-based materials

We evaluated the catalytic performance of 5A-OGNR by transferring the GNRs grown on electrodes onto Si substrates and exposing them to a vapor mixture of hydrofluoric acid and hydrogen peroxide at 50 °C. The silicon surface was then examined using SEM before and after etching to assess the catalytic activity of 5A-OGNR. As shown in Figure 4.7a and b, the Si regions covered with 5A-OGNR were significantly etched, whereas the uncovered areas remained intact. The cross-sectional SEM image (Figure 4.7c) reveals an etching rate of approximately $2.0 \mu\text{m h}^{-1}$ for 5A-OGNR. These observations confirm that Si etching almost does not occur in the absence of a suitable catalyst. The smallest observed etched area was approximately $2 \mu\text{m}^2$ (Figure 4.8). The experiment was repeated multiple times to verify reproducibility, as demonstrated in Figure 4.9. Furthermore, the precursor molecule, 2-butoxynaphthalene, exhibited no catalytic activity toward Si etching (Figure 4.10). To further highlight the superior catalytic performance of 5A-OGNR, comparative etching experiments were conducted using other catalysts. As shown in Figure 4.11, the etching rate of 5A-OGNR ($2.0 \mu\text{m h}^{-1}$) exceeds those of gold ($1.4 \mu\text{m h}^{-1}$), metallic CNT ($0.1 \mu\text{m h}^{-1}$), semiconducting CNT ($0.4 \mu\text{m h}^{-1}$), graphene ($0.1 \mu\text{m h}^{-1}$), 5-AGNR ($0.8 \mu\text{m h}^{-1}$), and 7-AGNR ($0.2 \mu\text{m h}^{-1}$). As a result, electrochemically produced 5A-OGNR exhibits the highest etching rate among these carbon-based materials and even higher than that of gold, making it an excellent Si-etching catalyst (Figure 4.12).

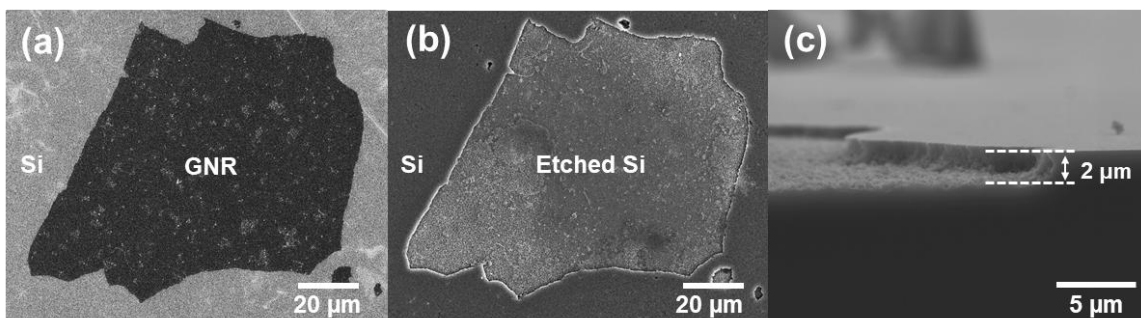


Figure 4.7. SEM images of GNR-covered Si (a) before and (b) after vapor-phase chemical etching by HF and H₂O₂. (c) Cross-sectional image of (b).

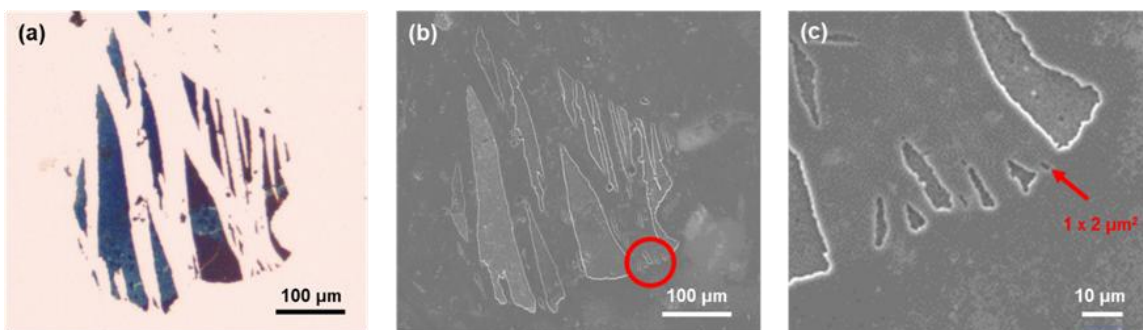


Figure 4.8. (a) Optical microscope image of GNR-covered Si before etching. (b) SEM image after etching. (c) Magnified SEM image of the red circle in (b).

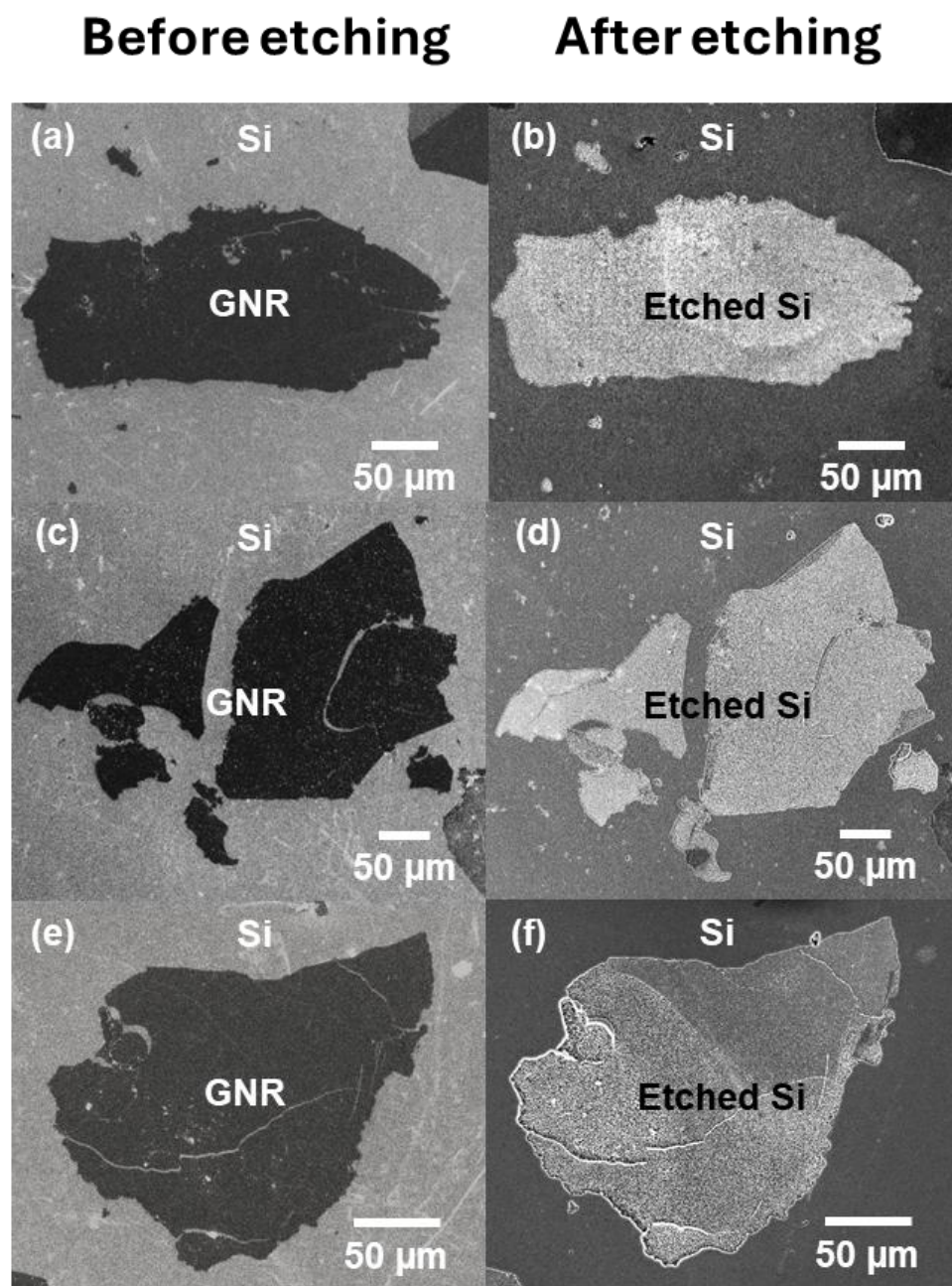


Figure 4.9. SEM images of GNR-covered Si (a, c and e) before and (b, d and f) after etching.

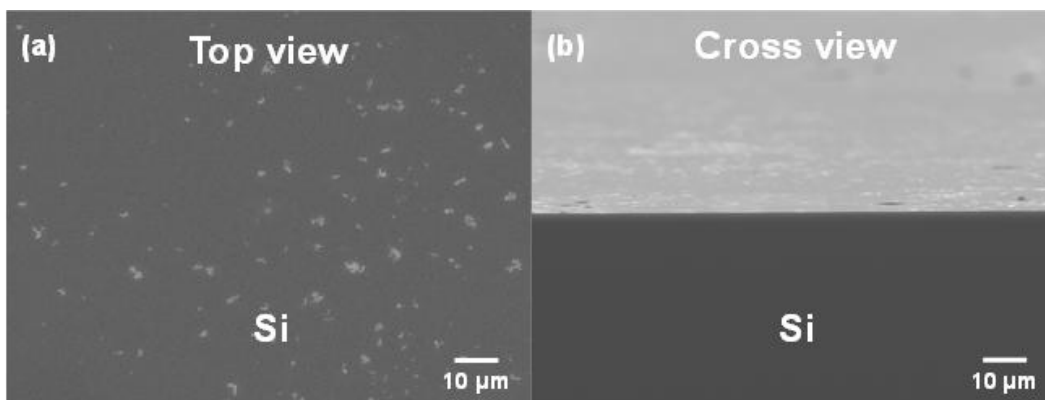
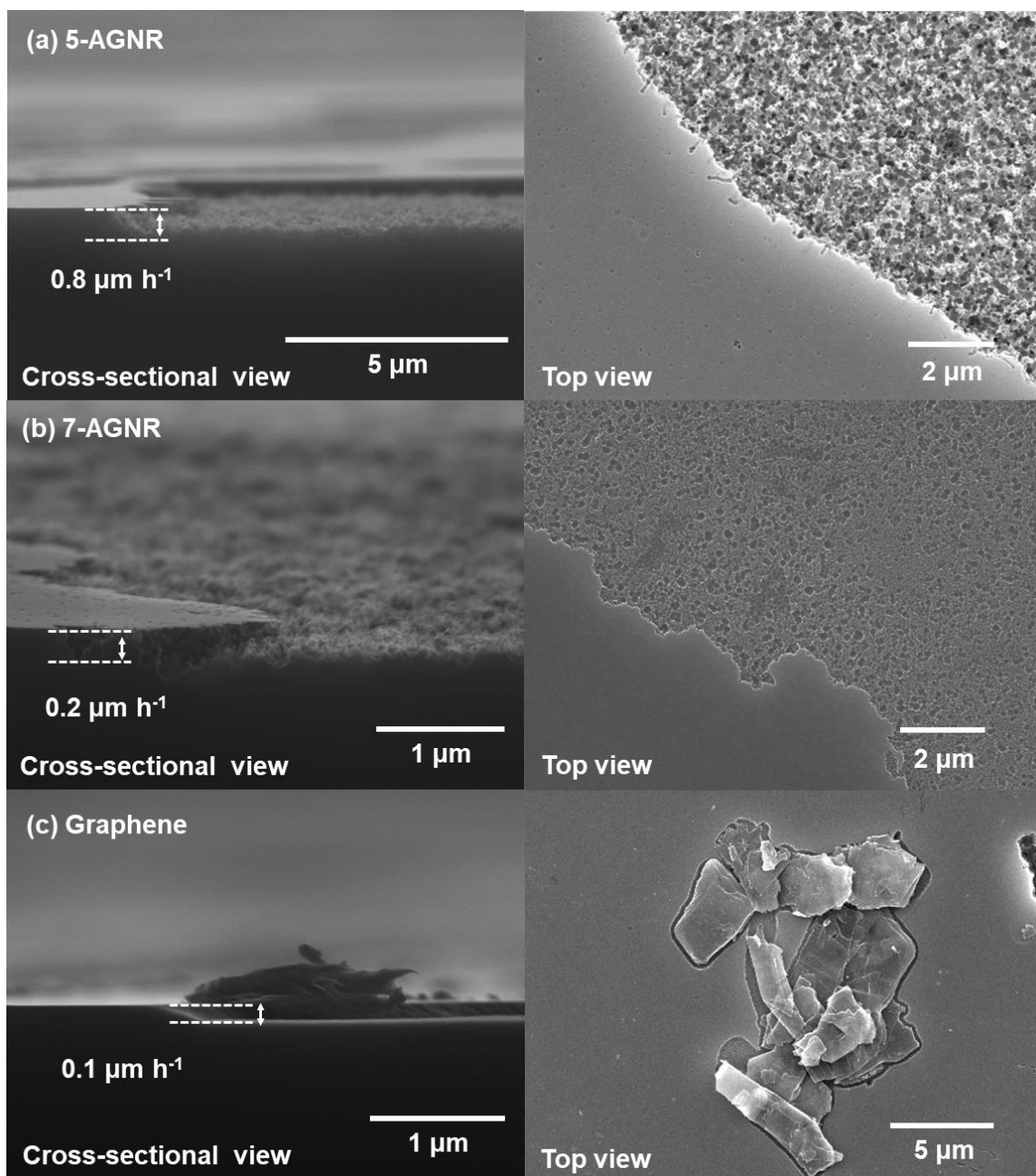


Figure4.10. SEM images of top view (a) and cross-sectional view (b) of the 2-butoxynaphthalene precursor-covered Si after etching.



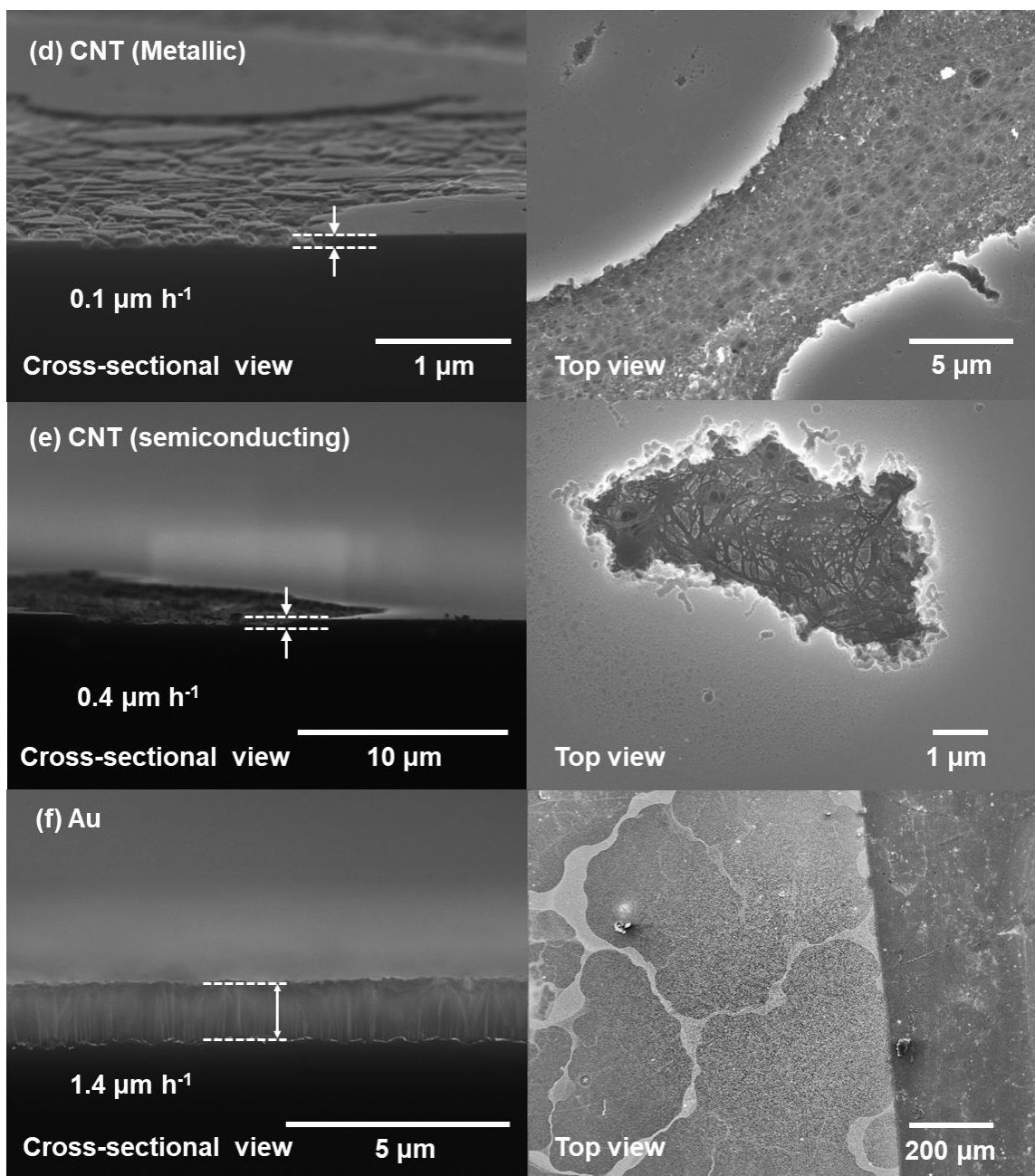


Figure 4.11. Cross-sectional view (left) and top view (right) of etched-Si substrates catalyzed by (a) 5-AGNR, (b) 7-AGNR, (c) graphene, (d) metallic CNT, (e) semiconducting CNT, and (f) gold.

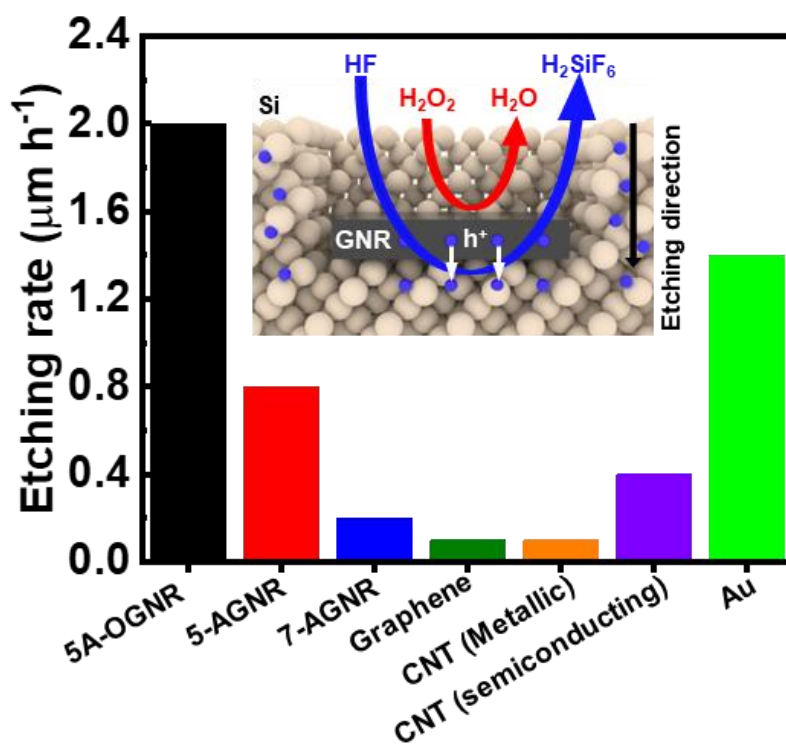


Figure 4.12. Catalytic performance of Si etching of electrochemically produced 5A-OGNR, 5-AGNR, 7-AGNR, graphene, metallic CNT, semiconducting CNT, and gold. The inset shows the mechanism of GNR-assisted Si etching.

4.3.3 Other applications of 5A-OGNR

We further investigated the photoconductive properties of electrochemically synthesized 5A-OGNR. To fabricate the sample cell, FeCl_3 was introduced into the 5A-OGNR film as an electron acceptor to reduce the bandgap, thus enhancing its photoconductivity¹⁵⁻¹⁷. The doped film, prepared on a glass substrate, was then patterned with gold electrodes separated by a 25- μm gap. Upon irradiation with a 532-nm laser (1 mW), the device exhibited pronounced current changes due to photoconductivity, with an ON/OFF ratio of 1.68 (Figure 4.12). For comparison, control experiments were conducted using 5-AGNR and 7-AGNR synthesized via chemical vapor deposition, which were also doped with FeCl_3 . However, no measurable photocurrent was detected in these samples (Figure 4.13). These findings demonstrate that the introduction of butoxy substituents into the GNR backbone significantly enhances the electronic properties of 5-AGNRs compared to hydrocarbon-based GNRs. We also found that FeCl_3 doping is necessary for the photoconductivity of 5A-OGNR under 532 nm laser radiation. The sample without FeCl_3 doping showed no photoconductivity (Figure 4.14).

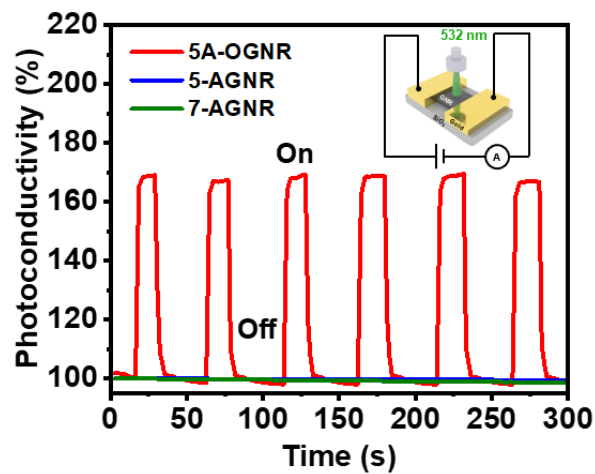


Figure 4.13. Photoconductivity of 5A-OGNR, 5-AGNR and 7-AGNR with FeCl_3 doping. The inset shows the experimental setup.

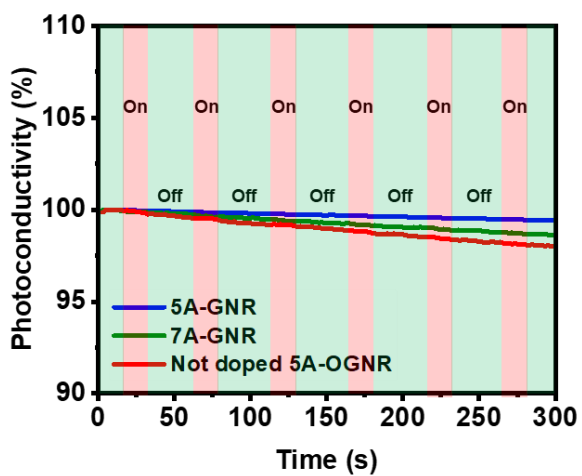


Figure 4.14. Photoconductive properties of FeCl_3 -doped 5-AGNR and 7-AGNR and undoped 5A-OGNR.

4.4 Conclusion

In summary, the electrochemically synthesized 5A-OGNR demonstrates exceptional catalytic performance in vapor-phase silicon etching, surpassing that of gold and other carbon-based catalysts, including carbon nanotubes and graphene. The strong electron-donating nature of the alkoxy-functionalized edges promotes efficient charge transfer from hydrogen peroxide to silicon, accelerating their oxidation and subsequent removal by hydrogen fluoride. Besides, 5A-OGNR also exhibits remarkable photoconductive behavior upon FeCl_3 doping. These findings highlight the potential of electrochemically synthesized GNRs as next-generation functional materials for nanoscale electronics, optoelectronics, and semiconductor processing. Furthermore, the versatility of this electrochemical approach provides a general platform for producing various edge-engineered GNRs, opening new pathways for the design of carbon-based catalysts, sensors, and energy-conversion devices.

References

1. Saraswat, V., Jacobberger, R. M. & Arnold, M. S. Materials Science Challenges to Graphene Nanoribbon Electronics. *ACS Nano* **15**, 3674–3708 (2021).
2. Lou, S. *et al.* Graphene nanoribbons: current status, challenges and opportunities. *Quantum Front* **3**, 3 (2024).
3. Nakada, K., Fujita, M., Dresselhaus, G. & Dresselhaus, M. S. Edge state in graphene ribbons: Nanometer size effect and edge shape dependence. *Phys. Rev. B* **54**, 17954–17961 (1996).
4. Houtsma, R. S. K., De La Rie, J. & Stöhr, M. Atomically precise graphene nanoribbons: interplay of structural and electronic properties. *Chem. Soc. Rev.* **50**, 6541–6568 (2021).
5. Huang, Z., Geyer, N., Werner, P., De Boor, J. & Gösele, U. Metal-Assisted Chemical Etching of Silicon: A Review: In memory of Prof. Ulrich Gösele. *Advanced Materials* **23**, 285–308 (2011).
6. Han, H., Huang, Z. & Lee, W. Metal-assisted chemical etching of silicon and nanotechnology applications. *Nano Today* **9**, 271–304 (2014).
7. Srivastava, R. P. & Khang, D. Structuring of Si into Multiple Scales by Metal-Assisted Chemical Etching. *Advanced Materials* **33**, 2005932 (2021).

8. Wilhelm, T. S. *et al.* Ordered Si Micropillar Arrays via Carbon-Nanotube-Assisted Chemical Etching for Applications Requiring Nonreflective Embedded Contacts. *ACS Appl. Nano Mater.* **2**, 7819–7826 (2019).
9. Xu, Y., Zhao, Q., Chen, J., Zhang, J. & Xu, B. Rapid graphene oxide assisted chemical etching of silicon in HF/H₂O₂ solution. *Phys. Scr.* **99**, 085914 (2024).
10. Kim, J., Lee, D. H., Kim, J. H. & Choi, S.-H. Graphene-Assisted Chemical Etching of Silicon Using Anodic Aluminum Oxides as Patterning Templates. *ACS Appl. Mater. Interfaces* **7**, 24242–24246 (2015).
11. Lehmann, V. *Electrochemistry of Silicon: Instrumentation, Science, Materials and Applications*. (Wiley, 2002). doi:10.1002/3527600272.
12. Sakaguchi, H., Song, S., Kojima, T. & Nakae, T. Homochiral polymerization-driven selective growth of graphene nanoribbons. *Nature Chem.* **9**, 57–63 (2017).
13. Romano, L. *et al.* Metal-assisted chemical etching of silicon in the gas phase: a nanofabrication platform for X-ray optics. *Nanoscale Horiz.* **5**, 869–879 (2020).
14. Ahmed, A. & Alwan, Alwan. Light-Induced Etching of Silicon. *ETJ* **25**, 467–474 (2007).

15. Bouabdallah Daho, Fontanesi, C., Messori, M., Dehbi, A. & Belfedal, A. Synthesis and Characterization of Semiconductor Polymer Doped with FeCl_3 and I_2 . *Semiconductors* **53**, 1656–1664 (2019).
16. Chen, Y., Shih, I. & Xiao, S. Effects of FeCl_3 doping on polymer-based thin film transistors. *Journal of Applied Physics* **96**, 454–458 (2004).
17. Jones, T. E., Ogden, T. R., McGinnis, W. C., Butler, W. F. & Gottfredson, D. M. Electronic properties of polyacetylene doped with FeCl_3 . *The Journal of Chemical Physics* **83**, 2532–2537 (1985).

Chapter 5. Theoretical Investigation of the Catalytic Activity of Oxygen-Doped Graphene Nanoribbons

5.1 Introduction

In the Chapter. 4, we found that the 5A-OGNR shows excellent catalytic performance in the vapor-phase Si etching process. To elucidate the underlying mechanism of this superior catalytic activity, DFT calculations together with experiments were carried out in this chapter. Based on mechanisms reported in previous studies, the silicon etching process at the catalyst/Si interface can be described by three main steps¹⁻³. First, H_2O_2 is adsorbed onto the catalyst surface and subsequently reduced to water, generating holes in the process. Second, the holes produced in this step diffuse through the catalyst and are injected into the underlying Si. Third, the Si in contact with the catalyst is oxidized by the injected holes and etched by HF, producing gaseous silicon tetrafluoride (SiF_4) or hexafluorosilicic acid (H_2SiF_6) that diffuses away along the interface. Among these steps, because hole diffusion occurs much more rapidly than mass transport in the chemical reaction^{4,5}, the rate-determining step of Si etching is generally considered to be governed by mass transport and reaction kinetics, which are influenced by reactant concentration and catalyst activity. Several studies indicate that when the H_2O_2 to HF ratio is low, the HF concentration is sufficient to dissolve the oxidized Si, and the overall etching rate becomes limited by the H_2O_2 reduction step⁶⁻⁸. Accordingly, under vapor-phase etching conditions, where the equilibrium vapor pressure of H_2O_2 is substantially lower than that of HF, the etching rate is primarily determined by the H_2O_2 reduction process. Understanding the detailed mechanism of H_2O_2

reduction at the catalyst interface is therefore critical for elucidating the high etching efficiency observed with GNRs.

In this chapter, the reaction pathway and mechanism of H_2O_2 reduction are investigated in detail. DFT calculations, combined with experimental vapor-phase Si etching, are performed for 5A-OGNR, undoped 5A-GNR, and 7A-GNR. The results demonstrate that oxygen doping via the $-\text{OC}_4\text{H}_9$ substituent significantly alters the charge distribution in 5A-OGNRs, generating high-charge-density active sites on the carbon atoms adjacent to the dopants. These active sites enhance the adsorption and reduction of H_2O_2 , reduce the activation energy during transition states, thereby facilitating hole generation and accelerating the overall Si etching reaction. Consequently, 5A-OGNRs exhibit superior catalytic performance in vapor-phase Si etching, surpassing that of both undoped GNRs and conventional noble metal catalysts.

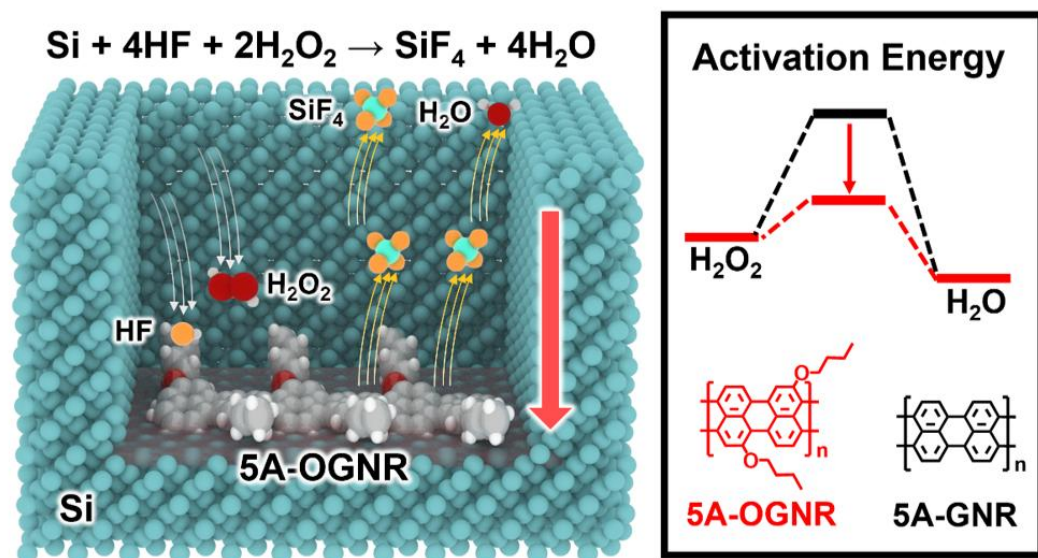


Figure 5.1. Graphic abstract of the Si etching process and activation energy in transition states research.

5.2 Experimental

5.2.1 Computational methods

The DFT calculations in our work were performed with the DMol3⁹ package in Materials Studio. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional was used to describe the electronic exchange–correlation functions¹⁰. The initial structures of GNRs were built based on the STM images in Figures 5.2a-c. The empirical dispersion correction proposed by Grimme was applied to the weak Van der Waals interaction¹¹. The all-electron method was adopted as the core treatment. The double numerical atomic orbital plus polarization function version 4.4 (DNP-4.4) was selected as the basis set¹¹. The self-consistent field (SCF) was determined with a tolerance value of 1.0×10^{-6} Ha. The vibrational frequencies were calculated to determine ZPE and the entropy contributions. T is chosen as 325 K based on our experimental conditions.

The adsorption energies of H₂O₂ molecules adsorbed on the graphene nanoribbon or graphene are defined by the formula:

$$E_{\text{ads}} = E_{\text{Substrate}+\text{H}_2\text{O}_2} - E_{\text{substrate}} - E_{\text{H}_2\text{O}_2}$$

where $E_{\text{substrate}}$, $E_{\text{H}_2\text{O}_2}$, and $E_{\text{Substrate}+\text{H}_2\text{O}_2}$ were the energy of the substrate, the energy of the substrate H₂O₂, and the total energy of the adsorption state, respectively. A lower E_{ads} indicates it is energetically favorable for GNR to adsorb the H₂O₂ molecules.

For each step, the reaction free energy ΔG is defined as the difference between the free energies of the initial and final states, which is determined by the formula:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$$

where ΔE is the electronic energy change, ΔE_{ZPE} is the zero-point energy change, T is the temperature, and ΔT is the entropy change.

The transition state (TS) searches were performed using the complete linear synchronous transit/quadratic synchronous transit (LST/QST) method. The activation energy (E_a) is defined by the formula:

$$E_a = E_{TS} - E_{IS}$$

where E_{TS} , E_{IS} are the total energy of the transition state and initial state, respectively.

5.2.2 Scanning tunneling microscopy (STM) characterization

All samples were degassed in UHV by annealing at 150°C for 1 hour before STM measurements. The STM experiments were performed in constant-current mode using a low-temperature scanning tunneling microscope (UNISOKU, USM-1100SA-2C) operated at 77 K. A tungsten tip, electrochemically etched to a sharp tip, was used for the measurements. The differential conductance map was recorded using a digital lock-in amplifier with a modulation frequency of 350 Hz and an AC voltage of 2 mV. The V_{sample} was set to -0.2 V, with a current of 80 pA. All STM images and data were analyzed using SPIP software.

5.3 Results and discussion

5.3.1 Si etching configuration of 5A-OGNR, 5A-GNR, and 7A-GNR

To evaluate the catalytic properties of graphene nanoribbons with different structures, 5-AGNRs and 7-AGNRs were synthesized using a two-zone chemical vapor deposition (2Z-CVD) method, whereas 5A-OGNRs were prepared electrochemically as described in Chapter 3. The molecular structures of these GNRs are characterized by using the LT-STM (Figure 5.2). Etching experiments were then performed under vapor-phase conditions containing H_2O_2 and HF at 50 °C, using the three types of GNRs as catalysts. Cross-sectional images of Si after etching with 5A-OGNRs, 5A-GNRs, and 7A-GNRs are shown in Figures 5.3a-c. The measured etching rates for these samples were $1.79 \mu\text{m h}^{-1}$, $0.72 \mu\text{m h}^{-1}$, and $0.16 \mu\text{m h}^{-1}$, respectively, indicating that Si covered with 5A-OGNRs exhibits the highest etching rate among the GNRs investigated.

Figures 5.3d-f show top views of Si etched by 5A-OGNRs, 5A-GNRs, and 7A-GNRs, respectively. In the 5A-OGNR sample, the etched Si surface is smooth. This is likely due to sufficient hole injections, in which the reaction between HF and the oxidized Si mainly limits the etching process. The excellent catalytic performance of 5A-OGNRs enables efficient H_2O_2 reduction, producing a large number of holes that diffuse and distribute uniformly across the exposed catalyst/Si interface. In stark contrast, both 5A-GNRs and 7A-GNRs show rough Si surfaces. The insufficient reduction of H_2O_2 reduces the number of holes produced, causing all available holes to be locally consumed¹. It suggests that the number of holes generated at the GNR/Si interface in 5A-

GNRs and 7A-GNRs is lower than in 5A-OGNRs. As a result, the etching rate is limited by the H_2O_2 reduction process that generates holes. To assess the stability of the three types of GNRs during etching, Raman spectra were characterized before and after etching (Figures 5.4a-c). The 5A-OGNRs showed sharp D-bands ($1000\text{-}1400\text{ cm}^{-1}$) and G-bands (1600 cm^{-1}) both before and after etching, indicating excellent stability under H_2O_2 and HF conditions. In sharp contrast, 5A-GNRs displayed a broadened D-band after etching. The D-band, a defect-induced Raman mode associated with disruptions in the sp^2 carbon lattice, is commonly used to evaluate the edge quality of graphene-based materials^{12,13}. Therefore, the broadening of the D-band indicates that the edge structures of 5A-GNRs are unstable during the Si etching process.

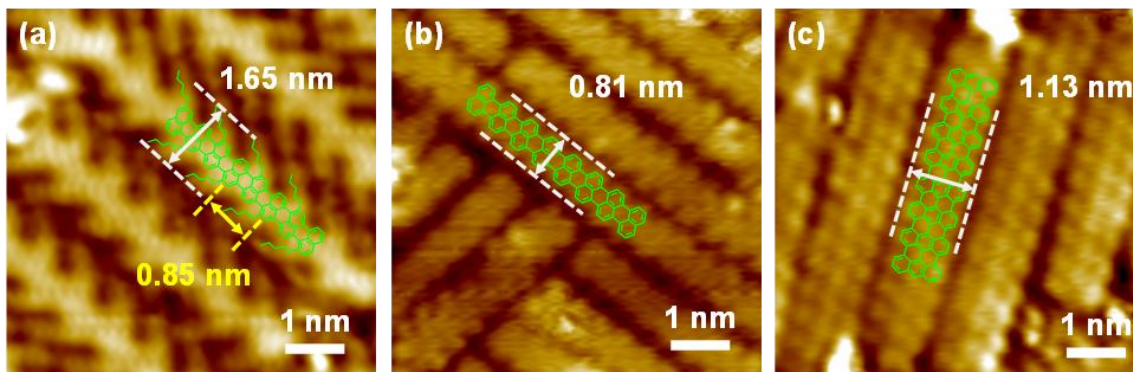


Figure 5.2. LT-STM images of (a) 5A-OGNR (Bias voltage = -0.71 V, feedback current = 580 pA), (b) 5A-GNR (Bias voltage = -0.14 V, feedback current = 275 pA), and (c) 7A-GNR (Bias voltage = -0.31 V, feedback current = 580 pA). The white dotted lines and arrows indicate the width of the GNRs; the yellow dotted lines and arrows indicate the periodicity of the 5A-OGNR. The chemical structures of GNRs are overlapped on the STM images.

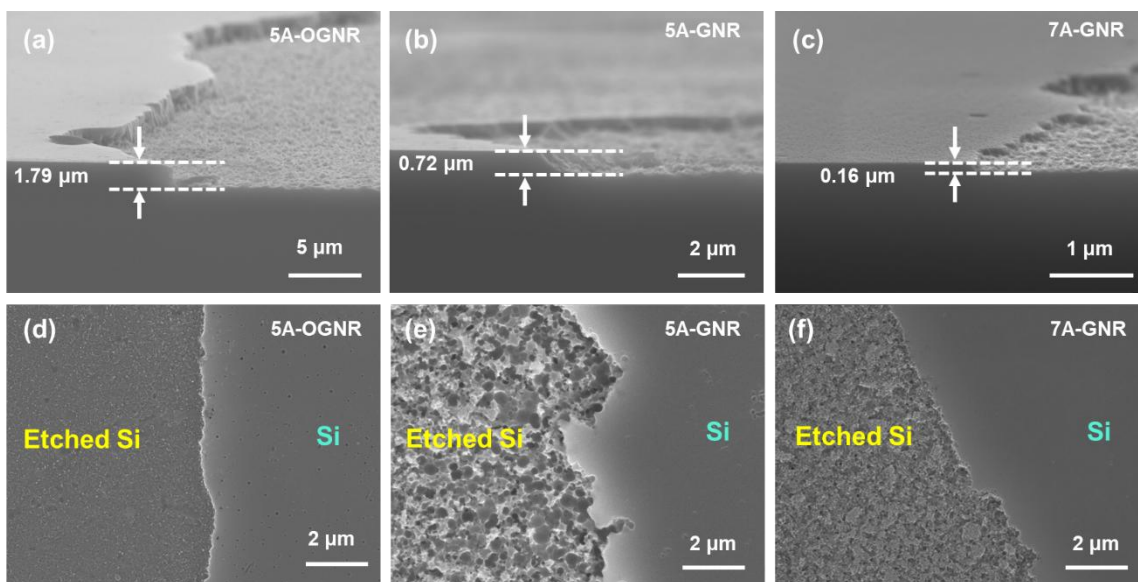


Figure 5.3. SEM images of the Si cross-sectional views and top views covered by (a, d) 5A-OGNR, (b, e) 5A-GNR, and (c, f) 7A-GNR after vapor-phase chemical etching in HF and H₂O₂. The white lines and arrows indicate the etching depth of Si after etching for one hour. The etched Si covered by the GNRs during the etching process is labeled in yellow text, while the non-etched Si is labeled in blue text.

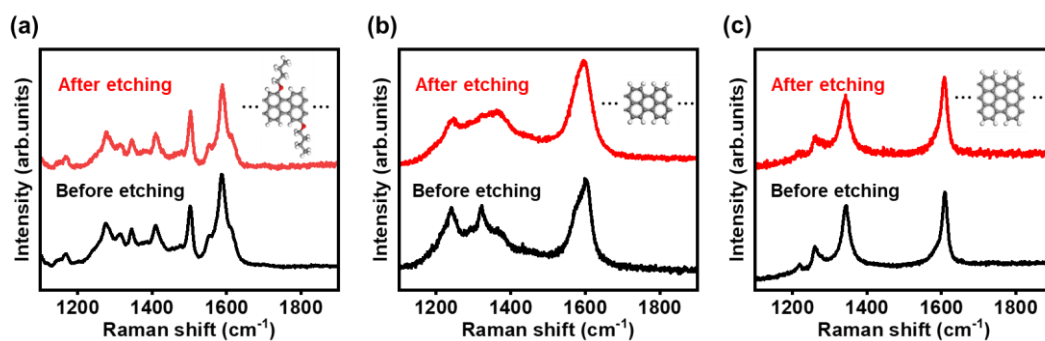


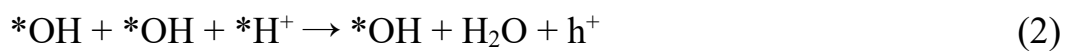
Figure 5.4. Raman spectra of (a) 5A-OGNR, (b) 5A-GNR, and (c) 7A-GNR before etching (black) and after etching (red). The insets show the chemical structures of GNRs.

5.3.2 Adsorption, reaction pathway, and Gibbs free energy simulations

The adsorption of reactants onto catalysts is a critical step in redox reactions¹⁴. One of the primary factors underlying the superior catalytic performance of 5A-OGNRs is the localized high charge density induced by oxygen doping, which promotes the adsorption of H_2O_2 molecules. To elucidate this effect, we simulated the charge distributions of 5A-OGNRs, 5A-GNRs, and 7A-GNRs and compared their corresponding H_2O_2 adsorption energies. As shown in Figure 5.5a, oxygen doping generates distinct regions of high charge density in 5A-OGNRs. Because oxygen (electronegativity 3.44) is more electronegative than carbon (2.55), a partial positive charge (0.295 |e|) is induced on the adjacent carbon atoms. In contrast, the undoped 5A-GNRs and 7A-GNRs (Figures 5.5b and c) display relatively uniform charge distributions without localized high-charge-density sites. Their charge densities are instead governed by the armchair edge effect arising from hydrogen passivation¹⁵, leading to a gradual decrease in charge density from the ribbon center toward the edges (from -0.025 |e| and -0.012 |e| at the center to -0.127 |e| and -0.130 |e| at the edges for 5A-GNRs and 7A-GNRs, respectively). Previous studies have demonstrated that regions with high charge density often serve as active sites owing to their increased reactivity toward adsorbates such as O_2 and $-\text{OOH}$ ^{16,17}. Because H_2O_2 also contains two lone electron pairs, a similar enhancement in adsorption is expected at these sites. Therefore, the carbon atoms exhibiting the highest charge density in 5A-OGNRs are predicted to function as active centers for H_2O_2 reduction.

To elucidate the correlation between charge distribution and adsorption energy, we calculated H₂O₂ adsorption energies at multiple positions along each GNR type, from the center to the edge. As illustrated in Figures 5.5d-f, 5A-OGNRs exhibit a pronounced advantage in H₂O₂ adsorption, which can be attributed to the incorporation of oxygen dopants. The adsorption energy at the site with the highest charge density in 5A-OGNRs is -0.597 eV, lower than that of 5A-GNRs (-0.557 eV) and 7A-GNRs (-0.559 eV). These computational results substantiate the hypothesis that oxygen-induced charge redistribution enhances the catalytic activity of 5A-OGNRs by promoting more energetically favorable H₂O₂ adsorption. Consequently, 5A-OGNRs offer a greater density of active sites, which is particularly beneficial for vapor-phase Si etching. In contrast, for 5A-GNRs and 7A-GNRs, the most favorable adsorption sites for H₂O₂ are located at the edge carbon atoms, corresponding to their lowest adsorption energies.

After H₂O₂ adsorption, the two possible pathways for the bond-cleaving process are studied¹⁸. One possibility is that the cracked adsorption pathway¹⁸ (Pathway 1) begins with the O-O bonds cleaving, as shown in Figure 5.6a, which can be expressed as (* denotes the surface of GNRs)



As shown in Figures 5.7-5.9, the reaction sites for step (1) in 5A-OGNRs, 5A-GNRs, and 7A-GNRs were identified by comparing the free energies of the

possible intermediates. The intermediates with the lowest free energies for step (1) correspond to the most favorable adsorption sites for each GNR type. Because bond cleavage generally occurs at the exact location of adsorption, all subsequent reaction steps were assumed to proceed at these identified sites. The free energy profiles for each reaction step are summarized in Figure 5.6b, with the reference energy level defined as that of the final product ($*$ + 2H₂O). The calculated data indicate that all steps are energetically downhill, suggesting that the overall reaction is thermodynamically favorable. The rate-determining step (RDS) is defined as the elementary step with the smallest reaction free energy change¹⁹. As summarized in Table 5.1, ΔG_1 is consistently lower than ΔG_2 and ΔG_3 for all GNR types, where ΔG_1 , ΔG_2 , and ΔG_3 represent the free energies of steps (1)-(3), respectively. Therefore, step (1) is identified as the rate-determining step in the H₂O₂ reduction process. In this step, 5A-OGNR exhibits the highest reaction free energy (0.83 eV), compared with 5A-GNR (0.61 eV) and 7A-GNR (0.18 eV). This result suggests that 5A-OGNR achieves a more thermodynamically stable configuration upon bonding with -OH, leading to a larger ΔG_1 during the H₂O₂ dissociative adsorption process and consequently enhanced catalytic activity. We attribute this to the influence of oxygen dopants, whose high electronegativity modulates the electronic distribution of adjacent carbon atoms, thereby strengthening the interaction between carbon and -OH groups. This mechanism is consistent with previous reports on N-doped graphene²⁰. Collectively, these findings corroborate the experimental observations, confirming that 5A-OGNRs exhibit the highest catalytic performance, whereas 7A-GNRs exhibit the lowest among the three GNR types.

Table 5.1. The reaction free energy change of the step (1-3) on 5A-OGNR, 5A-GNR, and 7A-GNR.

	5A-OGNR	5A-GNR	7-AGNR
ΔG_1 (eV)	0.83	0.61	0.18
ΔG_2 (eV)	1.09	1.14	1.46
ΔG_3 (eV)	1.71	1.88	1.99

The other possibility is that the ionized adsorption (Pathway 2) begins with the O-H bonds cleaving¹⁸, as shown in Figure 5.10a, which can be expressed as



However, as shown in Figure 5.10b, barriers of 1.66 eV, 1.53 eV, and 1.90 eV are found in the reaction free energy (ΔG_4) during the O-H bond cleaving process for 5A-OGNRs, 5A-GNRs, and 7-AGNRs, respectively. ΔG_4 denotes the reaction free energy of reaction (4). These results indicate that the H_2O_2 reduction reaction is more likely to proceed via Pathway 1, which exhibits a

downhill free energy profile, rather than Pathway 2, which involves an energetically unfavorable uphill process.

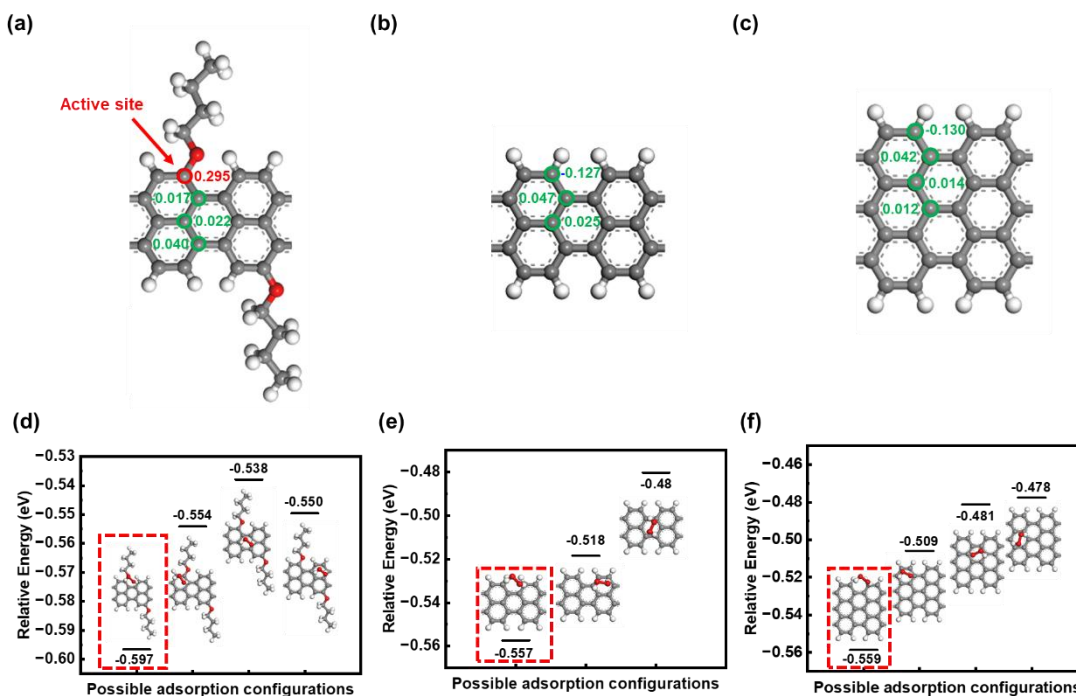


Figure 5.5. Top views of the simulation cells with the Mulliken charge values (green circles) on carbon atoms of (a) 5A-OGNR, (b) 5A-GNR, and (c) 7A-GNR. A red circle marks the active site in 5A-OGNR. Possible adsorption configurations during the H_2O_2 adsorption process on (d) 5A-OGNR, (e) 5A-GNR, and (f) 7A-GNR. These values denote the adsorption energy of each possible adsorption configuration. The red dotted rectangles denote the adsorption configurations with the lowest adsorption energy.

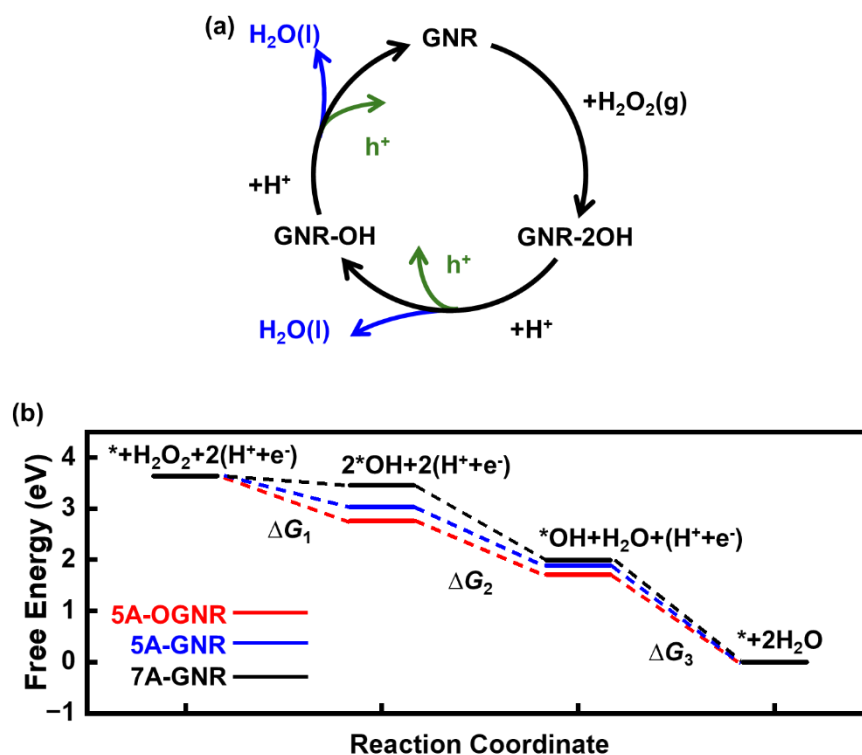


Figure 5.6. (a) Schematic illustration of the cracked adsorption pathway of the H_2O_2 bond-cleaving process on GNRs. The cracked adsorption pathway includes the reaction coordinates of GNR bonding with two -OH groups (GNR-2OH) and one -OH group (GNR-OH). (b) The corresponding free energies versus different reaction coordinates on 5A-OGNR (red), 5A-GNR (blue), and 7A-GNR (black). ΔG_1 , ΔG_2 , and ΔG_3 denote the reaction free energy changes of reaction (1-3) in the cracked adsorption pathway.

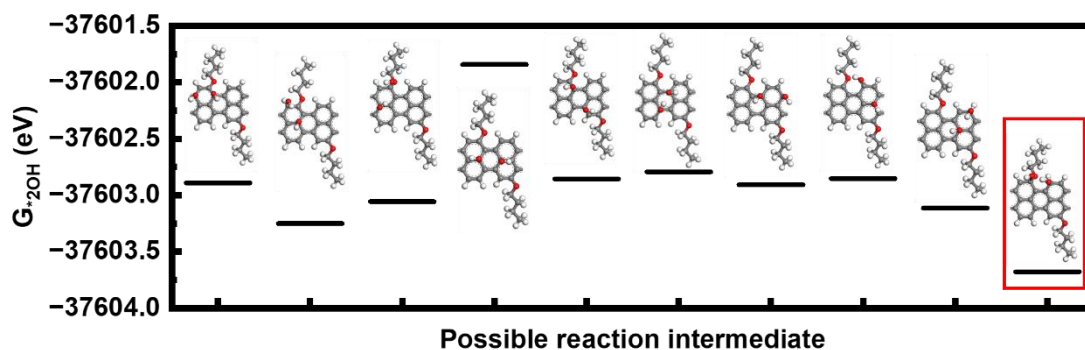


Figure 5.7. Possible reaction intermediates for cracked adsorption of H_2O_2 on 5A-OGNR. The insets show the molecular structures of possible reaction intermediates. The red rectangle denotes the reaction intermediate with the lowest Gibbs free energy.

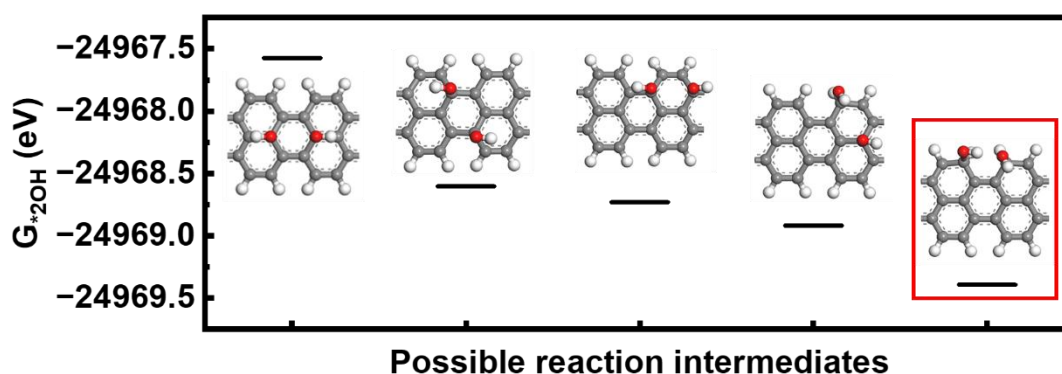


Figure 5.8. Possible reaction intermediates for cracked adsorption of H_2O_2 on 5A-GNR. The insets show the molecular structures of possible reaction intermediates. The red rectangle denotes the reaction intermediate with the lowest Gibbs free energy.

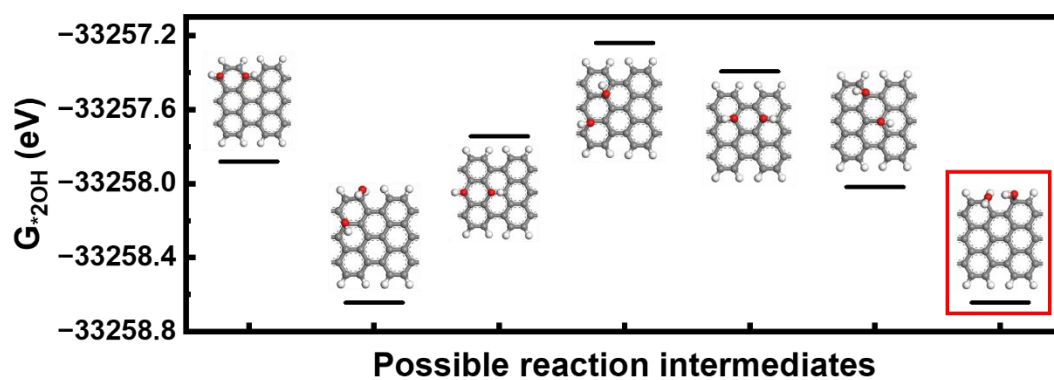


Figure 5.9. Possible reaction intermediates for cracked adsorption of H_2O_2 on 7A-GNR. The insets show the molecular structures of possible reaction intermediates. The red rectangle denotes the reaction intermediate with the lowest Gibbs free energy.

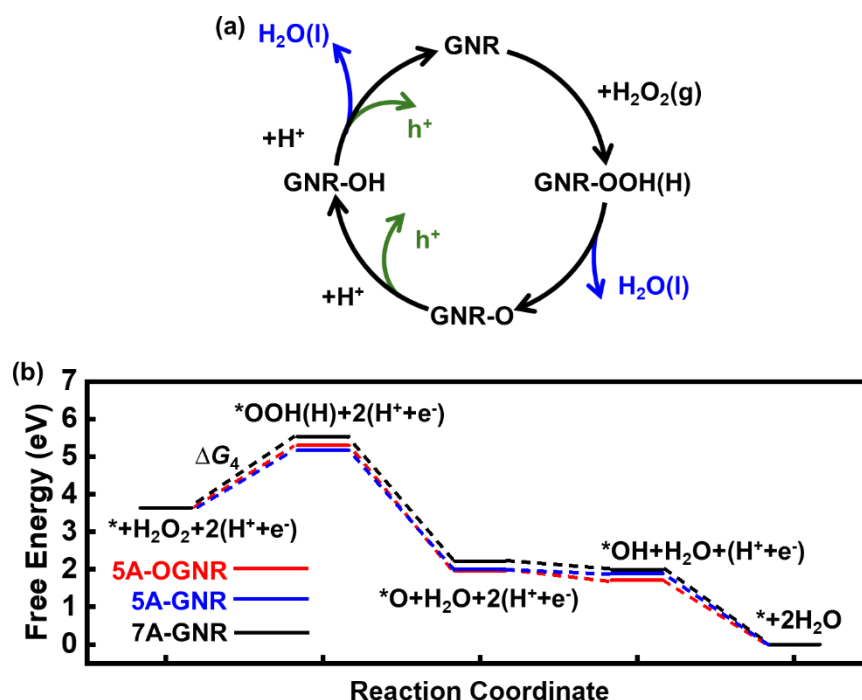


Figure 5.10. (a) Schematic illustration of the ionized adsorption pathway of the H_2O_2 bond-cleaving process on GNRs. The ionized adsorption pathway includes the reaction coordinates of GNR bonding with one -OOH and one H^+ (GNR-OOH(H)), one -O group (GNR-O), and one -OH group (GNR-OH). (b) The corresponding free energies versus different reaction coordinates on 5A-OGNR (red), 5A-GNR (blue), and 7A-GNR (black) along the ionized adsorption pathway. ΔG_4 denotes the reaction free energy change of reaction (4) in the ionized adsorption pathway.

5.3.3 Transition state and rate-determining step study of GNRs

To elucidate why the etching rate of 5A-OGNRs is significantly higher than that of 5A-GNRs, a transition-state analysis was conducted for each step of the H_2O_2 reduction reaction. As shown in Figure 5.11a-c, the activation energies for step (1) in 5A-OGNRs, 5A-GNRs, and 7A-GNRs are 0.08 eV, 0.08 eV, and 0.57 eV, respectively. These results indicate that the H_2O_2 bond-cleaving process can proceed easily on 5A-OGNRs and 5A-GNRs, whereas it is kinetically hindered on 7A-GNRs. The relatively high activation energy of 0.57 eV is considered one of the main factors contributing to the low etching rate ($0.16 \mu\text{m}\cdot\text{h}^{-1}$) observed for 7A-GNR-covered Si. Owing to the combination of a low reaction free energy and a high activation barrier, the H_2O_2 bond-cleaving process on 7A-GNRs is difficult to initiate, resulting in low catalytic performance in Si etching.

Figures 5.11d-f present the activation energies for step (2), which corresponds to the desorption process of the first -OH group. This step is crucial because it reflects both the reversibility of the redox process and the structural stability of the catalyst. The activation energies for 5A-OGNRs, 5A-GNRs, and 7A-GNRs are 0.50 eV, 0.76 eV, and 0.77 eV, respectively, indicating that 5A-OGNRs possess an advantage over the other two types of GNRs. As shown in Figure 5.11g, when we perform calculations about the desorption process of the second -OH in step (3), 5A-OGNRs show no activation energy. We think this advantage in the transition state of H_2O_2 reduction should be related to the electronic structure of the 5A-OGNR. Therefore, we characterize the STM constant-height differential conductance map of 5A-OGNRs (Figure 5.12) at

the HOMO level (-0.2 V). The result shows a bright contrast near the carbon atoms adjacent to the oxygen dopants. These regions correspond to the calculated active sites for the H_2O_2 reduction reaction. The increased local electron density near these oxygen-adjacent carbon atoms facilitates electron transfer from the catalyst to the reactant, thereby significantly reducing the activation energy for bond cleavage^{21,22}. In contrast, 5A-GNRs and 7A-GNRs exhibit higher activation energies of 0.94 eV and 0.84 eV (Figures 5.11h and 5.11i), respectively, showing no advantage in the desorption of the second -OH group. This limitation likely induces irreversible oxidation, leading to partial degradation of 5A-GNRs, as evidenced by the experimentally observed Raman spectra (Figure 5.4c). Consequently, the catalytic performance and the reversibility of 5A-GNRs are inferior to those of 5A-OGNRs.

Furthermore, as shown in Figures 5.13a-c, the transition state calculations for the ionized adsorption pathway of H_2O_2 (Pathway 2) on each GNR surface reveal higher activation energies of 2.23 eV, 2.05 eV, and 2.31 eV for 5A-OGNRs, 5A-GNRs, and 7A-GNRs, respectively. These high barriers indicate that the O-H bond cleavage of H_2O_2 is hard to proceed. Instead, the reaction preferentially follows Pathway 1, which features a downhill free energy profile and lower kinetic barriers, thereby offering a more thermodynamically and kinetically favorable route for H_2O_2 reduction.

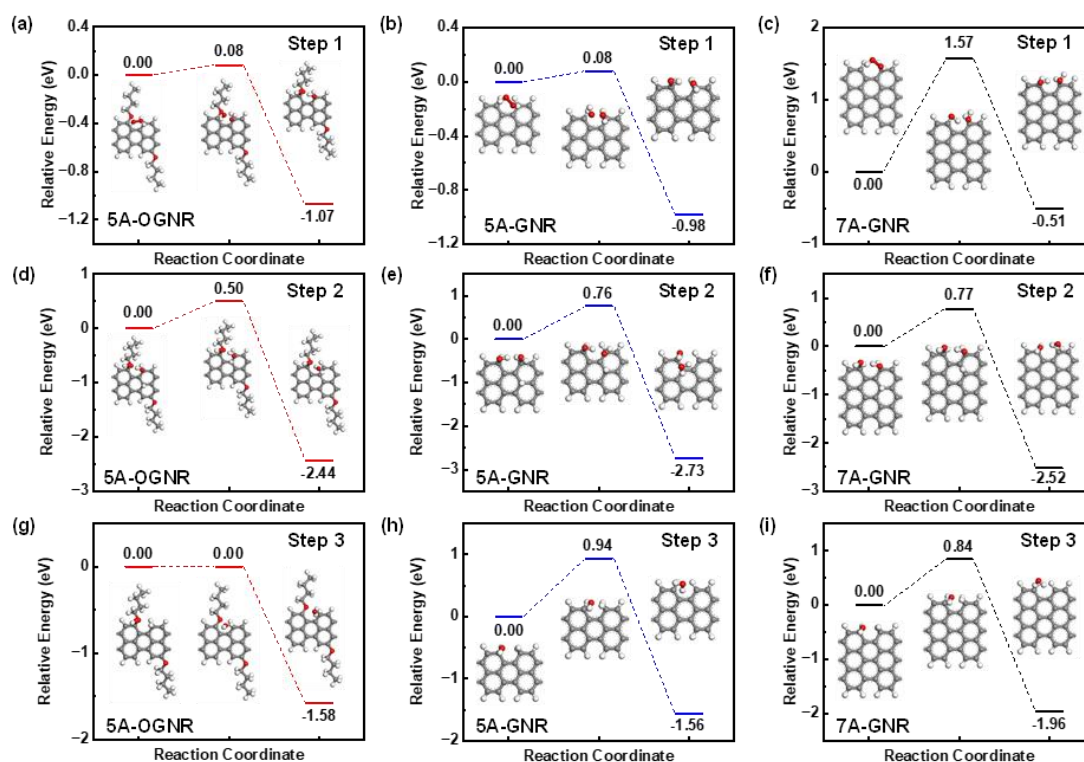


Figure 5.11. Optimized structures of the initial (IS), transition (TS), and final (FS) states of the H_2O_2 reduction reaction elemental steps on 5A-OGNR (red), 5A-GNR (blue), and 7A-GNR (black) and the corresponding activation energies for the reaction. (a-c) $* + \text{H}_2\text{O}_2 \rightarrow * \text{OH} + * \text{OH}$; (d-f) $* \text{OH} + * \text{OH} + * \text{H}^+ \rightarrow * \text{OH} + \text{H}_2\text{O} + \text{h}^+$; (g-i) $* \text{OH} + * \text{H}^+ \rightarrow * + \text{H}_2\text{O} + \text{h}^+$. The insets show the corresponding chemical structures of each reaction coordinate. The values denote the total energy of the reaction coordinates. The reference level of the total energy values is set as that of the initial state.

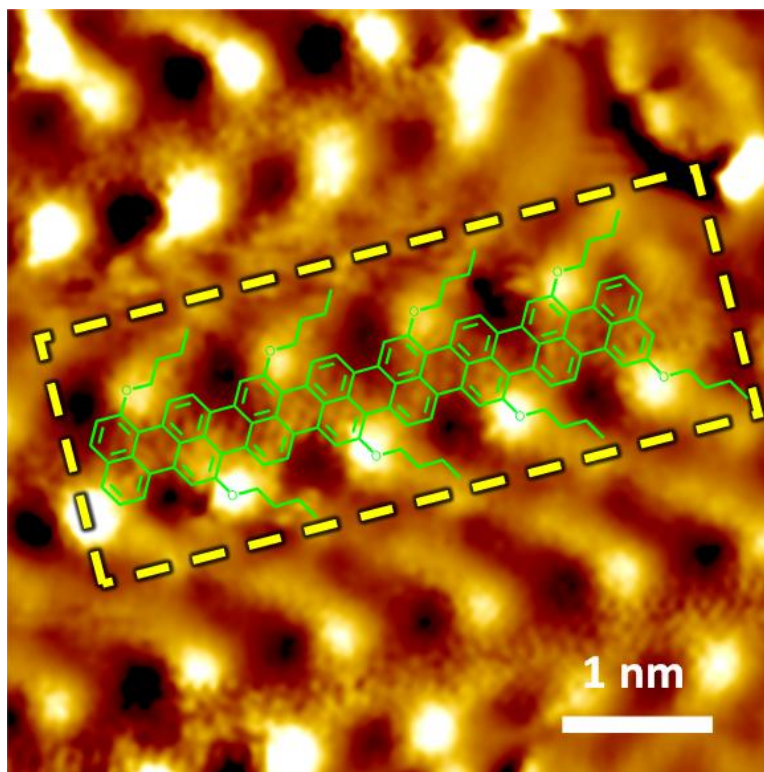


Figure 5.12. Experimental constant-height dI/dV maps of 5A-OGNR at HOMO (Bias voltage = -0.2 V, feedback current = 80 pA). The chemical structure of 5A-OGNR is overlaid with the STM image.

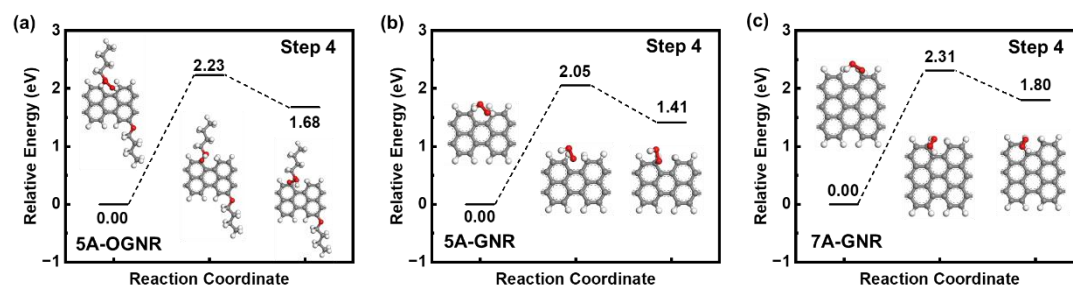


Figure 5.13. Optimized structures of the initial (IS), transition (TS), and final (FS) states of the H₂O₂ ionized adsorption ($* + \text{H}_2\text{O}_2 \rightarrow *\text{OOH} + \text{e}^- + *\text{H}^+$) on (a) 5A-OGNR, (b) 5A-GNR, and (c) 7A-GNR and the corresponding activation energies. The insets show the corresponding chemical structure of each reaction coordinate. The values denote the total energy of the reaction coordinates. The reference level of the total energy values is set as that of the initial state.

5.3.4 Comparison between graphene and GNRs in silicon etching

As shown in Figures 5.14 and 5.15, the reaction free energies and activation energy of the H_2O_2 reduction process on graphene were studied. In the H_2O_2 bond-cleaving process, the rate-determining step, graphene exhibits an uphill reaction free energy. The activation energies of 2.44 eV, 1.03 eV, and 0.93 eV in the transition states of steps (1-3) limit the catalytic performance in the H_2O_2 reduction reaction, resulting in lower catalytic performance in Si etching. It agrees well with the experimental data in Chapter 4, indicating that GNRs with abundant edge structures have advantages in the vapor-phase Si etching process over graphene.

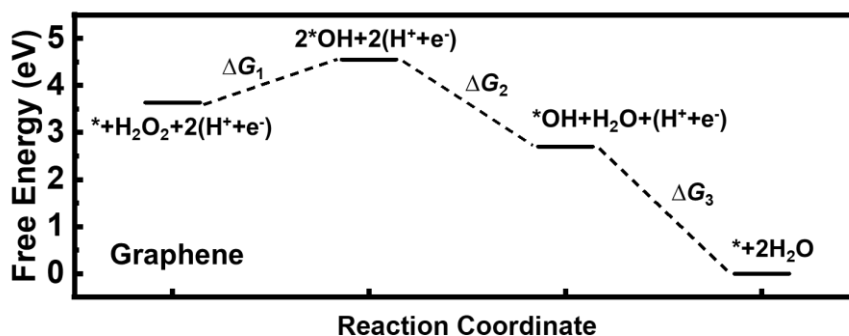


Figure 5.14. Schematic illustration of the cracked adsorption pathway of the H_2O_2 bond-breaking process on graphene and the corresponding free energies versus different reaction coordinates on graphene. ΔG_1 , ΔG_2 , and ΔG_3 denote the reaction free energy changes of reaction (1-3) in the cracked adsorption pathway.

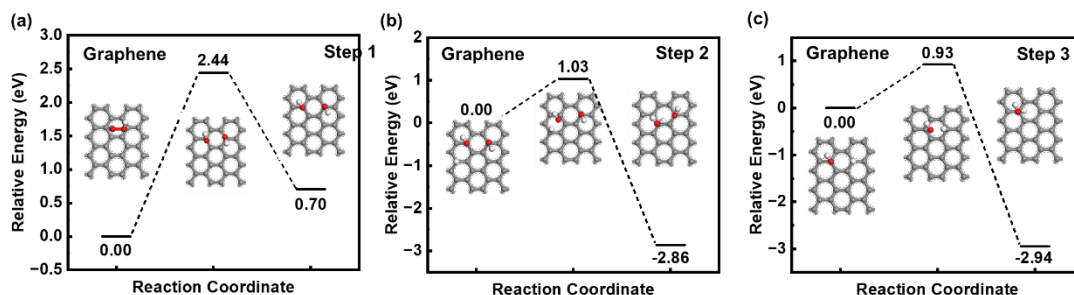


Figure 5.15. Optimized structures of the initial (IS), transition (TS), and final (FS) states of the H_2O_2 reduction reaction elemental steps on graphene and the corresponding activation energies for the reaction. (a) $* + \text{H}_2\text{O}_2 \rightarrow * \text{OH} + * \text{OH}$; (b) $* \text{OH} + * \text{OH} + * \text{H}^+ \rightarrow * \text{OH} + \text{H}_2\text{O} + \text{h}^+$; (c) $* \text{OH} + * \text{H}^+ \rightarrow * + \text{H}_2\text{O} + \text{h}^+$. The insets show the corresponding molecular structure of each reaction coordinate. The values denote the total energy of the reaction coordinates. The reference level of the total energy values is set as that of the initial state.

5.4 Conclusion

In conclusion, the 5A-OGNR demonstrates a significantly higher etching rate of $1.79 \mu\text{m h}^{-1}$ in vapor-phase chemical etching of silicon, surpassing 5A-GNR ($0.72 \mu\text{m h}^{-1}$) and 7A-GNR ($0.16 \mu\text{m h}^{-1}$). DFT calculations reveal that oxygen doping creates active sites on adjacent carbon atoms, enhancing the efficiency of H_2O_2 reduction in 5A-OGNR. The charge density near the active sites increases due to the high electronegativity of the oxygen atom, which improves H_2O_2 adsorption affinity. Moreover, 5A-OGNR exhibits a more energetically favorable rate-determining step in the H_2O_2 bond-cleaving process compared to 5A-GNR and 7A-GNR. Additionally, the activation energy for the desorption of the -OH group in 5A-OGNR is reduced due to the high HOMO energy level near the active sites, resulting in higher catalytic efficiency and reversibility compared to undoped 5A-GNR. Furthermore, the Raman spectra of 5A-OGNRs remain stable after Si etching, confirming their high stability. Our findings suggest that oxygen-doped GNRs, particularly 5A-OGNR, are promising alternatives to traditional metal-based catalysts for Si etching. Their stability, low contamination, and enhanced catalytic properties make them ideal candidates for improving the precision and efficiency of Si etching in industrial applications.

References

1. Huang, Z., Geyer, N., Werner, P., De Boor, J. & Gösele, U. Metal-Assisted Chemical Etching of Silicon: A Review: In memory of Prof. Ulrich Gösele. *Advanced Materials* **23**, 285–308 (2011).
2. Han, H., Huang, Z. & Lee, W. Metal-assisted chemical etching of silicon and nanotechnology applications. *Nano Today* **9**, 271–304 (2014).
3. Surdo, S. & Barillaro, G. Voltage- and Metal-assisted Chemical Etching of Micro and Nano Structures in Silicon: A Comprehensive Review. *Small* **20**, 2400499 (2024).
4. Kolasinski, K. W., Gogola, J. W. & Barclay, W. B. Test of Marcus Theory Predictions for Electroless Etching of Silicon. *J. Phys. Chem. C* **116**, 21472–21481 (2012).
5. Marcus, R. A. Electron Transfer Reactions in Chemistry: Theory and Experiment (Nobel Lecture). *Angew. Chem. Int. Ed. Engl.* **32**, 1111–1121 (1993).
6. Kumar, J. & Ingole, S. Effect of Silicon Conductivity and HF/H₂O₂ Ratio on Morphology of Silicon Nanostructures Obtained via Metal-Assisted Chemical Etching. *Journal of Electronic Materials* **47**, 1583–1588 (2018).

7. Chartier, C., Bastide, S. & Lévy-Clément, C. Metal-assisted chemical etching of silicon in HF–H₂O₂. *Electrochimica Acta* **53**, 5509–5516 (2008).
8. Lai, R. A., Hymel, T. M., Narasimhan, V. K. & Cui, Y. Schottky Barrier Catalysis Mechanism in Metal-Assisted Chemical Etching of Silicon. *ACS Appl. Mater. Interfaces* **8**, 8875–8879 (2016).
9. Delley, B. From molecules to solids with the DMol3 approach. *The Journal of Chemical Physics* **113**, 7756–7764 (2000).
10. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
11. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **27**, 1787–1799 (2006).
12. Ferrari, A. C. & Robertson, J. Interpretation of Raman spectra of disordered and amorphous carbon. *Phys. Rev. B* **61**, 14095–14107 (2000).
13. Inose, T. *et al.* Visualizing Ribbon-to-Ribbon Heterogeneity of Chemically Unzipped Wide Graphene Nanoribbons by Silver Nanowire-Based Tip-Enhanced Raman Scattering Microscopy. *Small* **20**, 2301841 (2024).

14. Wang, L. *et al.* Potential Application of Novel Boron-Doped Graphene Nanoribbon as Oxygen Reduction Reaction Catalyst. *J. Phys. Chem. C* **120**, 17427–17434 (2016).
15. Ritter, K. A. & Lyding, J. W. The influence of edge structure on the electronic properties of graphene quantum dots and nanoribbons. *Nature Mater.* **8**, 235–242 (2009).
16. Zhang, L. & Xia, Z. Mechanisms of Oxygen Reduction Reaction on Nitrogen-Doped Graphene for Fuel Cells. *J. Phys. Chem. C* **115**, 11170–11176 (2011).
17. Wang, S. *et al.* BCN Graphene as Efficient Metal-Free Electrocatalyst for the Oxygen Reduction Reaction. *Angewandte Chemie* **124**, 4285–4288 (2012).
18. Li, Y., Zhong, G., Yu, H., Wang, H. & Peng, F. O_2 and H_2 O_2 transformation steps for the oxygen reduction reaction catalyzed by graphitic nitrogen-doped carbon nanotubes in acidic electrolyte from first principles calculations. *Phys. Chem. Chem. Phys.* **17**, 21950–21959 (2015).
19. Ma, R. *et al.* A review of oxygen reduction mechanisms for metal-free carbon-based electrocatalysts. *npj. Comput. Mater.* **5**, 78 (2019).

20. Guo, D. *et al.* Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts. *Science* **351**, 361–365 (2016).
21. Zhao, L. *et al.* Visualizing Individual Nitrogen Dopants in Monolayer Graphene. *Science* **333**, 999–1003 (2011).
22. Sun, H. *et al.* Atomically imaging single atom catalysts and their behaviors by scanning tunneling microscopy. *EES. Catal.* **1**, 794–809 (2023).

Chapter 6. General Conclusions

In summary, this thesis presents the development, mechanistic understanding, and functional evaluation of electrochemically synthesized edge-functionalized GNRs. Through systematic investigation, we have demonstrated that electrochemical on-surface synthesis provides a versatile and scalable platform for constructing atomically precise GNRs with functionalized edges, opening new pathways for both fundamental studies and technological applications.

In Chapter 3, we established an electrochemical on-surface synthesis method as a novel approach for the controlled growth of edge-functionalized GNRs. The traditional UHV method faces two intrinsic limitations: the thermal instability of functional substituents and the restriction of growth to a single molecular layer. We solved these two problems by developing an on-surface electrochemical synthesis technique that harnesses redox reactions within the EDL at the solid-liquid interface. Within the EDL, typically confined to nanometer-scale thickness, the electric field provides a unique reaction environment capable of activating adsorbed molecules at room temperature. Moreover, because the EDL can continue to form on top of existing GNRs, the reaction can proceed continuously in the vertical direction, enabling layer-by-layer GNR growth and thus scalable fabrication. Mechanistic studies revealed that the reaction proceeds via a heterochiral dicationic polymerization pathway, a mechanism fundamentally distinct from conventional radical polymerization. This work establishes both a practical synthetic method and a conceptual

framework for the synthesis of edge-functionalized GNRs with atomic precision.

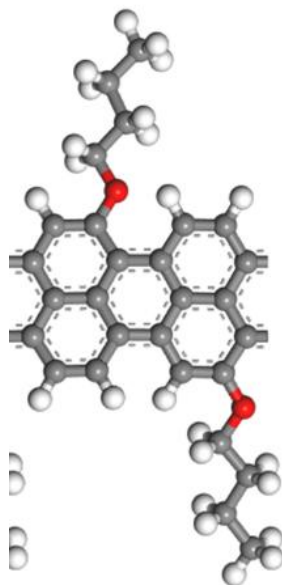
Chapters 4 and 5 focused on evaluating the functional properties of the electrochemically synthesized 5A-OGNRs. In vapor-phase silicon etching, 5A-OGNR demonstrated outstanding catalytic performance, surpassing conventional metal catalysts, such as gold, as well as other carbon-based materials, including graphene and carbon nanotubes. Oxygen doping at the edges not only enhances catalytic activity by creating highly active sites on adjacent carbon atoms to improve the H_2O_2 adsorption, but also facilitates efficient electron transfer from H_2O_2 to Si, accelerating oxidation and subsequent removal of Si. Density functional theory calculations revealed that 5A-OGNR exhibits a more favorable rate-determining step for H_2O_2 bond cleavage and reduced activation energy for -OH desorption, resulting in superior catalytic efficiency and reversibility compared to undoped GNRs. The high structural stability of 5A-OGNR during Si etching was confirmed by Raman spectroscopy, demonstrating its suitability as a metal-free catalyst for precision silicon processing. These findings highlight the potential of oxygen-doped GNRs as sustainable alternatives to traditional metal-based catalysts in industrial applications. Beyond catalysis, 5A-OGNRs exhibit remarkable photoconductive properties with FeCl_3 doping, indicating their multifunctional potential in optoelectronic applications. The combined tunability of electronic structure and chemical functionality underscores the versatility of electrochemically synthesized GNRs, making them promising candidates for nanoscale electronics, sensors, energy conversion devices, and other advanced technologies. The electrochemical synthesis platform provides a generalizable

approach for fabricating a variety of edge-functionalized GNRs with tailored properties, enabling the systematic exploration of structure-function relationships in carbon nanomaterials.

In conclusion, this thesis demonstrates that electrochemical on-surface synthesis is a powerful and flexible strategy for constructing functional, edge-engineered GNRs with atomic precision. The integration of mechanistic insight, precise structural control, and functional evaluation illustrates the unique advantages of this approach over conventional methods. Electrochemically synthesized 5A-OGNRs combine high structural fidelity, exceptional catalytic performance, and multifunctional electronic properties, offering a new class of metal-free nanomaterials with broad technological potential. Looking forward, the methodologies and findings presented herein provide a foundation for designing advanced carbon-based nanomaterials, extending the scope of electrochemical synthesis to other functional precursors, and enabling scalable production of next-generation catalysts, electronic devices, and energy-conversion systems.

Appendix

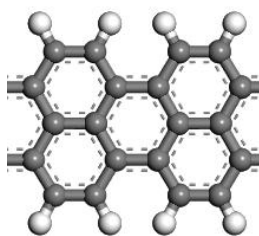
The Cartesian coordinates of GNRs, adsorption configurations, and the reaction coordinates. All GNRs were built along the x-direction with a periodicity of 8.52 Å. The vacuum region is set as 30 Å along the y- and z- directions.



Cartesian coordinates of 5A-OGNR

		X	Y	Z			X	Y	Z
1	C	-3.66926	15.95942	44.87349	28	H	0.830657	11.31577	45.06674
2	C	-2.96628	14.72089	44.73567	29	C	0.585332	15.92526	44.72487
3	C	-3.67563	13.49878	44.60856	30	C	1.293651	14.6959	44.72857
4	C	-2.91337	17.12097	45.1928	31	C	2.719999	14.73128	44.74045
5	C	-2.97546	12.30749	44.31034	32	C	3.428085	15.97456	44.72518
6	C	-1.60095	12.27552	44.2614	33	C	2.662197	17.17485	44.52079
7	C	-0.83171	13.44926	44.57697	34	C	1.286766	17.14127	44.55018
8	O	-5.1625	18.32704	44.25041	35	C	3.431128	13.49839	44.76021

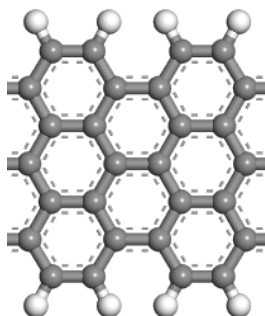
9	O	-0.91545	11.15018	43.87615	36	C	2.712735	12.28889	44.93113
10	C	-1.67275	9.986363	43.50064	37	C	1.345366	12.25759	44.91675
11	C	-0.69195	8.903084	43.08272	38	C	0.590776	13.44949	44.72655
12	C	-1.4032	7.615307	42.65504	39	H	-3.42576	18.03967	45.45525
13	C	-0.4276	6.520394	42.22035	40	H	-0.99414	17.98905	45.46363
14	H	-3.54805	11.41887	44.06446	41	H	0.717487	18.05221	44.38833
15	H	-2.35257	10.24092	42.66871	42	C	2.621259	19.50864	13.88717
16	H	-2.28657	9.650059	44.35434	43	C	3.636478	20.60356	13.60325
17	H	-0.00831	8.691689	43.921	44	C	2.988042	21.91	13.13681
18	H	-0.07032	9.283007	42.25642	45	C	4.01876	23.00806	12.87212
19	H	-2.09944	7.838941	41.82917	46	H	1.947388	19.80311	14.71091
20	H	-2.02519	7.246427	43.48799	47	H	2.003956	19.29654	12.99604
21	H	0.187659	6.852345	41.3709	48	H	4.343754	20.24159	12.83901
22	H	-0.95609	5.605922	41.9149	49	H	4.228835	20.78584	14.51595
23	H	0.257017	6.25242	43.03991	50	H	2.263322	22.25559	13.89465
24	C	-1.53985	14.68466	44.72909	51	H	2.403192	21.72262	12.2194
25	C	-0.82772	15.90936	44.87776	52	H	4.730938	22.69984	12.09105
26	C	-1.54543	17.0897	45.18998	53	H	4.60105	23.23098	13.78003
27	H	3.26164	11.36288	45.10509	54	H	3.542001	23.94179	12.54202



Cartesian coordinates of 5A-GNR

		X	Y	Z			X	Y	Z
1	C	0.440842	-11.8542	-14.0051	15	C	7.538258	-11.8542	-14.0051
2	C	1.146298	-13.0924	-14.0051	16	C	6.801333	-10.6419	-14.0051
3	C	2.572814	-13.0927	-14.0051	17	C	5.437131	-10.6421	-14.0051
4	C	3.278346	-11.8546	-14.0051	18	C	5.437838	-15.5433	-14.0051

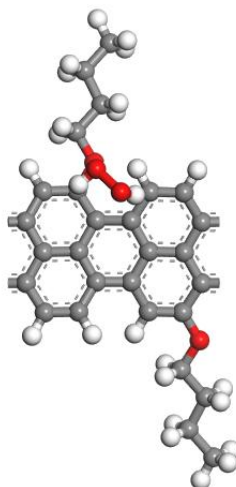
5	C	2.541938	-10.6421	-14.0051	19	C	6.801999	-15.5431	-14.0051
6	C	1.17774	-10.6419	-14.0051	20	C	7.538358	-14.3305	-14.0051
7	C	3.278277	-14.331	-14.0051	21	H	3.058533	-9.68539	-14.0051
8	C	2.541258	-15.5432	-14.0051	22	H	0.661527	-9.68501	-14.0051
9	C	1.177045	-15.543	-14.0051	23	H	3.057282	-16.5002	-14.0051
10	C	0.440705	-14.3305	-14.0051	24	H	0.660551	-16.4998	-14.0051
11	C	4.700753	-11.8546	-14.0051	25	H	7.317449	-9.68496	-14.0051
12	C	5.406261	-13.0927	-14.0051	26	H	4.92049	-9.6854	-14.0051
13	C	4.700831	-14.3309	-14.0051	27	H	4.921558	-16.5001	-14.0051
14	C	6.832822	-13.0924	-14.0051	28	H	7.318758	-16.4997	-14.0051



Cartesian coordinates of 7A-GNR

		X	Y	Z			X	Y	Z
1	C	0.500226	-11.6075	-14.1764	19	C	4.760175	-16.5513	-14.1764
2	C	1.201806	-12.8397	-14.1764	20	C	6.887573	-15.3194	-14.1764
3	C	2.627504	-12.8396	-14.1764	21	C	7.598274	-14.0796	-14.1764
4	C	3.329099	-11.6074	-14.1764	22	C	6.887538	-12.8397	-14.1764
5	C	2.597691	-10.3965	-14.1764	23	C	7.589125	-11.6075	-14.1764
6	C	1.231488	-10.3965	-14.1764	24	C	6.857843	-10.3965	-14.1764
7	C	3.338262	-14.0794	-14.1764	25	C	5.49164	-10.3965	-14.1764
8	C	2.627483	-15.3193	-14.1764	26	C	5.491231	-17.7624	-14.1764
9	C	1.201786	-15.3194	-14.1764	27	C	6.85738	-17.7625	-14.1764
10	C	0.491057	-14.0796	-14.1764	28	C	7.589062	-16.5516	-14.1764
11	C	0.500244	-16.5516	-14.1764	29	H	3.114196	-9.43986	-14.1764
12	C	1.231928	-17.7625	-14.1764	30	H	0.714715	-9.44004	-14.1764

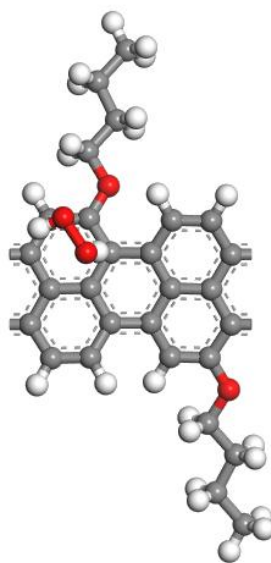
13	C	2.598143	-17.7624	-14.1764	31	H	0.7157	-18.7192	-14.1764
14	C	3.329185	-16.5513	-14.1764	32	H	3.114911	-18.7189	-14.1764
15	C	4.760249	-11.6074	-14.1764	33	H	7.374463	-9.43996	-14.1764
16	C	5.461833	-12.8396	-14.1764	34	H	4.974979	-9.43993	-14.1764
17	C	4.751074	-14.0794	-14.1764	35	H	4.974241	-18.7188	-14.1764
18	C	5.461823	-15.3193	-14.1764	36	H	7.374004	-18.7191	-14.1764



H₂O₂ adsorption on 5A-OGNR, configuration 1 in Figure 5.5

		X	Y	Z			X	Y	Z
1	C	-3.69137	15.96245	44.6846	30	C	1.272116	14.69746	44.58204
2	C	-2.98691	14.72238	44.57114	31	C	2.698978	14.73189	44.57003
3	C	-3.69585	13.4996	44.4466	32	C	3.40642	15.97476	44.53243
4	C	-2.93935	17.1308	45.00016	33	C	2.639613	17.17672	44.33069
5	C	-2.99489	12.30534	44.16949	34	C	1.264241	17.14564	44.40915
6	C	-1.61984	12.26886	44.14465	35	C	3.410788	13.49983	44.59691
7	C	-0.85267	13.44762	44.45024	36	C	2.69493	12.29272	44.78909
8	O	-5.1908	18.31141	44.01118	37	C	1.327751	12.26148	44.79138
9	O	-0.93383	11.13514	43.79733	38	C	0.570261	13.4507	44.5968
10	C	-1.68428	9.957607	43.44379	39	H	-3.45848	18.05897	45.21731
11	C	-0.69078	8.845259	43.15354	40	H	-1.02392	17.99868	45.29828
12	C	-1.37781	7.550906	42.70862	41	H	0.694265	18.05564	44.24573
13	C	-0.38107	6.422289	42.44207	42	C	2.599863	19.54579	13.86229

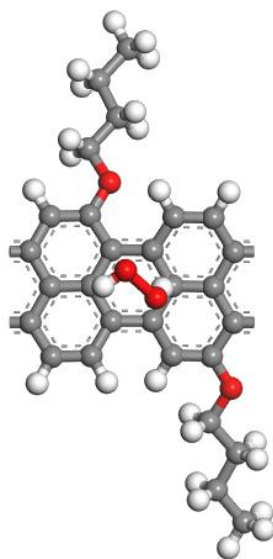
14	H	-3.56474	11.41469	43.92536	43	C	3.61117	20.64764	13.59458
15	H	-2.3103	10.17224	42.55992	44	C	2.946206	22.01067	13.38432
16	H	-2.34971	9.675669	44.27831	45	C	3.961481	23.12524	13.12743
17	H	-0.09124	8.656739	44.05996	46	H	2.032495	19.7488	14.7877
18	H	0.012516	9.186193	42.37641	47	H	1.885718	19.45363	13.02544
19	H	-1.96993	7.743846	41.79724	48	H	4.206796	20.3785	12.70726
20	H	-2.10009	7.231484	43.4798	49	H	4.313048	20.70148	14.44255
21	H	0.32452	6.699036	41.64362	50	H	2.337518	22.26282	14.26924
22	H	-0.88942	5.497697	42.13388	51	H	2.242722	21.94855	12.5365
23	H	0.21051	6.195956	43.34288	52	H	4.565349	22.91414	12.23113
24	C	-1.56043	14.68478	44.58591	53	H	4.653285	23.23404	13.97623
25	C	-0.84877	15.91034	44.73801	54	H	3.463587	24.09341	12.97465
26	C	-1.56963	17.0943	45.02985	55	O	-5.11496	18.04812	17.51845
27	H	3.24511	11.36882	44.96865	56	O	-4.12192	17.11278	18.07581
28	H	0.816106	11.32096	44.95518	57	H	-5.81974	17.41666	17.26512
29	C	0.5652	15.92798	44.58966	58	H	-3.53704	16.99763	17.29295



H₂O₂ adsorption on 5A-OGNR, configuration 2 in Figure 5.5

		X	Y	Z			X	Y	Z
1	C	-3.67586	15.94971	44.71818	30	C	1.284191	14.68501	44.56462

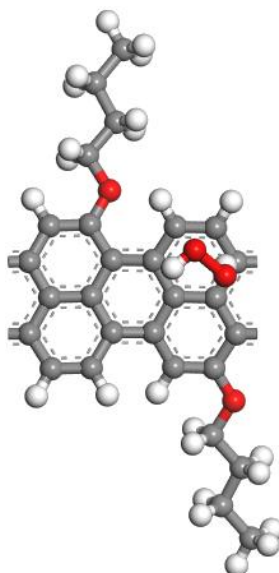
2	C	-2.97403	14.71117	44.57391	31	C	2.710755	14.7198	44.57217
3	C	-3.68363	13.48986	44.43673	32	C	3.419174	15.96601	44.56616
4	C	-2.92188	17.1096	45.04652	33	C	2.653504	17.16929	44.36463
5	C	-2.985	12.29975	44.13661	34	C	1.277488	17.13343	44.40132
6	C	-1.60983	12.2651	44.09644	35	C	3.422658	13.4877	44.58829
7	C	-0.84081	13.43922	44.41233	36	C	2.705004	12.27829	44.75803
8	O	-5.17114	18.31504	44.09456	37	C	1.337748	12.24724	44.74631
9	O	-0.92505	11.13901	43.72293	38	C	0.581969	13.43863	44.56021
10	C	-1.67549	9.952048	43.40232	39	H	-3.43519	18.02697	45.31107
11	C	-0.68333	8.845753	43.08584	40	H	-1.00381	17.97884	45.31738
12	C	-1.37757	7.514883	42.78158	41	H	0.708882	18.04569	44.24739
13	C	-0.38699	6.390129	42.47752	42	C	2.614633	19.53578	13.87143
14	H	-3.55668	11.41309	43.88261	43	C	3.62819	20.63211	13.59339
15	H	-2.33319	10.15281	42.53873	44	C	2.969659	21.99103	13.33792
16	H	-2.30903	9.671859	44.26189	45	C	3.993392	23.0988	13.08904
17	H	-0.00331	8.720168	43.94432	46	H	2.011625	19.7708	14.76599
18	H	-0.05892	9.153671	42.23207	47	H	1.930839	19.40389	13.01566
19	H	-2.06482	7.64318	41.92827	48	H	4.240693	20.33996	12.72557
20	H	-2.00843	7.229036	43.64052	49	H	4.31619	20.70945	14.45112
21	H	0.220974	6.624296	41.5903	50	H	2.335848	22.2588	14.20021
22	H	-0.90606	5.439567	42.2873	51	H	2.28967	21.914	12.47269
23	H	0.302043	6.231537	43.32069	52	H	4.607959	22.8798	12.20219
24	C	-1.5479	14.67438	44.56844	53	H	4.674655	23.20849	13.94622
25	C	-0.83633	15.89882	44.72552	54	H	3.503855	24.06948	12.92558
26	C	-1.55343	17.0777	45.04512	55	O	-6.76803	17.19589	17.9128
27	H	3.253585	11.35227	44.931	56	O	-5.95675	15.96618	17.95153
28	H	0.824381	11.30548	44.89788	57	H	-7.63237	16.81686	17.65187
29	C	0.577619	15.91606	44.56966	58	H	-5.54876	16.00007	17.05892



H₂O₂ adsorption on 5A-OGNR, configuration 3 in Figure 5.5

		X	Y	Z			X	Y	Z
1	C	-3.66417	15.9655	44.87693	30	C	1.298912	14.70125	44.72889
2	C	-2.9601	14.72557	44.73545	31	C	2.72591	14.73618	44.73905
3	C	-3.6699	13.5023	44.60249	32	C	3.433373	15.9801	44.7244
4	C	-2.9086	17.12553	45.20431	33	C	2.66903	17.18163	44.52118
5	C	-2.96942	12.31301	44.304	34	C	1.293118	17.14766	44.55488
6	C	-1.59404	12.27971	44.25953	35	C	3.436537	13.50212	44.75701
7	C	-0.82531	13.45366	44.57701	36	C	2.718639	12.2929	44.93086
8	O	-5.15519	18.33002	44.2503	37	C	1.351135	12.26262	44.91853
9	O	-0.91	11.15464	43.87944	38	C	0.596965	13.45446	44.72741
10	C	-1.67041	9.990195	43.50566	39	H	-3.4217	18.04087	45.47577
11	C	-0.69708	8.900931	43.08687	40	H	-0.98974	17.99044	45.48263
12	C	-1.4238	7.618713	42.6687	41	H	0.724427	18.0593	44.39545
13	C	-0.46381	6.503596	42.25072	42	C	2.630344	19.50543	13.85826
14	H	-3.54143	11.42374	44.06039	43	C	3.644647	20.59225	13.54204
15	H	-2.34975	10.24658	42.67417	44	C	2.989736	21.89006	13.06067
16	H	-2.2836	9.658261	44.3611	45	C	4.01483	22.98676	12.76902
17	H	-0.01087	8.686734	43.9223	46	H	1.962125	19.82287	14.67752
18	H	-0.07769	9.273161	42.2555	47	H	2.008292	19.27024	12.97669
19	H	-2.11345	7.843117	41.83753	48	H	4.343441	20.2168	12.77654

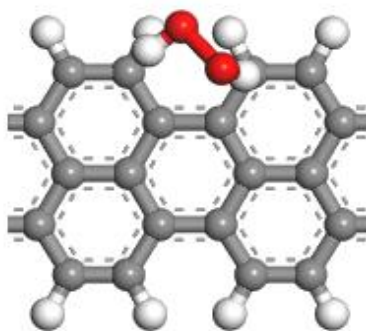
20	H	-2.05489	7.26846	43.5027	49	H	4.246946	20.79025	14.44455
21	H	0.156276	6.813831	41.39657	50	H	2.272735	22.2459	13.8209
22	H	-1.0074	5.594115	41.95751	51	H	2.395144	21.68759	12.15297
23	H	0.215701	6.236566	43.07462	52	H	4.722081	22.66902	11.98741
24	C	-1.53222	14.68943	44.73017	53	H	4.603136	23.22709	13.66817
25	C	-0.82181	15.91496	44.88131	54	H	3.531719	23.91304	12.42743
26	C	-1.54024	17.09338	45.20074	55	O	-4.59251	15.26152	18.52112
27	H	3.267285	11.36756	45.10723	56	O	-3.53467	14.30761	18.14238
28	H	0.836342	11.32157	45.07184	57	H	-5.38325	14.7123	18.34563
29	C	0.591983	15.93185	44.72762	58	H	-3.31812	14.64174	17.24515



H₂O₂ adsorption on 5A-OGNR, configuration 4 in Figure 5.5

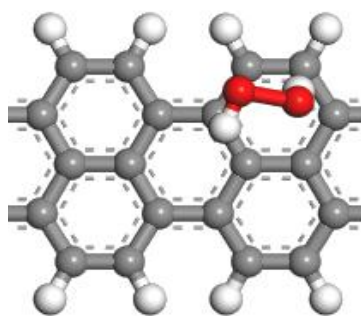
		X	Y	Z			X	Y	Z
1	C	-3.57179	15.83023	44.72969	30	C	1.392162	14.56753	44.57175
2	C	-2.86851	14.5938	44.57009	31	C	2.818449	14.60516	44.57422
3	C	-3.5772	13.37384	44.41963	32	C	3.525428	15.85036	44.58226
4	C	-2.8175	16.98518	45.07463	33	C	2.757898	17.05663	44.42168
5	C	-2.8775	12.18721	44.10766	34	C	1.382425	17.01688	44.46049
6	C	-1.50219	12.15055	44.07802	35	C	3.529543	13.37207	44.57134
7	C	-0.73348	13.32136	44.40587	36	C	2.813195	12.16068	44.73324

8	O	-5.07743	18.22149	44.19366	37	C	1.44582	12.12841	44.72983
9	O	-0.81583	11.0258	43.70422	38	C	0.689528	13.32105	44.55529
10	C	-1.56306	9.847839	43.34548	39	H	-3.32894	17.89816	45.3552
11	C	-0.56302	8.741949	43.05386	40	H	-0.90144	17.84758	45.37675
12	C	-1.23696	7.444277	42.599	41	H	0.811392	17.93072	44.33179
13	C	-0.22738	6.326933	42.33259	42	C	2.684652	19.43078	13.99412
14	H	-3.44843	11.30395	43.84058	43	C	3.662575	20.56356	13.73482
15	H	-2.186	10.06366	42.45933	44	C	2.945862	21.90047	13.51753
16	H	-2.23091	9.562016	44.17649	45	C	3.912744	23.05416	13.24969
17	H	0.035078	8.552776	43.96124	46	H	2.073243	19.63719	14.89031
18	H	0.141313	9.092065	42.28155	47	H	2.004858	19.29941	13.13441
19	H	-1.82547	7.636208	41.68497	48	H	4.275753	20.31596	12.85328
20	H	-1.96044	7.114796	43.36484	49	H	4.355008	20.64605	14.58871
21	H	0.482171	6.617096	41.54247	50	H	2.329253	22.13288	14.40281
22	H	-0.72406	5.399795	42.01337	51	H	2.243066	21.80504	12.67227
23	H	0.358521	6.099556	43.23684	52	H	4.507578	22.87059	12.34107
24	C	-1.44207	14.55462	44.56906	53	H	4.61537	23.18576	14.08609
25	C	-0.72932	15.7769	44.7456	54	H	3.375257	24.0034	13.10917
26	C	-1.44814	16.95291	45.08023	55	O	-2.1561	16.18242	18.66753
27	H	3.36359	11.23396	44.89691	56	O	-1.11745	15.31179	18.08806
28	H	0.933749	11.18539	44.87794	57	H	-2.92148	15.57436	18.63136
29	C	0.685277	15.79661	44.59749	58	H	-1.103	15.65491	17.16683



H₂O₂ adsorption on 5A-GNR, configuration 1 in Figure 5.5

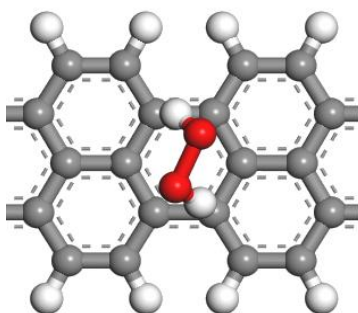
		X	Y	Z			X	Y	Z
1	C	0.424004	-11.8719	-14.0233	17	C	5.418716	-10.6596	-13.9313
2	C	1.129433	-13.1103	-14.0329	18	C	5.42057	-15.5593	-14.143
3	C	2.555638	-13.1109	-14.0404	19	C	6.785415	-15.559	-14.1394
4	C	3.260997	-11.8727	-14.044	20	C	7.521385	-14.3483	-14.0645
5	C	2.525348	-10.6583	-14.0776	21	H	3.044414	-9.70453	-14.1323
6	C	1.159366	-10.6586	-14.0614	22	H	0.642244	-9.70275	-14.1015
7	C	3.261214	-14.349	-14.0438	23	H	3.042218	-16.5168	-13.9712
8	C	2.525151	-15.561	-14.0074	24	H	0.642367	-16.5157	-13.9514
9	C	1.160109	-15.5607	-13.9984	25	H	7.302367	-9.70816	-13.833
10	C	0.423978	-14.3484	-14.0314	26	H	4.899921	-9.70676	-13.8547
11	C	4.682889	-11.8733	-14.013	27	H	4.903092	-16.5133	-14.2116
12	C	5.389319	-13.111	-14.0412	28	H	7.303401	-16.5127	-14.2088
13	C	4.683898	-14.3487	-14.0739	29	O	-3.79597	-10.5771	-10.7065
14	C	6.815904	-13.1106	-14.0332	30	O	-4.74454	-9.56641	-11.2081
15	C	7.521989	-11.8731	-13.9914	31	H	-3.27782	-10.7404	-11.5255
16	C	6.785659	-10.6619	-13.9135	32	H	-5.52289	-10.1357	-11.3822



H₂O₂ adsorption on 5A-GNR, configuration 2 in Figure 5.5

		X	Y	Z			X	Y	Z
1	C	0.483887	-11.8896	-14.1339	17	C	5.475995	-10.6828	-13.9157
2	C	1.188391	-13.1282	-14.1047	18	C	5.477781	-15.5744	-14.2619
3	C	2.614585	-13.1279	-14.1002	19	C	6.8447	-15.5743	-14.2646
4	C	3.319791	-11.8894	-14.1227	20	C	7.58042	-14.3666	-14.1407
5	C	2.585749	-10.6803	-14.2416	21	H	3.109753	-9.73396	-14.3596

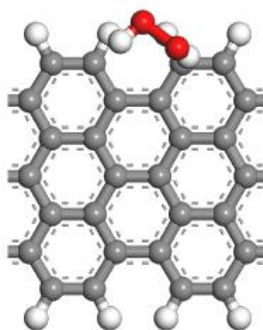
6	C	1.218946	-10.6806	-14.248	22	H	0.695803	-9.73426	-14.3715
7	C	3.320123	-14.3662	-14.071	23	H	3.107868	-16.5207	-13.8286
8	C	2.5845	-15.5747	-13.9535	24	H	0.693572	-16.5203	-13.8323
9	C	1.217625	-15.5746	-13.9561	25	H	7.369485	-9.73614	-13.7944
10	C	0.482678	-14.3661	-14.0769	26	H	4.952234	-9.74102	-13.7679
11	C	4.741685	-11.8909	-14.0527	27	H	4.953803	-16.5192	-14.3928
12	C	5.448299	-13.1284	-14.0967	28	H	7.367956	-16.5193	-14.3966
13	C	4.742627	-14.3666	-14.1347	29	O	-1.83277	-11.5596	-10.6731
14	C	6.875048	-13.1288	-14.1019	30	O	-3.25091	-11.3015	-10.3739
15	C	7.581863	-11.8909	-14.0657	31	H	-1.81103	-11.2944	-11.6192
16	C	6.845783	-10.6815	-13.9241	32	H	-3.59963	-12.2148	-10.4149



H₂O₂ adsorption on 5A-GNR, configuration 3 in Figure 5.5

		X	Y	Z			X	Y	Z
1	C	0.438513	-11.8613	-14.0483	17	C	5.435735	-10.6489	-14.1525
2	C	1.14397	-13.0994	-14.0666	18	C	5.43556	-15.5503	-13.9897
3	C	2.569766	-13.0997	-14.072	19	C	6.800626	-15.549	-13.9854
4	C	3.276282	-11.8612	-14.058	20	C	7.536627	-14.3371	-14.0439
5	C	2.539659	-10.6487	-13.9931	21	H	3.058489	-9.69443	-13.9365
6	C	1.174419	-10.6494	-13.99	22	H	0.655743	-9.69589	-13.9248
7	C	3.274662	-14.3383	-14.0912	23	H	3.057122	-16.5049	-14.1914
8	C	2.539178	-15.5503	-14.137	24	H	0.65609	-16.5042	-14.1764
9	C	1.174469	-15.5496	-14.1286	25	H	7.319461	-9.6959	-14.2097
10	C	0.43895	-14.3377	-14.0765	26	H	4.917351	-9.6953	-14.2221
11	C	4.699695	-11.8604	-14.0936	27	H	4.917092	-16.5047	-13.9338

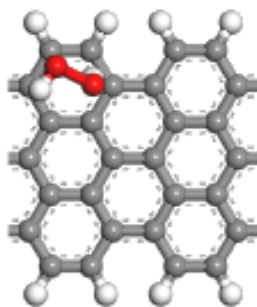
12	C	5.405179	-13.0988	-14.0705	28	H	7.319009	-16.5026	-13.921
13	C	4.698441	-14.3378	-14.0549	29	O	-4.74836	-13.7064	-10.7287
14	C	6.831238	-13.0991	-14.0653	30	O	-4.14594	-12.3672	-10.6021
15	C	7.53627	-11.8609	-14.0818	31	H	-4.1399	-14.1006	-11.3883
16	C	6.800471	-10.6496	-14.1468	32	H	-4.72609	-11.8659	-11.2113



H₂O₂ adsorption on 7A-GNR, configuration 1 in Figure 5.5

		X	Y	Z			X	Y	Z
1	C	0.47328	-11.6107	-14.0274	21	C	7.57052	-14.0823	-14.0979
2	C	1.173954	-12.8427	-14.0644	22	C	6.860037	-12.8426	-14.0663
3	C	2.599595	-12.8428	-14.0677	23	C	7.562274	-11.6115	-14.0298
4	C	3.300562	-11.611	-14.0359	24	C	6.830883	-10.3992	-14.0043
5	C	2.570923	-10.3984	-13.9957	25	C	5.461991	-10.3981	-14.0161
6	C	1.204085	-10.3993	-13.9918	26	C	5.463751	-17.764	-14.1916
7	C	3.310534	-14.0821	-14.101	27	C	6.829992	-17.7639	-14.1914
8	C	2.599616	-15.3214	-14.1319	28	C	7.561123	-16.553	-14.1618
9	C	1.174055	-15.3213	-14.1309	29	H	3.088321	-9.44337	-13.9587
10	C	0.463151	-14.082	-14.0978	30	H	0.687932	-9.44304	-13.9589
11	C	0.472431	-16.5528	-14.162	31	H	0.687029	-18.7198	-14.2153
12	C	1.20367	-17.7637	-14.1915	32	H	3.086435	-18.7199	-14.2148
13	C	2.569893	-17.7637	-14.1915	33	H	7.346484	-9.44219	-13.9845
14	C	3.301222	-16.5529	-14.163	34	H	4.944999	-9.44221	-13.9991
15	C	4.73146	-11.612	-14.042	35	H	4.947288	-18.7203	-14.2152
16	C	5.433812	-12.8429	-14.0702	36	H	7.346593	-18.7201	-14.2148
17	C	4.723156	-14.0826	-14.1007	37	O	-4.3358	20.94217	18.79393

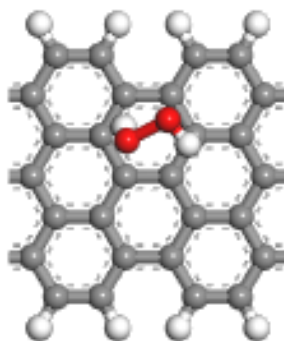
18	C	5.43407	-15.3217	-14.1316	38	O	-3.20881	20.10187	19.23951
19	C	4.732541	-16.5532	-14.1629	39	H	3.443934	20.31729	18.93421
20	C	6.859589	-15.3215	-14.1308	40	H	5.665024	19.8237	18.36491



H₂O₂ adsorption on 7A-GNR, configuration 2 in Figure 5.5

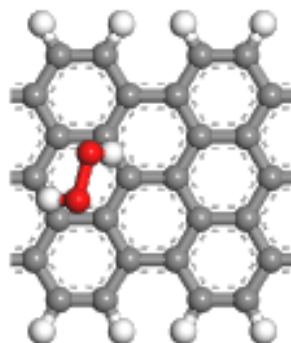
		X	Y	Z			X	Y	Z
1	C	0.504709	-11.6227	-14.0962	21	C	7.603386	-14.0936	-14.1604
2	C	1.206839	-12.8548	-14.1351	22	C	6.892876	-12.8538	-14.1591
3	C	2.632923	-12.8556	-14.1371	23	C	7.594475	-11.621	-14.1537
4	C	3.335842	-11.6228	-14.101	24	C	6.86445	-10.4108	-14.2315
5	C	2.603984	-10.4148	-13.9665	25	C	5.496726	-10.4109	-14.2348
6	C	1.234392	-10.4161	-13.9633	26	C	5.496707	-17.7762	-14.1874
7	C	3.343855	-14.0946	-14.1652	27	C	6.862935	-17.7762	-14.1873
8	C	2.632686	-15.3338	-14.1775	28	C	7.594324	-16.5653	-14.181
9	C	1.207295	-15.3337	-14.1761	29	H	3.125287	-9.46904	-13.8341
10	C	0.496244	-14.0943	-14.1626	30	H	0.712701	-9.4721	-13.824
11	C	0.505515	-16.5656	-14.1848	31	H	0.720333	-18.7331	-14.2044
12	C	1.236695	-17.7766	-14.1968	32	H	3.119507	-18.7331	-14.2053
13	C	2.602948	-17.7767	-14.1968	33	H	7.386038	-9.45925	-14.3101
14	C	3.334277	-16.5657	-14.186	34	H	4.975051	-9.4594	-14.3154
15	C	4.766603	-11.621	-14.1586	35	H	4.980066	-18.7326	-14.1932
16	C	5.467491	-12.854	-14.1606	36	H	7.379485	-18.7326	-14.1921
17	C	4.756615	-14.0937	-14.1628	37	O	-7.10501	19.03819	19.73851
18	C	5.46719	-15.3333	-14.1717	38	O	-5.83911	18.41434	19.31641
19	C	4.76539	-16.5653	-14.1822	39	H	0.859129	18.23878	19.83259

20	C	6.892581	-15.3333	-14.1704	40	H	2.660791	18.62881	18.3591
----	---	----------	----------	----------	----	---	----------	----------	---------



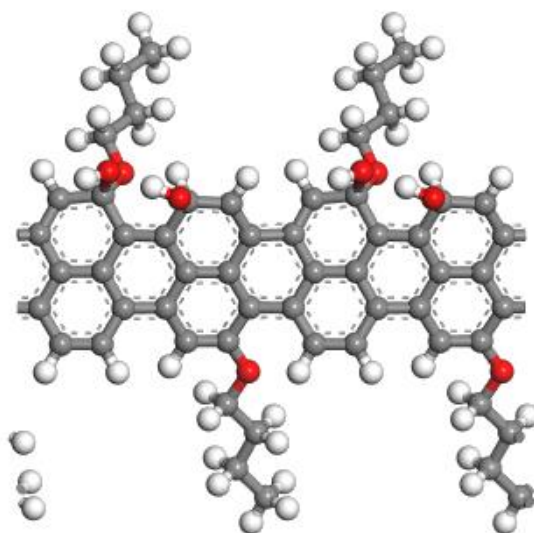
H₂O₂ adsorption on 7A-GNR, configuration 3 in Figure 5.5

		X	Y	Z			X	Y	Z
1	C	0.499705	-11.6196	-14.123	21	C	7.598079	-14.0915	-14.1534
2	C	1.200527	-12.8519	-14.1369	22	C	6.88774	-12.8515	-14.1446
3	C	2.627169	-12.8523	-14.1357	23	C	7.588776	-11.619	-14.1362
4	C	3.329581	-11.6185	-14.1163	24	C	6.857959	-10.4077	-14.1413
5	C	2.59709	-10.4072	-14.0835	25	C	5.49209	-10.4071	-14.1364
6	C	1.231134	-10.4084	-14.0899	26	C	5.491334	-17.7745	-14.1594
7	C	3.338388	-14.093	-14.1544	27	C	6.857578	-17.7744	-14.16
8	C	2.627121	-15.3321	-14.1636	28	C	7.589061	-16.5635	-14.1641
9	C	1.201729	-15.3316	-14.1627	29	H	3.113935	-9.45156	-14.0478
10	C	0.490712	-14.092	-14.1528	30	H	0.713701	-9.45286	-14.0613
11	C	0.500193	-16.5636	-14.1713	31	H	0.714681	-18.7308	-14.2046
12	C	1.231409	-17.7745	-14.1883	32	H	3.11428	-18.7311	-14.2016
13	C	2.597584	-17.7748	-14.1876	33	H	7.374542	-9.45131	-14.1503
14	C	3.328818	-16.5638	-14.1713	34	H	4.975217	-9.45094	-14.1386
15	C	4.761524	-11.6185	-14.1316	35	H	4.974657	-18.7309	-14.1527
16	C	5.46197	-12.8515	-14.144	36	H	7.374215	-18.7308	-14.1555
17	C	4.751206	-14.0918	-14.154	37	O	-5.12503	16.99172	19.30237
18	C	5.461897	-15.3317	-14.1591	38	O	-3.87045	17.63131	19.73925
19	C	4.759937	-16.5636	-14.1639	39	H	3.299039	17.39892	18.4157
20	C	6.887362	-15.3315	-14.1587	40	H	5.267757	16.88236	19.62048



H₂O₂ adsorption on 7A-GNR, configuration 4 in Figure 5.5

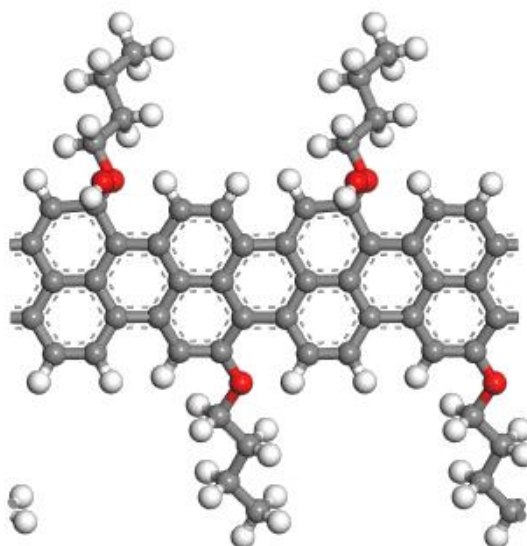
		X	Y	Z			X	Y	Z
1	C	0.499198	-11.6057	-14.123	21	C	7.596858	-14.0782	-14.1264
2	C	1.200357	-12.8377	-14.1271	22	C	6.886839	-12.838	-14.1269
3	C	2.626504	-12.8377	-14.1277	23	C	7.588364	-11.6058	-14.1279
4	C	3.328678	-11.6048	-14.1211	24	C	6.857236	-10.3947	-14.1323
5	C	2.596772	-10.3941	-14.1052	25	C	5.491171	-10.3944	-14.1307
6	C	1.230679	-10.3949	-14.1078	26	C	5.490598	-17.7616	-14.148
7	C	3.337494	-14.079	-14.1292	27	C	6.856613	-17.7618	-14.1436
8	C	2.626816	-15.3192	-14.1298	28	C	7.588172	-16.5507	-14.1309
9	C	1.201267	-15.3188	-14.1288	29	H	3.112583	-9.43742	-14.0864
10	C	0.490398	-14.0781	-14.128	30	H	0.713764	-9.43884	-14.0906
11	C	0.499318	-16.5512	-14.1245	31	H	0.715306	-18.7188	-14.0993
12	C	1.230973	-17.762	-14.1152	32	H	3.113455	-18.7181	-14.109
13	C	2.597079	-17.7617	-14.1209	33	H	7.373477	-9.43815	-14.1371
14	C	3.32843	-16.5509	-14.1302	34	H	4.974132	-9.43829	-14.1348
15	C	4.759858	-11.6056	-14.1261	35	H	4.973624	-18.7176	-14.1609
16	C	5.46126	-12.8381	-14.127	36	H	7.373948	-18.7178	-14.153
17	C	4.751187	-14.0784	-14.1278	37	O	-6.7351	15.23594	19.39353
18	C	5.461013	-15.3185	-14.131	38	O	-6.37273	16.66367	19.34322
19	C	4.75924	-16.5504	-14.1367	39	H	0.933134	15.26306	18.91167
20	C	6.88663	-15.3183	-14.1293	40	H	2.785125	16.64976	18.59952



5A-OGNR + 2*OH in Figure 5.6

		X	Y	Z			X	Y	Z
1	C	-3.71731	15.80522	45.62807	30	C	1.284129	14.61744	45.20683
2	C	-3.00238	14.60654	45.31727	31	C	2.703176	14.63244	45.24673
3	C	-3.6997	13.41649	45.00696	32	C	3.430213	15.85103	45.44448
4	C	-2.97257	16.9831	46.21996	33	C	2.708138	17.18549	45.39422
5	C	-3.00167	12.29237	44.52309	34	C	1.239257	17.06243	45.23721
6	C	-1.62598	12.29979	44.43712	35	C	3.398383	13.39973	45.13032
7	C	-0.87686	13.42904	44.91349	36	C	2.671614	12.19246	45.13899
8	O	-5.15894	17.92624	44.3712	37	C	1.299679	12.19202	45.11156
9	O	-0.92629	11.27311	43.85727	38	C	0.575986	13.40928	45.05769
10	C	-1.6641	10.18058	43.2779	39	H	-3.31318	17.91015	45.72833
11	C	-0.66124	9.22939	42.64735	40	H	-0.95113	17.7698	46.41134
12	C	-1.33539	8.024747	41.98434	41	H	0.688318	18.00201	45.20629
13	C	-0.32721	7.065749	41.3511	42	C	2.784645	19.19885	14.00552
14	H	-3.56852	11.44348	44.15366	43	C	3.798552	19.90799	13.12074
15	H	-2.36831	10.56935	42.52097	44	C	3.291962	21.24951	12.58571
16	H	-2.25074	9.67066	44.06207	45	C	4.320102	21.94361	11.68952
17	H	0.044435	8.883879	43.42102	46	H	2.56971	19.78972	14.91211
18	H	-0.06457	9.783649	41.9051	47	H	1.841335	19.03836	13.4532
19	H	-2.0457	8.376957	41.21664	48	H	4.057166	19.2428	12.2805

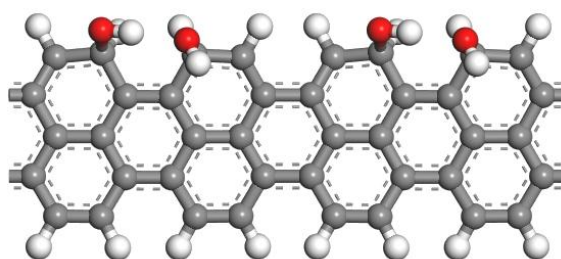
20	H	-1.93983	7.484637	42.73265	49	H	4.728385	20.06199	13.69415
21	H	0.263597	7.570381	40.57194	50	H	3.030918	21.90917	13.43081
22	H	-0.82563	6.202536	40.88573	51	H	2.35667	21.09057	12.0212
23	H	0.37928	6.680747	42.10304	52	H	4.564877	21.3222	10.81435
24	C	-1.58364	14.59663	45.24888	53	H	5.258338	22.12819	12.23609
25	C	-0.86547	15.83404	45.53242	54	H	3.950409	22.91179	11.32111
26	C	-1.5096	16.90472	46.05343	55	O	2.889072	17.97347	16.65037
27	H	3.203509	11.24264	45.19484	56	H	2.131313	17.73167	17.21664
28	H	0.767005	11.24849	45.13564	57	O	5.283111	17.08246	17.64053
29	C	0.577516	15.87862	45.30835	58	H	4.373573	17.45721	17.65706



5A-OGNR + *OH in Figure 5.6

		X	Y	Z			X	Y	Z
1	C	-3.6948	15.78816	45.39589	29	C	0.571778	15.81148	45.23014
2	C	-2.98201	14.57363	45.13652	30	C	1.28129	14.56101	45.11271
3	C	-3.6843	13.37332	44.88844	31	C	2.70741	14.59271	45.15082
4	C	-2.94756	16.94955	45.72977	32	C	3.417615	15.81006	45.30467
5	C	-2.98537	12.23007	44.45231	33	C	2.702903	17.13965	45.33467
6	C	-1.60507	12.21838	44.37179	34	C	1.239612	17.00754	45.23909
7	C	-0.84853	13.34656	44.81169	35	C	3.416383	13.35863	45.02882

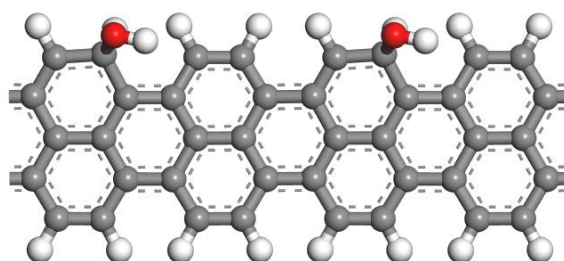
8	O	-5.23761	17.93542	44.29926	36	C	2.697906	12.14388	45.04999
9	O	-0.92201	11.15113	43.84479	37	C	1.329396	12.12803	45.01973
10	C	-1.67239	10.04822	43.3021	38	C	0.587353	13.34092	44.96112
11	C	-0.67836	9.068652	42.70235	39	H	-3.47033	17.85499	46.01363
12	C	-1.36109	7.84749	42.07887	40	H	-1.04146	17.81752	46.02137
13	C	-0.35925	6.869791	41.46491	41	H	0.695852	17.94772	45.2724
14	H	-3.55225	11.36416	44.12589	42	C	2.669345	19.21751	14.05038
15	H	-2.37203	10.41914	42.53232	43	C	3.609726	20.01317	13.15831
16	H	-2.26368	9.567904	44.10148	44	C	3.044495	21.38965	12.79555
17	H	0.025445	8.743071	43.48626	45	C	3.977899	22.1943	11.88979
18	H	-0.07861	9.592813	41.94141	46	H	2.495097	19.74528	15.00243
19	H	-2.07476	8.181461	41.30615	47	H	1.698224	19.07842	13.5423
20	H	-1.96249	7.330632	42.84555	48	H	3.803802	19.43279	12.24055
21	H	0.2296	7.355518	40.67224	49	H	4.580462	20.12623	13.66859
22	H	-0.86139	5.998182	41.0203	50	H	2.846278	21.95943	13.72037
23	H	0.349316	6.499835	42.22241	51	H	2.067131	21.26484	12.29883
24	C	-1.55988	14.55386	45.10407	52	H	4.15889	21.66607	10.94105
25	C	-0.86027	15.76559	45.35771	53	H	4.954596	22.35567	12.3705
26	C	-1.58061	16.92017	45.72394	54	H	3.554589	23.18072	11.64954
27	H	3.236751	11.19888	45.11489	55	O	2.957997	17.88975	16.587
28	H	0.80607	11.17957	45.05026	56	H	2.568855	17.35107	17.2994



5A-GNR + 2*OH in Figure 5.6

		X	Y	Z			X	Y	Z
1	C	0.451475	-11.8246	-14.1607	17	C	5.400758	-10.5973	-13.5608
2	C	1.1546	-13.0957	-14.0614	18	C	5.42836	-15.5381	-14.2135
3	C	2.573589	-13.0978	-14.0158	19	C	6.79932	-15.5203	-14.2432

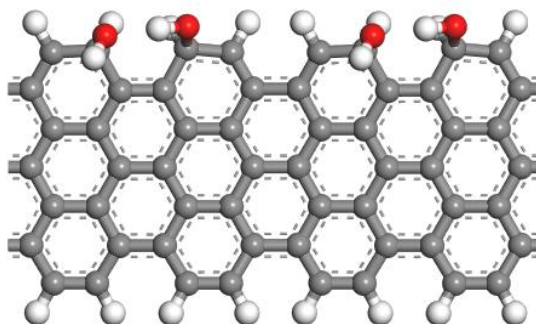
4	C	3.293751	-11.8627	-13.9575	20	C	7.516218	-14.3074	-14.1183
5	C	2.570047	-10.5352	-13.9948	21	H	3.072728	-9.89351	-14.7479
6	C	1.13244	-10.6678	-14.3219	22	H	0.608983	-9.72706	-14.4884
7	C	3.26776	-14.3383	-13.9895	23	H	3.046451	-16.4941	-13.8067
8	C	2.531696	-15.5411	-13.9129	24	H	0.626426	-16.4673	-13.8499
9	C	1.161675	-15.5242	-13.9383	25	H	7.392863	-9.73326	-13.6097
10	C	0.449472	-14.3077	-14.0528	26	H	4.969694	-9.76283	-14.1381
11	C	4.670905	-11.8775	-13.8537	27	H	4.909234	-16.4839	-14.3545
12	C	5.394312	-13.1066	-13.9704	28	H	7.330726	-16.4578	-14.393
13	C	4.697233	-14.3415	-14.0413	29	O	2.542955	20.15768	17.27848
14	C	6.811387	-13.0975	-14.0426	30	H	3.448786	20.08547	17.67151
15	C	7.515332	-11.8243	-14.0134	31	O	5.158129	19.84845	17.8366
16	C	6.853634	-10.6669	-13.764	32	H	5.498924	19.13796	18.41337



5A-GNR + *OH in Figure 5.6

		X	Y	Z			X	Y	Z
1	C	0.423652	-11.8156	-14.0005	16	C	6.766061	-10.6415	-14.2446
2	C	1.129179	-13.0832	-14.0235	17	C	5.396278	-10.6387	-14.2114
3	C	2.556022	-13.0788	-14.0041	18	C	5.421462	-15.5301	-13.9549
4	C	3.263313	-11.858	-13.9717	19	C	6.795225	-15.5204	-13.9621
5	C	2.570386	-10.5447	-13.7594	20	C	7.516739	-14.3164	-14.0381
6	C	1.101592	-10.638	-13.8449	21	H	2.908132	-9.81807	-14.5292
7	C	3.25884	-14.3221	-14.0534	22	H	0.574061	-9.69445	-13.7177
8	C	2.526386	-15.5278	-14.1399	23	H	3.045264	-16.4801	-14.2277
9	C	1.160497	-15.5213	-14.1394	24	H	0.634076	-16.4692	-14.222
10	C	0.433839	-14.3034	-14.0656	25	H	7.290861	-9.6977	-14.3804
11	C	4.664846	-11.8549	-14.0859	26	H	4.866781	-9.69054	-14.3022

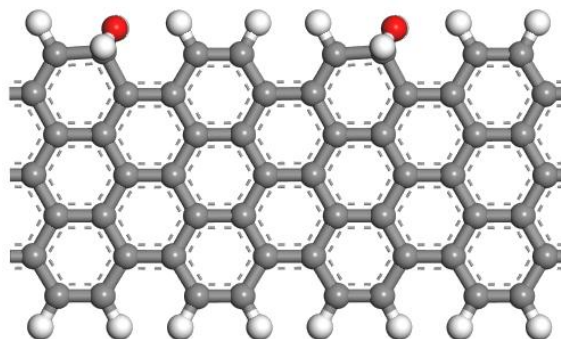
12	C	5.384795	-13.0909	-14.0732	27	H	4.908504	-16.4858	-13.8728
13	C	4.686341	-14.3265	-14.0292	28	H	7.316824	-16.4722	-13.8894
14	C	6.808128	-13.0789	-14.0762	29	O	2.882733	20.02831	17.55359
15	C	7.502052	-11.8389	-14.1124	30	H	3.82994	19.86101	17.71328



7A-GNR + 2*OH in Figure 5.6

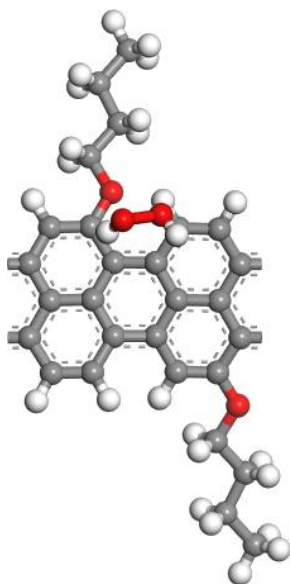
		X	Y	Z			X	Y	Z
1	C	0.543076	-11.6184	-14.1006	21	C	7.6119	-14.0984	-14.1593
2	C	1.24218	-12.8883	-14.1094	22	C	6.90443	-12.8864	-14.1551
3	C	2.662531	-12.8898	-14.0428	23	C	7.605877	-11.6189	-14.2324
4	C	3.382684	-11.6677	-13.9397	24	C	6.924021	-10.4581	-14.381
5	C	2.655867	-10.3852	-13.6559	25	C	5.487793	-10.3277	-14.0566
6	C	1.206485	-10.4557	-13.867	26	C	5.517981	-17.7942	-14.0656
7	C	3.365678	-14.1217	-14.1061	27	C	6.891501	-17.7867	-14.0661
8	C	2.654449	-15.3572	-14.1679	28	C	7.614183	-16.5812	-14.1572
9	C	1.233327	-15.3482	-14.1774	29	H	3.093189	-9.55088	-14.2284
10	C	0.532724	-14.0987	-14.1551	30	H	0.667759	-9.52129	-13.7182
11	C	0.530741	-16.5803	-14.2213	31	H	0.728036	-18.726	-14.487
12	C	1.253592	-17.7826	-14.3548	32	H	3.146514	-18.737	-14.4831
13	C	2.627424	-17.7897	-14.3527	33	H	7.446225	-9.51627	-14.5427
14	C	3.355785	-16.5912	-14.215	34	H	4.990375	-9.68149	-14.8096
15	C	4.767279	-11.6546	-14.033	35	H	4.99989	-18.7469	-13.9756
16	C	5.482169	-12.8814	-14.1157	36	H	7.416806	-18.7352	-13.9746
17	C	4.780732	-14.1179	-14.1208	37	O	2.88965	20.06384	17.74529
18	C	5.491065	-15.3563	-14.1457	38	O	5.507733	20.35963	17.22047

19	C	4.789063	-16.5919	-14.1511	39	H	2.53064	19.36018	18.31962
20	C	6.911651	-15.3484	-14.1541	40	H	4.596797	20.29111	17.60346



7A-GNR + *OH in Figure 5.6

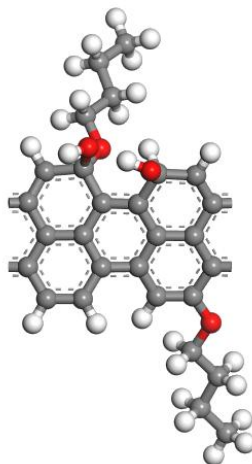
		X	Y	Z			X	Y	Z
1	C	0.519121	-11.6426	-14.0641	20	C	6.915814	-15.3725	-14.1459
2	C	1.224108	-12.9032	-14.0814	21	C	7.619578	-14.1361	-14.1291
3	C	2.654252	-12.8934	-14.0588	22	C	6.905956	-12.8977	-14.1118
4	C	3.36015	-11.6812	-14.0073	23	C	7.59434	-11.661	-14.0982
5	C	2.664733	-10.3595	-13.8831	24	C	6.85806	-10.4574	-14.0974
6	C	1.20395	-10.4554	-13.9946	25	C	5.492561	-10.4559	-14.0555
7	C	3.363505	-14.1374	-14.1054	26	C	5.521819	-17.8204	-14.131
8	C	2.655117	-15.3752	-14.1541	27	C	6.892188	-17.8174	-14.1307
9	C	1.232197	-15.3746	-14.1564	28	C	7.619683	-16.6092	-14.1658
10	C	0.523642	-14.1267	-14.1197	29	H	3.04905	-9.65645	-14.6439
11	C	0.532387	-16.604	-14.2065	30	H	0.684529	-9.50159	-13.9421
12	C	1.261248	-17.8106	-14.324	31	H	0.739505	-18.7581	-14.4387
13	C	2.629518	-17.8132	-14.3235	32	H	3.148996	-18.7621	-14.4376
14	C	3.358726	-16.6088	-14.2053	33	H	7.371212	-9.49892	-14.1162
15	C	4.769004	-11.6765	-14.0493	34	H	4.965127	-9.50754	-14.0021
16	C	5.483638	-12.9078	-14.0978	35	H	5.004496	-18.776	-14.0871
17	C	4.777262	-14.141	-14.1162	36	H	7.412126	-18.7716	-14.0864
18	C	5.489942	-15.3797	-14.1428	37	O	3.003566	20.32777	17.37432
19	C	4.79059	-16.6109	-14.1643	38	H	2.643578	19.76593	18.08621



5A-OGNR TS calculation step 1, configuration of IS in Figure 5.11

		X	Y	Z			X	Y	Z
1	C	-3.69722	15.95009	44.75385	30	C	1.26557	14.68757	44.60489
2	C	-2.99415	14.71186	44.61159	31	C	2.692524	14.72283	44.6121
3	C	-3.70277	13.48965	44.47952	32	C	3.400471	15.96664	44.60328
4	C	-2.94228	17.1092	45.08368	33	C	2.63281	17.16992	44.41874
5	C	-3.00257	12.29886	44.17947	34	C	1.257999	17.13577	44.46549
6	C	-1.62854	12.26956	44.12384	35	C	3.403686	13.48929	44.62634
7	C	-0.85949	13.44246	44.44357	36	C	2.684815	12.27915	44.7896
8	O	-5.19497	18.32429	44.15806	37	C	1.317765	12.24841	44.77428
9	O	-0.94156	11.15197	43.72276	38	C	0.562934	13.44138	44.59224
10	C	-1.68375	9.955336	43.42972	39	H	-3.45553	18.02655	45.34769
11	C	-0.68773	8.883344	43.0161	40	H	-1.02612	17.97352	45.37824
12	C	-1.35383	7.524636	42.78258	41	H	0.688482	18.0487	44.31817
13	C	-0.36293	6.456688	42.31683	42	C	2.58315	19.53269	13.91355
14	H	-3.57309	11.40941	43.93101	43	C	3.584933	20.6378	13.6245
15	H	-2.40396	10.15137	42.61649	44	C	2.90704	21.98376	13.34971
16	H	-2.25341	9.643822	44.32292	45	C	3.912	23.1011	13.06894
17	H	0.08217	8.790587	43.79993	46	H	1.970854	19.77946	14.79928
18	H	-0.16852	9.213043	42.10209	47	H	1.902139	19.38347	13.05791
19	H	-2.15886	7.630051	42.03507	48	H	4.204676	20.34296	12.76292

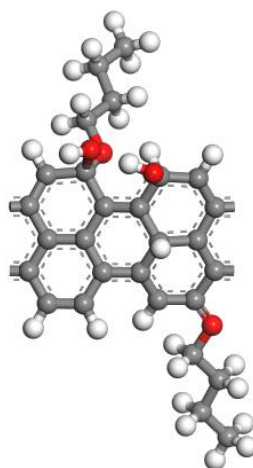
20	H	-1.84379	7.19456	43.71408	49	H	4.267988	20.735	14.48424
21	H	0.108459	6.744967	41.36531	50	H	2.279775	22.26026	14.21411
22	H	-0.85706	5.486405	42.1664	51	H	2.218669	21.88038	12.49386
23	H	0.441632	6.313184	43.05413	52	H	4.530324	22.86847	12.18801
24	C	-1.56771	14.67595	44.60735	53	H	4.592443	23.24499	13.92155
25	C	-0.85586	15.89897	44.7714	54	H	3.405454	24.05849	12.88034
26	C	-1.57467	17.07662	45.09156	55	O	-4.81411	17.37924	22.02407
27	H	3.232807	11.3521	44.9602	56	O	-3.52128	17.55441	21.33408
28	H	0.803248	11.30582	44.9189	57	H	-5.33085	16.97817	21.29704
29	C	0.557654	15.9172	44.62169	58	H	-2.99412	16.88014	21.80709



5A-OGNR TS calculation Step 1, configuration of FS in Figure 5.11

		X	Y	Z			X	Y	Z
1	C	-3.71731	15.80522	45.62807	30	C	1.284129	14.61744	45.20683
2	C	-3.00238	14.60654	45.31727	31	C	2.703176	14.63244	45.24673
3	C	-3.6997	13.41649	45.00696	32	C	3.430213	15.85103	45.44448
4	C	-2.97257	16.9831	46.21996	33	C	2.708138	17.18549	45.39422
5	C	-3.00167	12.29237	44.52309	34	C	1.239257	17.06243	45.23721
6	C	-1.62598	12.29979	44.43712	35	C	3.398383	13.39973	45.13032
7	C	-0.87686	13.42904	44.91349	36	C	2.671614	12.19246	45.13899
8	O	-5.15894	17.92624	44.3712	37	C	1.299679	12.19202	45.11156
9	O	-0.92629	11.27311	43.85727	38	C	0.575986	13.40928	45.05769
10	C	-1.6641	10.18058	43.2779	39	H	-3.31318	17.91015	45.72833

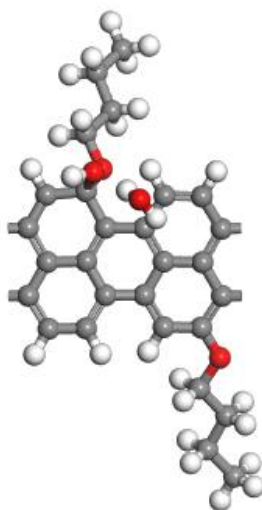
11	C	-0.66124	9.22939	42.64735	40	H	-0.95113	17.7698	46.41134
12	C	-1.33539	8.024747	41.98434	41	H	0.688318	18.00201	45.20629
13	C	-0.32721	7.065749	41.3511	42	C	2.784645	19.19885	14.00552
14	H	-3.56852	11.44348	44.15366	43	C	3.798552	19.90799	13.12074
15	H	-2.36831	10.56935	42.52097	44	C	3.291962	21.24951	12.58571
16	H	-2.25074	9.67066	44.06207	45	C	4.320102	21.94361	11.68952
17	H	0.044435	8.883879	43.42102	46	H	2.56971	19.78972	14.91211
18	H	-0.06457	9.783649	41.9051	47	H	1.841335	19.03836	13.4532
19	H	-2.0457	8.376957	41.21664	48	H	4.057166	19.2428	12.2805
20	H	-1.93983	7.484637	42.73265	49	H	4.728385	20.06199	13.69415
21	H	0.263597	7.570381	40.57194	50	H	3.030918	21.90917	13.43081
22	H	-0.82563	6.202536	40.88573	51	H	2.35667	21.09057	12.0212
23	H	0.37928	6.680747	42.10304	52	H	4.564877	21.3222	10.81435
24	C	-1.58364	14.59663	45.24888	53	H	5.258338	22.12819	12.23609
25	C	-0.86547	15.83404	45.53242	54	H	3.950409	22.91179	11.32111
26	C	-1.5096	16.90472	46.05343	55	O	2.889072	17.97347	16.65037
27	H	3.203509	11.24264	45.19484	56	H	2.131313	17.73167	17.21664
28	H	0.767005	11.24849	45.13564	57	O	5.283111	17.08246	17.64053
29	C	0.577516	15.87862	45.30835	58	H	4.373573	17.45721	17.65706



5A-OGNR TS calculation Step 2, configuration of IS in Figure 5.11

		X	Y	Z			X	Y	Z
--	--	---	---	---	--	--	---	---	---

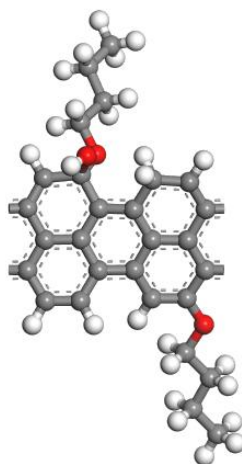
1	C	-3.71687	15.82341	45.77298	31	C	2.721714	14.62583	45.29624
2	C	-2.96655	14.51252	45.81341	32	C	3.474754	15.86117	45.47448
3	C	-3.69332	13.37012	45.18336	33	C	2.744995	17.19603	45.3716
4	C	-2.95524	17.01557	46.30086	34	C	1.267548	17.07056	45.25359
5	C	-3.00933	12.33758	44.56676	35	C	3.407795	13.38251	45.21399
6	C	-1.62233	12.33852	44.46389	36	C	2.673741	12.18169	45.13505
7	C	-0.85105	13.44804	44.9559	37	C	1.304621	12.19661	45.03989
8	O	-5.13665	17.89908	44.31587	38	C	0.597471	13.41886	45.02199
9	O	-0.95352	11.36411	43.7749	39	H	-3.32191	17.92874	45.80717
10	C	-1.69473	10.26087	43.21682	40	H	-0.93683	17.82487	46.38092
11	C	-0.69224	9.310379	42.58421	41	H	0.719916	18.01293	45.25256
12	C	-1.36339	8.094647	41.93862	42	C	2.78492	19.15368	13.92242
13	C	-0.35272	7.13754	41.30629	43	C	3.773367	19.86566	13.01264
14	H	-3.5869	11.55951	44.07521	44	C	3.238391	21.20168	12.49095
15	H	-2.40905	10.63732	42.46328	45	C	4.231005	21.91277	11.56897
16	H	-2.26807	9.757845	44.01461	46	H	2.568238	19.76124	14.81732
17	H	0.023278	8.976924	43.35429	47	H	1.838633	18.96425	13.38487
18	H	-0.1064	9.861339	41.83092	48	H	4.019272	19.20255	12.167
19	H	-2.08175	8.43526	41.17305	49	H	4.71393	20.02895	13.56519
20	H	-1.95822	7.557269	42.69655	50	H	2.990692	21.85613	13.34428
21	H	0.230149	7.640812	40.52012	51	H	2.290338	21.03314	11.9515
22	H	-0.84777	6.268094	40.84942	52	H	4.455447	21.30013	10.68202
23	H	0.360971	6.762663	42.05673	53	H	5.183171	22.10433	12.08735
24	C	-1.52597	14.59725	45.39361	54	H	3.83839	22.87852	11.21855
25	C	-0.83938	15.8342	45.60321	55	O	2.94321	18.01309	16.60433
26	C	-1.49446	16.93384	46.09451	56	H	2.139209	17.86673	17.13804
27	H	3.199245	11.22841	45.19772	57	O	5.324284	17.13017	17.73314
28	H	0.764433	11.25747	45.0147	58	H	4.410289	17.49068	17.75641
29	C	0.603576	15.88914	45.33592	59	H	5.603236	14.28159	16.91204
30	C	1.31773	14.62746	45.21838					



5A-OGNR TS calculation Step 2, configuration of FS in Figure 5.11

		X	Y	Z			X	Y	Z
1	C	-3.25869	16.04863	45.34162	31	C	3.143823	14.8386	45.2028
2	C	-2.54622	14.82046	45.16413	32	C	3.852877	16.06115	45.27831
3	C	-3.24839	13.60395	45.0059	33	C	3.136079	17.38796	45.31943
4	C	-2.51284	17.23131	45.59762	34	C	1.675827	17.2567	45.21488
5	C	-2.54642	12.43327	44.65937	35	C	3.852654	13.59922	45.15275
6	C	-1.16587	12.41577	44.58159	36	C	3.133767	12.38955	45.26201
7	C	-0.41081	13.57347	44.94179	37	C	1.76536	12.37215	45.23695
8	O	-4.81317	18.20167	44.29349	38	C	1.02356	13.57936	45.09953
9	O	-0.48411	11.31342	44.13334	39	H	-3.02475	18.16434	45.79775
10	C	-1.23884	10.19455	43.62573	40	H	-0.61395	18.11259	45.8695
11	C	-0.2523	9.195742	43.04735	41	H	1.130621	18.19608	45.17799
12	C	-0.94861	7.972713	42.44194	42	C	3.123241	19.50803	14.10805
13	C	0.040725	6.981296	41.82946	43	C	4.070493	20.32843	13.24706
14	H	-3.11014	11.54102	44.40646	44	C	3.524545	21.7304	12.961
15	H	-1.94259	10.54614	42.8513	45	C	4.458713	22.56507	12.0842
16	H	-1.8245	9.738612	44.44365	46	H	2.965878	19.99004	15.08614
17	H	0.446128	8.876232	43.83832	47	H	2.146318	19.41336	13.59981
18	H	0.35445	9.700328	42.27883	48	H	4.249544	19.79082	12.30145
19	H	-1.66571	8.304949	41.6716	49	H	5.047066	20.40348	13.75381
20	H	-1.54789	7.467765	43.21813	50	H	3.347855	22.25586	13.91508

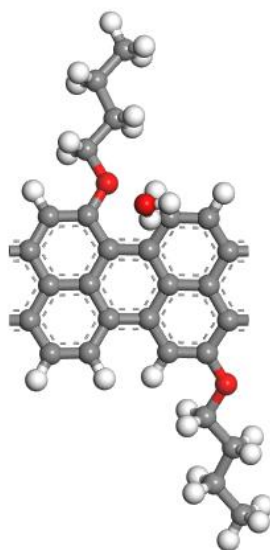
21	H	0.625753	7.455417	41.02694	51	H	2.538701	21.64651	12.47216
22	H	-0.47251	6.110382	41.3968	52	H	4.631538	22.07696	11.11338
23	H	0.75301	6.613511	42.58437	53	H	5.438745	22.70098	12.56622
24	C	-1.12351	14.79839	45.14073	54	H	4.040808	23.56325	11.88896
25	C	-0.42547	16.02257	45.32902	55	O	13.61942	17.08807	18.8362
26	C	-1.147	17.19886	45.61521	56	H	14.2095	16.40726	18.47357
27	H	3.67294	11.45143	45.39221	57	H	13.15197	17.41621	18.0408
28	H	1.24109	11.42828	45.33156	58	O	3.407176	18.08574	16.61165
29	C	1.00894	16.05994	45.23448	59	H	2.619073	17.92106	17.16331
30	C	1.717112	14.8056	45.18127					



5A-OGNR TS calculation Step 3, configuration of IS in Figure 5.11

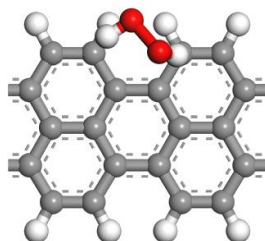
		X	Y	Z			X	Y	Z
1	C	-3.6443	15.74305	45.5094	30	C	1.362972	14.54248	45.11518
2	C	-2.92425	14.5415	45.20836	31	C	2.78164	14.56364	45.13758
3	C	-3.62151	13.35153	44.89576	32	C	3.505041	15.78548	45.32948
4	C	-2.90018	16.93001	46.04628	33	C	2.78397	17.11969	45.34288
5	C	-2.92234	12.22199	44.42739	34	C	1.31588	16.98663	45.20991
6	C	-1.5469	12.22171	44.35269	35	C	3.477862	13.33276	45.01794
7	C	-0.79681	13.35178	44.82557	36	C	2.755041	12.12258	45.03279
8	O	-5.13433	17.91753	44.31846	37	C	1.383683	12.11734	45.01245
9	O	-0.85206	11.1806	43.79008	38	C	0.65655	13.33363	44.96569

10	C	-1.59837	10.06642	43.26611	39	H	-3.23277	17.85152	45.54304
11	C	-0.60936	9.073481	42.68111	40	H	-0.86715	17.69274	46.3062
12	C	-1.30654	7.847879	42.08101	41	H	0.763285	17.9243	45.22023
13	C	-0.32029	6.849213	41.47605	42	C	2.757106	19.19159	14.0679
14	H	-3.49085	11.37296	44.06196	43	C	3.680621	20.02401	13.19327
15	H	-2.30176	10.42215	42.49256	44	C	3.075934	21.39533	12.87432
16	H	-2.18702	9.599949	44.07587	45	C	3.964879	22.24995	11.97086
17	H	0.093454	8.75497	43.46865	46	H	2.562219	19.70683	15.02304
18	H	-0.00776	9.579796	41.90978	47	H	1.794565	19.0374	13.5483
19	H	-2.02292	8.17648	41.30847	48	H	3.885107	19.47354	12.25982
20	H	-1.90738	7.349179	42.86016	49	H	4.649504	20.15119	13.70427
21	H	0.266221	7.314214	40.66922	50	H	2.883502	21.93561	13.81747
22	H	-0.8362	5.975387	41.0521	51	H	2.09105	21.25716	12.39665
23	H	0.39095	6.484966	42.23381	52	H	4.133683	21.75825	11.00105
24	C	-1.50305	14.52167	45.15952	53	H	4.949526	22.4217	12.43127
25	C	-0.78387	15.75328	45.46221	54	H	3.511109	23.23235	11.77454
26	C	-1.43739	16.82946	45.96042	55	O	3.01026	17.85601	16.59987
27	H	3.290285	11.17452	45.08743	56	H	2.391111	17.46527	17.24336
28	H	0.854168	11.17223	45.03621	57	H	5.311401	17.09401	17.09472
29	C	0.658491	15.80077	45.24918					



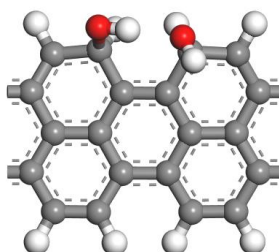
5A-OGNR TS calculation Step 3, configuration of FS in Figure 5.11

		X	Y	Z			X	Y	Z
1	C	-3.63825	15.79185	44.82767	30	C	1.325536	14.53042	44.67162
2	C	-2.93393	14.55526	44.67402	31	C	2.751951	14.56537	44.67391
3	C	-3.64289	13.3358	44.51806	32	C	3.458796	15.80938	44.67604
4	C	-2.88321	16.94943	45.16846	33	C	2.692999	17.01381	44.49474
5	C	-2.94314	12.15151	44.19587	34	C	1.317529	16.97966	44.54026
6	C	-1.56764	12.11732	44.16494	35	C	3.463648	13.33251	44.67018
7	C	-0.79972	13.2852	44.50471	36	C	2.746978	12.12089	44.82782
8	O	-5.1326	18.16436	44.2329	37	C	1.379197	12.09011	44.82282
9	O	-0.87955	11.00082	43.76525	38	C	0.623243	13.28395	44.65326
10	C	-1.62743	9.831161	43.38369	39	H	-3.39427	17.87032	45.42774
11	C	-0.62847	8.743572	43.02367	40	H	-0.96498	17.8113	45.46709
12	C	-1.30774	7.463393	42.52708	41	H	0.748801	17.89369	44.3969
13	C	-0.3038	6.350316	42.22426	42	C	2.651301	19.37524	13.97362
14	H	-3.51434	11.27141	43.91926	43	C	3.663409	20.47114	13.6852
15	H	-2.2742	10.07292	42.5218	44	C	2.999285	21.82241	13.40575
16	H	-2.27091	9.510259	44.22062	45	C	4.016668	22.9282	13.12181
17	H	-0.00963	8.517121	43.90842	46	H	2.035045	19.63123	14.85318
18	H	0.057626	9.131229	42.25275	47	H	1.978879	19.21943	13.11257
19	H	-1.89569	7.688099	41.62018	48	H	4.281595	20.16953	12.82469
20	H	-2.03422	7.112719	43.28137	49	H	4.344742	20.56212	14.54688
21	H	0.40588	6.660738	41.44187	50	H	2.373629	22.10953	14.26761
22	H	-0.80429	5.435188	41.87748	51	H	2.311994	21.72325	12.54836
23	H	0.282879	6.09326	43.1195	52	H	4.613712	22.70047	12.22497
24	C	-1.50754	14.51822	44.67552	53	H	4.715373	23.04777	13.96347
25	C	-0.79523	15.7402	44.84897	54	H	3.522242	23.89634	12.95822
26	C	-1.51321	16.91502	45.17797	55	O	4.753643	17.40935	18.50514
27	H	3.296852	11.19301	44.98747	56	H	4.926041	16.88722	17.70106
28	H	0.865929	11.1465	44.96571	57	H	5.623386	17.45415	18.93515
29	C	0.618628	15.76049	44.69571					



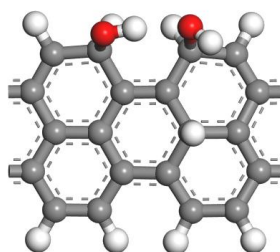
5A-GNR TS calculation Step 1, configuration of IS in Figure 5.11

		X	Y	Z			X	Y	Z
1	C	0.42368	-11.8719	-14.0351	17	C	5.420381	-10.6618	-13.9148
2	C	1.129277	-13.1101	-14.0346	18	C	5.419938	-15.5586	-14.1435
3	C	2.555737	-13.1099	-14.0343	19	C	6.784486	-15.5588	-14.1431
4	C	3.261261	-11.8715	-14.0317	20	C	7.521427	-14.348	-14.0672
5	C	2.524839	-10.6592	-14.0731	21	H	3.042919	-9.70409	-14.1191
6	C	1.159932	-10.6594	-14.0766	22	H	0.641025	-9.70481	-14.1247
7	C	3.261389	-14.3481	-14.0361	23	H	3.043699	-16.5158	-13.9598
8	C	2.525108	-15.5608	-14.0008	24	H	0.642388	-16.5163	-13.9622
9	C	1.160399	-15.561	-14.0017	25	H	7.30483	-9.7091	-13.8432
10	C	0.423684	-14.3485	-14.0368	26	H	4.901644	-9.70864	-13.8404
11	C	4.683716	-11.8721	-13.9961	27	H	4.901031	-16.5116	-14.2188
12	C	5.389177	-13.11	-14.0317	28	H	7.303082	-16.512	-14.2172
13	C	4.683497	-14.3477	-14.0674	29	O	-3.82068	19.3864	23.26913
14	C	6.815824	-13.1102	-14.0323	30	O	-4.7322	20.42261	22.74844
15	C	7.521438	-11.8724	-14.0003	31	H	-3.2395	19.27724	22.49017
16	C	6.785133	-10.6615	-13.9199	32	H	-5.54878	19.89089	22.66276



5A-GNR TS calculation Step 1, configuration of FS in Figure 5.11

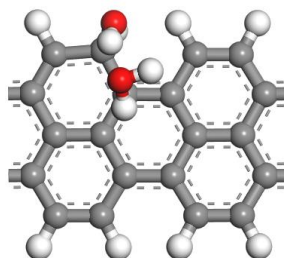
		X	Y	Z			X	Y	Z
1	C	0.540465	-11.6266	-14.1006	17	C	6.900528	-12.8983	-14.1395
2	C	1.244042	-12.8997	-14.1249	18	C	7.603283	-11.627	-14.24
3	C	2.660632	-12.9088	-14.0513	19	C	6.921924	-10.4701	-14.3977
4	C	3.384552	-11.6792	-13.9393	20	C	5.48596	-10.3397	-14.0618
5	C	2.654719	-10.3973	-13.6548	21	H	3.088046	-9.56443	-14.2319
6	C	1.202828	-10.4672	-13.862	22	H	0.665135	-9.53214	-13.7128
7	C	3.357673	-14.1438	-14.1195	23	H	7.442424	-9.52816	-14.5653
8	C	2.627334	-15.3402	-14.2931	24	H	4.982231	-9.68719	-14.8041
9	C	1.256466	-15.3225	-14.325	25	O	2.891957	20.05486	17.74278
10	C	0.539339	-14.1101	-14.1989	26	O	5.517985	20.33479	17.22136
11	C	4.761749	-11.6656	-14.0346	27	H	2.528005	19.35709	18.32089
12	C	5.482185	-12.901	-14.0908	28	H	4.605573	20.28031	17.60155
13	C	4.787645	-14.1409	-14.0676	29	H	3.146992	13.71412	15.56566
14	C	5.523239	-15.3439	-13.9944	30	H	0.725717	13.73972	15.52386
15	C	6.893189	-15.3269	-14.0204	31	H	5.008824	13.70228	16.10837
16	C	7.605707	-14.1105	-14.1341	32	H	7.428047	13.72943	16.06709



5A-GNR TS calculation Step 2, configuration of IS in Figure 5.11

		X	Y	Z			X	Y	Z
1	C	0.422267	-11.8224	-14.1234	18	C	5.407295	-15.5509	-13.9083
2	C	1.141908	-13.0917	-14.135	19	C	6.792013	-15.5272	-13.8939
3	C	2.54356	-13.1024	-14.0227	20	C	7.513239	-14.3078	-14.0263
4	C	3.267986	-11.8522	-13.8929	21	H	2.924957	-9.79514	-14.4544
5	C	2.523623	-10.5402	-13.7365	22	H	0.528398	-9.71606	-13.8251
6	C	1.071462	-10.6506	-13.9557	23	H	3.038702	-16.4721	-14.5143
7	C	3.247685	-14.347	-14.0877	24	H	0.61042	-16.4478	-14.5635

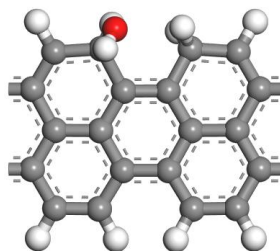
8	C	2.516248	-15.5307	-14.3555	25	H	7.271484	-9.74536	-14.5456
9	C	1.144185	-15.5144	-14.3926	26	H	4.834981	-9.81526	-14.4903
10	C	0.428957	-14.3104	-14.2118	27	H	4.91038	-16.5195	-13.9407
11	C	4.625904	-11.8335	-13.8211	28	H	7.326993	-16.4733	-13.8545
12	C	5.380406	-13.1024	-13.5675	29	O	2.648751	19.97266	17.60874
13	C	4.654265	-14.3746	-13.9074	30	H	3.612579	20.13244	17.76023
14	C	6.825698	-13.0953	-13.9619	31	O	5.360473	20.18306	17.46286
15	C	7.47599	-11.8422	-14.1561	32	H	5.985601	19.70242	18.03931
16	C	6.767796	-10.672	-14.2765	33	H	5.445967	16.85963	17.55742
17	C	5.368273	-10.5338	-13.8533					



5A-GNR TS calculation Step 2, configuration of FS in Figure 5.11

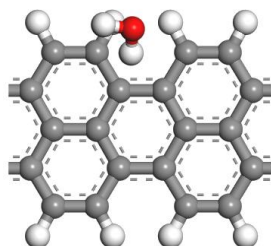
		X	Y	Z			X	Y	Z
1	C	0.622863	-11.6746	-14.0903	18	C	5.622615	-15.3784	-13.7502
2	C	1.328962	-12.939	-14.0108	19	C	6.99687	-15.3692	-13.7646
3	C	2.757097	-12.9286	-13.9895	20	C	7.718189	-14.1707	-13.9257
4	C	3.467092	-11.7067	-14.039	21	H	3.140072	-9.77366	-14.8962
5	C	2.772857	-10.3735	-14.0426	22	H	0.789213	-9.53525	-14.1616
6	C	1.308317	-10.4902	-14.1283	23	H	3.249198	-16.3386	-13.9982
7	C	3.46013	-14.1743	-13.9397	24	H	0.837804	-16.3317	-14.0114
8	C	2.728546	-15.3843	-13.9609	25	H	7.477132	-9.55066	-14.3608
9	C	1.362238	-15.3802	-13.9702	26	H	5.063919	-9.55142	-14.2439
10	C	0.635515	-14.1604	-13.9644	27	H	5.108631	-16.3248	-13.599
11	C	4.870705	-11.7135	-14.0884	28	H	7.52103	-16.3116	-13.6225
12	C	5.587501	-12.9485	-14.0138	29	O	3.11222	20.44951	17.11186
13	C	4.888294	-14.1794	-13.9031	30	H	2.99356	19.87876	17.91051
14	C	7.0103	-12.9377	-14.0269	31	O	3.309908	18.71852	19.37107

15	C	7.700851	-11.6991	-14.1322	32	H	4.221483	19.00262	19.56057
16	C	6.962588	-10.5027	-14.2525	33	H	11.94571	17.88545	18.87872
17	C	5.596417	-10.498	-14.2124					



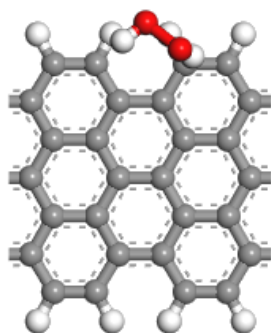
5A-GNR TS calculation Step 3, configuration of IS in Figure 5.11

		X	Y	Z			X	Y	Z
1	C	0.756072	-11.6819	-13.8124	17	C	5.675887	-10.4231	-14.0737
2	C	1.453842	-12.9596	-13.877	18	C	5.731929	-15.4055	-13.7687
3	C	2.872049	-12.9687	-13.8444	19	C	7.101962	-15.385	-13.7755
4	C	3.596287	-11.7393	-13.785	20	C	7.815828	-14.1689	-13.8916
5	C	2.899599	-10.4273	-13.5415	21	H	3.23538	-9.67807	-14.2823
6	C	1.430383	-10.5252	-13.5912	22	H	0.898921	-9.58791	-13.4264
7	C	3.566853	-14.2047	-13.925	23	H	3.350508	-16.3468	-14.2314
8	C	2.832437	-15.4018	-14.0791	24	H	0.926436	-16.3191	-14.2331
9	C	1.461602	-15.3835	-14.0848	25	H	7.685679	-9.58858	-14.3037
10	C	0.748332	-14.1687	-13.9471	26	H	5.27542	-9.88552	-14.9584
11	C	4.96553	-11.7358	-13.929	27	H	5.215943	-16.3551	-13.64
12	C	5.691518	-12.9659	-13.9333	28	H	7.639182	-16.3239	-13.6565
13	C	4.996296	-14.2051	-13.8841	29	O	3.320011	20.18094	17.72747
14	C	7.112753	-12.9564	-13.9247	30	H	3.022751	19.5649	18.42265
15	C	7.81962	-11.681	-13.9683	31	H	5.413682	20.23298	16.77612
16	C	7.142655	-10.5225	-14.1541					



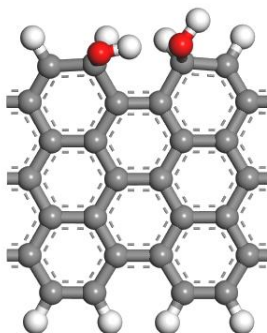
5A-GNR TS calculation Step 3, configuration of FS in Figure 5.11

		X	Y	Z			X	Y	Z
1	C	0.725399	-11.7065	-13.8909	17	C	5.723023	-10.4919	-13.8752
2	C	1.431292	-12.9451	-13.887	18	C	5.722455	-15.3946	-13.9773
3	C	2.857546	-12.9452	-13.8883	19	C	7.086963	-15.3946	-13.9761
4	C	3.563427	-11.706	-13.8903	20	C	7.823719	-14.183	-13.9187
5	C	2.826766	-10.4922	-13.8873	21	H	3.340674	-9.53484	-13.8738
6	C	1.461291	-10.494	-13.8887	22	H	0.9469	-9.53632	-13.8901
7	C	3.56365	-14.1831	-13.8917	23	H	3.345516	-16.3507	-13.8118
8	C	2.827144	-15.3958	-13.8524	24	H	0.944814	-16.351	-13.8119
9	C	1.462669	-15.3958	-13.8527	25	H	7.604034	-9.5375	-13.8646
10	C	0.72583	-14.1834	-13.8899	26	H	5.206183	-9.53639	-13.8575
11	C	4.987534	-11.7061	-13.889	27	H	5.204254	-16.3489	-14.0348
12	C	5.691858	-12.9448	-13.9037	28	H	7.605083	-16.3492	-14.0305
13	C	4.985946	-14.1827	-13.9196	29	O	3.983492	20.257	19.22818
14	C	7.118244	-12.9448	-13.9045	30	H	3.055695	20.38831	19.48472
15	C	7.822752	-11.7066	-13.8919	31	H	12.46235	19.48702	18.63447
16	C	7.086996	-10.4934	-13.8776					



7A-GNR TS calculation Step 1, configuration of IS in Figure 5.11

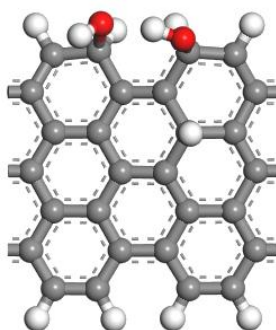
		X	Y	Z			X	Y	Z
1	C	0.472501	-11.6106	-14.0329	21	C	7.570521	-14.0818	-14.0959
2	C	1.174042	-12.8423	-14.0632	22	C	6.859667	-12.8423	-14.065
3	C	2.599726	-12.8423	-14.0627	23	C	7.561243	-11.6104	-14.0367
4	C	3.301211	-11.6105	-14.0311	24	C	6.830053	-10.3995	-14.0138
5	C	2.569918	-10.3998	-13.9978	25	C	5.46379	-10.3996	-14.0108
6	C	1.203686	-10.3997	-13.9985	26	C	5.463718	-17.7637	-14.1908
7	C	3.310487	-14.0818	-14.0952	27	C	6.829914	-17.7638	-14.1907
8	C	2.599721	-15.3212	-14.1276	28	C	7.561266	-16.5529	-14.1597
9	C	1.174006	-15.3213	-14.1277	29	H	3.086653	-9.44363	-13.9722
10	C	0.463236	-14.0818	-14.0957	30	H	0.686674	-9.44381	-13.9713
11	C	0.472461	-16.5529	-14.1598	31	H	0.687024	-18.7198	-14.2163
12	C	1.203813	-17.7638	-14.1909	32	H	3.086873	-18.7198	-14.2165
13	C	2.570016	-17.7637	-14.191	33	H	7.34718	-9.44342	-13.9964
14	C	3.301279	-16.5529	-14.1597	34	H	4.94709	-9.44321	-13.9952
15	C	4.732514	-11.6103	-14.0341	35	H	4.946815	-18.7198	-14.2165
16	C	5.434033	-12.8423	-14.0644	36	H	7.346733	-18.7198	-14.2162
17	C	4.723214	-14.0817	-14.0954	37	O	-4.33284	20.92986	23.26881
18	C	5.434016	-15.3212	-14.1275	38	O	-3.22627	20.07037	23.72977
19	C	4.732453	-16.5529	-14.1595	39	H	3.431668	20.3397	23.46325
20	C	6.859717	-15.3213	-14.1276	40	H	5.691789	19.84276	22.86608



7A-GNR TS calculation Step 1, configuration of FS in Figure 5.11

		X	Y	Z			X	Y	Z
--	--	---	---	---	--	--	---	---	---

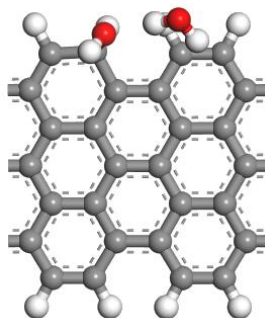
1	C	0.553099	-11.6657	-14.0229	21	C	7.630277	-14.1399	-14.1291
2	C	1.259042	-12.9334	-14.0571	22	C	6.919583	-12.9284	-14.102
3	C	2.679297	-12.9342	-13.987	23	C	7.618745	-11.6623	-14.165
4	C	3.394183	-11.713	-13.8493	24	C	6.92959	-10.5008	-14.326
5	C	2.661858	-10.4411	-13.4953	25	C	5.505855	-10.3888	-13.962
6	C	1.208566	-10.5179	-13.7213	26	C	5.537213	-17.8355	-14.1606
7	C	3.382838	-14.1636	-14.0849	27	C	6.90955	-17.8297	-14.1591
8	C	2.672317	-15.3986	-14.1668	28	C	7.633371	-16.6221	-14.186
9	C	1.251499	-15.3907	-14.1711	29	H	3.059893	-9.60649	-14.1109
10	C	0.550686	-14.1419	-14.1289	30	H	0.660956	-9.59904	-13.5137
11	C	0.549908	-16.6218	-14.2297	31	H	0.750995	-18.7715	-14.4659
12	C	1.27338	-17.8242	-14.3531	32	H	3.161771	-18.7822	-14.4673
13	C	2.64592	-17.8312	-14.3546	33	H	7.456635	-9.5684	-14.5375
14	C	3.374159	-16.6317	-14.2306	34	H	4.977006	-9.6675	-14.6095
15	C	4.776748	-11.7016	-13.965	35	H	5.022036	-18.7928	-14.128
16	C	5.49764	-12.9243	-14.0714	36	H	7.430374	-18.7836	-14.1242
17	C	4.797904	-14.1598	-14.1004	37	O	2.821266	19.89538	17.90248
18	C	5.509212	-15.3968	-14.1486	38	O	5.456731	20.16289	17.42584
19	C	4.80762	-16.6314	-14.1846	39	H	6.012518	20.96448	17.4355
20	C	6.930248	-15.3894	-14.1539	40	H	12.30195	20.10322	17.9976



7A-GNR TS calculation Step 2, configuration of IS in Figure 5.11

		X	Y	Z			X	Y	Z
1	C	0.563411	-11.6306	-14.2514	22	C	6.953506	-12.8986	-13.9777
2	C	1.282916	-12.8979	-14.1495	23	C	7.626836	-11.6383	-14.0457
3	C	2.682494	-12.8955	-14.096	24	C	6.963938	-10.4672	-13.7908

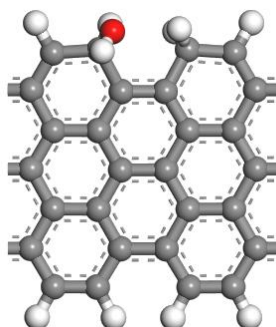
4	C	3.422217	-11.6477	-14.0658	25	C	5.510211	-10.3654	-13.5405
5	C	2.685346	-10.3338	-14.2273	26	C	5.534009	-17.8054	-14.3946
6	C	1.238055	-10.4786	-14.5039	27	C	6.900173	-17.7966	-14.3776
7	C	3.39107	-14.1431	-14.0653	28	C	7.627643	-16.5879	-14.215
8	C	2.672449	-15.3772	-14.1659	29	H	3.1858	-9.70296	-14.9761
9	C	1.25035	-15.3651	-14.1792	30	H	0.704776	-9.54956	-14.7068
10	C	0.55648	-14.1192	-14.1511	31	H	0.742593	-18.761	-14.1483
11	C	0.543256	-16.598	-14.2017	32	H	3.151867	-18.7771	-14.1567
12	C	1.2664	-17.8087	-14.1874	33	H	7.513506	-9.53317	-13.675
13	C	2.637105	-17.8196	-14.1902	34	H	5.107546	-9.55487	-14.1779
14	C	3.371923	-16.6115	-14.2004	35	H	5.016735	-18.7476	-14.5613
15	C	4.761594	-11.6417	-13.8109	36	H	7.428749	-18.7343	-14.5317
16	C	5.511137	-12.9157	-13.5577	37	O	2.760387	20.50449	17.00025
17	C	4.782947	-14.1659	-13.9399	38	O	5.341034	20.02272	17.85077
18	C	5.50031	-15.376	-14.0807	39	H	2.092081	20.12864	17.60686
19	C	4.799771	-16.6072	-14.2284	40	H	4.405141	20.33126	17.87638
20	C	6.932544	-15.367	-14.0958	41	H	14.09497	17.05071	17.56291
21	C	7.642616	-14.1088	-14.0862					



7A-GNR TS calculation Step 2, configuration of FS in Figure 5.11

		X	Y	Z			X	Y	Z
1	C	0.553813	-11.6211	-13.9993	22	C	6.939672	-12.8747	-14.0843
2	C	1.257912	-12.882	-14.0259	23	C	7.629441	-11.6388	-14.0604
3	C	2.688067	-12.8734	-14.0065	24	C	6.893629	-10.4346	-14.0686
4	C	3.392778	-11.6617	-13.9417	25	C	5.526829	-10.4346	-14.0271
5	C	2.694353	-10.3553	-13.73	26	C	5.555656	-17.797	-14.1224

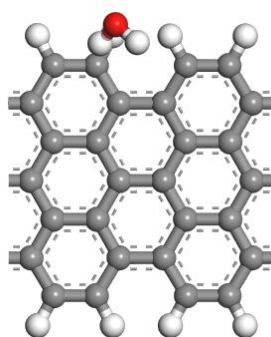
6	C	1.238307	-10.4355	-13.8918	27	C	6.925936	-17.7944	-14.1207
7	C	3.397459	-14.1159	-14.0761	28	C	7.653458	-16.5863	-14.1473
8	C	2.688835	-15.3528	-14.1284	29	H	3.099579	-9.58081	-14.4005
9	C	1.266001	-15.3521	-14.1276	30	H	0.718533	-9.48209	-13.834
10	C	0.557236	-14.1046	-14.0827	31	H	0.774204	-18.7361	-14.4076
11	C	0.566357	-16.5811	-14.1828	32	H	3.181675	-18.7406	-14.4065
12	C	1.295124	-17.7877	-14.2979	33	H	7.405247	-9.47565	-14.0882
13	C	2.663328	-17.7906	-14.298	34	H	5.007081	-9.48083	-13.9866
14	C	3.392508	-16.5861	-14.1843	35	H	5.039072	-18.7532	-14.0882
15	C	4.8009	-11.6533	-14.0168	36	H	7.444712	-18.7493	-14.0846
16	C	5.517026	-12.8849	-14.0745	37	O	2.991066	20.20642	17.61208
17	C	4.811185	-14.1183	-14.0926	38	O	5.444428	20.68016	19.16684
18	C	5.523849	-15.3567	-14.1232	39	H	2.521776	19.6329	18.24806
19	C	4.824557	-16.5876	-14.1479	40	H	4.661421	20.5622	18.58997
20	C	6.949494	-15.3496	-14.125	41	H	6.052654	19.99229	18.85086
21	C	7.653315	-14.1136	-14.1008					



7A-GNR TS calculation Step 3, configuration of IS in Figure 5.11

		X	Y	Z			X	Y	Z
1	C	0.534918	-11.6411	-13.9752	21	C	7.598406	-14.1234	-14.1226
2	C	1.228137	-12.9154	-14.0419	22	C	6.893223	-12.9119	-14.1149
3	C	2.650158	-12.917	-14.0114	23	C	7.59756	-11.6394	-14.1198
4	C	3.369515	-11.6961	-13.9463	24	C	6.919142	-10.4751	-14.2787
5	C	2.67675	-10.3879	-13.6791	25	C	5.453926	-10.3764	-14.2025
6	C	1.209603	-10.4839	-13.7418	26	C	5.504937	-17.8234	-14.2049
7	C	3.352001	-14.1486	-14.0964	27	C	6.876758	-17.8138	-14.2054

8	C	2.640419	-15.3843	-14.1433	28	C	7.599269	-16.6063	-14.1818
9	C	1.219425	-15.3742	-14.144	29	H	3.022247	-9.61878	-14.3934
10	C	0.519641	-14.1224	-14.1095	30	H	0.676625	-9.54999	-13.5636
11	C	0.516958	-16.6056	-14.1827	31	H	0.720469	-18.7672	-14.2509
12	C	1.239823	-17.8128	-14.2201	32	H	3.123609	-18.7796	-14.2502
13	C	2.611744	-17.8207	-14.2207	33	H	7.462528	-9.54037	-14.4201
14	C	3.341686	-16.6185	-14.1838	34	H	5.060353	-9.81311	-15.0737
15	C	4.746997	-11.6908	-14.0878	35	H	4.993524	-18.7826	-14.2244
16	C	5.468231	-12.912	-14.1271	36	H	7.396537	-18.7684	-14.2242
17	C	4.766476	-14.148	-14.1218	37	O	3.090883	20.18283	17.61148
18	C	5.477652	-15.385	-14.1525	38	H	2.760611	19.56292	18.28829
19	C	4.775919	-16.6199	-14.1799	39	H	5.186518	20.2608	16.66189
20	C	6.898093	-15.3745	-14.1545					



7A-GNR TS calculation Step 3, configuration of FS in Figure 5.11

		X	Y	Z			X	Y	Z
1	C	0.514249	-11.6821	-14.0816	21	C	7.614325	-14.1538	-14.1172
2	C	1.217372	-12.9141	-14.0989	22	C	6.903541	-12.9146	-14.073
3	C	2.643403	-12.9147	-14.1012	23	C	7.603691	-11.683	-14.0224
4	C	3.346698	-11.6829	-14.0902	24	C	6.873532	-10.4771	-13.8778
5	C	2.615204	-10.4712	-14.1665	25	C	5.505114	-10.4757	-13.8787
6	C	1.244695	-10.4714	-14.1569	26	C	5.507786	-17.836	-14.1972
7	C	3.354264	-14.1545	-14.1164	27	C	6.874011	-17.8359	-14.1973
8	C	2.643517	-15.3939	-14.1419	28	C	7.605313	-16.625	-14.1738
9	C	1.217998	-15.3937	-14.1416	29	H	3.136604	-9.52047	-14.259

10	C	0.507054	-14.1542	-14.1148	30	H	0.723973	-9.51934	-14.2404
11	C	0.516531	-16.6253	-14.1719	31	H	0.731094	-18.7923	-14.2268
12	C	1.247781	-17.8362	-14.2012	32	H	3.130702	-18.7925	-14.2267
13	C	2.614013	-17.8364	-14.2012	33	H	7.396882	-9.53366	-13.7356
14	C	3.345175	-16.6254	-14.1721	34	H	4.981011	-9.53426	-13.7281
15	C	4.777088	-11.683	-14.0281	35	H	4.991322	-18.7924	-14.2143
16	C	5.477707	-12.9146	-14.0753	36	H	7.390561	-18.7923	-14.2146
17	C	4.767071	-14.1539	-14.1193	37	O	3.230731	20.82833	18.76952
18	C	5.477962	-15.3933	-14.1488	38	H	3.927776	20.26064	19.13853
19	C	4.776386	-16.6251	-14.174	39	H	2.732098	20.22292	18.1909
20	C	6.903622	-15.3932	-14.1482					

List of publications

(1) Sakaguchi, H.; Kojima, T.; **Cheng, Y.**; Nobusue, S.; Fukami, K. Electrochemical On-Surface Synthesis of a Strong Electron-Donating Graphene Nanoribbon Catalyst. *Nature Communications* **2024**, 15 (1), 5972.

(Chapters 3 and 4)

(2) **Cheng, Y.**; Kojima, T.; Fukami, K.; Sakaguchi, H. Oxygen-Doped Graphene Nanoribbons with High Catalytic Performance in Chemical Etching of Silicon. *Journal of Physical Chemistry C* **2025**, 129, 4086–4096.

(Chapter 5)

Presentations at conferences

(1) **Yingbo Cheng**, Takahiro Kojima, Hiroshi Sakaguchi. Electrochemical Room Temperature growth of Functionalized GNR, *The 14th International Symposium of Advanced Energy Science*.

(2) **Yingbo Cheng**, Takahiro Kojima, Shunpei Nobusue, Kazuhiro Fukami, Hiroshi Sakaguchi. Electrochemical on-surface synthesis of oxygen-doped graphene nanoribbon catalyst, *The 105th CSJ Annual Meeting*.

Acknowledgement

I feel lucky to have had the chance to study abroad for my doctoral degree in Japan. It is not only an experience of study, but also a good memory in my life. I want to express my appreciation to all the professors and students I studied with over the past three years.

I would like to express my deepest gratitude to my supervisor, Prof. Hiroshi Sakaguchi, whose guidance, encouragement, and support have been central to the completion of this doctoral thesis. I am truly fortunate to have had the opportunity to learn under his supervision.

I am also grateful to all members of the Sakaguchi Laboratory:

Assoc. Prof. Takahiro Kojima, Asst. Prof. Shunpei Nobusue, Asst. Prof. Krishnamoorthy Sathiyar, Qiu Pengcheng, Tang Hong, Xie Cong, Wu Wei, Gui Fukang, Wang Jiameng, Matsuyama Ren, Fu Yuxin, Wang Ziwei, Nakajima Jo, Li Jiaxuan, Oh Junseok, Tateyama Shutaro, Liu Hao Yang, Li Zexiao, Jiang Dehao.

They fostered an inspiring research environment and offered invaluable support throughout my studies. I extend my sincere gratitude to my colleagues and friends, whose insightful discussions, thoughtful advice, and warm camaraderie have made this journey both intellectually enriching and personally meaningful.

Thanks to Prof. Toshiyuki Nohira and Prof. Eiji Nakata for reviewing this thesis.

Thanks to Prof. Kazuhiro Fukami and Atsuya Tada for their support in the

Si etching experiment.

Finally, I would like to express my heartfelt gratitude to my family for their unwavering love, understanding, and encouragement. Their support has been my most significant source of strength throughout this journey.