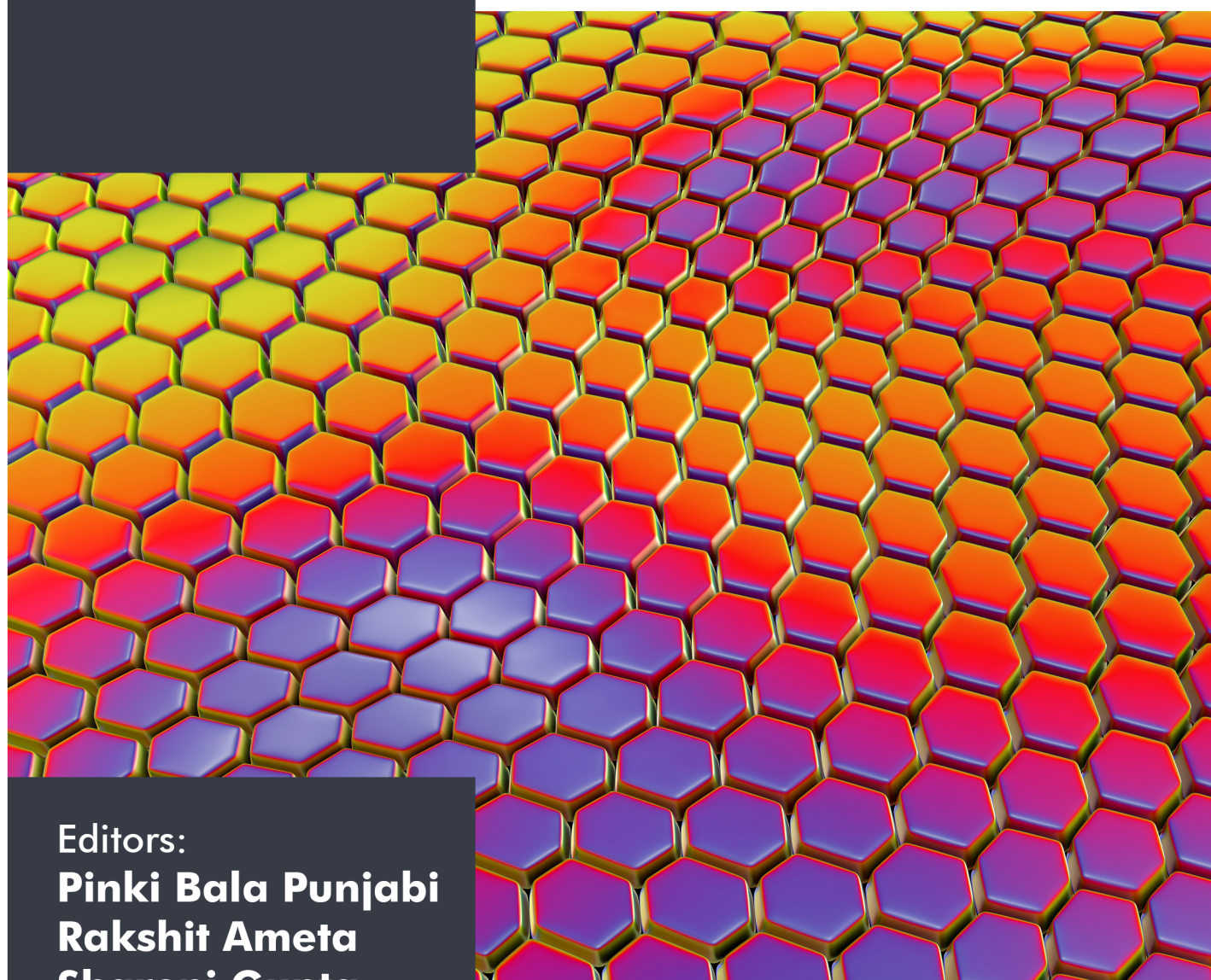


# GRAPHENE-BASED CARBOCATALYSTS

SYNTHESIS, PROPERTIES  
AND APPLICATIONS



Editors:  
**Pinki Bala Punjabi**  
**Rakshit Ameta**  
**Sharoni Gupta**

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# **Graphene-based Carbocatalysts: Synthesis, Properties and Applications**

*(Volume 1)*

Edited by

**Pinki Bala Punjabi**

*Department of Chemistry, University College of Science,  
Mohanlal Sukhadia University, Udaipur-313001, Rajasthan,  
India*

**Rakshit Ameta**

*Department of Chemistry, J.R.N. Rajasthan Vidyapeeth  
University, Udaipur-313001, Rajasthan,  
India*

**&**

**Sharoni Gupta**

*Department of Chemistry, University College of Science,  
Mohanlal Sukhadia University, Udaipur-313001, Rajasthan,  
India*

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## FOREWORD

Graphene is an allotrope of carbon, which is in the form of a thin layer with a two-dimensional honeycomb-like structure. It exhibits unique properties such as lightweight, excellent thermal and electrical conductivities, large specific surface area, easy preparation and functionalization, high intrinsic mobility, chemical stability, simple recovery, recyclability, *etc.* Therefore, it has emerged as the most successful entity with a wide range of applications in various medical, chemical and industrial processes, such as flexible electric/photonics circuits, solar cells, drug delivery, tissue engineering, bioimaging, optoelectronics, photodetectors, generation and storage of energy, biosensors, removal of contaminants, catalyst, water and sound proofing, and many more. The editors have made a very judicious choice in selecting graphene and its applications as a topic covering major fields of interest. I appreciate their efforts in compiling the different areas related to graphene and putting them all in a single arena. I believe that this book will get an overwhelming response from the readers.

**Suresh C. Ameta**  
Past President & Life Time Advisor  
Indian Chemical Society, Kolkata  
Professor of Eminence (Distinguished Professor)  
Faculty of Science  
PAHER University  
Udaipur-313003 (Raj.) India

## PREFACE

Catalysis is a fundamental and multidisciplinary phenomenon that has been ruling the energy sector and chemical industry for centuries impacting the world's economy. Not only production processes but even biological and natural reactions are catalytically controlled by enzymes and other substances to maintain life on Earth. Various manufacturing units including petrochemicals, pharmaceuticals, food, polymers, materials, and fine chemicals-based industries along with pollution-abating firms are highly dependent on catalysts. This is because catalysts offer green means for accelerating chemical transformations *via* energy-saving and atom economic pathways. Until today, multitudes of homogeneous and heterogeneous catalysts have been explored for carrying out several conversions and enhancing the feasibility of reactions. However, the issues of catalyst recoverability and efficiency have been a cause of concern across the globe. More recently, the necessity of environmental conservation has further accentuated the search for sustainable catalysts. In such a scenario, graphene-based catalysts or carbocatalysts have emerged as a boon to meet the growing demand for efficacious, benign and inexpensive heterogeneous catalysts.

Graphene with its distinguished opto-electronic, thermo-mechanical, surface and chemical characteristics is renowned as the most invincible nanomaterial. Ever since the path-breaking discovery of graphene in 2004, the two-dimensional, honeycomb lattice-based material has enthralled the scientific community throughout the world. The exceptional conductivity, tensile strength, stability, large surface area, recoverability, recyclability and ease of functionalization of graphene materials have especially captivated the researchers working in the field of catalysis. Owing to the surge in demand for graphene-based catalysts, graphene research is being carried out at a very rapid pace. Every year new additions to the knowledge and scope of graphene carbocatalysts appear at a considerably large scale. Consequently, this book is an attempt to acquaint readers with the recent advances in the field of graphene carbocatalysis.

The book encapsulates the recent developments involving the syntheses, properties, characterizations, functionalization, and catalytic applications of graphene, its derivatives and composites. The book is in two volumes. The first volume is divided into 10 chapters. In Chapter 1, a brief introduction to carbocatalysis has been laid out. The properties, syntheses and scope of carbocatalysts have been discussed to highlight their significance. Chapter 2 discusses the fundamental structure and properties of graphene and chemically modified graphene contributing to their applications in diverse fields. Chapter 3 describes the diverse synthetic strategies for the preparation of graphene and its derivatives. The advantages of present methods and future challenges related to industrial-scale synthesis have also been outlined in this chapter. Chapter 4 focuses on the latest and most commonly employed characterization techniques used for investigating the morphological, structural, and thermal properties of graphene materials. In Chapter 5, recent trends in functionalization and its role in the catalytic activity of graphene have been put forward. Chapter 6 summarizes the recent progress in the synthesis of graphene-based composites along with their properties and applications in catalytic reactions. The future prospects and challenges towards the design and development of graphene-based nanocomposites for catalytic reactions have also been addressed in the chapter. Chapter 7 reviews the recent advances in graphene-supported palladium catalysts for coupling reactions. It also underscores the synthesis of these catalysts and their mechanistic aspects spanning across a variety of cross-coupling reactions. A comparison of graphene-supported catalysts with traditional catalysts has also been included in this chapter. Chapter 8 provides an in-depth review of recent applications of graphene-based catalysts in multicomponent and domino reactions. In Chapter 9, current progress made

in the field of oxidation and reduction reactions of organic molecules catalyzed by graphene materials has been explored. Chapter 10 accounts for the contemporary trends in the area of graphene-based biocatalysts.

The second volume includes six chapters. Chapter 1 of the second volume incorporates the most recent advances in photocatalytic applications of graphene-based materials such as graphene-based semiconductor photocatalysts for the degradation of various contaminants (treatment of waste water), production of hydrogen, and photocatalytic reduction of carbon dioxide to energy-rich synthetic fuels (combating against global warming and energy crisis), *etc.* Chapter 2 discusses the latest advances in electrocatalysis by graphene materials with a special focus on the electrocatalytic activities of non-metal doped graphene, graphene-2D materials heterostructures, and graphene-plasmonic nanostructures. Chapter 3 provides an overview of the recent advancement made by graphene-based materials including graphene oxide, reduced graphene oxide and graphene oxide quantum dots for hydrogen evolution from light-driven water splitting and future prospects. Chapter 4 highlights the modern trends in the fabrication of graphene-based smart energy materials for applications in various energy storage systems. The future trends and challenges have also been underlined. Chapter 5 underscores the potential utility of graphene materials in electrochemical sensing devices. Chapter 6 concludes the book and reports state-of-the-art graphene carbocatalysis with the future challenges accompanying graphene-based catalysts.

The book covers multidimensional applications of graphene-based materials cutting across various fields ranging from energy generation, chemical synthesis, and electrochemical sensing to photocatalysis. Hopefully, this book will serve as a reference work for all those researchers, students, industry workers and engineers who are interested in graphene research as well as its emerging applications in catalysis and beyond.

At last, we would like to thank all the authors of this book for their invaluable contribution to enriching the content of this book. We are also extremely indebted to the managers, editors, and reviewers of Bentham Science Publications for their magnanimous help throughout the creation and publication of this book. Finally, we are highly grateful to our families for their constant support and inspiration.

**Pinki B Punjabi**

Department of Chemistry,  
University College of Science,  
Mohanlal Sukhadia University,  
Udaipur-313001, Rajasthan,  
India

**Rakshit Ameta**

Department of Chemistry,  
J.R.N. Rajasthan Vidyapeeth University,  
Udaipur-313001, Rajasthan, India

&

**Sharoni Gupta**

Department of Chemistry,  
University College of Science,  
Mohanlal Sukhadia University,  
Udaipur-313001, Rajasthan, India

## **DEDICATION**

*In fond memory of my beloved uncle Mr. Anil Kothari who taught me how to smile through difficult times.*

Dr. Sharoni Gupta

## List of Contributors

|                                     |  |
|-------------------------------------|--|
| <b>Abhilasha Jain</b>               | Department of Chemistry, St. Xavier's College (Autonomus), Mumbai, Maharashtra-400001, India   |
| <b>Akella Sivaramakrishna</b>       | Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology (VIT), Vellore 632014, Tamil Nadu, India                       |
| <b>Anamika Srivastava</b>           | Department of Chemistry, Banasthali Vidyapith, Banasthali, Rajasthan, India  |
| <b>Anjali Banger</b>                | Department of Chemistry, Banasthali Vidyapith, Banasthali, Rajasthan, India  |
| <b>Chetna Ameta</b>                 | Photochemistry Laboratory, Department of Chemistry, University College of Science, Mohanlal Sukhadia University, Udaipur (Raj.), India               |
| <b>Dharmendra Dharmendra</b>        | Photochemistry Laboratory, Department of Chemistry, University College of Science, Mohanlal Sukhadia University, Udaipur (Raj.), India               |
| <b>Dinesh Kumar Yadav</b>           | Department of Chemistry, Mohanlal Sukhadia University, Udaipur, 313001, India  |
| <b>G.S. Sahoo Navneet</b>           | Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology (VIT), Vellore 632014, Tamil Nadu, India                       |
| <b>H.S. Sushma</b>                  | Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology (VIT), Vellore 632014, Tamil Nadu, India                       |
| <b>Ivaturi Sai Vighnesh</b>         | Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology (VIT), Vellore 632014, Tamil Nadu, India                       |
| <b>K. M. Sreeranjani</b>            | Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology (VIT), Vellore 632014, Tamil Nadu, India                       |
| <b>Manish Srivastava</b>            | Department of Chemistry, Banasthali Vidyapith, Banasthali, Rajasthan, India  |
| <b>Monika Jangid</b>                | Department of Chemistry, PAHER University, 313001-Udaipur, Rajasthan, India  |
| <b>Munsaf Ali</b>                   | College of Nanoscale Science and Engineering, State University of New York, Polytechnic Institute - CNSE, 257 Fuller Rd., Albany, NY 12203, New York |
| <b>Nirmala Kumari Jangid</b>        | Department of Chemistry, Banasthali Vidyapith, Banasthali, Rajasthan, India  |
| <b>Nitinkumar Satyadev Upadhyay</b> | College of Nanoscale Science and Engineering, State University of New York, Polytechnic Institute - CNSE, 257 Fuller Rd., Albany, NY 12203, New York |
| <b>Priyanka Chundawat</b>           | Photochemistry Laboratory, Department of Chemistry, University College of Science, Mohanlal Sukhadia University, Udaipur (Raj.), India               |
| <b>Pinki Bala Punjabi</b>           | School of Basic and Applied Sciences, Sangam University, Bhilwara-311001, Rajasthan, India   |
| <b>Pradeep Kumar Jaiswal</b>        | Department of Biochemistry and Biophysics, Texas A&M University, College Station, Texas 77843, USA   |



|                            |   |
|----------------------------|---|
| <b>Priy Brat Dwivedi</b>   | National University of Science and Technology, AlHail South, Seen 111, Muscat, Oman   |
| <b>Reema Agarwal</b>       | Photochemistry Laboratory, Department of Chemistry, University College of Science, Mohanlal Sukhadia University, Udaipur (Raj.), India                                    |
| <b>Rajagopal Desikan</b>   | Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology (VIT), Vellore 632014, Tamil Nadu, India  |
| <b>Rakesh R Panicker</b>   | Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology (VIT), Vellore 632014, Tamil Nadu, India  |
| <b>Rakshit Ameta</b>       | Department of Chemistry, J.R.N. Rajasthan Vidyapeeth University, Udaipur-313001, Rajasthan, India   |
| <b>Ramesh L. Gardas</b>    | Department of Chemistry, Indian Institute of Technology Madras, Chennai - 600 036, India  |
| <b>S. Ahallya</b>          | Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology (VIT), Vellore 632014, Tamil Nadu, India  |
| <b>S. Haripriya</b>        | Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology (VIT), Vellore 632014, Tamil Nadu, India  |
| <b>S. Sathish</b>          | Department of Physics, MVJ College of Engineering, Bangalore – 560067, India  |
| <b>Sagar Ulkesh Patil</b>  | Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology (VIT), Vellore 632014, Tamil Nadu, India  |
| <b>Siddharth Sharma</b>    | Department of Chemistry, Mohanlal Sukhadia University, Udaipur, 313001, India   |
| <b>Sharoni Gupta</b>       | Department of Chemistry, University College of Science, Mohanlal Sukhadia University, Udaipur-313001, Rajasthan, India  |
| <b>Sunita Panchawat</b>    | Department of Pharmaceutical Sciences, Mohanlal Sukhadia University, Udaipur, Rajasthan-313001, India   |
| <b>Vepa Jagannadha Rao</b> | Department of Chemistry, Anil Neerukonda Institute of Technology and Sciences, Affiliated to Andhra University, Sanghivalasa, Visakhapatnam 531162, Andhra Pradesh, India |
| <b>Vickramjeet Singh</b>   | Department of Chemistry, Dr B R Ambedkar National Institute of Technology, Jalandhar-144011, Punjab, India  |
| <b>Yogeshwari Vyas</b>     | Photochemistry Laboratory, Department of Chemistry, University College of Science, Mohanlal Sukhadia University, Udaipur (Raj.), India                                    |

**CHAPTER 1****Introduction to Carbocatalysis****Pinki Bala Punjabi<sup>1,\*</sup> and Sharoni Gupta<sup>1</sup>**<sup>1</sup> *Department of Chemistry, University College of Science, Mohanlal Sukhadia University, Udaipur-313001, Rajasthan, India*

**Abstract:** Carbocatalysis has emerged as a promising field of catalysis. The exceptional surface morphology, pore distribution, thermal conductivity, chemical inertness, electrical property and renewability of carbon materials have rendered them suitable for various catalytic processes namely, photocatalysis, electrocatalysis, biocatalysis and chemical catalysis. Therefore, the introductory chapter on carbocatalysis describes the useful properties of carbonaceous materials which govern their catalytic behaviour. Moreover, synthetic approaches for the fabrication of diverse carbon polymorphs such as active carbon, graphite, fullerene, glassy carbon, carbon black, carbon nanotubes, carbon nanofibres, nanodiamonds, carbon nano-onions, and graphene have also been briefly discussed in this chapter. The scope of carbocatalysts over broad areas has also been elucidated by quoting instances.

**Keywords:** Carbocatalysis, Electrical Properties, Surface Properties, Sustainability, Synthesis, Thermal Conductivity.

**INTRODUCTION**

Catalysis is the backbone of chemical transformations which facilitates a sustainable and efficacious means to convert starting raw materials to useful chemical compounds. One of the twelve principles of green chemistry states that the “use of catalysts should be encouraged as these enhance selectivity, reduce the formation of by-products, reaction time and energy requirements” [1]. Therefore, catalytic transformations have become an integral part of environmentally benign chemical processes. Homogenous and heterogeneous catalysts are the two main classes of catalysts that over the past several decades have served as a driving force in achieving high performance conversions by abating the activation energy. Both homogeneous and heterogeneous catalysts have their high points, for instance, homogeneous catalysts have excellent catalytic efficiency owing to

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\* **Corresponding author Pinki Bala Punjabi:** Department of Chemistry, University College of Science, Mohanlal Sukhadia University, Udaipur-313001, Rajasthan, India; E-mail: pb\_punjabi@yahoo.com

readily accessible active sites [2] while heterogeneous catalysts are quite stable and easy to separate and recover [3]. However, with growing awareness of environmentally friendly protocols, the use of conventional catalysts has become a debatable topic. This is primarily because the traditional catalysis employs acids, bases, transition and non-transition metals which are toxic, expensive, get easily deactivated by impurities and non-reusable.

Sustainability being an essential element of modern chemistry has coerced researchers and chemists globally to look for renewable and cost-effective catalytic systems. The recent emergence of graphene based catalysts has paved way for a green alternative to conventional catalysts. Carbocatalysis *viz.* catalysis driven by carbonaceous materials is not a novel avenue of study. Several carbon based catalyst have been used in the past. Perhaps the beginning of carbocatalysis can be traced back to the year 1854 when Stenhouse observed that activated carbon was capable of oxidizing a mixture of organic gases coming from putrefied biomass [4]. Since then there have been several reports where carbon allotropes were used as catalytic materials. In 1925, Rideal and Wright employed charcoal as a catalyst for the oxidation of oxalic acid [5]. In the 1930s, Kutzelnigg and Kolthoff separately confirmed that activated charcoals were highly suitable for catalyzing the aerobic oxidation of ferrocyanide to ferricyanide [6, 7]. Thereafter in 1979, charcoal was used to catalyze the oxidative dehydrogenation (ODH) reaction of ethylbenzene to styrene [8]. Also, graphite catalyst was employed for the first time by Lucking and co-workers for the oxidative cleavage of 4-chlorophenol, which yielded CO<sub>2</sub>, H<sub>2</sub>O, and HCl [9]. In another instance, Fortuny *et al.* have also reported oxidation of phenol using active carbon as a catalyst [10]. Despite the good catalytic performance of carbonaceous materials attributable to their versatile porosity and surface properties, carbocatalysis did not achieve the desired level of attention until the discovery of fullerene, carbon nanotubes, and graphene. Further, mostly the carbon polymorphs such as charcoal [11], graphite [12], carbon black [13], and diamond [14] have been used as support in catalytic systems because of their advantages including ease of metal immobilization on carbon, resistance to attack by acids and bases, simple as well as cost-effective preparation, high thermal stability and straightforward recovery of the active phase. Regardless of the beneficial features, some shortcomings such as lack of active sites, microporous structure, hydrophobic character and poor resistance to oxidation stalled the growth of carbon based catalysts in earlier days [15]. However, the recent developments in the synthetic chemistry of carbon have allowed easy modification of the pore size distribution, surface chemistry, and hydrophilicity to afford carbocatalyst with desirable electronic and physicochemical properties, large surface to weight ratio, and better biocompatibility.

The discovery of fullerenes in 1985 was a landmark in the field of carbon science [16]. The unique three dimensional structure of fullerene comprises intricately arranged five and six membered rings of covalently bonded carbon atoms arranged to form spherical shape. The high conductivity (narrow band gap) of fullerene arises from the pi electron delocalization within carbon layers which favours its catalytic behaviour. Functionalization of fullerenes also aids in tuning their electrical properties and serves as a precursor for the preparation of fullerene based nanocatalyst. Ever since their discovery, fullerene based catalysts have been used to catalyze several reactions such as reduction [17], oxidation [18], photodegradation [19], dehydration [20], proton transfer [21], deallylation [22], *etc.*

The birth of nanotechnology proved to be a boon for carbocatalysis. The designing of nanodimensional carbon tubes with readily accessible sites on large surface area revolutionized the field of catalysis. The breakthrough invention of carbon nanotubes in 1991 by Iijima [23] followed by its use as catalyst support in 1994 [24] led to a new generation of catalysts dominated by carbon nanomaterials. Carbon nanotubes belong to the fullerene family and are basically graphite sheets rolled in the form of cylindrical shapes. The excellent electrical conductivity, striking mechanical and thermal stabilities, tolerance against poisoning effect, easily modifiable surface area, and ease of functionalization of carbon nanotubes make them promising catalytic systems [25]. Carbon nanotubes have been widely applied and employed in heterogeneous catalysis [26], photocatalysis [27], and electrocatalysis [28].

One of the lightest and strongest known materials, graphene is a single layered allotrope of carbon that has honeycomb structure and is the most famous carbocatalyst of recent times. The discovery of graphene dates back to 1859 when Brodie while examining the structure of graphite, observed graphene and named it “graphone” [29]. In 2004, the isolation of graphene sheets by Novoselov *et al.* brought about a storm in the field of carbonaceous materials [30]. The extraordinary physicochemical and thermoelectrical properties of graphene such as large specific surface area (theoretically 2630 m<sup>2</sup>/g for single-layer graphene) [31], amazing electronic properties and electron transport potential [32, 33], unparalleled flexibility and impermeability [34, 35], sturdy mechanical property [36] and excellent thermal and electrical conductivities [37, 38] attracted enormous interest and resulted in an explosion of research studies in the domain of graphene based materials. In 2009, Lu *et al.* highlighted the use of gold embedded graphene based catalyst for oxidation of CO [39]. Jafri *et al.* also reported nitrogen doped graphene nanoplatelets as a potent catalyst for oxygen reduction reaction [40]. In 2010, Dreyer *et al.* demonstrated graphene oxide as a compatible carbocatalyst for oxidation and hydration reactions [41]. In the same

**CHAPTER 2****Structure and Properties of Graphene and Chemically Modified Graphene Materials****Manish Srivastava<sup>1</sup>, Anjali Banger<sup>2</sup>, Anamika Srivastava<sup>2</sup>, Nirmala Kumari Jangid<sup>2,\*</sup> and Priy Brat Dwivedi<sup>3</sup>**<sup>1</sup> Department of Chemistry, Central University of Allahabad, Allahabad – 211002, Uttar Pradesh, India<sup>2</sup> Department of Chemistry, Banasthali Vidyapith, Banasthali – 304022, Rajasthan, India<sup>3</sup> National University of Science and Technology, AlHail South, Seen 111, Muscat, Oman

**Abstract:** Graphene is an allotrope of carbon that is made up of very strongly bonded carbon atoms. The structure of graphene is a hexagonal lattice. Graphene shows  $sp^2$  hybridization and an extremely thin atomic thickness of approximately 0.345nm. This chapter deals with graphene structure, including hybridization, critical parameters of the unit cell, the formation of  $\sigma$  and  $\pi$  bonds, electronic band structure, edge orientations, and the number and stacking order of graphene layers. The remarkable characteristics of graphene occur because of the extended chain of  $\pi$  conjugation that results in high charge mobility, high conductivity & high Young's modulus value. Due to these attractive properties, graphene has gained much attention. Graphene, with the unique combination of bonded carbon atom structures with its myriad and complex physical properties is balanced to have a big impact on the future of material sciences, electronics, and nanotechnology. Graphene is converted to Graphene nanoparticles, Graphene oxide nanoparticles; Polymer-based graphene composite materials and Graphene nanoribbons, etc by chemical methods. Some of the application areas are batteries and ultracapacitors for energy storage and fuel cell and solar cell for energy generation and some of the possible future directions of research have been discussed.

**Keywords:** Actuators, Application of Graphene, Chemical Properties, Electrical Properties, Electrochemical Capacitors, Fabrication of Graphene Oxide, Functionality and Solubility, Graphene Aerogels, Graphene Composites, Graphene Derived Nanofiller, Graphene Oxide, Hybrid Graphene, Mechanical Properties, Optical Properties, Properties of Graphene, Quantum Dots of Graphene, Storage Material, Surface-Enhanced Raman Spectroscopy, Thermal Properties.

\* **Corresponding author Nirmala Kumari Jangid:** Department of Chemistry, Banasthali Vidyapith, Banasthali – 304022, Rajasthan, India; E-mail:nirmalajangid.111@gmail.com

## 1. INTRODUCTION

The 6th element of the periodic table *i.e.*, Carbon has always attracted researchers and technologists and the most studied allotrope of the Carbon family is Graphene. It is a single atomic planar layer of graphite [1]. By chemical vapor deposition, chemical or mechanical methods, can be obtained from graphite [2, 3].

Theoretically, for the last sixty years, graphene or two-dimensional graphite had been studied [4]. Earlier, it was assumed that graphene does not exist in the free state. Peierls and Landau contended that since two-dimensional crystals were chemically not stable so they do not exist [5, 6]. Hence, it was proclaimed that graphene has large three-dimensional structures [7]. Without a three-dimensional base, two-dimensional structures do not exist, later in 2004, Novoselov *et al.* accidentally discovered graphene. Using a micromechanical cleavage technique single-layer graphene was established [8].

After several broadcasts on nanotubes of carbon (1991) [9], fullerenes (1985) [10], and intercalated graphite [11], graphene gained immense interest [12, 13]. It is a flat  $sp^2$  hybridized planar sheet of C atoms densely packed in a 2D hexagonal pattern. It can be coated into zero-dimensional fullerenes, twirled into a one-dimensional nanotube, or can be bundled into three-dimensional graphite.

The uncommon characteristics of graphene involve that its charge carriers behave as Dirac fermions, and under encompassing situations they scatter. This distinct attitude resulted in exceptional phenomenal changes [12]. Firstly, it is a two-dimensional semiconductor with minimal overlapping between the conduction band and valence band and has a bandgap of zero. Secondly, for measuring deviation in room temperature (up to  $10000 \text{ cm}^{-2} \text{ s}^{-1}$ ) and charge carrier concentration (up to  $10^{13} \text{ cm}^{-2}$ ) it shows a strong bipolar electric field effect. Thirdly, by modifying chemical potential with the help of the electric field effect, exceptional half-integer QHE for hole and electrons carrier can be seen [13, 14]. At room temperature, a single layer of a sheet, shows great thermal conductivity ( $5000 \text{ WmK}^{-1}$ ). Additionally, it's transparent with 2.3% absorption towards visible light [15, 16]. Transistors can be produced with narrower (1-2 nm thick) ribbons of graphene having variable band gaps [17 - 19].

In past years, graphene is being used instead of carbon-based nanofiller in preparing nanocomposites of polymer and showed great thermal, electrical, and mechanical properties [20 - 27]. Chemically unstable indium tin oxide in displays and screens can be replaced by graphene [28, 29]. Hence, it is assumed that a single layer is responsible for the uniqueness of graphene although its preparation is severe in encompassing conditions. Due to inappropriate separation of graphene

sheets, it aggregates and restacks leading to the formation of graphite *via* Vander Waals interaction and p–p stacking [30, 31]. Graphene has vast applications in the fields of microwave absorption shields, nanocomposites of polymer, super-capacitor devices, drug delivery, biosensing, *etc.*

According to IUPAC, graphene can be explained as a single sheet of C with a graphitic structure and similar to a polycyclic aromatic hydrocarbon. During a discussion of various properties of monatomic sheets, graphene is prescribed [32, 33]. In 1987, for the first time, the word “graphene” was used by Mouras *et al.* [34], although in 1840 Schafhaeutl (German scientist) narrated the exfoliation and intercalation of graphite by making use of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. From that time researchers predict the presence of graphene. But it was not until 2004 that two physicists at the University of Manchester, Andre Geim and Konstantin Novoselov, obtained graphene in the laboratory and could prove it. These researchers developed an easy procedure for obtaining graphene from graphite. Using tape, a thin sample of graphite was extracted from a greater one.

This procedure was repeated several times to finally obtain a monoatomic layer, which was then electrically isolated with a thin layer of silicon dioxide on a silicon wafer. The importance of this event lies in having isolated graphene at room temperature since in the past this material was considered thermodynamically unstable. For their innovative experiments, in 2010 they received the Nobel Prize in Physics [35].

The important discoveries of a few scientists have been summarized below (Table 1).

**Table 1. Scientists with their discoveries.**

| S.No. | SCIENTISTS                                       | DISCOVERIES   |
|-------|--|---|
| 1.    | Schafhaeutl (1840)                               | Narrated exfoliation and intercalation of graphite by making use of HNO <sub>3</sub> and H <sub>2</sub> SO <sub>4</sub> . |
| 2.    | B.C. Brodie (1859)                               | First discovered graphite oxide properties [97].  |
| 3.    | Brodie, Staudenmaier, Hummers and Offeman (1958) | First synthesized graphene oxide through graphitic oxidation [109 - 111].   |
| 4.    | Mouras <i>et al.</i> (1987)                      | For the first time, used the word “graphene” [34].  |
| 5.    | Andre Geim and Konstantin Novoselov (2004)       | Fabricated graphene from graphite in the laboratory and received Nobel Prize in Physics (2010) for this.                  |
| 6.    | Novoselov <i>et al.</i> (2004)                   | Discovered graphene using a micromechanical cleavage technique [8].   |
| 7.    | Wu <i>et al.</i> (2011)                          | Established remote control graphene-based robot in the presence and absence of IR radiations [89].                        |

## Preparation Methods for Graphene and its Derivatives

Sharoni Gupta<sup>1,\*</sup>, Pinki Bala Punjabi<sup>1</sup> and Rakshit Ameta<sup>2</sup>

<sup>1</sup> Department of Chemistry, University College of Science, Mohanlal Sukhadia University, Udaipur-313001, Rajasthan, India

<sup>2</sup> Department of Chemistry, J.R.N. Rajasthan Vidyapeeth University, Udaipur-313001, Rajasthan, India

**Abstract:** Over the past few decades, graphene and its derivatives have carved a niche for themselves in material science. These carbon nanomaterials exhibit a broad range of applications owing to their enchanting features like high specific surface area, chemical inertness, astonishing electrical and thermal properties, elevated intrinsic mobility, inimitable optical properties, and huge mechanical strength. Considering the ubiquitous applications of graphene in different industries, diverse top-down and bottom-up methods have been developed. This chapter outlines the various methods used for the synthesis of graphene and graphene-based derivatives, such as exfoliation, unrolling or unzipping of carbon nanotubes, electric arc discharge method, laser ablation technique, oxidative exfoliation-reduction of graphene oxide, chemical vapour deposition, epitaxial growth, template synthesis, pyrolysis, substrate-free synthesis, total organic synthesis, and biological methods, highlighting the advantages of these methods. Upcoming challenges concerning the commercial synthesis of graphene have also been addressed in the concluding part.

**Keywords:** Bottom-up Strategies, Graphene, Graphene Oxide, Reduced Graphene Oxide, Top-down Methods.

### INTRODUCTION

Graphene, a 2-D carbon allotrope, is one of the thinnest and strongest materials known. Graphene has a honeycomb lattice structure comprising a monolayer of sp<sup>2</sup> hybridized carbon atoms assembled as hexagonal rings [1]. In 1859, Brodie, while examining the structure of graphite for the first time, observed graphene and

\* Corresponding author Sharoni Gupta: Department of Chemistry, University College of Science, Mohanlal Sukhadia University, Udaipur-313001, Rajasthan, India; E-mail:sharoni290490@gmail.com



coined the name “graphone” [2]. Later, Boehm *et al.* were the first to use the term ‘graphene’ [3]. For a long time since its first discovery, very little work has been reported on graphene. Then in 2004, Novoselov, Geim, and their research group isolated graphene from graphite with a simple exfoliation method [4]. The reinstating of graphene by Geim and Novoselov, who were awarded the Noble Prize in 2010 for their work on graphene [5], paved the way for “Graphene Science”. Ever since then, a plethora of methods for the synthesis of graphene and its applications in various areas have been explored by researchers worldwide.

The incredible properties namely, enlarged specific surface area (up to  $2630 \text{ m}^2 \text{ g}^{-1}$ ), enormous intrinsic mobility ( $200,000 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ ), stupendous thermal conductivity ( $< 5000 \text{ W m}^{-1} \text{ K}^{-1}$ ), extremely large Young’s modulus ( $< 1.0 \text{ TPa}$ ), exceptional optical transmittance ( $< 97.7\%$ ), outstanding electrical conductivity, and tremendous chemical stability, displayed by graphene arise from its distinctive structure and arrangement of carbon framework [6 - 9].

The arrangement of mono graphitic lamellae of carbon particles in hexagonal planar sheet stacked in one or few layers forms bi-dimensional graphene. It has been reported that graphene lamella has a thickness of about 0.35 nm, comparable to  $1/200,000^{\text{th}}$  of the diameter of a strand of a human’s hair [10]. The bi-layer and few-layer graphenes consist of two and three to ten layers of graphitic sheets, respectively. Graphene with twenty to thirty sheets is identified as multilayer or thick graphene or nanocrystalline thin graphite [11]. The monolayer graphene has a wavy sheet without any stacking. While, in the bi or few-layered graphene, the graphitic sheets are arranged in AA (hexagonal) or AB (Bernal) or ABC (rhombohedral) stacking [12]. Also, the few-layered graphene with no appreciable stacking order is commonly termed turbostratic [13].

The  $\text{sp}^2$  bonding of carbon atoms in graphene exhibits three  $\sigma$  bonds (in-plane) formed by hybridization of s,  $\text{p}_x$ , and  $\text{p}_y$  orbitals and a  $\pi$  bond formed by  $\text{p}_z$  orbital perpendicular to the plane [10, 14]. The  $\sigma$  bonds form a firm backbone of hexagonal geometry, whereas the out-of-plane  $\pi$  bonds result in inter-lamellar interaction between graphene layers [10]. The existence of free electrons in the  $\pi$  bands is thus responsible for the exclusive electrical and optical properties of graphene [15]. Furthermore, the electrical conductivity of graphene is governed by the type of edges. Generally, armchair or zigzag edges exist in graphene. The variety and density of edges can generate metallic or semiconducting behaviour in graphene [16].

In spite of the desirable features of graphene, the lack of industrial-scale production is a major hindrance to its applicability in diverse fields. In such a scenario, the surfacing of graphene oxide and reduced graphene oxide has been a

relief for material chemists and industrial workers. This is because preparative protocols for GO and rGO are quite simple, require inexpensive starting materials, and result in mass production of these materials [17].

The oxidized form of graphene, *viz.* graphene oxide (GO), is structurally similar to graphene but with the presence of oxygen functionalities [17]. The precise structure of GO has been a highly controversial subject owing to its amorphous, berthollide character and hygroscopic nature [18]. Despite its debatable structure, several models have been proposed to elucidate the structural architecture of GO. Hofmann and Holst were the first to put forth a model suggesting that the epoxy groups exist at the basal planes of the graphite layer, with an overall molecular formula of  $C_2O$  [19]. Next, Ruess anticipated a model which elucidated that the carbon sheets were puckered instead of planar and the oxygen-containing groups like hydroxyl and ether-like oxygen formed bridges between the carbon atoms at positions 1 and 3 of the graphite framework [20]. Thereafter, Clause and co-workers [21], to explain the acidic nature of GO, further illustrated an enol- and keto-type model. In 1969, Scholz and Boehm [22] presented a novel arrangement of GO, which encompassed grooved carbon layers bearing hydroxyl and carbonyl functional groups. Nakajima and his research group [23, 24] also proposed a model elucidating the structural attributes of GO. According to them, GO comprises two carbon layers anchored to each other by  $sp^3$  hybridized carbon-carbon bonds at right angles to the layers with the presence of relative numbers of carbonyl and hydroxyl groups based on the hydration scale. In 1997, Lerf and his colleagues [25] suggested the most widely accepted model for GO. As per their model, GO consists of haphazardly dispersed planar aromatic sections comprising un-oxidized benzene rings and crumpled zones of six-membered alicyclic rings with C=C, C-OH and ether groups at 1 and 2 positions [26]. Finally, Szabó *et al.* presented the most recent structural model for GO [27]. The model revealed that the carbon framework exhibits two kinds of zones, one with trans-linked cyclohexane chairs and the other one bearing ribbons of flat hexagonal rings with C=C bonds as well as functionalities, including tertiary OH, 1,3-ether, ketone, quinone, and phenol. Overall, it is clear that the structure of GO comprises graphitic regions, disordered oxidized areas, and regions with defects (which arise due to holes *via* the release of CO and  $CO_2$  during the belligerent oxidation and exfoliation of the sheet in GO) [28].

Additionally, the partial reduction of graphene oxide restores the carbon framework of a graphene layer with the presence of a few oxygen functional groups. This form is known as reduced graphene oxide (rGO). The atomic structure of rGO was studied by Navarro *et al.* [29], and it was explicated that rGO sheets include large areas of undamaged graphene along with considerable regions rich in defects, namely, pentagonal-hexagonal pairs and planar, quasi

## Characterization Techniques for Graphene-Based Materials

Vickramjeet Singh<sup>1</sup> and Ramesh L. Gardas<sup>2\*</sup>

<sup>1</sup> Department of Chemistry, Dr B R Ambedkar National Institute of Technology, Jalandhar-144011, Punjab, India

<sup>2</sup> Department of Chemistry, Indian Institute of Technology Madras, Chennai - 600 036, India

**Abstract:** Graphene bearing 2D (dimensional) layer of carbon atoms bonded in  $sp^2$  hybridized state are only 1 atomic-scale thick. However, the graphene can be extended along the horizontal dimension. The alternate double bonds leading to perfect conjugation with  $sp^2$  hybridization are exhibited in the hexagonal structure (*honeycomb*) of graphene. Theoretically and experimentally, the thicknesses of graphene have been determined and are in the nano-meter range. The extraordinary mechanical and electrical properties exhibited by such a 2D material have inspired scientists for device fabrication methodologies that can shift the synthesis from lab scale to large scale. It is considered the strongest material on earth, almost 100 times stronger (*i.e.*, strength) than the best steel. Since graphene is only 1 atomic-scale thick and transparent, the characterization of graphene is complex but essential. The thickness down to one atomic layer in graphene can be identified by the light interference causing color contrast. Thus, optical microscopy-based methods enable the identification of graphene or its derivatives; on the other hand, Raman spectroscopy, which is sensitive to molecular bonding and geometric structure, is commonly employed for the quality determination of graphene-based materials. In this chapter, various characterization techniques are discussed, enabling the characterization of graphene and graphene-based materials (GBMs).

**Keywords:** Characterization, Fourier-transform infra-red Spectroscopy (FT-IR), Graphene, Graphene Sayers, Graphene Oxide, Optical Microscopy, Raman Spectroscopy, Reduced Graphene Oxide, Scanning Tunneling Microscope (STM), Transmission Electron Microscope (TEM), X-ray Photoelectron Spectroscopy (XPS).

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\* Corresponding author Ramesh L. Gardas: Department of Chemistry, Indian Institute of Technology Madras, Chennai - 600 036, India; E-mail: gardas@iitm.ac.in

## 1. INTRODUCTION

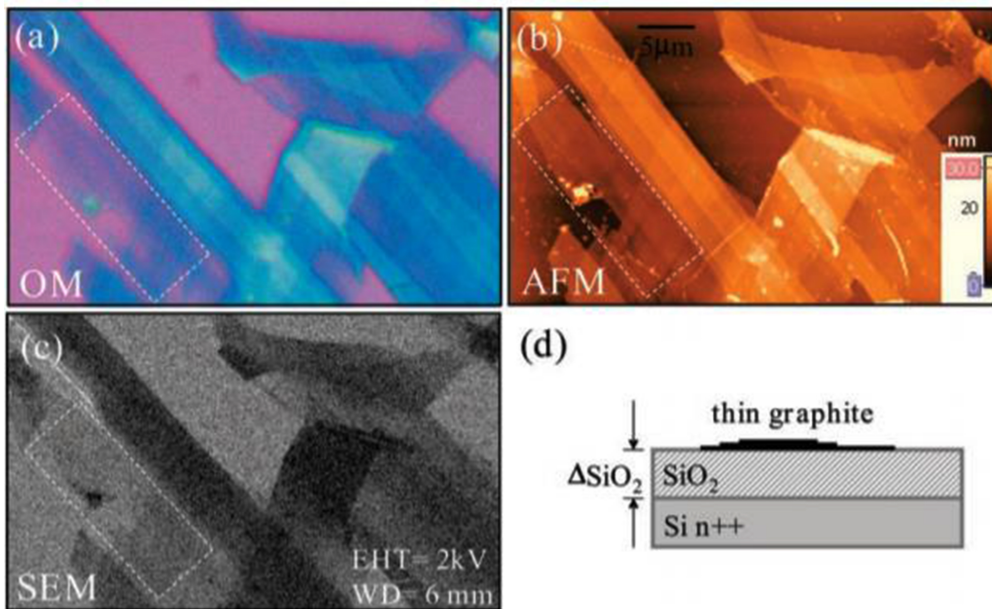
Graphene is a 2D nano crystallite material composed of a single carbon atom layer packed in a hexagonal arrangement (honeycomb) with alternating single and double bonds [1, 2]. The  $sp^2$  hybridized state of carbon atoms has  $\pi$ -bonds (out-of-plane) responsible for conduction (delocalized  $\pi$ -electrons) and weak interaction between graphene layers [1, 2]. The strongest bond in this carbon allotrope is the in-plane C-C bond [2, 3]. The graphene is thus a 2D semiconductor with zero band gaps or nil band gap energy, *i.e.*, having a minor overlap among the conduction and valence bands [2, 4]. While maintaining the  $sp^2$  hybridization, graphene sheets can be rolled up to make materials with dimensions as 3 D (graphite), 1 D (nanotubes), and 0D (fullerenes) [5]. Since graphene is 1 atomic layer thick, the first report of graphene discovery (structural analysis) was still based on optical microscopy [4, 6]. The ease of analysis by the visualization using an optical microscope is possible for graphene synthesized by mechanical peeling and transferred on a few layers of thick  $SiO_2$  (onto a silicon surface) [6]; however, when deposited on cleaned Si surfaces, this visualization of graphene is lost [6]. The graphene-based materials (GBMs) can be single or multi-layered, graphene oxide, graphene reduced oxide, graphene ribbons, and graphene nano sheets [1, 6, 7]. Graphene with various layers or GBMs can be characterized by a number of techniques, and in this chapter following techniques are being discussed:

1. Optical Microscopic techniques
2. Raman Spectroscopy
3. FT-IR Spectroscopy
4. X-ray Photoelectron Spectroscopy
5. Thermogravimetric Analysis

## 2. OPTICAL METHODS

As mentioned above, optical methods can be used to characterise graphene synthesized by mechanical peeling unless the graphene is pasted onto a clean Si substrate [6]. The graphene layers onto a  $SiO_2$  substrate can cause light interferences, so the color and the contrast depend upon graphene layers [3, 6, 8, 9]. Besides  $SiO_2$ -based surfaces, other substrates for supporting graphene layers that can be visibility distinct are polymethylmethacrylate and silicon nitride ( $Si_3N_4$ ) [3, 6, 8, 9]. Mechanical exfoliation may form flakes of various thicknesses; the image of graphite on  $SiO_2$  substrate (oxide thickness of 500 nm)

is shown in Fig. (1) [8]. Besides the optical image, the SEM (scanning electron microscope) and AFM (atomic force microscope) images are also shown in Fig. 1 b and c, respectively. The picture shows the regions having varied thicknesses [8]. The rectangular box (broken lines) in these images indicates the region with a few monolayer thicknesses. The images can be resolved to get a better picture with an electron microscope, such as SEM with better electron detectors [8].



**Fig. (1).** The image of graphite flake having regions with different thicknesses, as obtained from (a) optical microscope (OM), (b) AFM, (c) SEM. The graphite was deposited on a Si substrate with a SiO<sub>2</sub> thickness of about 500 nm. Reprinted (adapted) with permission from ref [8]. Copyright (2007) American Chemical Society.

The AFM analysis can directly identify the layer number of graphene, but this technique can damage the crystal lattice while performing the measurement, and the true thickness cannot be estimated [10]. Ni *et al.* [10] developed a method based on contrasting graphene and the substrate onto which graphene layers were transferred. The light reflection makes graphene visible from ten layers down to one layer. Furthermore, experimental data were correlated with theoretical analysis and a good agreement was reported [10]. An analytical expression for determining the number of graphene layers was also provided [10]. Blake *et al.* [3] represented the optical microscopic images of graphene transferred onto the SiO<sub>2</sub> layer. It was demonstrated that the optically visualized contrast depends upon the opacity of graphene and the optical path, that is, the dependence on the SiO<sub>2</sub> layer as well as light wavelength [3]. The images of graphene obtained under

## Functionalization of Graphene and Factors Affecting Catalytic Performance

Gopal Avashthi<sup>1,2,3</sup> and Man Singh<sup>1,\*</sup>

<sup>1</sup> School of Chemical Sciences, Central University of Gujarat, Gandhinagar-382030, Gujarat, India

<sup>2</sup> Department of Chemistry, Sankalchand Patel University, Visnagar-384315, Gujarat, India

<sup>3</sup> School of Sciences, P P Savani University, Kosamba-394125, Surat, Gujarat, India

**Abstract:** Carbon and its driven materials have been a foundation of living and non-living systems for centuries due to their amazing experimental expressions in light, temperature, pressure, and pH. Being light-weighted and electronically active with equal energy partitioning in its four orbitals ( $2s^1 2p_x^1 2p_y^1 2p_z^1$ ), the C atoms have been at the core of natural sciences, providing valuable resources like high-grade wood, cotton, and many others. Thus, carbon-driven materials like diamond, graphite, and graphene ink have been attracting the attention of scientists, researchers, and industries. The chapter reviews recent chemical methodologies for the synthesis and structural investigation of graphene and its derivatives by various analytical techniques that provide information about basic knowledge to understand the role of graphene and graphene-based composites in various qualitative and quantitative applications. Here, several methods have been enlisted for the surface alteration of graphene oxide by a synthetic approach, such as ultrasound, a microwave-assisted synthesis that avoids the use of hazardous chemicals. Also, conventional methods have been discussed, including various types of reactions, such as nucleophilic, electrophilic, condensation, and cycloaddition. This review article highlights the key points to understanding the 2D carbon material for researchers and users to learn about the chemical modification of graphene at the initial stage. This write-up also discusses a brief explanation of various carbon nanomaterials that concern graphene and its oxide forms. We have explained the synthetic value of 2D carbon materials so that it covers a lot of the needs of researchers for synthetic aspects in graphene and allied fields of interest. Currently, such unique experiments are noted as milestones in the field of material synthesis for various applications. So, a review of chemically altered graphene materials reinforced with structural multi-functionalities is highly informative as a ready reckoner for needed information and understanding.

\* Corresponding author Man Singh: School of Chemical Sciences, Central University of Gujarat, Gandhinagar-382030, Gujarat, India. Tel: +91-079-23260210; Fax: +91-079-23260076. E-mail: mansingh50@hotmail.com

**Keywords:** Covalent Functionalization, Graphene, Non-covalent Functionalization, Surface Modified Carbon Materials, Ultrasound and Microwave-assisted Functionalization.

## INTRODUCTION TO CARBON CHEMISTRY

Carbon is the fourth most abundant chemical element in the universe and the second most abundant in the human body by mass [1]. The atomic number of carbon is six and it belongs to the second period of the fourteenth group [IVA group] of the periodic table. A carbon atom has six electrons with  $1s^2$ ,  $2s^2$ , and  $2p^2$  electronic configurations, which infer tetravalency. Two inner shell electrons are spherically symmetric; out of which,  $1s$  orbital is tightly close to the nucleus. The energy difference between  $1^{\text{st}}$  and  $2^{\text{nd}}$  shells is far from the Fermi energy levels, and remaining four valence electrons ( $2s^2$ ,  $2p^2$ ) have very similar energy to silicon. The energy difference between the  $2s$  and  $2p$  orbitals of carbon is relatively low compared to the bond enthalpy. The tetravalent nature of carbon and its distinctive catenation property can be accessible for hybridization, forming new compounds. Thus,  $2s$  and  $2p$  orbitals hybridize (Fig. 1a,b). The catenation property of carbon results in stable allotropes of 0D, 1D, 2D, and 3D dimensionality compared to other elements [2].

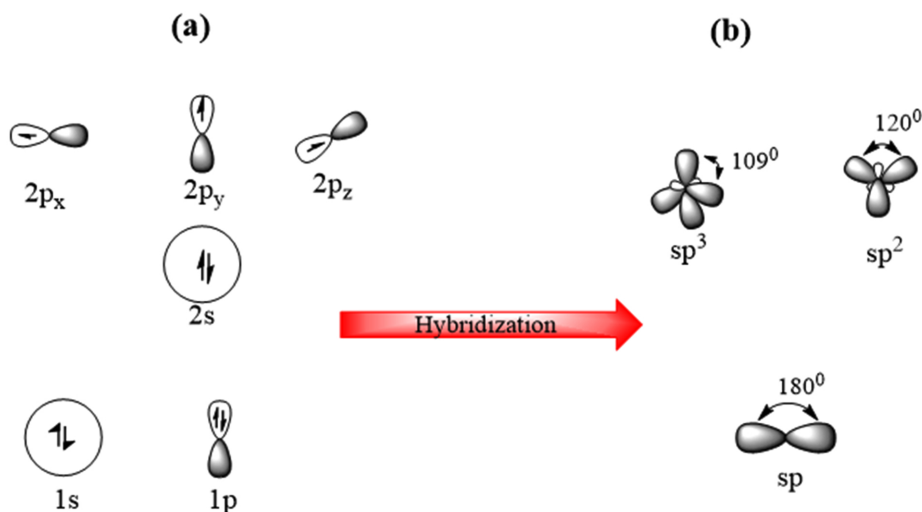
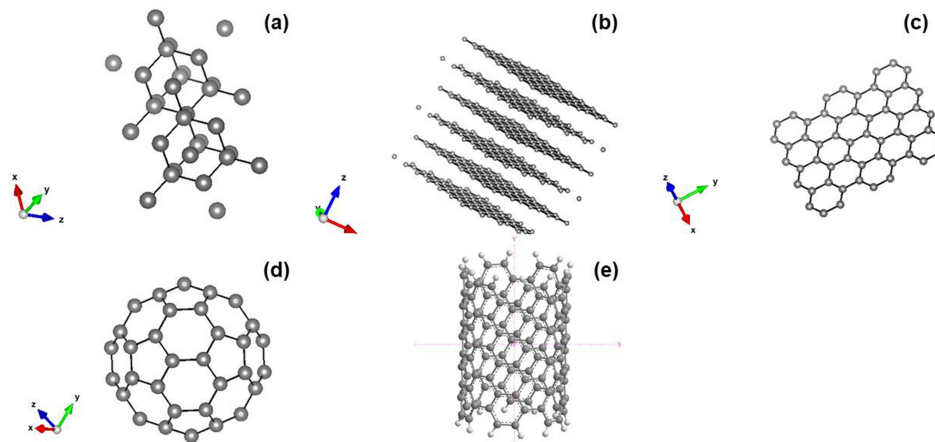


Fig. (1). (a) Diagram of atomic orbitals, and (b) hybrid orbitals of carbon.

## POLYMORPHISM OF CARBON

Carbon has the ability to bind with various elements like H, Si according to optimal hybridization, supporting the synthesis of compounds with different

structural properties and applications. Therefore, newly synthesized compounds have different geometrical features, like  $sp$  hybridized carbon which is linear in nature, while  $sp^2$  and  $sp^3$  have trigonal planar and tetrahedral structures, respectively [2]. The one  $p$  and one  $s$ -orbital hybridize as  $sp$  while, two  $p$  and one  $s$ -orbital hybridize as  $sp^2$  carbon, and remaining unhybridized orbitals participate in forming an additional  $\pi$  bond. Therefore, the tetrahedral lattice of the diamond (Greek 'adamant' meaning impossible to tame) belongs to  $sp^3$ -hybridized carbon atoms in terms of strong covalent bonding to itself [1, 2]. The wave function of four valence electrons ( $2s^2$  and  $2p^2$ ) of carbon, hybridize easily and it adds to the solid-state features of  $sp^2$  hybridized graphite (Gt). The diamond and Gt are two natural allotropes of carbon. The diamond and Gt allotropes have been known since prehistoric times for their distinctive properties such as hardness, thermal conductivity, and lubrication behaviour [3, 4]. In the last few decades, the surprising discoveries of three artificial allotropes of carbon, *i.e.*, 0D fullerene, 1D carbon nanotube, and 2D graphene (Gr) have confirmed the efficiencies of carbon materials for their amazing applications [1 - 8] (Fig. 2a-e).



**Fig. (2).** Carbon allotropes (a) Diamond, (b) Graphite, (c) Graphene, (d) Fullerene, and (e) Carbon nanotube.

## Natural Allotropes

### *Diamond*

Diamond is a  $sp^3$  hybridized natural allotrope of carbon with structurally strong C-C covalent bonds [1, 2]. The crystal structure (Figs. 3a, b) of the diamond is known for its excellent properties; such as high Young's modulus, hardness (hardest material with a supreme Mohs value of 10), chemical inertness, low electrical conductivity, high thermal conductivity (900–2,320 W/m/K), high X-ray, and high optical scattering ability of visible spectrum 1-1.5 eV [1, 9, 10].



## Graphene-based Nanocomposite Catalysts: Synthesis, Properties and Applications

Pradeep Kumar Jaiswal<sup>1,\*</sup>, Munsaf Ali<sup>2</sup>, Siddharth Sharma<sup>3</sup>, Dinesh Kumar Yadav<sup>3</sup> and Nitinkumar Satyadev Upadhyay<sup>2</sup>

<sup>1</sup> Department of Biochemistry and Biophysics, Texas A&M University, College Station, Texas 77843, USA

<sup>2</sup> Colleges of Nanoscale Science and Engineering, State University of New York, Polytechnic Institute, 257 Fuller Rd. Albany, NY 12203, New York, USA

<sup>3</sup> Department of Chemistry, Mohanlal Sukhadia University, Udaipur, 313001, India

**Abstract:** In recent years, the progress of doped carbon catalysts (such as graphene-based nanocomposites), has attracted the tremendous attention of the scientific community because of their broad area of applications involving unique mechanical, electrical and industrial chemical production processes. The catalytic nature of metal-doped graphene-based nanocomposites has significantly improved, and provides alternatives to traditional transition metal-based catalysts. In addition, the progress of simple and easy synthetic approaches for graphene-based nanocomposites provides a wide range of opportunities for the synthesis of graphene-based nanocomposites *via* incorporating various metal or polymer-based nanomaterials for diverse applications. In this context, the recent development in the synthesis of graphene-based nanocomposites, their properties and applications are summarized in this chapter. The future insights and challenges towards the design and utilization of graphene-based nanocomposites with decent stability and enhanced catalytic performance are also outlined in this chapter.

**Keywords:** Electrochemical Biosensor, Graphene, Graphene Nanocomposite Catalysts, Graphene Oxide, Reduced Graphene Oxide.

### INTRODUCTION

Since the discovery of carbon-related catalysts, the hydrocarbon-based compounds such as activated carbon, carbon fibers, graphite, and graphite-intercalation compounds, have gained significant attraction from chemists, in the last decades. Nowadays, carbon-based materials like graphene-based nanomaterial synthesis have become an attractive field in chemistry, physics, biology, and

\* Corresponding author Pradeep Kumar Jaiswal: Department of Biochemistry and Biophysics, Texas A&M University, College Station, Texas 77843, USA; E-mail:pradeepjais@gmail.com

materials science [1]. Graphene is a two-dimensional carbon-based material having a single layer of  $sp^2$  hybridized bonded carbon atoms that are closely packed in a honeycomb lattice [2]. Since the remarkable work of Prof. Novoselov's group in carbon-based chemistry research, the fast development in graphene-based research has envisioned the great potential of graphene in optoelectronics, nanoelectronics, electrochemical drug delivery, and biosensor applications due to its unique 2D structure, excellent electrical capacity, high adsorption susceptibility, high mechanical strength, and high thermal conductivity [3 - 5]. Although graphene sheets were well explored in fundamentals by a physicist at the discovery time, graphene metal-nanocomposites are drawing more attention to real applications for industry [6 - 9]. Until now, various synthetic procedures, such as covalent as well as non-covalent methods, electrochemical, micro-mechanical, solvo-thermal, chemical oxidation–reduction, chemical vapour deposition, photochemical reaction, physical deposition, and mixing [10 - 14] have been fabricated for the synthesis of well-defined functional graphene-based nanocomposites [15 - 20]. It was investigated that the graphene-based sheets can be doped with several components such as metal, metal oxides, or polymers [15, 21, 22] and developed as graphene-based-hybrids which can be employed in multiple applications [23 - 29]. In this view, extensive efforts have been devoted towards the study of graphene-based hybrids and many reviews on their design, development, synthesis, properties, characterization, and applications in recent decades are documented [29 - 32]. The significant potential growth of graphene-based nanocomposites toward their application in a variety of fields motivated us to present its synthesis, properties, and potential applications in a single chapter.

It is well established that the design of a heterogeneous catalyst plays an important role in its catalytic activity [33, 34]. As a new carbon family member, the extraordinary properties of graphene-based nanocomposites provide an ideal catalytic support [32, 35]. Therefore, we hope that this chapter will draw significant attention to the recent developments and advancements in the synthetic protocols and catalytic utilization of graphene-based nanocomposites. It is noteworthy that almost all graphene supports in the nanocomposites are developed *via* chemical reduction–oxidation methodology. The catalytic reactions, which are demonstrated, are an extension of the model reactions towards industrial-based reactions and the utilization of non-selective reactions towards more challenging and selective hydrogenation, coupling, oxidation, or reduction reactions. In the present chapter, a brief overview of the characteristic synthetic approaches and catalytic potential of graphene-based nanocomposites is presented, along with the enhanced catalytic behavior. A summary of some of the scientific opportunities and challenges is also presented at the end of the chapter.

## APPROACHES TOWARDS GRAPHENE-BASED NANOCOMPOSITES SYNTHESSES

Many versatile synthetic approaches have been documented to synthesize the graphene-based nanocomposites, such as covalent/non-covalent interaction, photochemical reactions, chemical/physical deposition or mixing, hydrothermal/solvothermal growth, electrophoresis, and electrochemical deposition. These developed approaches have several advantages as well as limitations, along with the improved recent development of specific graphene nanocomposites by adoption of appropriate preparation methods.

### Non-covalent Interactive Approach

Non-covalent interaction is a leading applied methodology to design and synthesize graphene-based nanocomposites. Non-covalent association of organic and inorganic species with graphene leads to the attachment of organic and inorganic species on graphene incorporated surfaces. *in-situ* Small molecules, such as surfactants and polymers, are bonded to graphene surfaces *via* - stacking and/or hydrophobic interactions, providing an important way to modify graphene surfaces for graphene nanocomposites [36 - 40]. Because of the strong -stacking interaction with the graphene sheet of the pyrene moiety in the molecule, Xu and colleagues used PB- to synthesize enhanced hydrophilic graphene [40]. This was provided by *in-situ* chemical reduction of GO by hydrazine in the presence of 1-pyrenebutyrate (PB-). The resultant water-soluble graphene can be utilized to develop large scale conductive graphene films with higher conductivity in comparison to graphene oxide.

Metal ions can also be doped in graphene sheets through non-covalent congregation of graphene to form 3-D composites or hydrogel [41, 42]. For example, graphene oxide and metal precursors are hydrothermally decomposed to furnish three dimensional graphene-supported metal nanocomposites. Novel metal nanocomposites (Ag, Au, Pd, Rh, Ir, or Pt) on graphene material exhibit active sites, which enhance the porosity in graphene metal composites. The catalytic activity of 3-D composite with respect to Heck reaction has shown excellent and selective physical behavior [41]. GO sheets also undergo metal ions promoted self-assembly based reaction *via* the reduction of GO and produce magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles with macroscopic graphene based nanocomposites [42].

### Covalent Interactive Approach

Another method that can be used to design and synthesis graphene nanocomposites is covalent reaction. Ionic liquids, polymers, porphyrin,

## CHAPTER 7

# Graphene Supported Palladium Nanocatalyst for Cross-Coupling Reactions

Mukesh Kumar<sup>1</sup>, Meenakshi Singh Solanki<sup>2</sup> and Siddharth Sharma<sup>3,\*</sup>

<sup>1</sup> Department of Chemistry, Sahu Jain College, Najibabad, Bijnor 246763, India

<sup>2</sup> Department of Chemistry, PAHER University, Udaipur, Rajasthan 313003, India

<sup>3</sup> Department of Chemistry, Mohanlal Sukhadia University Udaipur, Rajasthan 313001, India

**Abstract:** The catalytic potential of graphene oxide (GO) and graphite oxide has been well explored in recent years. The reactivity of metal-supported graphite oxide as a solid-phase heterogeneous catalyst has started to be an exceptionally powerful tool for the construction of C-C bonds in synthetic organic chemistry. Among them, palladium has been widely used in different catalysts for a variety of cross-coupling reactions such as Mizoroki-Heck, Suzuki-Miyaura, Kumada, Stille, Negishi, Hiyama, and Buchwald-Hartwig, *etc.*, because of its high catalytic activity and the rapid installation of a complex molecular structure with selectivity in comparison to other transition metal catalysts. A description of recent advances in graphene-supported palladium nanocatalysts for cross-coupling reactions is presented in this chapter. Catalyst synthesis and mechanistic aspects are also given, followed by comparisons with traditional methods.

**Keywords:** C-C Bond Formation, Cross-coupling Reaction, Graphene Oxide, Graphite Oxide, Reduced Graphene Oxide (r-GO).

## INTRODUCTION

Transition metal-catalyzed cross-coupling reactions have emerged as an exceptionally powerful tool for the construction of C-C and C-Hetero atoms bonds in synthetic organic chemistry and continue to have widespread application, especially in drug development programmes and agrochemicals [1, 2]. In the last decades, many transition metals have been employed to carry out cross-coupling reactions. Among them, palladium has been widely used in different catalysts for a variety of cross-coupling reactions such as Mizoroki-Heck, Suzuki-Miyaura, Kumada, Stille, Negishi, Hiyama, Buchwald-Hartwig, *etc.*, because of its high catalytic activity and the rapid installation of complex molecular structure with

\* Corresponding author Siddharth Sharma: Department of Chemistry, Mohanlal Sukhadia University Udaipur, Rajasthan 313001, India; E-mail: [siddharth@mlsu.ac.in](mailto:siddharth@mlsu.ac.in)

selectivity in comparison to other transition metal catalysts [3]. The impact of palladium-catalyzed reactions in the scientific community has been recognized after getting the Nobel Prize in chemistry by three renowned scientists in this area: Professor Richard F. Heck, Professor Eichi Negishi, and Professor Akira Suzuki [4].

Despite the high impact of homogenous palladium-catalyzed cross-coupling reactions in all fields of science, there are many issues associated with homogenous catalysis, such as the use of a high-cost catalytic system, lack of reusability of catalyst, and potential contamination of the drug by residual heavy metals, which strongly limit their use in the pharmaceutical industry [5, 6]. To address these issues, synthetic chemists started channeling their efforts to innovate environmentally benign processes by developing new catalysts with high efficiency and reusability, applying efficient energy sources, and avoiding the use of ligands and auxiliaries. For these reasons, synthetic chemists moved on to heterogeneous catalysis, in which palladium catalysts immobilized on solid support (organic, inorganic, and hybrid materials) have become an important alternative to address all the issues associated with homogenous catalysis. Several heterogeneous palladium catalysts have been generated using silica [7, 8], zeolites [9, 10], ionic liquids [11 - 13], alumina [14], clay [15], zinc ferrite [16], organic, and inorganic polymers as supports [17 - 22]. There are many carbon-based nanomaterials such as one-dimensional (1D) carbon nanotubes (CNTs), two-dimensional (2D) graphene, amorphous activated carbon (AC), and mesoporous carbon (MC), which have also been applied as supports for the synthesis of palladium nanoparticles catalysts [23 - 26].

Among them, graphene and modified graphene has recently become more attractive support in the field of catalysis and have attracted much attention from the scientific community because of their extraordinary properties. Graphene, a 2D material, is considered a “wonder material” formed by carbon atoms that are arranged in a hexagonal monolayer pattern (a honeycomb crystal lattice). Each carbon atom of graphene is  $sp^2$  hybridized and 200 times harder than steel, very feathery, and flexible [27 - 29]. In addition, graphene possesses a large surface area, and excellent chemical, thermal and electrical stability. Moreover, it showed a strong hydrophobic interaction with metal and was easily modified to other forms [30]. Graphene-based architectures are highly desirable in the synthesis of metal nanoparticles, especially as a support for palladium nanoparticles (PdNPs), and displayed exceptional catalytic efficiency for C-C cross-coupling reactions because graphene has high binding energy with palladium and good charge storage performance [31]. Moreover, due to the presence of transparency and conductive properties of graphene it also plays a vital role in the areas of electrochemical applications such as sensors [32], electrodes [33], and fuel cells

[34]. Furthermore, graphene derivatives, such as graphene oxide (GO) and reduced graphene oxide (rGO) have also become useful support in nano metal-catalysis due to their structural defects, which allow an easy covalent and non-covalent (hydrogen-binding or  $\pi$ -stacking) functionalization of the material that can be used either as supports for immobilizing active species or as metal-free catalysts and enhancing the rate of interaction with anchored metal nanoparticles [35, 36]. Graphene oxide was first synthesized by oxidation of graphite in acidic conditions using the Hummers-Offeman method [37]. This method involves the treatment of graphite with sodium nitrite ( $\text{NaNO}_2$ ), potassium permanganate ( $\text{KMnO}_4$ ), and followed by hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).

Recently, Palladium nanoparticles (PdNPs) have established as an intensively investigated and rapidly growing area in ligand-free catalysis because of their high surface-to-volume ratio and highly active surface atoms in comparison to other bulk catalysts [38 - 42]. Palladium nanoparticles (PdNPs), used as a heterogeneous catalyst for the production of pharmaceutical agents, herbicides, fine chemicals, and polymers have a lot of advantages over the palladium-catalyzed homogenous reactions because of their remarkable features such as stability, selectivity, reusability, cost-effective, simple workup procedure and easy separation of the final product [43]. Palladium nanoparticles (PdNPs) supported on graphene/graphene oxide (GO) /reduced graphene oxide (rGO) increase the surface area of nanohybrids by expanding the distance between the sheets. This process enhances the catalytic performance of this type of heterogeneous catalyst. These heterogeneous catalysts have not only shown their catalytic efficiency for catalyzing the cross-coupling reactions in which carbon-carbon bond is formed but they have also been applied in other reactions, such as hydrogenation of alkenes, alkynes, and hydrogenation of carbonyl ( $-\text{CO}$ ) and nitro ( $-\text{NO}_2$ ) groups [44 - 52].

This chapter covers the graphene/graphene oxide (GO)/reduced graphene oxide (rGO) supported metal nanoparticles catalyzed cross-coupling reactions such as Suzuki, Heck, and Sonogashira, leading to the formation of biological importance molecules.

### **GRAPHENE SUPPORTED PALLADIUM NANOPARTICLES (PDNPS/G) CATALYZED CROSS-COUPLING REACTIONS**

Palladium nanoparticles supported on graphene (PdNPs-G) and reduced graphene oxide (PdNPs-rGO) have been used as catalysts for Suzuki cross-coupling reactions between aryl bromides and potassium aryltrifluoroborates by Gómez-Martínez and his co-workers in 2015 [53]. Potassium aryl- and heteroaryl-trifluoroborates efficiently coupled with various aryl halides in the presence of 0.1

## CHAPTER 8

# Domino and Multicomponent Reactions by Graphene-Based Carbocatalysts – A Boon for Organic Transformations

S. Haripriya<sup>1,ψ</sup>, K.M. Sreeranjana<sup>1,ψ</sup>, Sagar Ulkesh Patil<sup>1,ψ</sup>, G.S. Sahoo Navneet<sup>1,ψ</sup>, H.S. Sushma<sup>1</sup>, S. Ahallya<sup>1</sup>, Rakesh R Panicker<sup>1</sup>, Ivaturi Sai Vighnesh<sup>1</sup>, Rajagopal Desikan<sup>1</sup>, Vepa Jagannadha Rao<sup>2</sup> and Akella Sivaramakrishna<sup>1,\*</sup>

<sup>1</sup> Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology (VIT), Vellore 632014, Tamil Nadu, India

<sup>2</sup> Department of Chemistry, Anil Neerukonda Institute of Technology and Sciences, Affiliated to Andhra University, Sanghivalasa, Visakhapatnam 531162, Andhra Pradesh, India

**Abstract:** The research on the development of high-performance metal-free carbocatalysis is one of the emerging areas in chemical sciences. The possible active sites of the surfaces of graphene, oxygenated, and reduced graphene oxide materials are responsible for diversified synthetic transformations, including redox reactions. At present, the advanced research is focused on scalable, sustainable, biocompatible, green, and cost-effective graphene-based carbocatalysts as wonderful alternatives over the noble metallic catalytic materials which are being employed despite their scarcity, high cost, and relative toxicity. The present chapter describes the utility of graphene-based carbocatalysts in multicomponent reactions.

**Keywords:** Catalytic Activity, Graphene Oxide Materials, Metal-Free Carbocatalysts, Multicomponent Reactions, Reduced Graphene Oxides.

## 1. INTRODUCTION

Numerous organic transformations have been reported by many homogeneous transition metal complexes including organometallics and heterogeneous catalysts [1 - 4]. Among these catalytic reactions, due to the significant medicinal properties of the reaction products, various multicomponent organic reactions yielding fused heterocyclic compounds have been designed employing a variety

\* Corresponding author Akella Sivaramakrishna: Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology (VIT), Vellore 632014, Tamil Nadu, India; E-mail: askrishna@vit.ac.in

ψ All these authors have equal contributions to this Chapter.

of metal and non-metal-based catalysts [5]. It would be appropriate to design alternative non-metal catalysts derived from renewable resources in terms of sustainability. Because of this, carbon materials resulting from biomass have been considered sustainable pathways [6, 7]. The economic burden and toxicity are the other specific factors besides sustainability, which favor the carbocatalysts since some of the precious metals (in particular noble metals) are very expensive over the carbon feedstock materials. Furthermore, it is sometimes a very difficult task to remove the residual catalyst from the final product, which can lead to undesired toxicity. These aspects are the driving force in developing metal-free catalysts by researchers. Among them, “carbocatalysis” is one of the promising sustainable routes to reduce metal-based reactions [8 - 10]. It was found that these carbocatalysts, especially the heteroatom doped graphene-based carbocatalysts are considered the best promising alternates of noble metals as an efficient and green catalyst.

In general, carbocatalysts are non-molecular entities and contain mostly carbon framework as an active component with a large surface area. But these carbonaceous catalytic materials are completely different from organocatalysts, which are active organic molecules [7, 11]. Furthermore, the incorporation of the active sites into the carbon materials by appropriate modifications is the key aspect for carbocatalysts, which makes the utilization of metals non-essential. Carbocatalyst is better suited for heterogeneous reactions over homogeneous systems when the particle sizes are large. However, the particle size of the graphene material can be reduced to the carbon dots having 2D morphology; carbocatalysts facilitate the single phased homogeneous catalysis [12]. The graphene derivatives can offer wonderful catalytic properties due to the presence of functional groups with heteroatoms on the G-sheet as active catalytic centers [13, 14]. The importance of graphene as catalytic material is highlighted based on the adsorption capacity, electron density, and morphology of the sheets and its efficiency is strongly dependent on the position and nature of active sites on the graphene sheets.

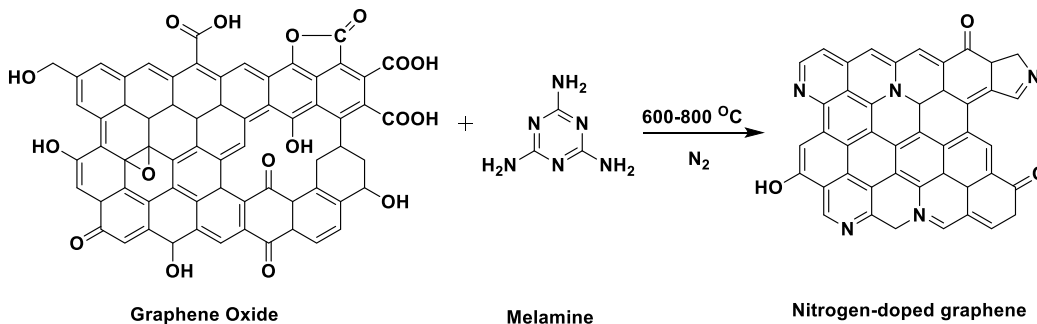
## **2. SYNTHESIS OF GRAPHENE-BASED CARBOCATALYSTS**

A large number of research articles have been reported on the method of preparation on various Gmat [12 - 33] and characterization techniques [17, 18, 23, 34], including their important structural properties for the applications in electronics [34 - 40] and conductivity [38 - 41]. Furthermore, the studies on electrocatalysis [42 - 47] and photocatalytic applications [48] of graphene derivatives have been widely carried out; however, there is a growing interest in the graphene oxide (GO) materials as semiconductors [49] and the synthesis of



organic heterocycles [50]. Notably, N and P double doped graphene carbon catalyst (NP-G) was employed for the reduction of nitrophenol over traditional graphene-based catalyst [14]. Nitrogen and sulfur co-doped graphene (NS-G) derived by one-pot thermal pyrolysis using heteroatom containing precursors like dopamine hydrochloride (DA) and 2-mercaptoethanol (ME) exhibits unusual catalytic activity due to its porous structure toward water splitting upon activation [51].

The synthesis of heteroatom donor graphene oxide (GO) is quite lengthy and cumbersome. Primarily, the modified Hummer's method [52] was employed to synthesize GO for the synthesis of N-doped rGO. By this process, GO was (1.0 g) dissolved in 50 mL ethanol, agitated for around 30 min, followed by sonication. After that, melamine (1.0 g) was incorporated into the mixture and the resulting suspension was heated to 50 °C on a hotplate while stirring (Scheme 1). The desiccated mixture was heated at 450 °C and then calcination was done at varying temperatures of 600, 700, and 800 °C under an inert N<sub>2</sub> atmosphere for 1 h to obtain NG-600, NG-700, NG-800, respectively. Further washing with ultrapure water and ethanol and after overnight drying at 60 °C, the (N)G attains the catalytic activity [53].



Scheme 1. Synthesis of N-doped graphene.

The graphene-based carbocatalytic reactions for various organic transformations are broadly classified into i) oxidation, ii) carbon-carbon bond formation, iii) hydrogenation, iv) aza-Michael addition, v) dehydration-hydrothiolation, and vi) Friedel-Crafts alkylation.

## CHAPTER 9

## Oxidation and Reduction Reactions Catalyzed by Graphene Based Catalysts

Chetna Ameta<sup>1,\*</sup>, Priyanka Chundawat<sup>1</sup>, Yogeshwari Vyas<sup>1</sup>, Reema Agarwal<sup>1</sup> and Dharmendra Dharmendra<sup>1</sup>

<sup>1</sup> Photochemistry Laboratory, Department of Chemistry University College of Science, Mohanlal Sukhadia University, Udaipur (Raj.), India

**Abstract:** Graphene has several features, such as charge mobility, high conductivity, and a large specific surface area with a two-dimensional structure. It also has exceptional electrical, mechanical, and thermal properties. Graphene has exceptional mechanical, physical, and chemical properties, which are responsible for the development of efficient graphene-based catalysts for selective organic synthesis. This chapter recapitulates the various applications of graphene-based catalysts in oxidation and reduction reactions. It gives a complete overview of graphene, reduced graphene oxide, functionalized graphene oxide, N-doped graphene oxide, and their catalytic applications in various oxidation and reduction reactions. The previous studies reveal that metal-free GO has many catalytic applications. Owing to its high surface area, graphene oxide has a high adsorption tendency for hydrocarbons, gases, and ions. When reacting with oxygenating functionalities, GO provides several paths for introducing and modifying various functional groups. The large potential is employed for the use of metal-free carbon catalysts to resolve the industrial problems arising from traditional catalysts. Since graphene/GO catalysts are synthesized from environmental-friendly material, their applications in green synthesis should be discovered vigorously. The graphene-based catalysts have several applications. They allow only selective, mild, and highly effective transformations and undergo the synthesis and synthesis in an easy, recyclable, regenerable, and environmentally friendly manner.

**Keywords:** Graphene, Reduced Graphene Oxide, Functionalized Graphene Oxide, Metal-free Structured Carbon Catalysts, Oxidation and Reduction Reactions, Green Method.

### INTRODUCTION

In the last decade, the utilization of nanomaterials as catalysts and supporting catalysts has propagated immensely. More exciting is the fast development in the research on the application of structured carbon nanomaterial in catalysis.

\* Corresponding author Chetna Ameta: Photochemistry Laboratory, Department of Chemistry University College of Science, Mohanlal Sukhadia University, Udaipur (Raj.), India; E-mail: chetna.ameta@yahoo.com

Graphene is composed of a two-dimensional carbon network and it is also used for the synthesis of other carbon materials such as single and multiwalled carbon tubes (1D), fullerenes (0D), and graphite (3D) [1]. All the above-mentioned carbon materials are used as a support system for catalytic active phase and metals, it can also be used as a metal-free catalyst.

Carbon nanomaterials own unique properties, such as electrochemical and chemical stability, the tendency for a high degree of functionalization, and high surface area. In the last few years, extensive studies have been done on single and multi-walled carbon nanotubes to explore their use in catalysis, energy and electronic devices, polymer fillers, biological applications, and drug delivery. In 2004 mechanically exfoliated single-layer graphene sheets were reported.

Graphene-based materials have a huge application in energy storage, photocatalysis, catalysis, solar cells, memory devices, drug delivery, nano circuitry, and sensing platforms [2]. Several unique thermal, electronic, mechanical, and optical properties are owned by pristine graphene, these above properties are different from other forms of carbon. But, pristine graphene has some limitations, such as complex synthesis procedures and poor processability. Graphene oxide, reduced graphene oxide, and chemically modified graphene can be used as alternatives to pristine graphene because they can be easily prepared and processed in large quantity and also they can be easily synthesized, processed and dispersed in water and other organic solvents. However, they have some mechanical and electrical properties which are somehow different from graphene and responsible for disturbance in few applications. Yet, they are the appropriate starting materials for several applications [3].

Pristine graphene has zero bandgap and is a stable and inert material, whereas graphene oxide and reduced graphene oxides are either insulators or semiconductors. Graphene consists of only carbon material, while graphene oxide and reduced graphene oxide contain several organic functional groups which can further undergo modifications. At present main function of GO, graphene, and CMGs (chemically modified Graphene) are to act as supporting materials for catalytically active transition metals. So, we need to find more striking alternatives concerning extended stability, low cost, flexibility, and ecological influence.

The biological grade synthesis processes are highly toxic processes which is a matter of great concern, particularly the leakage of metal from their supports. To solve these problems, heterogenous metal-free catalysts made up of carbon materials [4] and noncarbon materials [5] can be used as an alternative. Over the past two decades, innovation and growth in new forms of carbon like nanotubes,

fullerenes, graphene, and nanofibers have resulted in an emphasis on the development and use of metal-free carbon catalysts. Important applications of CMGs and metal-free graphene oxides are their use in various chemical reactions as green catalysts.

The application of graphene and graphene oxide in catalysis has been discovered recently. Because of their use in battery and fuel cells, these materials have gained much attention already, specially N-doped graphene shows excellent activity for electrocatalytic oxygen reduction reaction (ORR). In this chapter, we will emphasize recent development and synthesis and oxidation and reduction reactions catalyzed by GO, FGO (Functionalized graphene oxide), and heteroatom doped graphene, which does not gain much consideration.

## **SYNTHESIS OF GRAPHENE/GRAPHENE OXIDE**

### **Graphene**

The exfoliation method was used first time for the experimental research of a single atomic layer of graphene. But this synthesis method is not adaptable for producing high-quality graphene on a large scale. The development of graphene sheets from graphite is done by the use of various chemical methods. The solvent used in the chemical method can interrupt the  $\pi$ - $\pi$  interaction between sheets and result in individual stabilization of graphene [6], another alternative method is the bottom-up method in which, at high-temperature organic precursors are used for the direct growth of graphene [7].

The above methods have a large number of limitations, such as poor solubility, which results in graphitization and an increase in defect sites, and the number of unwanted side reactions. Even with the lots of development in the above alternative techniques, the mechanical exfoliation route is still the best method to produce graphene sheets of good quality.

### **Graphene Oxide and Reduced Graphene Oxide**

Brodie [8], Staudenmeier [9], and Hummers [10] proposed the most common method to prepare to GO. In this method, graphite is oxidized with a strong oxidizing agent and results in samples having the same degree of oxidation. In the last decade, a modified Hummers method has become much more popular because it does not produce hazardous  $\text{ClO}_2$  gas, has a short reaction time, and peroxidation steps promote further oxidation.

In Modified Hummers method, oxidization of flake graphite powder takes place, in these method flake graphite powder is mixed with phosphorus peroxide ( $\text{P}_2\text{O}_5$ )

## Graphene Based Biocatalysts

Monika Jangid<sup>1</sup>, Sunita Panchawat<sup>2</sup> and Abhilasha Jain<sup>3,\*</sup>

<sup>1</sup> Department of Chemistry, PAHER University, Udaipur, Rajasthan, 313001, India

<sup>2</sup> Department of Pharmaceutical Sciences, Mohanlal Sukhadia University, Udaipur, Rajasthan, 313001, India

<sup>3</sup> Department of Chemistry, St. Xavier's College (Autonomous), Mumbai, Maharashtra, 400001, India

**Abstract:** Enzymes have catalytic properties and can be used for different purposes as biocatalysts in some industrial processes. However, their applications are limited due to some drawbacks, such as lack of long-term stability and recovery under conditions of any particular process. Enzymes can improve their catalytic activity, stability, reusability, and half life, if these are immobilized on some support. Graphene and graphene based nanomaterials are good supports for enzymes as they are also non-toxic materials in nature. Such materials can also find applications in the fields of medical diagnostics, biofuel cells, biosensors, *etc.* These particular aspects have been discussed in this chapter.

**Keywords:** Biocatalyst, Biofuel Cell, Biosensors, Graphene, Graphene Oxide, Immobilization, Reduced Graphene Oxide.

### INTRODUCTION

Nowadays, graphene and its derivatives are attracting the attention of scientists all over the globe due to their unique properties such as chemical, optical, mechanical, electrical, *etc.* There could be multivalent functionalized and surface loaded efficiently with the number of biomolecules. Apart from it, abundance, easy synthesis, excellent solubility and processability, high surface area, conductivity, and biocompatibility are the added advantages of graphene-derivatives over other carbon-based materials like diamond, carbon nanotubes, fullerene, *etc.* Recent advancement in the synthesis and surface functionalization of this graphene or graphene-based nanostructured materials have opened up new horizons as a host material for polymers grafting and the designing of state-of-the-art nano-biocatalytic systems. Graphene-immobilized nanocatalyst varies from

\* Corresponding author **Abhilasha Jain:** Department of Chemistry, St. Xavier's College (Autonomous), Mumbai, Maharashtra, 400001, India; E-mail: jainabhilasha5@gmail.com

conventional nano-bioconjugates with respect to functional stability, catalytic efficacy, and applicability. Graphene-assisted biocatalysts find numerous applications in various fields such as enzyme engineering, biotransformation, biosensing, biofuel & energy production, and designing highly biocompatible, non-toxic (Arvidsson *et al.* [4]), and environmentally-friendly nanomaterials and assemblies.

The substances, which can catalyse different chemical reactions in living systems are called biocatalysts. Best examples are enzymes, which are biological compounds (derived from micro-organisms, plants or animal tissue) worked as nature's catalysts and promoted chemical reactions in biological as well as natural systems. Microbial lipases are a class of enzymes, well known as biocatalysts and these are used in a broad range of chemical and biological reactions. These enzymes find numerous applications such as pharmaceuticals, cosmetics, waste water treatments, foods, tanning, detergents, *etc.*

Various enzymes can be used as biocatalysts for different analytical purposes in medical diagnostics and manufacturing purposes in large-scale industrial processes. They have catalytic properties, but their industrial applications are limited due to a lack of long-term stability under process conditions. There is a demand to resolve the difficulties associated with recycling before the enzyme is implemented on an industrial scale. Here, immobilization of enzymes is a novel approach, which can improve half-life, stability, catalytic activity, and reusability of enzymes. Graphene-based nanomaterials are nanoscale and thermo stable inorganic carriers. There are also nontoxic materials and selective modulators for enzyme activity.

## APPLICATIONS OF GRAPHENE BASED BIOCATALYSTS

### Immobilization of Enzymes

Enzyme immobilization is an interesting field of research and many enzymes are useful in medical fields and food processing industries and this immobilization can improve their activity and stability. Immobilization has certain advantages such as increasing catalytic activity, improvement of stability, easy recovery of enzyme, reuse, *etc.*

A green and efficient Rassi has developed one-pot procedure and Baharfar [1] to achieve indole based amides using Passerini reaction, which involves indole--carboxylic acids, aromatic aldehydes and alkyl isocyanides in the presence of immobilized lipase on graphene oxide. This method has many advantages such as simple operation, mild reaction conditions, good to excellent yields, environmental compatibility and no side products.

The Passerini reaction was performed in the presence of GO@lipase as a green heterogeneous catalyst for the synthesis of indole based  $\alpha$ -acyloxycarboxamide derivatives. Activity, efficiency and reusability of *Aspergillus Niger* Lipase (ANL) immobilized on graphene oxide (GO@lipase) were demonstrated. As-prepared nanobiocatalyst was found applicable in multi-component reactions (MCRs) as a heterogeneous biocatalyst.

Adeel *et al.* [2] reported that graphene-based nanomaterials had attracted research interest in different fields related to proteins. They have exceptional physiochemical properties such as optical, thermal, electrical, and mechanical strength, so graphene-based nanostructured materials are considered suitable for many applications in varied fields such as electrochemical sensors, electroanalytical chemistry and immobilization of biomolecules and enzymes. Graphene oxide has different functionalities, such as epoxy, hydroxyl, and carboxylic group, which has opened new avenues to modify GO to achieve materials with desired properties.

Ariaeenejad *et al.* [3] reported bifunctional applications of a novel immobilized enzyme on the modified magnetic graphene oxide (GO) for the effective removal of dyes from water. The amine functionalized GO nano-carrier was covalently attached to a model enzyme (PersiManXyn1). It was observed that the specific activities of the free and immobilized enzymes were 856.05 and 1141.1  $\mu\text{mol min}^{-1}\text{mg}^{-1}$ , respectively based on enzyme assays. The free enzyme showed only 5% of its maximum activity, while the immobilized PersiManXyn1 preserved more than 35% of its activity at 90°C. It was revealed that the free enzyme was deactivated after four weeks of storage, but the immobilized enzyme retained 54% of its initial activity. Immobilized PersiManXyn1 was applied for the removal of dye from water. The immobilized PersiManXyn1 could catalytically reduce the dye solutions (94% dye removal after 15<sup>th</sup> cycle), while pristine nano-carrier and free enzyme showed no considerable catalytic ability within 150s. It retained its superior reusability. This immobilized PersiManXyn1 finds its practical applications in the treatment of real textile effluent.

Graphene oxide is a potential candidate for enzyme immobilization, because it has large specific surface area. GO was first functionalized with L-aspartic acid (GO-Asp) by Monajati *et al.* [5]. Then L-asparaginase was immobilized on the GO-Asp either physically or through chemical conjugation. It was reported that a significant enzyme loading could be achieved through covalent immobilization (almost 100% immobilization efficiency). They also examined stability of free and immobilized L-asparaginase in a wide range of temperatures (20–60°C) and pH (5–9). It was revealed that covalently immobilized L-asparaginase exhibited higher enzyme activity than the free enzyme at pH 8, with the maximum

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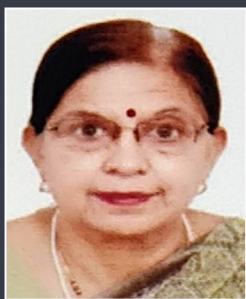
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## **Pinki Bala Punjabi**

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Prof. Pinki Bala Punjabi obtained her M.Sc., M. Phil. and Ph.D. degrees from Vikram University, Ujjain (M.P.), India. She secured the first position in M.Sc. (1980) as well as in M.Phil. (1981). She has 34 years of research and teaching experience and superannuated from the Department of Chemistry, Mohanlal Sukhadia University, Udaipur (Raj.) in 2019. She is also a lifetime member of various societies namely, the Indian Chemical Society, Kolkata; Indian Council of Chemists, Agra; Indian Science Congress, Kolkata; and Indian Association of Chemistry Teachers, Mumbai. She has published around 139 research papers in journals of international and national repute. She has authored several chapters and books for renowned publishers such as Taylor and Francis, Elsevier, Apple Academic Press, CRC Press, Materials Research Forum, Nova Science Publishers, etc. She is also a reviewer of several international journals. She has completed two major research projects sponsored by University Grants Commission, New Delhi. Prof. Pinki Bala Punjabi has delivered invited lectures and chaired technical sessions at various national and international conferences. She has also organized two national-level conferences. Her expertise includes nanochemistry, particularly graphene chemistry, photocatalysis, organic synthesis, and polymer synthesis.



## **Rakshit Ameta**

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Dr. Rakshit Ameta has a first-class career throughout securing the first position in the M. Sc. and was awarded a Gold Medal. He was also conferred Fateh Singh Award by Maharana Mewar Foundation, Udaipur for his meritorious performance. After completing his Ph.D., he served at Hindustan Zinc Limited, Vedanta Group for one year. He has served at M. L. Sukhadia University, Udaipur; University of Kota, Kota, PAHER University, Udaipur, and presently J. R. N. Rajasthan Vidyapeeth (Deemed to be University) Udaipur. 16 Ph.D. students have been awarded their Ph.D. degrees under his supervision in various aspects of green chemistry. He has around 150 research publications to his credit in the journals of national and international repute. He also has a patent to his credit. He is a reviewer of around 50 international journals.

Dr. Rakshit has successfully organized many national conferences at the University of Kota, Kota; PAHER University, Udaipur, and JRN Rajasthan Vidyapeeth, Udaipur. He has delivered invited lectures and chaired sessions at 20 national conferences in different parts of the country. Dr. Rakshit served as a Council Member (2011-2013 & 2020-2022) and an Associate Editor of Physical Chemistry Section (2014-16), a Scientist-in-Charge in the Industrial and Applied Chemistry Section (2014-2016) of the Indian Chemical Society, Kolkata, and an Executive Council Member (2012-2014). He was also a Zonal Secretary (2016-18) of the Indian Council of Chemists, Agra.

He has written books and chapters published by CRC Press (Taylor & Francis), UK; Academic Press, Elsevier; Nova Publishers, USA; and Trans-Tech Publications, Switzerland. In 2017, he received Prof. U.C. Pant Memorial Award instituted by the Indian Chemical Society for his significant contribution. His research specialization includes photochemistry, green chemistry, microwave-assisted reactions, environmental chemistry, waste-water treatment, nanochemistry, solar cells, bioactive and conducting polymers. Recently, he has been elected as the Vice-President of the Indian Chemical Society, India.



## **Sharoni Gupta**

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Sharoni Gupta obtained her Ph.D. degree from Mohanlal Sukhadia University, Udaipur (Raj.), India in the year 2020. She was awarded the University Gold Medal for securing the first position in M.Sc. (Chemistry) in the year 2015. She was also a recipient of the Maulana Azad National Fellowship from the University Grants Commission, New Delhi. She has contributed 10 articles and chapters to the journals and books of leading international publishers such as Apple Academic Press, CRC Press, Bentham Science, Elsevier, Springer Nature and Wiley & Sons. Her specialization fields include graphene-based chemistry, nanocatalysis, and sustainable organic synthesis.