2D MATERIALS: CHEMISTRY AND APPLICATIONS PART 1

Editor: Vinay Deep Punetha

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2D Materials: Chemistry and Applications

(Part 1)

Edited by

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PREFACE

In the rapidly evolving field of materials science, the exploration and utilization of twodimensional (2D) materials have marked a revolutionary shift in how scientists and engineers approach the empirical evidence in developing new technologies. Among these materials, graphene stands out due to its exceptional electrical, thermal, and mechanical properties, which have led to its exploration across various domains—from energy storage and environmental engineering to biomedicine and electronics. This book, "2D Materials: Chemistry and Applications," aims to capture the holistic view and essence of recent research and advancements by evidence based assessment of advancements in its fundamental chemistry and mushrooming usage in copious applications.

The opening chapter of this book provides a foundational understanding of graphene and its structure at the molecular level, various types of defects, synthesis methods, and functionalization techniques, with the inclusion of recent advancements. This groundwork is crucial for both seasoned researchers and newcomers to the field, helping them in understanding the differentiating properties of graphene along with strategies that allow surface revamping and exploration of this material in various applications.

As the chapters progress, the focus shifts to more complex constructs such as hybrid materials combining graphene with various nanoparticles. These hybrids exhibit unique resonance of individual properties of graphene and the nanoparticles that can be harnessed for several established and emerging applications, including sensors, catalysis, and energy conversion technologies. This discussion leads naturally into a detailed examination of multifunctional graphene-based nanocomposites, which are positioned at the cutting edge of materials research with their ability to perform multiple functions simultaneously.

Further, the book investigates the life sciences applications of graphene, illustrating its potential in gene and drug delivery systems where it promises to increase efficiency and targeting accuracy. The subsequent chapters explore the role of graphene in biomedical imaging and its emerging significance in microbial control, where its properties can be leveraged to offer new solutions in fighting infections and enhancing hygiene.

One of the most compelling areas of graphene application covered in this book is in cancer therapy. Graphene-based materials have been identified as potent tools in the diagnosis and treatment of cancer, reflecting a major theme of contemporary research efforts. Additionally, the application of graphene in tissue engineering is discussed, providing insights into its use in constructing scaffolds that mimic the extracellular matrix for tissue regeneration.

The final chapter looks at the broader implications of graphene derivatives in biotechnology, underscoring the vast potential of these materials to influence future developments in science and engineering.

"2D Materials: Chemistry and Applications" is designed to serve as a comprehensive resource for scientists, engineers, and students who are engaged in or entering the field of graphene research. It aims to inspire further innovations and applications of this remarkable material, paving the way for new solutions to some of the world's most pressing challenges. Through this book, we invite readers to explore the multifaceted world of graphene and envision the future it is capable of creating.

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CHAPTER 1

1

Graphene: Understanding its Structure, Synthesis, and Functionalization

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Abstract: Material science has gone through several evolutionary stages; especially the discovery of graphene has added one of the most defining chapters in this journey. Owing to the enormous potential of this material in various applications, a tremendous pace can be seen in the development of graphene-derived materials and technologies. The 2D revolution in material science can be marked by the shift from the bulk form of materials to their intelligent and efficient two-dimensional (2D) analogs and their use in developing innovative contrivances. Various forms of 2D graphene have recently evolved, including mainly monolayer graphene, bilayer graphene, graphene oxide, graphene nanoribbons, and graphene quantum dots. These materials have shown great potential to revolutionize various aspects of human life, from electronics and actuation to healthcare and energy.

Its exceptional properties make it an ideal candidate for various applications. Continuing explorations and epistemological pieces of evidence will likely reveal even more prospective applications. The book chapter deals with a concise overview of the structural aspects of graphene, the presence of defects, methods of synthesis, and functionalization. The chapter will help develop an essential understanding of the critical aspects of science and recent developments around it. This chapter aims to provide a quick and easily understandable summary of various complex aspects of it by reducing irrelevant or extraneous information.

Keywords: Applications, Armchair, Cove, Defects, Fjord synthesis, Functionalization, Graphene, Gulf, 2D materials.

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INTRODUCTION

Two-dimensional (2D) materials are characterized by their nano-dimensions, which fall between 0.3 and 100 nanometers. They consist of mostly a single layer of atoms in two dimensions with atomic thickness. However, a few layers of atoms can also be seen if left for a period due to stacking or agglomeration. The 2D materials include Xenes (2D materials of 14 group elements), transition metal dichalcogenides (TMDs), such as molybdenum disulfide (MoS2), boron nitride (BN), and black phosphorus (BP) [1], The scientific community is particularly interested in the 14 group 2D materials due to their chemical and optoelectronic properties. Recent efforts have concentrated on exploring and realizing the vast potential of these materials. The critical elements of this class include 2D structures of carbon (C), silicon (Si), germanium (Ge), tin (Sn), and lead (Pb) with graphene, silicene, germanene, tinene, and plumbene as their respective 2D analogs. Graphene is the most studied material with concrete experimental evidence. Primarily theoretical investigations using density functional theory (DFT) have been performed so far with heavier 2D analogs such as tinene and plumbene. The reduced dimension and high surface-to-volume ratio of these materials offer exceptional physics with significant applications in optoelectronics, mechanical, thermal, and biological applications [2]. Graphene, in particular, and its derivatives have found astounding applications in various fields due to nonpareil properties, such as its ability to transmit electric current and the potential to bear mechanical forces or stresses such as tension, compression, bending, or torsion. In addition, graphene allows tuning various matrices as reinforcing material with opportunities to develop the next generations of composite materials [2]. As a reinforcement material, graphene offers excellent strength, stiffness, and several other desirable properties. These composites have shown incredible potential in developing numerous applications such as remote actuation, soft robotics, disease diagnosis, cancer therapy, targeted drug delivery, bio-imaging, and many more and quite elaborately discussed in the review article by Punthea et al. [3]. Several forms of graphene have been studied extensively in recent times. A summary of these forms is given in Table 1. Monolayer graphene, graphene oxide, and functionalized graphene oxide are the most investigated forms of graphene in various applications (Fig. 1). However, graphene structures such as nanoribbons, quantum dots, and 3D graphene are relatively new in their exploration journey [4]. Nanoribbons are thin strips of nanomaterials that are only a few nanometers wide and can be made from a variety of materials, quantum dots are tiny semiconductor particles that are only a few nanometers in size and 3D graphene, on the other hand, is a three-dimensional form of graphene that has a complex, porous structure. All three materials are currently being studied and developed for a wide range of applications, and their unique properties make them promising candidates for future technologies.

Graphene

S. No.	Form of Graphene	Description	Refs.
1.	Monolayer Graphene	The simplest form of graphene with a consistent sp ² framework.	[2]
2.	Multilayer graphene	Inter-planer interaction between sheets to form multilayers due to stacking.	[4]
3.	Graphene oxide (GO)	Graphene with oxidized surface	[3, 5]
4.	Reduced GO	It is synthesized by reducing GO with less oxygen-containing functional moieties.	[3, 6]
5.	Functionalized Graphene	Form of graphene synthesized by adding different active guest molecules <i>via</i> covalent or non-covalent interactions.	[3]
6.	Graphene nanoribbons	A form of graphene in narrow 1D strips with starkly unique physics.	[4, 7]
7.	Graphene quantum dots	Zero-dimensional form of graphene with all three dimensions less than 10nm.	[4, 7]
8.	Graphene foam	Porous interconnected graphene sheets.	[4, 7]
9.	Graphene Nano flakes	Small pieces of graphene have a thickness ranging from a few to several hundred nanometers.	[4, 7]
10.	3D graphene	Creating a 3D scaffold of graphene monolayers by creating deliberate defects on the surface.	[8]

Table 1. Various forms of graphene with their short description.

One of the most sophisticated tasks is to synthesize pristine graphene; especially the commercial production of monolayer graphene has witnessed many obstacles [5]. Various methods have been proposed recently for synthesizing graphene and graphene derivatives. These methods can be categorized into top-down and bottom-up methods [6]. In the top-down method, the bulk precursor is broken down to the required size by applying mechanical forces. Simultaneously, the bottom-up approach deals with the synthesis of graphene structure by using atomic precursors. The top-down approach is good when it comes to the commercial production of these materials. At the same time, the bottom-up method generally deals with producing consistent 2D graphene-like skeletons with high quality [6, 7]. The chapter, in detail, discusses these approaches with extended discussions of their added pros and cons.

The functionalization of graphene is another crucial aspect, which has been discussed in detail in this chapter. Functionalization refers to the surface revamping of graphene to modify its properties by structural manipulations on its atomic organization. Functionalization plays a pivotal role in significantly altering the characteristics of graphene, opening up a multitude of possibilities for its widespread utilization across various applications (Fig. 2). In popular science,

Hybrid Materials of Graphene and Nanoparticles: Synthesis and Emerging Applications

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Abstract: Recently, nanoparticle-functionalized graphene materials have been in the spotlight due to their exceptional properties. A pristine graphene sheet is an attractive candidate for the dispersion of nanoparticles due to its large active surface area compared to other carbon allotropes. Moreover, pristine graphene possesses electrical and mechanical strength, which gives it a unique architecture. The chemical functionalization of graphene intends to revamp its properties and elevate its use in multiple applications by incorporating different functional groups. There are two main approaches to the functionalization process, either based on covalent or noncovalent. This chapter elaborates on the major strategies employed for the nanoparticles functionalized graphene. The precursors of nanoparticles are metal salts which are reduced in the solvent of the desired substrate. The strategies above involve the deposition of metal nanoparticles, metal oxide nanoparticles, and quantum dots on graphene substrate. The functionalization of graphene improves its dispersion capacity and sets forth new properties, which broadens its scope of applications. Furthermore, we aim to focus on the potential of materials derived from nanoparticle functionalization in various applications such as wastewater management, biomedical devices, photocatalysis, food additives detection, supercapacitors, electrochemical gas sensors, and energy storage, flexible electronics, photonics, photovoltaic systems, and catalysts. We aspire that the readers will learn the synthetic strategies for the functionalization of graphene along with guidance and inspiration on the emerging trends towards applications of interest. This chapter surveys various properties and applications of nanoparticle-functionalized graphene.

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Hybrid Materials of Graphene

Keywords: Applications, Biomedical, Functionalization, Graphene, Nanoparticles, Photocatalysis, Sensors, Wastewater.

INTRODUCTION

In terms of mass, carbon is the most common element in the universe, and it has several intriguing characteristics. Three main carbon types are diamond, graphite, and charcoal. It may be further classified due to its chemical makeup, namely its hybridization state and molecular configurations. The carbon isotope found in graphite is the subject of the current study. Diamond, fullerene, and carbon nanotubes are more carbon allotropes. Carbon-based materials exhibit increased viability features and structural changes by incorporating additional functions [1]. Due to its distinctive structure, graphene is the newest substance in materials research. In two and three-dimensional orientations, graphene exhibits excessive mechanical strength and electrical characteristics [2]. The most scholarly focus over the past 20 years has been fabricating graphene/graphene oxide with tailored shapes [3]. Hybrid materials of graphene refer to composites or combinations where graphene is integrated with other materials to create new functional properties. These materials leverage the unique properties of graphene, such as high mechanical strength, electrical conductivity, and thermal conductivity, to enhance the performance of the composite material [4]. The integration of graphene into different matrices, such as polymers, metals, ceramics, and carbonbased materials, allows for the development of hybrid materials with improved mechanical, electrical, and thermal properties. They offer advantages such as increased strength, enhanced conductivity, improved thermal management, and superior barrier properties. Fig. (1) showcases a momentous historical event in material science, revealing the pioneering instance when a graphene layer was delicately separated from the commonplace graphite typically found in an everyday pencil.



Fig. (1). A graphene layer peeled away from the graphite found in a standard pencil.

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Several pathways and chemical techniques are used to carry out graphene's oxidation and reduction processes. Graphene oxide (GO) and reduced graphene oxide (rGO) synthesis are becoming increasingly urgent. It distinguishes itself from comparable compounds thanks to its strong electrical conductivity, large surface area, Young's modulus, optical transmittance, and thermal conductivity. Its plane, single-layered structure is what gives it properties like a high Young's modulus of about 1100 GPa, a high fracture strength of about 125 GPa, outstanding electrical and excellent thermal conductivity of about 5000 W/mK, the brisk charge carrier mobility of about 200,000 cm²/V s, and a large specific surface area of the theoretical value of 2630 m²/g [5]. Due to its wide range of uses in industries, including nano-electronics, biosensors, drug delivery, supercapacitors, fuel cells, H₂ storage, transistors, and polymer nanocomposites, graphene has generated a great deal of attention, Fig. (2).

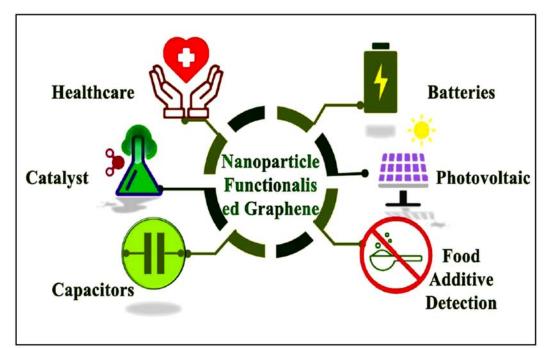


Fig. (2). Nano-functionalized graphene applications.

According to Park *et al.* (2010), employing pure graphene can occasionally be challenging due to its susceptibility to aggregation and processing challenges. Researchers have begun to concentrate on using functionalized graphene to solve this issue [6]. Despite its ongoing theoretical and practical accomplishments, we have yet to be able to use graphene's unique features, and this is because well-dispersed graphene is challenging to manipulate reliably [7]. Because of its

Harnessing Graphene-Based Nanocomposites for Multifunctional Applications

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Abstract: Due to the distinctive 2D lattice structure, graphene, and its derivatives have received much interest in recent years to advance technology into the era of stretchable, bendable, and flexible technology. Graphene has advantageous features that create diversely effective devices when combined with other materials to create composites. Compared to graphene, its composites exhibit improved features such as excellent mechanical strength, tunable electrical and thermal conductivity, and optical properties. Graphene composites utilize graphene fillers, films, or nanosheets with several other organic and inorganic groups, such as polymers, metal oxides, metal nanowires and nanoparticles, quantum dots, ceramics, and cement through covalent or noncovalent interactions. Numerous factors help tune the characteristics of the composites, such as graphene concentration, filler dispersion, chemical bonding, and others. The chapter discusses various methods for synthesizing graphene-based composites, including melt intercalation, in-situ polymerization, solution processing, etc. It also discusses factors that affect the composite's mechanical, electrical, thermal, photonic, and photocatalytic properties and its wide range of uses in electronics, sensors, transistors, energy storage, and environmental remediation. In addition, the problems and obstacles encountered in the manufacture of composites have been highlighted.

Keywords: Applications, Ceramics, Composites, Electrical properties, Graphene composites, Metal oxides, Polymers, Thermal conductivity, 2D structure.

INTRODUCTION

Graphene is an allotropic form of carbon. It has a 2D honeycomb-like structure in which carbon atoms are arranged in flat sheets. Graphene has a planar hexagonal lattice structure. Four valance electrons exist in each carbon atom of the graphene sheet; two e are in 2s orbital, and the remaining two are in 2px and 2py orbitals

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forming sp² hybrid orbitals. One electron in the p orbital is free to move and form a π bond (Fig. 1) [1].

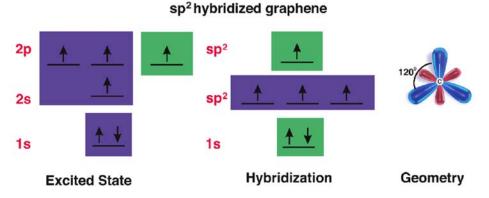


Fig. (1). Hybridization of graphene.

Although the concept of graphene had been known, it was not until 2004 that Professor Andre Geim and Professor Kostya Novoselov at the University of Manchester successfully extracted graphene from graphite. This discovery marked a significant breakthrough due to the extraordinary thermal and electronic properties exhibited by graphene. The synthesis of graphene can be approached using two distinct methods: the top-down approach and the bottom-up approach (Fig. 2). In the top-down approach, graphite is broken down into layers that are just one atom thick. The methods employed in top-down synthesis are an extension of those utilized to create particles with diameters smaller than a micron. These strategies involve the removal or division of bulk material or the downsizing of existing manufacturing methods to attain the desired structure with specific properties. Top-down approaches are relatively simpler but often suffer from surface structural flaws. On the other hand, the bottom-up approach, as its name suggests, involves constructing a substance from its constituent atoms, molecules, or clusters. This approach offers the advantage of generating less waste and being more cost-effective. For the synthesis of graphene, bottom-up techniques utilize a carbonaceous gas source to build the material atom by atom. These techniques represent a bottom-up pathway for graphene synthesis.

SYNTHESIS OF GRAPHENE AND DERIVATIVES

Liquid Phase Exfoliation

The primary technique for generating two-dimensional (2D) materials on a large scale with a favorable cost-quality ratio is liquid-phase exfoliation (LPE) [1],

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which is now widely employed by both the academic and industrial sectors. The force produced by ultrasound and its interaction with the solvent molecules have generally been assumed to be the only sources of the fragmentation and exfoliation mechanisms involved. How gigantic, thick graphite crystals can be exfoliated into tiny, small graphene flakes is currently unknown. According to Z. Li *et al.* [1], there are three distinct stages in transforming graphite flakes into graphene when subjected to ultrasonic LPE. Secondly, sonication causes large flakes to separate and leave behind kink band striations, typically in a zigzag pattern on their surfaces. Second, fissures begin to appear along these striations. When a solvent is intercalated, these cracks induce the unzipping and peeling off of small strips of graphite, which eventually exfoliate into graphene. In order to maximize the lateral dimensions, the information will be of great use.

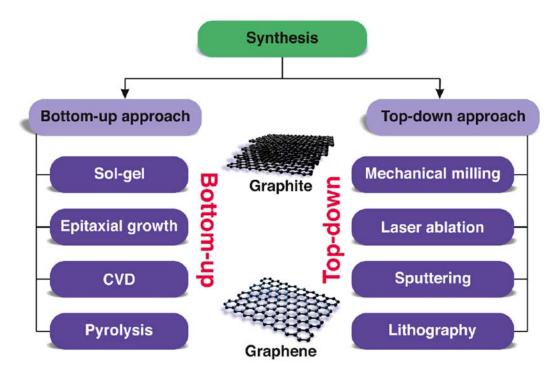


Fig. (2). Approaches for the synthesis of graphene.

Chemical Vapor Deposition

It is a bottom-up approach for fabricating single-layer and few-layer graphene films. CVD uses chemical processes to cast material as a thin coating from vapor species on the surfaces. Many intricate variables, such as the system configuration, reactor configuration, gas flow state, gas ratios, both reactor pressure and partial gas pressures, reaction temperature, deposition time,

Graphene-Based Gene and Drug Delivery Systems Innovations and Applications

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Abstract: Recent progress in the nanotechnology sector has abetted to mitigate the drawbacks associated with conventional therapies' limited effectiveness and medication efficacy after the *in vivo* drug delivery. In this regard, graphene; a 2D nanomaterial; has emerged as one of the wonder materials in medication delivery systems. Since the discovery of its capabilities in a biological system in 2008, numerous improvements and developments have been made till now in the therapeutic application of graphenebased materials. Additionally, it has been imparted with specific biological activities by both covalent and non-covalent surface revamping which further improves their biocompatibility and colloidal stability. Due to their hexagonal lattice and high surface area, they possess the astounding ability to provide high drug loading capacity via simple preparation methods, which makes them a more fecund material in comparison with other drug delivery systems. The present chapter outlines the exclusive drug and gene delivery applications of graphene-based materials and discusses their up-to-date advances. The chapter also discusses in detail how the integration of graphene and polymers makes them ideal as a delivery system in tissue engineering and nanomedicine for therapeutic approaches. The outlook presented here may help invoke deep insights into the nanotechnology-based drug delivery system for future research.

Keywords: Graphene, Drug, Gene, Biocompatibility.

INTRODUCTION

What exactly happens when a pill/drug (any pharmaceutical compound) is administered to our body ailing from some diseases? That drug is supposed to reach the target site inside the body without any hindrance and exert its therapeutic effect, helping our body recover over the period with fewer or no adverse effects at all. But, it is not always the scenario. Before reaching its target, the drug has to face several pharmacological aspects of drug delivery. The

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drug/gene delivery system merely depends on the pharmacodynamics of the drugs and the pharmacokinetics of the body [1]. Enhancing the performance of medications can be achieved by identifying the optimal drug molecule delivery system. A drug delivery system pertains to a channel or carrier that facilitates the administration of pharmaceutical or therapeutic substances into the body of a patient. Repurposing standing medications into novel drug formulations, that result in improved release and directed delivery, in addition to innovative pharmaceuticals, is garnering increasing attention, with a focus on nano-drug delivery systems in particular. Nanotechnology employs therapeutic materials at the molecular level to make nanomedicines. Nanoparticles are the major dynamic strength supporting the advancement as well as the development of nanobiotechnology, drug transport, biosensors, and tissue editing in the biomedical (BM) field [2]. Nano-based drug delivery systems (DDS) are a fast-emerging science in which nanomaterials are utilized to transport therapeutic agents to the target sites in a regulated way [3]. NMs have undergone extensive research because of their small size (10-100nm), vast surface area, and potential for surface functionalization. These characteristics make them highly suitable for use as gene and drug carriers, offering exceptional biocompatibility in medical applications [4, 5]. Owing to their extremely small sizes they have a significant impact on the limitations of nanomedicine, influencing everything from biosensors to tissue engineering.

Furthermore, increasing health hazards as manifested in humans in the forms of life-threatening diseases have compelled the scientific community to explore alternative means of theranostics. Therefore, considering the vast and diverse applicability of graphene (Gr) and its related materials, they have been explored for use in BM so that diseases could be minimized aiding mankind. Since the discovery of Gr in 2004, it has been used in diverse applications ranging from electronics to robotics, construction to BM, forming a never-ending list. In this context, several graphene materials have shown their capabilities as potent materials in the fabrication of various energy storage and energy-producing devices. These materials are also used as a catalysts in different biofuel, biodiesel, and other bioenergy-related reactions and processes [6 - 8]. Besides that, the material is also used in a number of biological applications involving detection and identification as well as antibacterial, antiviral and antifungal activities [9 -13]. These properties make it very significant in several biomedical applications. Their multitude of applications is owed to their remarkable mechanical, optical, electrical, and thermal along with diverse functionalization capabilities [14]. However, till 2008 it was not employed in BM applications when Liu and coworkers first revamped their functional utility as an effective carrier molecule in drug delivery systems [15, 16]. Following this research, it has embarked as a potent material for use in the BM sector and gained impetus ranging from delivery

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of drugs/genes to bioimaging as well as in biosensors and tissue engineering [17 -19]. Gr-based therapeutic approaches have gained worldwide attention among researchers and the scientific community. This approach consists of the delivery of medicament including drug molecules and/or therapeutic nucleotide agents to the target cell. Nucleotides are delivered to the target nucleus to correct the defective gene function either by regulating the protein expression or by gene knockdown. Gr due to the extraordinary physicochemical characteristics including high surface area, and electrical, thermal, mechanical as well as chemical properties have aided in delivering drugs as well as gene molecules to cure varieties of illnesses including cancer, genetic diseases, etc. Gr and its materials have been employed as nanocarriers (NC) in delivery systems aiding in the highly efficient delivery of the therapeutic drug and gene molecule in the target cells. It consists of a thin monolayer C-sheet and is frequently utilized as a carrier material for drug as well as gene delivery applications, owed to its extraordinary physicochemical characteristics including electrical, mechanical, thermal, magnetic as well as large surface area, imparted as an evolving material for these BM applications. More precisely the enhanced biocompatibility and extensive functionalization have supplemented their role in delivery in biomedicines. With the advancement of nanomaterials, the Gr-based drug/gene delivery system has evolved to a great extent such as improvement in bioavailability, increased permeability, specificity, and circulation time along with the sustained release and multimodality. Fig. (1) depicts the advancement in graphene-mediated drug and gene delivery.



Fig. (1). Advancement in graphene-mediated drug/gene delivery.

Graphene and its Derivatives: A Potential Solution for Microbial Control

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Abstract: Graphene-based materials (GMs) are the most promising materials in this era of antimicrobial and antiviral materials. Their excellent physicochemical properties and biocompatibility have opened new doors in this field. Graphene has good mechanical properties, a large surface area, high barrier mobility, excellent electronic transport performance, and resistance to degradation. Antimicrobial and antiviral materials have been used in the health sector for many years to fight off pathogens. Antibiotics, metal ions, and quaternary ammonium hydroxide are used for bacteria, while metals and organic materials are effective against viruses. Although metals are effective against viruses, their toxicity, high cost, and unintended leaching restrict their use as antivirals. Viral strains are progressively mutating, emerging as new threats to our species' survival. Bacterial resistance has developed as a result of the excessive use of antibiotics. The antimicrobial materials used so far have a high cost, cause environmental pollution, and are complex to process. To overcome these challenges, graphene-based materials have been in the limelight for antiviral and antibacterial abilities against pathogens. The combined properties of graphene alongside metals, polymers, metal oxides, and many other materials enable the perfect tool to protect human health. Their efficacy and broad-spectrum activities against gram-positive and gram-negative bacteria can potentially improve the quality of life. This chapter examines the detailed application of graphene-based materials towards wound healing, antibacterial coatings, biosensors, bioimaging, antibacterial sutures, anti-bio films, photocatalytic degradation of bacteria, and antibacterial packaging.

Keywords: Antibacterial, Antiviral, Antibiotics, Barrier, Biofilms, Bioimaging, Biosensors, Degradation, Graphene, Packaging, Pathogens, Photocatalytic, Wound healing.

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INTRODUCTION

Graphene is a two-dimensional (2D) material with carbon atoms forming an sp² hybridized sheet. It exhibits unrivaled mechanical, thermal, and electrical properties [1]. Geim and Novoselov shared the Nobel Prize in physics for their discovery of the thinnest material ever known. Since the discovery, graphene's numerous intriguing features, including its ability to efficiently conduct both charges and heat, significant surface area, and exceptional mechanical robustness, have come under discussion. Graphene research has grown tremendously, examining various features and uses for photoconductivity in photovoltaics, imaging medical aspects, tissue engineering, targeted drug delivery, and optoelectronic device [2].

MECHANISM OF ACTION

Despite extensive research efforts to investigate the antibacterial effects of graphene and its derivatives, such as graphene oxide (GO) and reduced GO (rGO), a comprehensive understanding of the underlying mechanism is still elusive. Experimental studies have generated more questions than answers, highlighting the need for further investigation. Graphene-based materials exhibit antibacterial properties that can alter bacterial physiology and induce the release of internal compounds. The antibacterial activity of Graphene Materials (GMs) is likely influenced by the physicochemical interactions between the materials and microbial entities. Several proposed mechanisms contribute to the antibacterial effects of GMs. Firstly, GMs can exert stress on the cell membrane, causing structural damage and compromising bacterial integrity. This mechanism is often referred to as "nano knives." Secondly, GMs can induce oxidative stress within bacterial cells, disrupting vital cellular processes and leading to antibacterial effects. Another mechanism involves the ability of GMs to wrap around bacterial cells or trap them, preventing their proliferation and resulting in antibacterial outcomes. Lastly, GMs possess intrinsic properties that enable them to directly kill bacteria through physical interactions or the release of toxic substances, known as the "self-killing effect." It is important to note that the specific mechanisms may vary depending on the type of graphene material and bacterial strain under investigation. The mechanism have been discussed in detail in the following segment of the chapter. Mechanisms of various antibacterial actions have been been illustrated in Fig. (1).

Nano Knives

GMs have defects in their structure, such as sharp edges, which can come in direct contact with the bacteria and destroy their membranes. This mechanism is known as Nanoknives' Action of Sharp-Edged GMs. This mechanism of GMs'

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interaction with bacteria was studied and proved by many researchers. One such work was performed by Akhavan and Ghaderi *et al.*, where they studied the effect of GONWs and rGONW's sharp edges on bacteria such as *E. coli* or S. aureus. The cell membrane of the bacteria gets destroyed, and the leakage of the RNA occurs, which ultimately induces cell death [3].

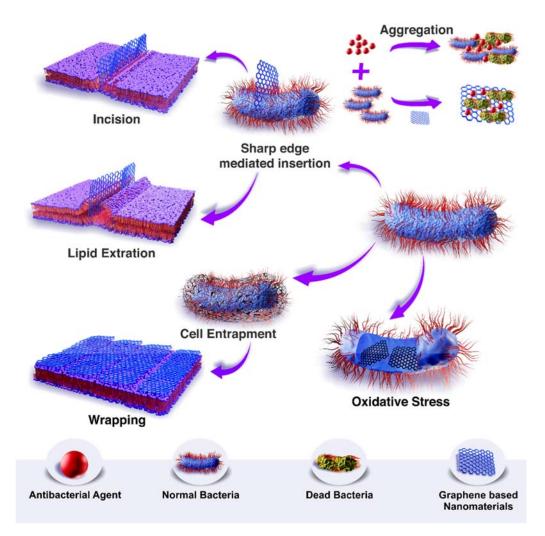


Fig. (1). Schematic representation of the three different GO antibacterial mechanisms of action.

Oxidative Stress

Typically, the oxidative stresses can either be ROS-dependent or ROSindependent. In both cases, it interferes with cellular processes, leading to cellular

The Role of Graphene in Revolutionizing Biomedical Imaging Techniques

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Abstract: Graphene possesses exceptional structural, mechanical, electrical, optical, and thermal properties. These properties have provided researchers worldwide with a vast horizon for their application in diverse fields including electronics, energy, sensing, drug/gene delivery, photothermal therapy, and the biomedical field. Moreover, in recent years, we have come across enormous research on graphene and its functional analogs, especially in the biomedical imaging field. Therefore, the present chapter provides impetus on bio-imaging modalities including optical imaging, magnetic resonance imaging, positron emission tomography/single-photon emission computed tomography, Raman imaging, and multimodal imaging. This chapter will provide its readers with deep insights into the advances in bio-imaging using graphene-based materials such as graphene, graphene oxide, and reduced graphene oxide. Finally, a brief discussion on the challenges and prospects of using graphene materials in bioimaging is provided.

Keywords: Bio-imaging, Fluorescence imaging, Graphene, Graphene oxide, Magnetic imaging, Reduced graphene oxide.

INTRODUCTION

Graphene (Gr) consists of a monolayer of sp² hybridized carbon (C) atoms with a two-dimensional (2D) honeycomb lattice that functions as the fundamental constructing entity for other forms of C, including carbon nanotubes and fullerene [1]. Gr derivatives namely graphene oxide (GO) and reduced GO (rGO) get arranged similarly as graphene along with the possession of different oxygen-containing functional groups such as hydroxyl (OH), carbonyl, and carboxyl (–COOH). Aromatic ring shape has repeating C-C bonds which are in the plane and provide free pi (π)-electrons as well as reactivity sites [2]. Its oxidation yields

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GO, which is soluble in water and consists of functional groups including -OH and epoxide (-O-) on the double open sides, and -COOH groups at its edges [3]. Certain portions of Gr in GO that were not altered during the chemical reduction of Gr retain free electrons that give it a hydrophobic character and enable the loading of drugs and non-covalent modification *via* π -stacking and hydrophobic interactions [4]. The presence of functional groups provides a polar character to GO allowing for weak interactions including H-bonding [5]. rGO is produced by the reduction of GO such that surface charge, oxygen content as well as hydrophobicity are minimized, producing rGO with repaired electrical as well as increased optical characteristics [6].

Like Gr, its derivative possesses extraordinary electrical, mechanical, thermal as well as optical properties which have gained worldwide recognition for being used in biomedical including bioimaging (BI), biomedicine, biosensor, *etc.* The research community has also focused their study in this direction so that the medical fraternity be bestowed with supplementary things in the form of sensing and medicine. Several studies have been performed to emphasize the biomedical applications involving Gr and its derivatives (GrAD) for BI, delivery of drugs, and photothermal treatment using near-infrared (NIR) light [7, 8]. Amongst all applications, BI has emerged as a potent tool for the detection and analysis of various biological processes at molecular as well as cellular levels in the biological system most prominently during diseased processes [9]. Furthermore, envisaging and tracing molecular and physical activities in living cells is a critical method for understanding cellular biology and has a potentially significant impact on the research and development of the biomedical sector. Advancement in this will surely lead to the up-leveling of medical diagnosis and treatment.

Visualizing tiny animal cells which are translucent, and colorless with a diameter of 10-20 µm which is usually one-fifth of the size of the tiny particle that is observable to the bare naked eye, becomes a most promising task. Thus, one of the most crucial issues in BI has been the creation of efficient and reliable probes. By using specialized probes or contrasting agents, it can recognize the early onset of disease as well as offer an effective way to monitor the disease progression and therapeutic response. In this context, the nanotechnology sector is always looking for novel materials that may be developed for BI applications to enable the nonintrusive *in vivo* studies of biological phenomena at the cellular as well as molecular levels. The last two decades have seen a continuous advancement in this involving Gr and imaging science methodologies for the research and development of Gr-based BI probes for potential application in biosensing and BI. Due to their extensive range of surface functionalization possibilities and extraordinarily high surface area, GrAD is easily modified by small nanoparticles (NPs), drugs, polymers, dyes, or other biomolecules to fabricate graphene-based Role of Graphene

nanomaterials (GBNs) intended for various BI applications.

This article provides insight into Gr-based BI techniques. We have emphasized techniques, as depicted in Fig. (1), such as PET/SPECT (positron emission tomography/single-photon emission computed tomography) Raman, multimodal imaging, magnetic resonance imaging (MRI), fluorescence [FL], and two-photon FL imaging [TPFI]). Functional as well as imaging procedures of each of these techniques have been thoroughly elaborated. Finally, we have outlined the opportunities and potential obstacles to using GrAD in future BI applications.

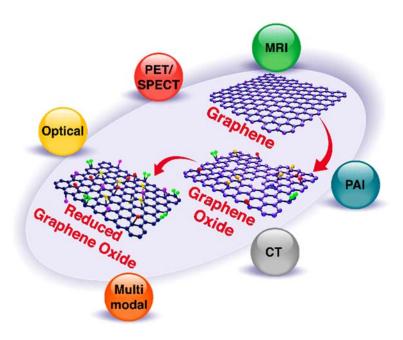


Fig. (1). Various graphene based bioimaging techniques.

GRAPHENE PROPERTIES: FUNDAMENTAL FOR BIOIMAGING

GrAD are well-suited for use in BI systems because of their numerous special physical as well as chemical characteristics. Initially, unusual optical properties including photoluminescence, remarkable fluorescence quenching ability, and Raman characteristics make Gr an excellent BI material [10]. Furthermore, extensive surface coverage may be attained by absorption or direct contact by functional groups on their surface. More probe molecules would increase the sensitivity of the detecting device. For BI, functionalized graphene materials can be combined with various recognition molecules and other functional components, such as proteins, metal NPs, or conducting polymers. The following

Recent Advances in Graphene-Based Materials for Application in Cancer Therapy

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Abstract: The surge in morbidity and death rates among patients suffering from cancer call for innovation towards efficient therapeutic strategies. Conventional therapy fails to treat cancer or to provide prolonged survival rate due to its toxic side effects on normal cells and lack of target specificity. In recent years, 2D materials (graphene and graphene analogues) have gained remarkable attention owing to their intriguing potential for therapeutic and targeted delivery in cancer therapostics. Due to their tunable physicochemical properties, π - π conjugated structure, optical characteristics, modifiable active moieties, strong photothermal effect, high compatibility, and ease of fabrication, graphene-based materials are highly suited for cancer treatment. This book chapter meticulously discusses the synthesis, modifications, and biomedical applications of graphene-based materials, explicitly focusing on graphene oxide (GO) and reduced graphene oxide (rGO). The authors detail the various methods for synthesizing GO and rGO, their physicochemical properties, and how these properties can be tailored for specific applications in drug delivery systems for cancer therapy. Notably, this work highlights the versatility of GO and rGO in enhancing the solubility and efficacy of chemotherapeutic agents, supported by examples such as the improved solubility of doxorubicin and the use of graphene for targeted drug delivery, which leverages the nano-scale properties of graphene for effective cancer treatment. By compiling and synthesizing recent research findings, the chapter is a valuable resource for nanotechnology and biomedical sciences researchers, providing a solid foundation for future studies and technological advancements in using graphene-based materials for cancer therapy. This work underscores the critical advancements in graphene technology and its promising future in medical applications, especially in enhancing the effectiveness and safety of cancer treatments.

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Keywords: 2D materials, Anticancer therapy, Biosensors, Graphene, Nanotechnology, Theranostics.

INTRODUCTION

Cancer has severely affected human life worldwide owing to its curability issues and high mortality rate. Although the fatality of cancer varies, its progression is linked to the body's failure to regulate cell growth and proliferation, resulting in the development of abnormal cells [1]. Considering the severity associated with cancer, clinicians and researchers have made tremendous efforts in advancing the treatment modalities for saving human life, including chemotherapy, radiation therapy, and surgery [2]. Conventional drug delivery systems and carriers have provided some relief. However, their effectiveness is compromised by challenges such as multi-drug resistance, the rapid metabolism, and elimination of drugs before they reach their target, non-specific cytotoxicity, and dose-dependent side effects [3, 4].

The limitations of traditional approaches have spurred the adoption of nanomaterials in biomedical research. Nanomaterials, especially biomaterials with unique properties, have revolutionized cancer treatment and have garnered significant attention as potential nanocarriers for the effective delivery of drugs [5]. A range of nanocarriers – micelles, lipid nanoparticles, liposomes, niosomes, peptides, nanocrystals, nanoparticles, nanocomposites dendrimers, and ethosomes have been extensively explored as drug delivery agent of anticancer drugs [6 - 12]. Amongst these, carbon-based nanomaterials, explicitly belonging to the graphene family, have fetched tremendous focus due to distinguishing properties suitable for the effective delivery of anticancer drugs [13, 14]. Nanomaterials have indispensable structural and surface functionalities enabling enhanced drug loading and pH-sensitive drug release at tumor sites. These nanomaterials have gained popularity for cancer treatment because of both physicochemical and biological properties, including endosomal escape after intracellular uptake for gene therapeutics and targeted delivery [15, 16].

A versatile property of graphene-based nanomaterials GO, rGO, graphene quantum dots, and graphene nanocomposites) is their ability to fine-tune from the original 2D structure into one/three dimensions, along with surface modifications [17]. Such exceptional and tunable properties have assured their new applications in constructing highly sensitive biosensors, high throughput bio-assays, drug delivery as well as tissue engineering. GO, the oxidized version of graphene is produced in a harsh oxidation environment. It contains various oxygen functionalities—hydroxyl, carboxylic, and epoxide groups—on its carbon surface, which enhance its hydrophilicity. These graphene and GO-based nanocomposites,

Graphene-Based Materials

with their increased surface area, ease of functionalization, high drug loading capacity, and potential to induce reactive oxygen species (ROS), are ideal carriers for the targeted delivery of anticancer drugs and diagnostic agents [18].

Similar to GO, rGO is a nanomaterial with a single-atom thick sheet layer of sp² hybridized carbon, synthesized by reducing GO either by chemical, thermal, or electrical methods [19]. The process of making rGO from GO is crucial as it influences the quality of the rGO formed. The reduced GO can later be functionalized for precise use in diverse applications. Functionalized rGO showed a high loading of genes and increased efficacy of nucleic acid therapeutics in targeted gene therapy [20]. An increase in surface area results in an increase in the loading of hydrophobic anticancer drugs for photodynamic therapy (PDT). Owing to good photo-absorption of light under near-infrared range, rGO has obtained its applications in cancer photo-thermal therapy (PTT) [21, 22]. Due to its facile synthesis, high water dispersibility, straightforward surface functionalization, and excellent biocompatibility, rGO has emerged as a superior multifunctional nanomaterial for photothermal therapy (PTT). In summary, surface functionalization with various therapeutic moieties or conjugation with targeting ligands on the surface of graphene and its derivatives underscores their use in targeted cancer therapies such as chemo-phototherapy and photothermal/immunotherapy [18, 23].

This chapter provides an in-depth outline of the current advancement established for using graphene-based materials in cancer therapy, placing particular emphasis on the outstanding potential of graphene in the drug delivery systems field. A number of intrinsic properties of such 2D materials, such as tunable properties according to specific biomedical applications, a sizeable area-to-volume ratio, and tailorable surface chemistry, make them an ideal choice for improving the therapeutic effectiveness of anticancer therapies. Therefore, it describes the synthesis, functionalization, and application of these materials for their further application. Briefly, it intends to respond to the unmet need for effective cancer therapy while calling attention to some of the current novelties that are taking place in the area of cancer nanomedicine. So, the synthesis reported here not only contributes to our knowledge in this specific field but also underlines the necessity for research to progress in this area to finally achieve *in vivo* the total therapeutic potential of these advanced materials.

A CACHE ON GRAPHENE-BASED MATERIALS

Structural re-arrangement of carbon atoms bonded through covalent bonds leads to the formation of materials collectively called carbon allotropes. Depending on the spatial arrangement of these carbon atoms, the allotropes that are formed have

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CHAPTER 8

2D Graphene for Tissue Engineering Advances and Perspectives

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Abstract: In recent years, there has been a surge in research studies exploring the potential of graphene-based materials for scaffold fabrication, with a particular emphasis on harnessing their exceptional properties such as high mechanical strength and high surface area. Significant advancements in tissue engineering have led to the development of innovative tools for creating artificial biotherapeutics. Among these, graphene-based composites have emerged as a thriving area of research in tissue engineering and regenerative medicine. The exceptional mechanical and cell-oriented properties of graphene have positioned it at the forefront of tissue engineering applications, encompassing various body systems such as nerve connections, the cardiovascular system, the skeletal system, cartilage, skin, and more. This chapter aims to succinctly explore the applications of graphene and its derivatives in tissue engineering, considering tissue engineering as a pinnacle of human-made biotherapeutics with immense therapeutic potential. Additionally, the prospects associated with the utilization of graphene-based composite scaffold materials have been reviewed in depth, providing valuable insights and a broad perspective on their application in tissue engineering.

Keywords: Biomedical applications, Biomaterials, Bio-therapeutics, Graphene, Tissue engineering.

INTRODUCTION

Graphene (Gr) has revolutionized the field of tissue engineering, offering remarkable advances and perspectives for the development of regenerative

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therapies. Its unique properties, including mechanical strength, flexibility, and electrical conductivity, make it an exceptional material for scaffold fabrication. Graphene-based scaffolds have demonstrated exceptional biocompatibility, promoting cell adhesion, proliferation, and differentiation, crucial for tissue regeneration. Moreover, graphene's surface chemistry and the ability to functionalize further enhance its potential in controlled drug delivery systems and targeted therapies. The integration of graphene in tissue engineering has opened new horizons, paving the way for innovative solutions in regenerative medicine and providing immense hope for patients in need of tissue repair and regeneration.

The development of effective scaffolds is crucial for successful tissue engineering applications, providing a supportive framework for cell adhesion, proliferation, and tissue regeneration [1, 2]. Gr has emerged as a highly promising candidate for scaffold fabrication due to its exceptional properties and versatility. Extensive research has been conducted to explore Gr-based materials and their underlying mechanisms, paving the way for the translation of Gr-based therapies from the laboratory to clinical settings [1, 2]. Gr exhibits significant biological activities, including antibacterial, antiviral, and antifungal properties, making it highly relevant in biomedical innovations [3, 4]. Its stretchability, flexibility, and highest thermal and electrical conductivity further enhance its potential for bioengineering applications [5 - 7]. In neural tissue engineering, Gr-based scaffolds have shown promise in promoting neural cell adhesion, differentiation, and signal transmission, potentially facilitating the regeneration of damaged neural pathways [8, 9]. The use of Gr derivatives holds promise in restoring lost functions necessary for patient survival, surpassing the limitations of traditional organ transplantation [10, 11]. The exceptional characteristics of Gr, including mechanical strength, stiffness, and electrical conductivity, make it highly desirable for various biomedical applications [12 - 15].

Moreover, Gr scaffolds have shown several promising aspects in bone tissue engineering, as their mechanical properties can be tailored to mimic natural bone characteristics, providing mechanical support during bone regeneration [16]. The unique surface chemistry of Gr allows for the controlled release of growth factors or osteogenic molecules, promoting bone cell proliferation and differentiation [16]. In addition, Gr holds significant potential in the field of cell and organ transplantation, offering a range of advantages [17]. Gr's versatility allows for the incorporation of additional functionalities into transplantation strategies. It can be functionalized with biomolecules or therapeutic agents to enhance cell or organ survival, modulate immune responses, or deliver a controlled release of drugs or growth factors. This ability to customize Gr-based materials opens up new possibilities for improving the success and outcomes of cell and organ transplantation procedures [18, 19]. However, the structure and uniformity of Gr

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become critical factors when considering its application in tissue regeneration [20, 21]. Exploring suitable composite formulations and ratios of Gr is imperative to address emerging clinical challenges in the field [22].

In addition to Gr, the incorporation of other materials and composites has been explored to enhance the properties and functionality of Gr-based scaffolds. [23, 24]. The intermolecular forces between particles have a significant impact on scaffold fabrication as they influence particle dispersion and interaction. Particularly, strong van der Waals forces among scaffold particles can affect their ability to disperse in physiological fluids and aqueous media, thereby affecting the overall performance of the scaffold [25]. Functionalization has played a pivotal role in scaffold fabrication by addressing the challenges associated with the dispersibility and solubility of pristine Gr. Through functionalization, the surface chemistry of Gr can be modified, enabling improved compatibility with physiological fluids and aqueous media. Functionalization techniques, such as chemical modifications or the introduction of functional groups, have been explored to enhance the dispersibility and solubility of graphene-based materials, making them more suitable for scaffold fabrication in tissue engineering applications [26 - 28].

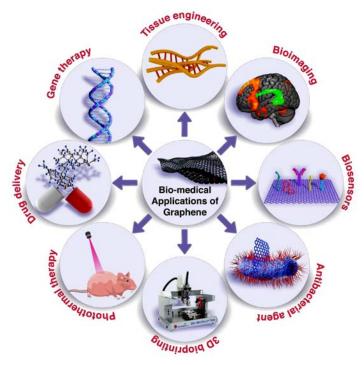


Fig. (1). Key biomedical applications of graphene.

The Promise and Potential of Graphene Derivatives in Biotechnology

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Abstract: The extensive range of applications associated with graphene and its derivatives has captivated the attention of nano biotechnologists due to their remarkable versatility. The 2D clan of graphene possesses exceptional physical, chemical, and mechanical characteristics, rendering it an extraordinary material with unparalleled properties. It is an allotrope of carbon which has a 2-dimensional hexagonal lattice structure. It has broad applicability in material science, physics, chemistry, biology, etc. Graphene is advantageous over other materials because (a) it is the finest and toughest material known to date; (b) It has a monolayer of carbon atoms that are transparent and also possess flexibility; (c) it acts as an excellent electrical and thermal conductor. Besides its natural availability, its demand has led to its synthesis using hierarchical and self-assembly methods. Modification of graphene according to various biological systems increases its solubility, selectivity, and compatibility. Graphene is used as a substrate interfacing with different biomolecules and cells as tissue scaffolds and to generate stem cells for regenerative medicines. Graphene and its derivatives are applied in drug delivery, gene delivery, biomolecule recognition, molecular medicine, bioassays, antibacterial compositions, biosensing, energy storage, and catalysis. Graphene derivatives have been recently used as theranostics in cancer because of their intrinsic photoluminescent properties and treatment of several microbial infections. Though graphene has been explored tremendously, studying the toxicity issues and its interaction with the environment and ecosystem is imperative. This chapter will uncover the different forms of graphene and its derivatives; its synthesis approaches, and various applications in biomedicine.

Keywords: Allotrope, Biosensors, Biomolecule, Fullerene, FRET, Graphane, Guantum dots, Graphene oxide, Graphdiyne, Hexagonal, Monolayer, Nanobiotechnology, Nanoflakes, Nanofilms, Reduced- GO, Synthesis, Scaffolds.

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INTRODUCTION

The origin of graphene (G) in 2004 led to the emergence of newer dimensions of nanomaterial science and technology [1]. Graphene is considered a wonder material composed of a 2-dimensional single graphite sheet. It is an allotrope of carbon that has a 2-dimensional hexagonal lattice structure. Carbon atoms are arranged in a planar monolayer with a carbon-carbon bond length of 0.142 nm. It has broad applicability in physics, material science, biology, chemistry, and, recently, biotechnology. Graphene is advantageous over other materials because (a) it is the most challenging and finest material known to date; (b) it has monolayered carbon atoms that are transparent in color and also poses flexibility; (c) it acts as an excellent electrical and thermal conductor.

Unlike the 3D bulk material, which hides most of the internal structure and limits observation, graphene's 2D surface is always exposed. It may be advantageous to inspect and modify its structure with greater ease. Graphite is brittle in nature; recall when humanity used to write with a pencil, the layers separated from each other as a result of the weak interlayer van der Waals forces. Exfoliation is a process that transforms natural or artificial graphite, the mother bulk material, into graphene, resulting in significant changes in its atomic properties and applications. For instance, graphene monolayers, with their unique characteristics, find applications in high-end technologies such as solar cells [2], semiconductors [3], and micro-super capacitors [4]. On the other hand, multilayer graphene is utilized in the production of composites [5], pastes, or powders [6]. Various methods, including thermal, mechanical, liquid-phase, or chemical vapor deposition (CVD) [7], can be employed for graphite exfoliation. Liquid-phase exfoliation involves the separation of single layers from the bulk material, while in CVD, graphene is deposited onto a substrate using a carbon-rich source like methane. Each graphene layer exhibits unique properties, enabling the production of high-quality versions suitable for photonics, sensing, and wafer-scale electronics.

Nanobiotechnology is just an addendum to nanotechnology. The concept behind nanotechnology is its fabrication and synthesis from bulk materials according to nanosize (<100 nm). When material is reduced to an atomic scale from bulk scale, the properties of the nanomaterial change, and interestingly it becomes more appealing. Similarly, graphene is a nanomaterial synthesized from its bulk material graphite and possesses unique chemical and physical properties. Due to this, it has developed a strong interest in many applications, especially in biotechnology [8], and published an excellent review on generating functional, more convenient, and dynamic DNA-based nanostructures. Materials of carbon-based 2D clan have been frequently investigated with DNA/RNA, proteins,

peptides, and cells. Graphene can quench electrons from the biomolecules, adsorb single-stranded DNA (ssDNA), protect biomolecules from enzymatic attack, and assist in cell-cell trafficking *in vivo* systems. This ability makes it an excellent candidate in biotechnology to study the interaction and response of vivid biological moieties with nanomaterials.

Not only graphene, but its derivatives like graphene oxide (GO), graphene quantum dots (GQDs), reduced graphene oxide (rGO), and nanocomposites are promising candidates in the development of nanobiotechnology. GQDs have proven their application in the detection of biomolecules, bioimaging of living cells, targeted drug delivery and cancer therapy [9], antimicrobial activity [10], and many more. Researchers recently described an efficient method of detecting different pollutants in natural water samples. They demonstrated using 0D luminescent nano lights to selectively and sensitively detect specific analytes in the sample. For developing various biotechnology tools, G, GO, CMG, and other derivates have proven successful [7]. Graphene is introduced to biotechnology by combining it with biomolecules; however, the achievements of graphene-based functional biosystems are reported by some authors [7]. Fluorescence resonance energy transfer (FRET) biosensors based on graphene and its derivatives have the sensing detection limit ranging from small molecules and DNA to proteins and cells [7, 11, 12]. GO, rGO, nanocomposites and graphene films have applications in tissue engineering, gene delivery, antimicrobial activities, molecular imaging, and bioelectronics [13].

Advances in imaging techniques also involve using GO, rGO, and GQDs as fluorescent markers for intracellular imaging *via* optical imaging for visualizing human carcinoma cells. Graphene films are also used for direct imaging of interfaces to gold nanoparticles [14]. Transmission Electron Microscopy (TEM) and High-Resolution Transmission Electron Microscopy (HRTEM) are used to study graphene related studies [15]. G-flakes are also used to study TMV without staining [16].

This chapter will provide information on emerging graphene derivatives, their properties, and their approaches w.r.t biotechnology per se. The role of G and GDs is illustrated in Fig. (1), where possibilities of gene therapy, tissue engineering, modified protective cloth fibers, and combating SARS-CoV2 are highlighted. This chapter aims to provide a comprehensive overview of the diverse applications of various graphene derivatives (GDs) enabled by advanced and cutting-edge technologies. Additionally, it will highlight the tremendous impact of graphene nanomaterials on the field of material science, making them one of the most promising advancements to date.

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