# Graphene

## Mechanical Properties, Potential Applications and Electrochemical Performance

### Bruce T. Edwards
Editor

*Chemistry Research and Applications*

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# GRAPHENE

# MECHANICAL PROPERTIES, POTENTIAL APPLICATIONS AND ELECTROCHEMICAL PERFORMANCE

BRUCE T. EDWARDS

EDITOR

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# PREFACE

Graphene has drawn considerable scientific and commercial interest thanks to its unique structure, including being single-atom thick, strictly two-dimensional and highly conjugated, which results in some superb electric, optical, mechanical and thermal properties. In this book the authors present current research in the application of graphene in sensing technology; the adsorption of hexavalent chromium from aqueous solutions by graphene modified with cetyltrimethylammonium bromide; graphene-non-noble metal hybrid nanomaterials as advanced electrocatalysts; the application of graphene in mass spectrometry; the incorporation of graphene into direct-patternable transparent conducting oxide thin films; graphene and related nanomaterials for environmental remediation; and configurations of structural defects in graphene and their effects on its transport properties.

Chapter 1 – Graphene has drawn considerable scientific and commercial interest thanks to its unique structure, including being single-atom thick, strictly two-dimensional and highly conjugated, which results in some superb electric, optical, mechanical and thermal properties. These properties combined with the inherent benefits of the nanocarbon materials make graphene a promising material for the applications in electronics, quantum physics, novel materials and chemistry. In this chapter the authors mainly discuss the recent advance of graphene-based materials in sensing technology including chemical sensors, biosensors, immunosensors for the application in security, enviromental safety and various diseases detection and analysis. The techniques for the preparation of graphene, such as mechanical exfoliation, thermal deposition, chemical vapor deposition (CVD), unzipping CNT, reduction of graphite oxide, particularly the matrix-assisted direct exfoliation of graphene from graphite are briefly introduced in this chapter.

Chapter 2 – In this study, cetyltrimethylammonium bromide was chosen to modify graphene which was prepared using a modified Hummers' method. The characteristics of graphene and modified graphene were characterized by X-ray diffraction, fourier transform infrared spectrum, X-ray photoelectron spectroscopy, transmission electron microscopy and scanning electron microscopy. The effect factors including pH, contact time, temperature and dosage on the adsorption properties of Cr(VI) onto graphene and modified graphene were investigated. Batch experiments were conducted to evaluate the adsorbance of Cr(VI) from aqueous solution using graphene and modified graphene as the adsorbent under different conditions. The results revealed that the optimal pH for the adsorption was about 2, and the best suitable temperature was at 293 K. The adsorption processes were rapid within the first 5 min and reached equilibrium in about 40 min. The adsorption kinetics fitted well with pseudo-second-order model. The adsorption capacity of Cr(VI) on modified graphene inferred from the Langmuir model was 21.57 mg/g at 293 K. The thermodynamic parameters indicated that the adsorption of Cr(VI) onto modified graphene was an exothermic and spontaneous process.

Chapter 3 – Graphene, as the fundamental 2D carbon structure with exceptionally high crystal and electronic quality, has emerged as a rapidly rising star in the field of material science. Its discovery in 2004 led to an explosion of interest in the study of graphene with respect to its unique physical, chemical, and mechanical properties, opening up a new research area for multidisciplinary fields, and aiming for wide-ranging and diversified technological applications. On the other hand, due to the large surface area and high catalytic activity, nanomaterials exhibit promising applications in fuel cells as advanced electrocatalysts. In this chapter, the authors highlight recent advances in the development of graphene-non-noble metal nanomaterials from the standpoint of electrocatalysts. The unique properties of graphene will be discussed firstly. The exciting progress related to graphene-based nanomaterials in electrocatalysts in recent years, including graphene or its derivative (heteroatom doped graphene, etc.), and graphene-supported metal non-noble nanoparticles are summarized in detail.

Chapter 4 – This chapter reviews the up-to-date research about the application of graphene and its relatives in mass spectrometry (MS). Due to its large specific surface area, large delocalized $\pi$-electrons, thermal conductivity, stability and rich interaction chemistry, graphene has been widely used in MS study. Graphene and graphene-based materials were applied as very effective matrices for many kinds small molecules in matrix-assisted laser desorption/ionization (MALDI) MS analysis. Many advantages of this novel

matrix have been proved, which included: low interference ions from matrix itself, good reproducibility, high salt tolerance, less accompanied reduction and so on. The unique properties of graphene also make it a superior sorbent used in solid-phase extraction (SPE). Further development of on-line SPE methods based on graphene coupled with MALDI-MS, GC-MS and LC-MS greatly simplifies the analytical procedure for complex samples and makes the high-throughput and automatic analysis possible. And its potential in rapid analysis of environmental contaminants has been gradually revealed by more and more research groups. Their applications as a platform in proteolysis for the rapid identification of proteins are also presented here. In addition, laser ablation mass spectra of graphene and graphene oxide have been studied. Graphene was also found to be a unique precursor for the generation of large-sized carbon cluster anions in the gas phase.

Chapter 5 – Transparent metal oxide thin films, such as zinc oxide (ZnO) and tin dioxide ($SnO_2$) thin films, have been increasingly studied due to their high optical transparency with electrical conducting property, high chemical durability and low cost. An incorporation of graphene into direct-patternable transparent metal oxide thin films was carried out to enhance the electrical conducting property. Metal precursors, solvent, and photosensitive additive were used for the synthesis of stock solutions. After addition of graphene, the solution was spin-coated and the coated film was exposed to ultraviolet (UV) light of 365 nm. Then, the UV exposed film was washed by solvent and the direct-patterned film was annealed to form a desired pure phase system. From the results of UV-vis spectra, X-ray diffractometer, Hall effect measurement and photoelectron spectroscopy of the graphene incorporated metal oxide thin films, the authors can deduce the effect of graphene in transparent metal oxide thin films.

Chapter 6 – It has been widely acknowledged that finding solutions to environmental problems that we are facing now has become a top priority. Environmental problems are highly complex and often vary in scale ranging from local to global dimensions. The advent of graphene revolution in recent years has provided immense scope and opportunities for environmental remediation. Graphene, and its related materials such as graphene oxide, reduced graphene oxide and their nanocomposites can all function as adsorbents and catalysts for the effective removal and degradation of recalcitrant organic pollutants (e.g., dyes, phenolic compounds, polycyclic aromatic hydrocarbons), toxic inorganic contaminants (e.g., heavy metals) and harmful biological substances (e.g., bacteria, microcystins), present invariably in the aquatic environment. Graphene-based materials are also popular in

decontaminating industrial waste gaseous streams containing various air pollutants such as $NH_3$, $H_2S$, $SO_x$, $NO_x$, etc. This chapter aims at bringing together the current knowledge available in the development and use of graphene and its related nanomaterials for environmental clean-up. This synthesis of advanced knowledge in graphene, an emerging field of interest, will help in fuelling further innovations in the development of novel graphene-based nanomaterials for environmental pollution control and abatement, a topic of current global interest.

Chapter 7 – The chapter combines analytical (statistical-thermodynamic and kinetic) with numerical (Kubo–Greenwood-formalism-based) approaches used to ascertain an influence of the configurations of point (impurities, vacancies) and line (grain boundaries, atomic steps) defects on the charge transport in graphene. Possible substitutional and interstitial graphene-based superstructures are predicted and described. The arrangements of dopants over sites or interstices related with interatomic-interaction energies governing the configurations of impurities. Depending on whether the interatomic interactions are short- or long-range, the low-temperature stability diagrams in terms of interaction-energy parameters are obtained. The dominance of intersublattice interactions in competition with intrasublattice ones results in a nonmonotony of orderingprocess kinetics. Spatial correlations of impurities do not affect the electronic conductivity of graphene for the most important experimentally-relevant cases of point defects, neutral adatoms and screened charged impurities, while atomic ordering can give rise in the conductivity up to tens times for weak and strong short-range potentials. There is no ordering effect manifestation for long-range potentials. The anisotropy of the conductivity along and across the line defects is revealed and gives rise in the conductivity of graphene with correlated line defects as compared with the case of random ones. Simultaneously correlated (and/or ordered) point and line defects in graphene can give rise in the conductivity up to hundreds times vs. their random distribution. On an example of different B or N doping configurations in graphene, results from the Kubo–Greenwood approach are compared with those obtained from DFT method.

# CONTENTS

*Chapter 1*

# APPLICATION OF GRAPHENE IN SENSING TECHNOLOGY

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## ABSTRACT

Graphene has drawn considerable scientific and commercial interest thanks to its unique structure, including being single-atom thick, strictly two-dimensional and highly conjugated, which results in some superb electric, optical, mechanical and thermal properties. These properties combined with the inherent benefits of the nanocarbon materials make graphene a promising material for the applications in electronics,

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quantum physics, novel materials and chemistry. In this chapter we mainly discuss the recent advance of graphene-based materials in sensing technology including chemical sensors, biosensors, immunosensors for the application in security, enviromental safety and various diseases detection and analysis. The techniques for the preparation of graphene, such as mechanical exfoliation, thermal deposition, chemical vapor deposition (CVD), unzipping CNT, reduction of graphite oxide, particularly the matrix-assisted direct exfoliation of graphene from graphite are briefly introduced in this chapter.

# 1. INTRODUCTION

In recent years, nanomaterials have evidenced rapidly advance since the emergence of a two-dimensional material, graphene, which consists of hexagonal configuration with $sp^2$ bonded carbon atoms. The experimental isolation of individual graphene sheets was first achieved with a simple repeated peeling process by Geim and Novoselov in 2004.[1] Since then, large numbers of scientists have created ingenious methods to synthesize monolayered graphene flakes, including mechanical and matrix assisted exfoliations,[2-4] thermal deposition,[5,6] chemical vapor deposition (CVD),[7,8] unzipping CNT,[9,10] and reduction of graphite oxide.[11,12] Each of these preparation methods has some advantages for specific applications, but also has some drawbacks. For example, graphene prepared by mechanical exfoliation and cleavage exhibits high carrier mobility and low density of defects, therefore it can be used for fabrication of electronics. However, mechanical exfoliation is a time consuming process which can not be applied for large-scale production of graphene. The oxidation-reduction method for producing graphene from graphite can be used for mass production, whereas the as-prepared graphene nanosheets usually retain smaller size, high defects and low electrical conductivity.

Though graphene is the most recently discovered member of the nanocarbon family, it has already been intensively applied in various fields due to its unique chemical and physical properties (such as superior electrical conductivity, excellent mechanical flexibility, large surface area and high thermal and chemical stability). For instance, graphene was explored for the wide application in energy field, attributed to its high conductivity, transparency and ultrathin sheets.[13-16] Owing to the large specific surface area (2630 $m^2$ $g^{-1}$),[17] excellent mechanical strength and aromatic–rich structure, graphene can be applied as pollutant adsorbents by strong interaction

between graphene surface and small molecules, as well as catalyst or catalytic support for fuels and photo degradation of organics.[18-22] Moreover, graphene plays a crucial role in sensing application which utilize graphene's exceptional electrical properties (e.g., extremely high carrier mobility and capacity), electrochemical properties (e.g., high electron transfer rate), optical properties (e.g., excellent ability to quench fluorescence), structural properties. In this chapter, we place the emphases on graphene-based materials for their applications for the detection of gas, heavy metal ions, protein, glucose and bacteria etc.

## 2. Preparation of Graphene

Since Geim and Novoselov et al.[1] were credited for the successful preparation of graphene by the now famous Scotch tape method in 2004, many methods have been reported on the synthesis of graphene. Generally speaking, these methods can be classified as exfoliation, thermal decomposition, chemical vapor deposition (CVD), unzipping CNT, thermal reduction and oxidation-reduction etc, which will be described below.

### 2.1. Mechanical and Matrix-Assisted Exfoliation

Exfoliation, a repeated peeling process to prepare graphene from highly-oriented pyrolytic graphite (HOPG).[1] Using this technique, graphene samples obtained were virtually free of crystal defects, resulting in high carrier mobility. Likewise, Shukla et al.[2] prepared mm-sized single- to few-layer graphene by bonding bulk graphite to borosilicate glass under a particular temperature and voltage, followed by exfoliation to leave single- or few-layer of graphene on the substrate. However, mechanical exfoliation is a time consuming process and cannot be scaled for industrial large-scale production. Therefore, other exfoliation methods have been developed.

It was found that graphene can be exfoliated directly from graphite in organic solvents such as N-methyl-pyrrolidone.[3] The monolayer graphene yield reached 7-12 wt % by further processing. Similar approach was adopted to obtain garphene sheets by sonication of natural graphite crystals in dimethylformamide (DMF).[23] Solution based exfoliation of graphite showed a new window for large-scale production of graphene. Graphene was prepared using a similar process of liquid based exfoliation in water-surfactant solutions

with the aid of ultrasound.[4] Another group also reported the exfoliation-reintercalation-expansion of graphite to produce high-quality single-layer graphene sheets (GSs) stably suspended in DMF (Figure 1).[24] Gram-scale carbon nanosheets can be prepared by low-temperature flash pyrolysis of a solvothermal product of sodium and ethanol, followed by mild sonication of the nanoporous carbon product.[25]
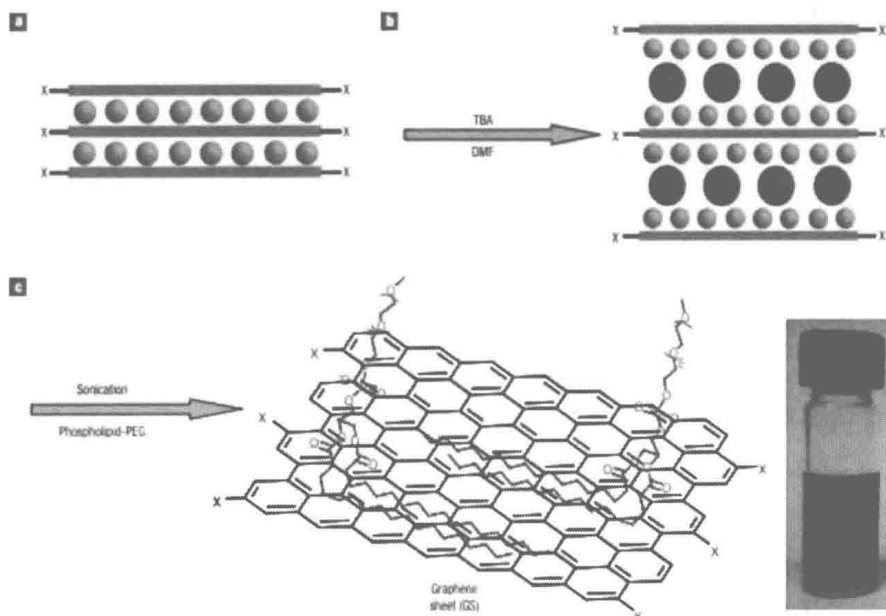


Figure 1. Chemically derived single-layer GS from the solution phase. a), Schematic of the exfoliated graphite reintercalated with sulphuric acid molecules (teal spheres) between the layers. b), Schematic of tetrabutylammonium hydroxide (TBA) (blue spheres) insertion into the intercalated graphite. c), Schematic of GS coated with 1,2-distearoyl-sn-glycero-3-phosphoethanolamine-N-[methoxy(polyethyleneglycol)-5000] (DSPE-mPEG) molecules and a photograph of a DSPE-mPEG / DMF solution of GS.

Moreover, enormous research focused on the preparation of graphene by non-destructive $\pi$–$\pi$ stacking interactions between the aromatic molecules and graphite microplatelets. Jang et al.[26] reported a supercritical fluid (SCF) method to obtain high quality graphene sheets by introducing 1-pyrene sulfonic acid sodium salt (1-PSA) during the SCF exfoliation. This process could result in homogeneously modified graphene nanosheets (GNS) via the $\pi$–$\pi$ interaction between the graphene layer and aromatic ring of the modifier molecules without any damages to the graphene surface and its electronic

conductivity. Likewise, single stranded DNAs modified 1-pyrenebutyric acid was also utilized to prepare a water-dispersible single-layered graphene from exfoliation of graphite flakes.[27] Later, the amphiphilic copolymers, consisting of a mono- or multi-pyrene units, were designed to selectively exfoliate graphite powder into single- and double-layer graphene sheets in aqueous or organic media.[28,29] Stable suspensions of graphene nanosheets were also successfully produced by using chemical exfoliation of graphite oxide and then reducing it to graphene.[30]

## 2.2. Thermal Decomposition

The thermal decomposition of silicon carbide (SiC) is a technique employed for the fabrication and processing of graphene materials. When SiC is heated in ultra-high vacuum (UHV) to temperatures between 1000 °C and 1500 °C, Si will sublimate and leave behind a carbon rich surface. Bergen et al.[5] prepared ultrathin epitaxial graphite films on the Si-terminated (0001) face of single-crystal 6H-SiC by thermal decomposition of SiC. The Si face was treated by oxidation or $H_2$ etching, followed by being heated via electron bombardment in ultrahigh vacuum to 1000 °C in order to remove the oxide. After deoxygenation, samples were heated to temperature ranging from 1250 °C to 1450 °C for 1-20 min and thin graphite layers were formed. The graphene layers were from 1 to 3 and the thickness of graphene mainly relies on the temperature. Likewise, graphite thin films were synthesized by thermal decomposition and demonstrated the successful growth of single crystalline films down to approximately one graphene layer.[31] Lin et al.[6] fabricated graphene field-effect transistors (FETs) on a 2-inch graphene wafer, made by epitaxially grown on the Si face of high-purity SiC wafer via thermal annealing at 1450 °C and further demonstrated the high potential application of graphene for electronic devices. However, vacuum decomposition of SiC yields graphene layers with small grains. To solve this problem, *ex* situ graphitization of SiC under 900 mbar of argon was performed to prepare monolayer graphene films with much larger domain sizes (more than 50μm in length) and high electronic mobility of 2,000 $cm^2$ $V^{-1}$ $s^{-1}$.[32] In addition, Juang et al.[33] presented a modified method of thermal decomposition to fabricate millimeter-scaled graphene films on silicon carbide substrates at low temperatures (750 °C).

In a similar approach by Sutter et al.,[34] epitaxial graphene was grown on the (0001) surface of ruthenium (Ru). They found that interaction between the

first graphene layer and metal substrate was strong, while the second layer was almost completely detached, showing weak electronic coupling to the metal. This result showed that graphene sheets obtained through this approach retained the inherent electronic structure of graphene. This finding provided a feasible route towards rational graphene synthesis on transition-metal templates. Another independent study[35] has also reported on epitaxial graphene monolayer grown on Ru (0001) covering uniformly the substrate over lateral distances larger than several microns, with periodical ripple and spatial extensibility.

## 2.3. Chemical Vapor Deposition (CVD)

In addition to the thermal decomposition of SiC, graphene with high structural quality and large area can also be obtained through low-pressure chemical vapor deposition, in which carbon is supplied in gas form and a metal is used as both catalyst and substrate to grow the graphene layer. Somani et al.[7] reported for the first time the synthesis of plane few-layer graphenes (PFLG) from camphor pyrolysis on nickel substrates by a simple, cost-effective thermal CVD method. Graphene sheets prepared by Acro et al.[36] via the CVD method exhibited high transmittance of 80 % in the visible wavelength range. Another recent study[37] has shown that the synthesis of large area, few-layer graphene films on polycrystalline Ni films via ambient pressure CVD, which can be transferred to arbitrary substrates, keeping its electrical properties unchanged. The as-prepared graphene films with 3 nm average thickness transferred onto a glass substrate exhibited high optical transmittance of ~ 90 % in the 500-1000 nm wavelength regime. Similarly, single- or multi-layered graphene sheets with high transmittance, electrical properties and large size have also been successfully prepared by a few other groups.[38,39] The CVD methods was also conducted on the copper substrate to prepare graphene sheets with similar properties.[40,41] It indicated that the process was the surface mediated and self-limiting. A roll-to-roll process has also been developed to produce graphene monolayer up to 30-inch by CVD on copper.[8]