NANOMATERIALS FOR CARBON DIOXIDE CAPTURE AND CONVERSION TECHNOLOGIES

Edited by
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Nanomaterials for Carbon Dioxide Capture and Conversion Technologies

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Dedication

This book would not have been possible without sacrifices from the family. I dedicate this book to my loving wife and my lovely daughter Aysha.

—Dr. Shaukat Ali Mazari

In the name of Allah, the Most Gracious and the Most Merciful. First of all, I would like to raise my heartfelt gratitude and appreciation to Allah SWT for the permission, guidance, wisdom, and blessing for all these years till now, when I have reached this important destination of my journey in life to accomplish my goal. Finally, I would like to present my most heartfelt and warmest appreciation to the great parents and parents-in-law (may Allah SWT bless and reward them), brothers and sisters who always encouraged and supported me during the completion of the book. Special and heartiest gratitude to my dearest wife, Muna Tasnim Mukhtaruddin, and kids, Muhammad Fayyad, Muhammad Fawwaz, and Mulaika Faleeha, for their invariable encouragement endless sacrifices, patience, understanding, ideas, and inspiration from time to time in finishing the book smoothly and timely.

—Dr. Nabisab Mujawar Mubarak

I offer my sincere gratitude and thanks to The Almighty for providing me energy, inspiration, and thoughtfulness within me to complete this book. Without His permission and blessings, I would not have been able to complete this book. I would like to dedicate this book to my family. From the first day, their encouragement, support, and motivation were instrumental. I appreciate their continuous efforts and sacrifices which helped me to focus on the book and complete it.

—Dr. Manoj Tripathi
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Dr. Tripathi has published more than 25 research articles in highly reputed international journals. He has authored around 10 book chapters in different edited books published by eminent publishers such as Elsevier and Springer Nature. Citation of his authored papers also explains his contribution to the research community. His overall citation in Google Scholar is more than 1300 and that of SCOPUS is around 1000, which of course is a significant number. Dr. Tripathi also has a patent under his name.

Dr. Manoj Tripathi is working on polymer composites and energy storage materials. His area of interest is biomass-based supercapacitor electrode, thermal energy storage systems, thermochemical conversion techniques, microwave pyrolysis of biomass, production of bio-oil from agricultural wastes, and solid waste management. His work
includes the study of thermophysical, dielectric, thermal, and mechanical properties of highly carbonaceous materials.

He has research collaborations with researchers at national and international level. He has jointly developed research labs in universities and is a member of various committees to promote academic and research activities. Moreover, Dr. Tripathi is member of many scientific and professional societies working in the field of science and technology and member of various research societies and communities as well. He is the advisor to the Optical Society of America (OSA) student chapter in JIIT-Noida.
CO₂-induced climate change has the characteristics of a gradually progressive disorder of the delicately balanced environment of the planet with an overwhelming concern over profuse CO₂ emissions from industries and the locomotives (transportation sector), making way for concerted efforts to arrest the debilitating effects of the phenomenon. Apart from CO₂ emissions, particulates of impurity have to be removed from natural gas streams. Nanomaterials—due to their excellent chemical, structural, and morphological characteristics—are being widely investigated for CO₂ capture and conversion processes. These materials are being applied to absorption, adsorption, membranes, and catalytic conversion processes of CO₂, given that the enhanced and tailormade properties of nanomaterials make them attractive for a wide range of CO₂ capture and conversion processes. Especially, nanomaterials have shown excellent catalytic characteristics for CO₂ conversion into fuels and chemicals. This book has the following aims: first, to focus on the applications of nanomaterials for CO₂ capture and conversion processes; secondly, to highlight the need for CO₂ mitigation, where carbon dioxide emissions can be regulated with knowledge from the basic principle for CO₂ capture and conversion processes using different nanomaterials, and to face the environmental challenges and perspectives for using nanomaterials for CO₂ mitigation technologies; and lastly, to act as a reference material helpful to both academicians and professionals, alike, with a need to know the basic principles for CO₂ capture and conversion techniques using nanomaterials and their synthesis. Given its alignment with pedagogical principles for teaching graduate students or using in lab-scale experiments or prototype design applications, and as a ready reckoner for professionals, especially engineers, scientists, policymakers, and environmentalists, the book makes for an excellent guide to develop nanotechnology for CO₂ capture and conversion. The book consists of 16 chapters.

Chapter 1 provides an extensive review of the presence of CO₂ in natural gas streams and their impact on the process equipment, especially corrosion. The chapter further explores types of CO₂ corrosion, their kinetics, and prevention techniques.

Chapter 2 discusses the basic principles of CO₂ capture and conversion technologies. The principles of absorption, adsorption, membrane separation, oxy-fuel combustion, chemical looping combustion, cryogenic separation, electrocatalysis, photocatalysis, CO₂-based polymer synthesis via chain insertion, etc. are well amplified from the point of view of giving an initial grip to the reader on the technologies which will be further developed later in the book.
Chapter 3 reports the chemical, physical, and morphological characteristics of nanomaterials. The chapter introduces nanomaterial fabrication and their characterization techniques, followed by detailed coverage of applications of nanomaterials in different CO$_2$ capture and conversion processes depending on their characteristics.

Chapter 4 begins with a discussion on the status of CO$_2$ emissions and introduces nanofluids. Detailed methods of preparation of nanofluids are provided for various nanofluids. Applications of different nanoparticles as nanofluids such as aluminum oxide, silica and silica oxide, iron oxide, titanium oxide, carbon nanotubes, nanocomposites, and MXene for CO$_2$ capture are described in detail. The chapter ends with a look at effective parameters for CO$_2$ absorption and the mechanism of CO$_2$ interaction with nanofluids.

Chapter 5 introduces waste and biomass sources and the synthesis methods for porous carbon materials from waste and biomass, followed by a discussion of nanomaterials with waste and biomass-derived adsorbents. The chapter provides details on the mechanism of CO$_2$ capture and ends with prospects for the commercialization of waste and biomass-based nano adsorbents.

Chapter 6 introduces various nanomaterials and focuses on titanium-based nanomaterials. It provides details on the fundamentals, mechanism, thermodynamics, and kinetics of CO$_2$ photocatalytic conversion over TiO$_2$ nanophotocatalysts, their modification strategies for enhanced CO$_2$ photoreduction, and ends with an overview of future research perspectives.

Chapter 7 begins with the discovery and history of perovskite photovoltaics and introduces products from CO$_2$ conversion and their applications. A detailed brief of perovskite materials for CO$_2$ conversion is provided in the chapter, along with a look at the synthesis and characterization methods followed by a sounding out of the challenges in the efficacy and application of perovskite nanomaterials for CO$_2$ conversion.

Chapter 8 introduces synthesis methods and characterization of graphene nanomaterials. The chapter's primary focus is on applying graphene-based nanomaterials for various CO$_2$ capture and conversion processes such as photocatalytic reduction, electrochemical CO$_2$ reduction, CO$_2$ hydrogenation, and membranes for CO$_2$ capture, CO$_2$ cycloaddition, and CO$_2$ adsorption. The chapter ends with foreshadowing the prospects and technological challenges in utilizing graphene-based nanomaterials for CO$_2$ capture and conversion.

Chapter 9 launches straightforward into a discussion of the synthesis methods and properties of carbon nanotubes for CO$_2$ capture and conversion. Focus has been given to the various types of carbon nanotubes, such as single-wall carbon nanotubes, multi-wall carbon nanotubes, functionalized carbon nanotubes, and carbon nanotube composites for CO$_2$ capture.

Chapter 10 introduces metal–organic frameworks as efficient CO$_2$ capture and conversion materials. A detailed view of applications of metal–organic frameworks for
CO$_2$ capture and conversion processes such as electrocatalysis, photocatalysis, and thermal catalysis is provided with an elucidation of the structure—activity relationship closing the chapter.

Chapter 11 introduces zeolite materials and their characteristics. A detailed account of zeolites as adsorbents in CO$_2$ capture is provided, along with the adsorption mechanisms effect of various parameters on CO$_2$ adsorption. The chapter also provides status on the development and application of multiple zeolites such as metal cation—exchanged zeolites, hydrophobic zeolites, hierarchical zeolites, zeolite membranes, and zeolites catalysts. The chapter ends with a presage of future challenges and perspectives on using zeolites for CO$_2$ capture technologies.

Chapter 12 describes the synthesis of dual-functional nano zeolites and highlights their properties and characteristics for CO$_2$ capture. The chapter's primary focus is on the conversion processes of CO$_2$ into value-added products such as methane, methanol, ethanol, gasoline, olefins, aromatics, and fine chemicals. The design of dual-functional materials and the effect of zeolite topology in the dual-functional materials for CO$_2$ conversion are drawn out in detail. The chapter wraps up with an insight into the environmental impact of dual-functional nano zeolites and their future challenges and prospects for transformation.

Chapter 13 details the synthesis of mesoporous silica nanoparticles, their characterization, and desired properties for CO$_2$ capture. A detailed review of the applications of mesoporous silica nanoparticles for CO$_2$ capture and conversion is provided, along with reaction mechanisms.

Chapter 14 delves into the synthesis and characterization of ionic liquid functionalized nanomaterials and their description for CO$_2$ capture. Applications of ionic liquid-based nanomaterials have been described for CO$_2$ hydrogenation, electrochemical fixation, electrochemical conversion, etc.

Chapter 15 enlightens with a techno-economic analysis of nanomaterials in CO$_2$ capture and conversion technologies. More specifically, process economic analysis using nanomaterials, the cost involved in the synthesis of nanomaterials, and the techno-economic aspect of CO$_2$ conversion processes using nanomaterials are clarified.

Chapter 16 gives the finishing touches to an exegesis on nanomaterials by digressing into the environmental impact of nanomaterials. The chapter introduces the application of various nanomaterials for CO$_2$ capture and conversion processes. Focus has been given to the toxicities of nanomaterials, the pathways to the environment and water bodies, and the impact of exposure to nanomaterials on animals, humans, food chains, etc.

Shaukat Ali Mazari
Nabisab Mujawar Mubarak
Manoj Tripathi
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—Dr. Shaukat Ali Mazari

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—Dr. Nabisab Mujawar Mubarak

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—Dr. Manoj Tripathi
CHAPTER 8
Graphene-based nanomaterials for CO₂ capture and conversion

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8.1 Introduction

The ever-increasing human population and growth in urbanization around the world has resulted in the excessive emission of greenhouse gases (GHGs), particularly carbon dioxide (CO₂), to the environment, which contributes to both environmental and health issues (Lu et al., 2021). This is because we are still heavily dependent on the use of fossil fuels for energy supply and most renewable source technologies are still not practiced commercially due to their uncompetitiveness when compared to the conventional fossil fuels as an energy source (Chin et al., 2016). It was evidently reported that the CO₂ emission increased drastically from 20.5 Gt to 31.5 Gt from 1990 to 2020 (IEA, 2020). According to Global Climate Change (2021), the CO₂ concentration was documented at the value of 410 ppm and this value indicates the global warming concerns which need to be taken seriously. There is an urgent need to find effective approaches to reduce and control the emission of the CO₂ to the environment for resolving this issue (Global Climate Change, 2021). A few strategies such as solar energy utilization (Li et al., 2019), green plants cultivation (Wang et al., 2016), and coal desulfurization (Liu et al., 2020) are alternatives for CO₂ reduction. However, these methods are said to be time consuming or involve complicated equipment with low efficiency (Lu et al., 2021). Recently, there is an increasing interest in the development of graphene-based nanomaterials for CO₂ capture and conversion by researchers and scientists (Balasubramanian & Chowdhury, 2015; Kudahi et al., 2017; Wang et al., 2014).
Graphene is a carbon allotrope that displays the properties of a semiconductor and it is grouped as a quasi-metal (Si et al., 2021). Furthermore, the existence of carbon in graphene allows the flexibility in different nanostructures such as zero-, one-, two-, or three-dimensional elemental structure (Le et al., 2021). Additionally, the graphene has a flat single layer of two-dimensional sheets a single-atom-thick derived from crystalline graphite (Balandin et al., 2008; Dragoman & Dragoman, 2009; Du et al., 2008; Ganganboina & Doong, 2020; Lee et al., 2008; Miao et al., 2007; Murali et al., 2009; Nair et al., 2008; Novoselov et al., 2004; Shen et al., 2009; Si et al., 2021; Stoller et al., 2008; Yu et al., 2010; Tombros et al., 2007) (Table 8.1).

In this chapter, the recent advances and development progress of graphene-derived nanomaterials particularly in CO2 capture and conversion are critically examined. Furthermore, the various synthesis methods of graphene nanomaterials such as Hummer’s method, mechanical exfoliation, electrochemical method, and chemical vapor deposition (CVD) method are presented. The different types of graphene-based nanomaterials (photocatalytic reduction, electrochemical CO2 reduction, graphene-based nanomaterials for CO2 hydrogenation, graphene-based nanomaterials membranes for CO2 capture, and graphene-based nanomaterials for CO2 cycloaddition) are compiled based on recent literature. Lastly, the future prospects and technological challenges for the utilization of graphene-based nanomaterials for CO2 capture and conversion are discussed.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus</td>
<td>1 TPa</td>
<td>Lee et al. (2008)</td>
</tr>
<tr>
<td>Fermi velocity</td>
<td>300–500 nm</td>
<td>Dragoman and Dragoman (2009)</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>5000 Wm(^{-1}) K(^{-1})</td>
<td>Balandin et al. (2008)</td>
</tr>
<tr>
<td>Current density</td>
<td>1,000,000 ms(^{-1})</td>
<td>Dragoman and Dragoman (2009)</td>
</tr>
<tr>
<td>Fracture strength</td>
<td>130 GPa</td>
<td>Lee et al. (2008)</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>2630 m(^2) g(^{-1})</td>
<td>Stoller et al. (2008)</td>
</tr>
<tr>
<td>Elaxation length</td>
<td>15,000 cm(^2) V(^{-1}) s(^{-1})</td>
<td>Novoselov et al. (2004)</td>
</tr>
<tr>
<td>Sheet resistance</td>
<td>(1.3 \times 10^{4} - 5.1 \times 10^{4}) Ω sq(^{-1})</td>
<td>Nair et al. (2008)</td>
</tr>
<tr>
<td>Mobility (Intrinsic)</td>
<td>(10^{8}) A cm(^{-2})</td>
<td>Murali et al. (2009), Yu et al. (2010)</td>
</tr>
<tr>
<td>Spin R</td>
<td>(1.5–2) μm</td>
<td>Tombros et al. (2007)</td>
</tr>
<tr>
<td>Optical transmittance</td>
<td>97.7%</td>
<td>Nair et al. (2008)</td>
</tr>
<tr>
<td>Phase coherence length</td>
<td>(3–5) μm</td>
<td>Miao et al. (2007)</td>
</tr>
<tr>
<td>Mobility (typical)</td>
<td>200,000 cm(^2) V(^{-1}) s(^{-1})</td>
<td>Du et al. (2008)</td>
</tr>
<tr>
<td>Thermal resistance (interface)</td>
<td>(4 \times 10^{-8}) km(^2) W(^{-1})</td>
<td>Shen et al. (2009)</td>
</tr>
</tbody>
</table>
8.2 Synthesis method and characterization of graphene nanomaterials

It is well-acknowledged in the literature that the rational design of graphene-based nanomaterials with well-defined morphology and structures plays a vital role in steering the selectivity and performance of graphene nanomaterials toward CO₂ capture and conversion. To date, a significant number of graphene synthesis methods have been developed to search for the most efficient and economical approach to produce high-quality graphene nanomaterials for the application of CO₂ capture and conversion. Generally, the graphene synthesis methods can be grouped into two main types, i.e., bottom-up and top-down. The former method typically used a carbonaceous gas source as the reactant to form a covalently linked two-dimensional (2D) carbon network, while the latter technique depends on exfoliation of graphite to break down the powder graphite materials into graphite sheets. Some of the graphene synthesis approaches include mechanical exfoliation, Hummers’ method, electrochemical method, and CVD (Ahmed et al., 2020; Bhuyan et al., 2016; Shams & Zhang, 2015; Taheri Najafabadi, 2015; Toh et al., 2014; Warner et al., 2013) (Table 8.2).

8.2.1 Mechanical exfoliation

Mechanical exfoliation, also known as adhesive tape technique is a top-down approach that requires mechanical energy to exfoliate graphite. Within the top–bottom concept, the graphene material is mechanically isolated from the bulk graphite layer by layer. Normal force or lateral force is applied to overcome the van der Waals attraction forces between the graphene flakes. In 2004, graphene sheet was successfully synthesized by Andre Geim and Kostantin Novoselov via a micromechanical cleaving method, also known as the “Scotch Tape Exfoliation” method (Novoselov et al., 2004). Novoselov et al. (2004) and his coworkers used an adhesive tape to extract a single layer of defect-free graphene atoms (1 mm thickness) from a three-dimensional (3D) highly ordered pyrolytic graphite (HOPG) (Novoselov et al., 2004). In a typical mechanical exfoliation procedure, a fresh piece of Scotch tape with a length of about 6 inches was pressed onto the HOPG and exerted normal force on it for about 10 seconds. After approximately 10 seconds, the tape was gently removed from the graphite and a thick layer of shiny graphite layer was attached to the adhesive side of the tape. Next, the tape with the graphite layer was refolded onto a clean adhesive part of the tape before it was unfolded. The same steps were repeated several times until the end of the tape turned into a dark color. Following, the graphite layers on the tape were transferred onto the surface of the silicate or silica oxide wafers by gently pressing them on the tape before peeling it off.

Although the micromechanical exfoliation approach can yield high-quality single-layer or bi-layer graphene nanomaterials with the lateral dimensions on the order of
<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>Strengths</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical exfoliation</td>
<td>Safe and simple sample preparation</td>
<td>Poor graphene yield</td>
</tr>
<tr>
<td></td>
<td>Graphite layer in nanoscale can be easily obtained</td>
<td>Requires skilled manual labor or mechanical energy</td>
</tr>
<tr>
<td></td>
<td>High graphene purity</td>
<td>Despite the tape residue does not affect the quality of the graphene nanomaterials significantly, however it does make those samples more difficult to find on the substrate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High production cost</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Uneven thickness of graphene nanomaterials</td>
</tr>
<tr>
<td>Hummer method</td>
<td>High graphene yield</td>
<td>Tedious, time-consuming, and labor-intensive procedures</td>
</tr>
<tr>
<td></td>
<td>Highly scalable</td>
<td>Longer preparation time</td>
</tr>
<tr>
<td></td>
<td>Excellent dispersibility in various solvents</td>
<td>Higher reaction temperature</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inevitable defects on graphene sheets</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>Easy to operate</td>
<td>Environment-unfriendly due to production of corrosive and toxic gaseous such as NO₂ and N₂O₄</td>
</tr>
<tr>
<td>method</td>
<td>Relatively faster approach</td>
<td>Presence of impurities (electrolyte salts) between the graphene sheets</td>
</tr>
<tr>
<td></td>
<td>High graphene yield</td>
<td>Poor thickness control</td>
</tr>
<tr>
<td></td>
<td>Scalable to industrial level</td>
<td>Presence of impurities (electrolyte salts) between the graphene sheets</td>
</tr>
<tr>
<td></td>
<td>Environmental-friendly</td>
<td>Poor thickness control</td>
</tr>
<tr>
<td></td>
<td>Allows functionalization of graphene sheet with different types of electrolyte</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Well-suited with organic compounds or polymers materials</td>
<td></td>
</tr>
<tr>
<td>Chemical vapor</td>
<td>Production of high-quality, impervious, and hard graphene sheets</td>
<td>Presence of wrinkled graphene nanomaterials at high temperatures over 900°C</td>
</tr>
<tr>
<td>deposition (CVD)</td>
<td>Allows mass production of graphene nanomaterials</td>
<td>Environment-unfriendly due to production of corrosive and toxic gaseous such as NO₂ and N₂O₄</td>
</tr>
<tr>
<td></td>
<td>High growth rates</td>
<td>Difficulty in locating a proper substrate to grow graphene layers</td>
</tr>
<tr>
<td></td>
<td>Excellent reproducibility</td>
<td>Difficulty in transferring and removing the film from the substrate to other surfaces without affecting the structure of the graphene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Difficulty in controlling the thickness and achieving uniform deposition of the carbon materials</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Further purification needed to remove residue catalyst</td>
</tr>
</tbody>
</table>
tens to hundreds of micrometers, this method has been condemned by many previous researchers for its extremely labor-intensive and time-consuming procedures (Yi & Shen, 2015). From the perspective of industrial practicability, it may be easy to isolate small amounts of this one-atom-thick carbon material, but it is technically impossible to produce large graphene sheets by using the tape exfoliation method for commercial applications like CO₂ capture and conversion. Thus, this technique is limited to laboratory scale and does not appear to be scalable for industrial production. Also, a major drawback of this technique is its inherent complexity in identifying and finding a proper substrate to grow graphene layers on as well as the difficulty in transferring and removing the film from the substrate to other surfaces without affecting the structure of the graphene. Recently, several researchers have been attempting to improve the scalability and efficiency of the mechanical exfoliation technique by using an advanced operational setup such as ultrasharp single-crystal diamond wedge and a three-roll mill machine with a polymer adhesive (Chen et al., 2012; Jayasena & Subbiah, 2011). These novel methods have reduced the labor cost and eliminated the need for manual operation. However, all of these new approaches still suffer from additional machinery complexity, high production cost, and high energy consumption, which limit their scalability for mass production (Lee et al., 2020).

8.2.2 Hummer’s method

Of all the chemical exfoliation approaches, Hummers’ method is one of the most commonly used techniques to synthesize graphene nanomaterials. Unlike the mechanical exfoliation technique, graphite substrates are chemically oxidized to graphite oxide (GO) by treatment with a mixture of concentrated oxidizing reagents such as sulfuric acid (H₂SO₄), sodium nitrate (NaNO₃), and potassium permanganate (KMnO₄). As reported by Hummers (Hummers & Offeman, 1958), the graphite powders were added into a solution mixture of NaNO₃ and H₂SO₄ in an ice bath. Moreover, KMnO₄ was also added to keep the suspension temperature at 20°C. As the suspension became concentrated, hot water was subsequently added to dilute the suspension and the diluted suspension was further treated with the addition of hydrogen peroxide (H₂O₂) to reduce the residual permanganate to soluble manganese ions. Lastly, the mixture was subsequently filtered and washed with warm water several times to remove the soluble salt of mellitic acid. The resulting GO solids were then dried under an air-free environment over phosphorus pentoxide (P₄O₁₀) at 40°C.

Due to the release of harmful and explosive gases like nitrogen dioxide (NO₂), dinitrogen tetroxide (N₂O₄), and chlorine dioxide (ClO₂) during the synthesis, the Hummers’ method has undergone several modifications over the years, mainly focused on eliminating the use of NaNO₃ and avoiding the release of toxic nitrous gases.
(Lee et al., 2019; Marcano et al., 2010). Thus most of the modified Hummer’s methods have introduced a greener and cheaper approach in producing a more stable GO colloidal suspension at a much shorter time frame and milder reaction conditions. Typically, it is carried out in the following three major steps: oxidation, reduction, and posttreatment. In oxidation, the natural graphite flakes are added into a solution mixture of H₂SO₄ and HNO₃ under continuous stirring in an ice bath, followed by the addition of KMnO₄ under room temperature. Next, warm water is added to the solution until the pH is about 7 before it is centrifuged and filtered. Lastly, a monolayer GO product is obtained from the ultrasonication process.

Instead of applying the conventional thermal reduction, a known volume of reducing agents such as hydrazine and sodium borohydride (NaBH₄) are added to the measured solution to further reduce the resulting GO product. This helps to remove the attached functional group on the GO. Furthermore, polar aprotic solvents can be added to improve the exfoliation performance. Lastly, the solution is filtered and washed with water until neutrality is achieved before the solid is dried and ground for further use. Despite the distinct advantages of Hummers’ methods for the synthesis of graphene oxide, the major drawbacks of this top-down approach are its inherent tedious preparation procedures, use of strong oxidizing agents, and high reaction temperatures.

8.2.3 Electrochemical method

In recent years, electrochemical exfoliation of graphite has emerged as an eco-friendly and efficient preparation technique potentially capable of synthesizing high-quality few-layer graphene (FLG) in mass amounts. Unlike other methods, the production of graphene nanomaterial via electrochemical technique involves a single hybridization step without the use of any volatile solvents or strong oxidizing agents. In this method, a fixed potential or electrical voltage is usually applied to drive the ionic species in the electrolyte solution into the graphite electrode before weakening the van der Waals forces between the graphite layers. The evolution of locally formed gaseous species intercalate the adjacent sheets of graphene and cause the graphene sheet to expand. As a result, the graphene sheets disintegrate during the intercalation and the interlayer distance of graphene layers increases.

To date, electrochemical exfoliation of graphite has been conducted in ionic liquids (Lei et al., 2017; Liu et al., 2008; Yan et al., 2017) and conventional inorganic electrolytes such as HCl, HF, H₂SO₄, HNO₃, H₃PO₄, NaClO₄, and others (Lee et al., 2020; Lin et al., 2016; Lowe et al., 2019). It has been well-reported in the literature that both ionic liquids and inorganic electrolytes have their respective strengths and limitations for use in electrochemical exfoliation. For example, electrochemical exfoliation of graphene materials in acidic electrolytes can yield a higher
quality of graphene flakes with a larger lateral size. However, the resulting graphene flakes will still possess a significant amount of oxygen-containing functional groups due to the fact that the graphite is being oxidized by the products of the acid electrolysis (Li et al., 2020). In contrast, the usage of ionic liquid as an electrolyte solution in electrochemical exfoliation of graphene can promote a better functionalization performance at the expanse of the graphene yield and lateral size (Li et al., 2020).

As a whole, electrochemical exfoliation has several advantages over the traditional mechanical and chemical methods. The single-step technique is versatile in terms of chemical functionalization and allows the potential of mass production of graphene. This environment-friendly method is easy to operate and able to operate at ambient conditions. Furthermore, this synthesis method also encourages the facile production of graphene flakes within several minutes or hours. On the other hand, this electrochemical method also suffers a number of major downfalls that are required to be addressed promptly in the future before it can be applied at a larger manufacturing scale. For example, loose graphite powder may not be applicable as the electrode needs to be continuous and electrically conductive (Achee et al., 2018). Thus, only graphite monoliths are suitable to be used as the carbon source for electrochemical exfoliation. Secondly, the electrochemical exfoliation process tends to halt when the graphite electrodes disintegrate and interrupt the entire circuit, which leads to the need for further intercalation of unexfoliated materials (Achee et al., 2018).

8.2.4 Chemical vapor deposition (CVD) method

Chemical vapor deposition (CVD) is a bottom-up technique that decomposes, combines, and deposits volatile carbon-containing gases (methane, acetylene, ethylene, hexane, and other biomass materials) onto a substrate in a reaction chamber in the presence of a metallic catalyst (copper or nickel film). By heating up the carbonaceous material at elevated temperatures (650°C—1000°C), the carbon precursor decomposes into volatile gas molecules and it dissociates into individual carbon and hydrogen atoms upon contacting the surface of the metal catalysts (Lee et al., 2019). Afterwards, the carbon atom diffuses through the surface and bulk of metal catalysts before forming the graphene sheets. At the same times, the by-product gases are pumped out from the chamber. In short, the graphene films can be produced from CVD in merely two steps. The first step involves thermal pyrolysis of a precursor materials at high temperature to form carbon atoms on a substrate materials. In the second step, the dissociated carbon atoms are assembled onto a substrate in the presence of a metal catalyst before forming a monolayer or multilayer graphene film. In CVD, reaction temperature plays an important role as it has a significant effect on the type of reaction that
occurs and the properties of the resulting products. Although CVD can produce high-quality and high-purity graphene films with low defects and high surface area, the by-products produced from the reactions can be very toxic due to the volatile nature of the precursor gases. Furthermore, the resulting graphene needs to be transferred from the metal surface to the target substrate, which makes the production process difficult to control and further hinders its potential industrial applications in CO$_2$ capture and conversion (Li et al., 2020).

8.3 Applications of graphene-based nanomaterial

8.3.1 Graphene-based nanomaterials for CO$_2$ adsorption

Graphene-based nanomaterials have emerged as promising solid sorbents for CO$_2$ separation and capture, owing to their high specific surface area, lower production cost, superior structural, chemical, mechanical, thermal, and electrical characteristics (Abergel et al., 2010; Wang et al., 2014). Studies on graphene-derived materials on adsorption of CO$_2$ have been reported by several researchers. Generally, the adsorption of CO$_2$ by sorbents is controlled by five stages of mass transport mechanism, namely CO$_2$ external diffusion, film diffusion, pore diffusion, intraparticle diffusion, and surface adhesion (Kudahi et al., 2017).

To enhance the CO$_2$ adsorption capacity, selectivity, and kinetics for industrial applications, several techniques such as heat/electric/chemical treatment, surface functionalization and modification, nanoparticles doping, development of hybrid graphene or graphene oxide nanocomposites have been proposed and attempted. These treatments aim to enhance the surface area, porosity, available active sites, and surface chemistry of the sorbents, hence facilitating better diffusion and binding (adsorption) of CO$_2$ molecules on the surface of the sorbents. Stanly et al. (2019) synthesized polyphosphoric acid and amino-modified montmorillonite clays (PMMT and AMMT) and hybridized them with reduced graphene oxide (rGO) to study the performance of the developed sorbents (Stanly et al., 2019). The BET surface area of PMMT/rGO hybrid was increased tremendously to 50.77 m$^2$ g$^{-1}$ as compared to that of pristine MMT (14.90 m$^2$ g$^{-1}$) and GO (1.14 m$^2$ g$^{-1}$), leading to its improved CO$_2$ adsorption capacity of 0.49 mmol g$^{-1}$ at low pressure (900 mmHg) (Stanly et al., 2019). Ning et al. (2021) developed a graphene-based semicoke porous carbon and found it boosted the CO$_2$ adsorption capacity (7.11 mmol g$^{-1}$ at 25°C and 30 bar) and selectivity (CO$_2$/N$_2$ = 28.24, at 25°C) (Ning et al., 2021). This was attributed to the nitrogen-rich layered sandwich-like structure of the materials, which greatly improved the CO$_2$ mass transport (Ning et al., 2021).

While isotherms and equilibrium studies of CO$_2$ adsorption have been widely reported, the kinetics of CO$_2$ adsorption on various sorbents is also equally important. Kudahi et al. (2017) investigated the kinetics of CO$_2$ adsorption on various novel
Graphene-based nanomaterials for CO₂ capture and conversion

Graphene-based sorbents, namely mesoporous graphene oxide/TiO₂ nanocomposite, thermally treated graphene nanosheets, holey graphene frameworks, and 3-D graphene-based porous adsorbent (Kudahi et al., 2017). Several kinetic correlations (pseudo-first order model, pseudo-second order model, Avrami model, and fractal-like exponential kinetic model) were used to describe the CO₂ adsorption kinetics, in addition to the investigation of interparticle diffusion model, intraparticle diffusion model, and Boyd’s film diffusion model in determining the rate-limiting mechanism of adsorption (Kudahi et al., 2017). Pajdak et al. (2019) compared the equilibrium isotherms and kinetics of CO₂ adsorption in rGO, multi-walled carbon nanotubes (MWCNT) and coals, and reported that the sorption equilibrium was attained almost instantaneously by rGO and MWCNT following a pressure change in the reactor (Pajdak et al., 2019) (Figs. 8.1 and 8.2).

Other than that, several computational modeling studies have also been reported on CO₂ adsorption by graphene-based nanomaterials to complement the empirical studies. Sathishkumar et al. (2020) explored the (reversible) effect of charge-induced density

![Figure 8.1 CO₂ adsorption isotherms (Langmuir) on different types of sorbents: (A) Multi-walled carbon nanotube (MWCNT), (B) rGO, (C) Sobieski coal, and (D) Budryk coal. From Pajdak, A., Skoczylas, N., Dębski, A., Grzegorek, J., Maziarz, W., & Kudasik, M. (2019). CO₂ and CH₄ sorption on carbon nanomaterials and coals — Comparative characteristics. Journal of Natural Gas Science and Engineering, 72, 103003. https://doi.org/10.1016/j.jngse.2019.103003 (Original work published 2019).](image-url)
and external electric field on the stronger adsorption of CO₂ by N-doped penta-graphene sheet (chemisorption) through density functional theory (DFT) computations (Sathishkumar et al., 2020). Another study by Osouleddini and Rastegar (2019) also applied DFT calculations to study and compare the adsorption energies of CO₂ on the surface of intrinsic graphene and tetracyanoethylene (TCNE)-modified graphene and found stronger interaction of CO₂ on the surface of TCNE-modified graphene due to the reduction of electron accumulation on the graphene by TCNE molecule (Osouleddini & Rastegar, 2019). These computational studies have paved the way toward fundamental understanding and insights of the chemistry between graphene-based adsorbents and CO₂ (and other gas mixtures), which are beneficial for the selection and synthesis of novel adsorbents (Chowdhury & Balasubramanian, 2016a,b,c; Chowdhury et al., 2015; Kudahi et al., 2017; Li et al., 2016; Liu et al., 2021; Ning et al., 2021; Stanly et al., 2019) (Table 8.3).

<table>
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<tr>
<th>References</th>
<th>Adsorbent material</th>
<th>Surface area/pore volume of adsorbent</th>
<th>Adsorption temperature and pressure</th>
<th>CO₂ equilibrium adsorption capacity (qₑ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kudahi et al.</td>
<td>Graphene oxide/TiO₂ nanocomposite</td>
<td>- BET surface area: 83.12—99.54 m² g⁻¹ (Chowdhury et al., 2015)</td>
<td>- Temperature: 0°C—50°C</td>
<td>1.091—2.389 mmol g⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Pore volume: 0.269—0.382 cm³ g⁻¹ (Chowdhury et al., 2015)</td>
<td>- Pressure: 0—1 bar</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- BET surface area: 185—484 m² g⁻¹ (Chowdhury &amp; Balasubramanian, 2016a)</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Thermally treated graphene nanosheets</td>
<td>- Pore volume: 0.268—0.682 cm³ g⁻¹ (Chowdhury &amp; Balasubramanian, 2016a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Holey graphene frameworks</td>
<td>- BET surface area: 439.11—524.18 m² g⁻¹ (Chowdhury &amp; Balasubramanian, 2016b)</td>
<td>- Temperature: 0°C—50°C</td>
<td>0.974—2.109 mmol g⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Pore volume: 1.06—1.27 cm³ g⁻¹ (Chowdhury &amp; Balasubramanian, 2016b)</td>
<td>- Pressure: 0—1 bar</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3-D graphene-based porous adsorbent</td>
<td>- BET surface area: 885.34—1315.98 m² g⁻¹ (Chowdhury &amp; Balasubramanian, 2016c)</td>
<td>- Temperature: 0°C—50°C</td>
<td>1.588—3.412 mmol g⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Pore volume: 0.71—1.07 cm³ g⁻¹ (Chowdhury &amp; Balasubramanian, 2016c)</td>
<td>- Pressure: 0—1 bar</td>
<td></td>
</tr>
<tr>
<td>Stanly et al.</td>
<td>Polyphosphoric acid modified montmorillonite clay/reduced</td>
<td>- BET surface area: 50.77 m² g⁻¹</td>
<td>- Temperature: 25°C</td>
<td>0.49 mmol g⁻¹</td>
</tr>
<tr>
<td>(2019)</td>
<td>graphene oxide hybrids</td>
<td>- Pore volume: 0.0788 cm³ g⁻¹</td>
<td>- Pressure: 0—900 mmHg</td>
<td></td>
</tr>
</tbody>
</table>

(Continued)
<table>
<thead>
<tr>
<th>References</th>
<th>Adsorbent material</th>
<th>Surface area/pore volume of adsorbent</th>
<th>Adsorption temperature and pressure</th>
<th>CO$_2$ equilibrium adsorption capacity ($q_e$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ning et al.</td>
<td>N-rich layered sandwich-structure of graphene-based semi coke porous carbon</td>
<td>BET surface area: 467.96–701.53 m$^2$ g$^{-1}$</td>
<td>Temperature: 25°C</td>
<td>3.99–7.11 mmol g$^{-1}$</td>
</tr>
<tr>
<td>(2021)</td>
<td></td>
<td>Pore volume: 0.23–0.37 cm$^3$ g$^{-1}$</td>
<td>Pressure: 0.1–30 bar</td>
<td></td>
</tr>
<tr>
<td>Liu et al.</td>
<td>Graphene oxide/core shell ZIF-8@ZIF-67 nanocomposite hybrid</td>
<td>BET surface area: 532–1490 m$^2$ g$^{-1}$</td>
<td>Temperature: 0°C</td>
<td>0.90–2.15 mmol g$^{-1}$</td>
</tr>
<tr>
<td>(2021)</td>
<td></td>
<td>Pore volume: 0.29–1.60 cm$^3$ g$^{-1}$</td>
<td>Pressure: 0–1 bar</td>
<td></td>
</tr>
<tr>
<td>Li et al.</td>
<td>ZnO based N-doped rGO porous nanomaterial</td>
<td>BET surface area: 1122 m$^2$ g$^{-1}$</td>
<td>Temperature: 25°C</td>
<td>3.55 mmol g$^{-1}$</td>
</tr>
<tr>
<td>(2016)</td>
<td></td>
<td>Pore volume: 0.60 cm$^3$ g$^{-1}$</td>
<td>Pressure: 0–1 atm</td>
<td></td>
</tr>
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</table>
8.3.2 Graphene-based nanomaterials membranes for CO₂ reduction

8.3.2.1 Photocatalytic reduction of CO₂ using graphene-based materials

To date, graphene-based materials have been hailed to have an immense potential for large range of industrial applications including semiconductors, optoelectronics, CO₂ capture, hydrogen (H₂) storage, catalysts, and sensors to name a few (Bardi et al., 2020; Loy et al., 2019; Stoller et al., 2008; Yamamoto et al., 2020). On this ground, large interests have been dedicated to photocatalytic activities owing to their unique characteristics such as large surface area, high adsorption capacity, high stability, and flexible tuning physiochemical characteristics, as well as high carrier mobility (Bonaccorso et al., 2015; Purkait et al., 2017; Szcześniak et al., 2017). For example, graphene oxide (GO) has been elucidated as a semiconductor photocatalyst due to an apparent bandgap of 2.4–4.3 eV, which is suitable for generating H₂ through H₂O splitting under a wide range of solar energy from UV to near infrared light (Giovannetti et al., 2017; Gusain et al., 2016; Kuang et al., 2020) (Fig. 8.3).

Figure 8.3 (A) Photocatalyst scheme of TiO₂-assisted graphene-based nanocomposite (copyright from Giovannetti et al., 2017); (B) graphene nanoparticles simulated using crystal maker software; (C) SEM image of TiO₂-RGO 0.5% (copyright from Leal et al., 2020); (D) TEM images of the RGO/Pt4 nanocomposite with (E) high resolution image, the insets of Fig. 8.3D. Data from Kasturi, S., Torati, S. R., Eom, Y. J., Ahmad, S., Lee, B.-J., Yu, J.-S., & Kim, C. (2020). Real-time monitored photocatalytic activity and electrochemical performance of an rGO/Pt nanocomposite synthesized via a green approach. RSC Advance, 10(23), 13722–13731. https://doi.org/10.1039/D0RA00541Ja.
Lately, nanocomposites of TiO$_2$ with graphene-family materials have been reported as very efficient photocatalysts (Jin et al., 2020; Kandulna et al., 2020; Phukan & Sahu, 2020). Graphene is a two-dimensional carbon nanomaterial with a honeycomb structure made of SP$^2$ carbons (see AlShammari et al., 2020; Chen et al., 2020; He et al., 2020; Leal et al., 2020).

Besides using TiO$_2$ as cocatalyst, some researchers incorporated Pt ions on GO via a cheap reducing agent to form RGO/Pt nanocomposites. Kasturi et al. (2020) have reported honey as a reducing agent which plays a role in the in situ functionalization of the Pt ions on the surface of RGO via a reduction method (Kasturi et al., 2020). Interestingly, the increase of Pt precursor concentration will lead to a highly efficient photocatalytic rate, implying that the Pt could induce a better electron transfer property with higher current and conductivity as compared to the pure RGO. Based on the TEM images (Kasturi et al., 2020; Neppolian et al., 2012), a well uniform and good distribution of Pt nanoparticles with an average size of 2.5 nm on the surface of rGO can be observed, suggesting that no agglomeration of Pt nanocluster was formed. Owing to the remarkable high electron transfer property, the optimized photocatalyst (20 wt% Pt precursor) exhibited a remarkable photocatalytic activity and degraded 98% of methylene blue in the presence of sunlight at an ambient temperature under 180 minutes. Neppolian et al. also synthesized a TiO$_2$ doped Pt-GO nanomaterial through ultrasound-assisted method (Neppolian et al., 2012). They tested the catalyst using an anionic surfactant, dodecylbenzenesulfonate (DBS) in an aqueous solution was carried out using Pt—GO—TiO$_2$ nanoparticles in order to evaluate the photocatalytic efficiency. As expected, the Pt doped GO—TiO$_2$ exhibited an enhanced rate of mineralization of DBS under visible light irradiation.

### 8.3.2.2 Electrochemical CO$_2$ reduction using graphene-based materials

By exploiting the presence of carboxylic groups (—COOH) on GO nanosheets, GO tends to be an ideal platform for covalent immobilization of ions (Rowley-Neale et al., 2018; Shaban et al., 2019; Smith et al., 2017). Apart from the —COOH functional groups, GO also exhibits high electron mobility at room temperature, high thermal conductivity, and strong mechanical properties (high Young’s modulus) (Hasani et al., 2019). On this ground, GO can be classified as a relatively simple, economic, fast, and environmentally benign electrochemical CO$_2$ reduction method. In 2019 the first graphene-based single-atom catalyst for CO$_2$ reduction reaction (CO2RR) was revealed (Cheng et al., 2019). The authors doped the Ni single atom on the highly porous defect-rich microwave exfoliated GO support via the impregnation method. Interestingly, the exfoliated GO provides a large surface area and abundant defects on the pore edge as anchoring sites for Ni, yielding a 3D structure connected with a nanotube shape with a diameter of 30 nm, as observed in the TEM image (see Fig. 8.4).
In 2020, Hwang’s group reported that RGO layers can effectively alter the Faradaic efficiency for CO production in electrocatalysis (Nguyen et al., 2020). They have synthesized a the R-ZnO/rGO electrode that exhibited both of the diffraction peaks associated with Zn metal and Zn cations (See Fig. 8.4).

**Figure 8.4** (A) TEM image of Ni single atom/microwave exfoliated GO nanosheet (copyright from Cheng et al., 2019); (B) DFT study of Ni-N species on the graphene plane (copyright from Cheng et al., 2019), (C) Structure of R-ZnO/rGO electrodes (copyright from Nguyen et al., 2020); (D) Raman Spectra of R-ZnO/RGO and ZnO/GO. GO, graphite oxide; DFT, density functional theory. Data from Cheng, Y., Zhao, S., Li, H., He, S., Veder, J.-P., Johannessen, B., Xiao, J., Lu, S., Pan, J., Chisholm, M. F., Yang, S.-Z., Liu, C., Chen, J. G., & Jiang, S. P. (2019). Unsaturated edge-anchored Ni single atoms on porous microwave exfoliated graphene oxide for electrochemical CO₂. Applied Catalysis B: Environmental, 243, 294–303. https://doi.org/10.1016/j.apcatb.2018.10.046.

In 2020, Hwang’s group reported that RGO layers can effectively alter the Faradaic efficiency for CO production in electrocatalysis (Nguyen et al., 2020). They have synthesized a the R–ZnO/rGO electrode that exhibited both of the diffraction peaks associated with Zn metal and Zn cations (See Fig. 8.4).

### 8.3.2.3 Graphene-based nanomaterials for CO₂ hydrogenation

The motivation underlying CO₂ hydrogenation process is to convert CO₂ to useful products (Van-Dal & Bouallou, 2013). This not only creates a window for profitable business but also minimizes CO₂ emission, which is the root cause of global
warming (Van-Dal & Bouallou, 2013). Nonetheless, the challenge arises because CO$_2$ is considered to be an inert molecule that is relatively difficult to be activated for the hydrogenation process (Liu et al., 2019). In this context, the utilization of an appropriate and well-distributed catalyst is substantially important to ensure a sufficient conversion, yield, and reaction rate of the hydrogenation process (Liu et al., 2019). In this context, graphene-based nanomaterials have been proposed to be a strong support to be utilized in CO$_2$ hydrogenation owing to their favorable characteristics, which include a large effective surface area, outstanding stability with respect to thermal and chemical interaction, ease in surface alteration, and existence of various active sites for catalytic activity (Tang et al., 2016). In this context, the graphene serves as a bridge between different catalysts, which allows the uniform distribution of catalysts and enhances the catalytic activity by strengthening the hydrogen spillover phenomenon. During this process, activated H$_2$ species migrate from the catalyst particle that binds them to the carbon species of graphene nanomaterial. Subsequently, the graphene works as a binding platform that enhances the absorption of hydrogen species to the other catalysts that preferentially bind CO$_2$, which forms a platform for the hydrogenation process to occur. The mechanism of graphene oxide as a catalyst support and bridging agent is shown in Witoon et al. (2018) (Fig. 8.5).

Summary of utilization of graphene-based nanomaterials for different applications of CO$_2$ hydrogenation is provided in Table 8.4 (Deerattrakul et al., 2016; Fan & Wu, 2016; Jurca et al., 2019; Liu et al., 2019; Ma et al., 2019; 2019; Mohd Ridzuan et al., 2020; Nguyen et al., 2015; Primo et al., 2019; Witoon et al., 2018).

### 8.3.2.4 Graphene-based nanomaterials membranes for CO$_2$ capture

Membrane is an emerging separation process for CO$_2$ separation due to its many benefits, such as flexible operating conditions, effective energy utilization and operating cost, its chemical free process, as well as the smaller footprint (Bernardo & Drioli, 2010). Polymeric membranes dominate membrane separation technology in industry at present since they have huge reproducibility for large-scale production and low fabrication cost (Hwang et al., 2012). However, the performance of polymeric membranes is limited by the trade-off between permeability (high gas transport to cater for large feed flux and high CO$_2$ concentration) and selectivity (preference of membrane to allow transport of CO$_2$ while retaining the product gas to constitute two concentrated streams) (Jusoh et al., 2016). To overcome the limitations, the incorporation of inorganic fillers into polymer matrix to constitute mixed matrix membranes (MMMs) has been proposed as a viable solution. Over recent years, graphene-based nanomaterial has been studied extensively since it inherits active functional groups such as epoxy, hydroxyl, and carboxyl groups that can enhance dispersion within polymeric material while serving as active sorption sites for CO$_2$ separation. In this context, the uniformly distributed nanomaterial disrupts
efficient polymer, which further contributes to the formation of bigger void spaces that act as channels to enhance CO$_2$ gas transport property. In addition, the higher affinity for CO$_2$ as compared to its counterpart also enhances the membrane selectivity that increases product purity. The enhancement in the separation mechanism of membranes using graphene-based nanomaterial is illustrated in Fig. 8.6 (Goh et al., 2019).

Realizing the benefits of graphene-based nanomaterial, research groups have begun to incorporate it within MMM, as summarized in Table 8.5 (Casadei et al., 2019; Dai et al., 2016; Dong et al., 2016, 2018; Ebrahimi et al., 2016; He et al., 2019; Karunakaran et al., 2015; Li, Cheng, et al., 2015; Li, Ma, et al., 2015; Pazani & Aroujalian, 2020; Prasad & Mandal, 2018; Raouf et al., 2020; Rea et al., 2018; Sarfraz & Ba-Shammakh, 2016a,b; Shen et al., 2015; Wong et al., 2019; Xin et al., 2015; Xue et al., 2017; Yang et al., 2020; Ying et al., 2018; Zahri et al., 2016; Zhao, Cheng, et al., 2015; Zhao, Ren, et al., 2015).
<table>
<thead>
<tr>
<th>References</th>
<th>Catalyst nanocomposite</th>
<th>Synthesis method</th>
<th>Product</th>
<th>Catalytic activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liu et al. (2014)</td>
<td>CuO-ZnO-Al2O3/graphene-modified support</td>
<td>High energy ball milling</td>
<td>Methanol</td>
<td>CO\textsubscript{2} conversion = 14.6% Yield = 12.6% Product selectivity = 62.3% (10 wt% graphene, 3 MPa, 250°C)</td>
</tr>
<tr>
<td>Nguyen et al. (2015)</td>
<td>PdNi alloy/carbon nanotube/graphene support</td>
<td>Wet impregnation and reduction</td>
<td>Formic Acid</td>
<td>Yield = 1.92 mmol/1 mmol (Pd + Ni) catalysts (Pd/Ni = 3/7, 5 MPa, 40°C)</td>
</tr>
<tr>
<td>Fan &amp; Wu (2016)</td>
<td>CuO-ZnO-ZrO\textsubscript{2}-Al2O\textsubscript{3}/reduced graphene oxide (rGO)</td>
<td>Coprecipitation</td>
<td>Methanol</td>
<td>CO\textsubscript{2} conversion = 14.7% Yield = 18.4% Product selectivity = 78.0% (80 wt% rGO, 2 MPa, 240°C)</td>
</tr>
<tr>
<td>Deerattrakul et al. (2016)</td>
<td>Cu-Zn/rGO</td>
<td>Incipient wetness impregnation</td>
<td>Methanol</td>
<td>CO\textsubscript{2} conversion = 20.0% Yield = 424 mg g\textsuperscript{-1} h\textsuperscript{-1} Product selectivity = 15.6% (90 wt% rGO, 1.5 MPa, 250°C)</td>
</tr>
<tr>
<td>Witoon et al. (2018)</td>
<td>CuO-ZnO-ZrO\textsubscript{2}/GO</td>
<td>Reverse coprecipitation</td>
<td>Methanol</td>
<td>CO\textsubscript{2} conversion = 63.5% Yield = 275 mg g\textsuperscript{-1} h\textsuperscript{-1} Product selectivity = 55.0% (1 wt% GO, 2 MPa, 250°C)</td>
</tr>
<tr>
<td>Ma et al. (2019)</td>
<td>Cu-ZnO-Al2O\textsubscript{3}/N-doped graphene (NG)</td>
<td>Coprecipitation</td>
<td>Methanol</td>
<td>CO\textsubscript{2} conversion = 8.2% Yield = 6.9% Product selectivity = 84.0% (10 wt% GO, 3 MPa, 200°C)</td>
</tr>
<tr>
<td>Ma et al. (2019)</td>
<td>Ni-SiO\textsubscript{2}/GO-Ni-foam</td>
<td>Hydrothermal</td>
<td>Methane</td>
<td>CO\textsubscript{2} conversion = 84.0% Yield = 82.0% Product selectivity = 98.0% (500 h\textsuperscript{-1} Gas hourly space velocity, 0.1 MPa, 470°C)</td>
</tr>
<tr>
<td>Jurca et al. (2019)</td>
<td>N-doped defective graphene from biomass</td>
<td>Pyrolysis</td>
<td>Methane</td>
<td>CO\textsubscript{2} conversion = 52.3% Product selectivity = 99.2% (2.5 MPa, 500°C)</td>
</tr>
<tr>
<td>Primo et al. (2019)</td>
<td>MoS\textsubscript{2}/Defective flat layer graphene MoO\textsubscript{3}/Defective flat layer graphene</td>
<td>Pyrolysis</td>
<td>Methane</td>
<td>MoS\textsubscript{2}/Defective flat layer graphene CO\textsubscript{2} conversion = 67.0% Product selectivity = 98.0% (95.8 wt% graphene, 1 MPa, 600°C)</td>
</tr>
<tr>
<td>Mohd Ridzuan et al. (2020)</td>
<td>Ni/rGO</td>
<td>Incipient wetness impregnation</td>
<td>Methane</td>
<td>CO\textsubscript{2} conversion = 55.3% Yield = 24.9 mg g\textsuperscript{-1} h\textsuperscript{-1} Product selectivity = 100% (85 wt% rGO, 1 MPa, 240°C)</td>
</tr>
</tbody>
</table>

Graphene oxide (GO) consists of sp²-hybridized carbon atom basic building blocks that consist of various oxygen functional groups. The oxygen functional groups could be either hydroxyl, epoxide, carbonyl, or carboxyl, which allows the material to be changed easily (Dreyer et al., 2010). It is evidently proven that GO is a great adsorbent for CO₂ capture (Kim et al., 2014; Shen et al., 2015) and acts as a good CO₂ conversion catalyst (Lan et al., 2014; Luo et al., 2014). Furthermore, the GO has been reported to be an outstanding performance catalyst specifically for cycloaddition reactions (Lan et al., 2014; Luo et al., 2014; Qu et al., 2012). The presence of homogenous nucleophiles (e.g., quaternary ammonium salt) is said to be important. It is proven that the catalytic activity improves when the hydrogen bonding donor and nucleophilic anion interact with each other (Lan et al., 2014; Ma et al., 2012; Qu et al., 2012; Song et al., 2008; Sun et al., 2014). Hence, this indicates that the GO multifunctionalized with silanol group, salt derived from quaternary ammonium, and amine provides a good catalytic activity for the cycloaddition of CO₂ to epoxides when the effects of amine on CO₂ adsorption and activation are observed (Pinto et al., 2011; Srivastava et al., 2005).

Carboxylic acid is considered a prospective chemical for building blocks as a fundamental material for pharmaceutical and conjugated functional materials (Garg & Ling, 2013). Carboxylic acid is known for its stable chemical properties, and it is derived from the by-products of the decarboxylative coupling reaction, and considered as a natural benign CO₂ (Feng & Loh, 2010; Kolarović et al., 2011; Moon et al., 2008). Kim et al. (2012) investigated the Ag-decorated graphene oxide catalyst (GOSH-Ag) for the application into the decarboxylative cycloaddition reaction (J. D. Kim et al., 2012). The chemical reactions involved in this study are shown in Fig. 8.7 (Garg & Ling, 2013; Kim et al., 2012).

### 8.3.2.5 Graphene-based Nanomaterials for CO₂ cycloaddition

Graphene-based nanomaterials offer a more sustainable future for fossil-fuel-based economies in CO₂ capture and conversion through the development of new adsorbents with...
<table>
<thead>
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<th>References</th>
<th>Membrane</th>
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<th>Permeability CO₂ (barrer)</th>
<th>Selectivity</th>
<th>Test condition</th>
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</thead>
<tbody>
<tr>
<td>Zhao, Ren, et al. (2015)</td>
<td>GO/Polyimide MMM</td>
<td>CO₂/N₂</td>
<td>15.94</td>
<td>84.36</td>
<td>1 wt.% GO, 1 MPa, 35°C</td>
</tr>
<tr>
<td>Shen et al. (2015)</td>
<td>GO/Pebax MMM</td>
<td>CO₂/N₂</td>
<td>100</td>
<td>91</td>
<td>0.1 wt.% GO, 0.3 MPa, 25°C</td>
</tr>
<tr>
<td>Karunakaran et al. (2015)</td>
<td>GO/copolymer PEO—PBT (PolyActive) composite</td>
<td>CO₂/N₂</td>
<td>143</td>
<td>73</td>
<td>0.065 wt.% GO, 0.05 MPa, 25°C</td>
</tr>
<tr>
<td>Zhao, Cheng, et al. (2015)</td>
<td>GO/Pebax MMM</td>
<td>CO₂/CH₄CO₂/N₂</td>
<td>108</td>
<td>16.7, 48.5, 8.9</td>
<td>0.99 wt.% GO, 0.7 MPa, 25°C</td>
</tr>
<tr>
<td>Li, Ma, et al. (2015)</td>
<td>GO–CNT/ Matrimid³ MMM</td>
<td>CO₂/CH₄CO₂/N₂</td>
<td>38.07</td>
<td>84.6, 81</td>
<td>5 wt.% GO, 5 wt.% CNT, 0.2 MPa, 30°C</td>
</tr>
<tr>
<td>Li, Ma, et al. (2015)</td>
<td>Polyethylene glycol- and polyethylenimine-functionalized (PEG–PEI)–GO nanosheets/Pebax MMM</td>
<td>CO₂/CH₄CO₂/N₂</td>
<td>1330</td>
<td>45, 120</td>
<td>10 wt % PEG – PEI – GO, 0.2 MPa, 30°C</td>
</tr>
<tr>
<td>Xin et al. (2015)</td>
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<td>CO₂/CH₄CO₂/N₂</td>
<td>1247</td>
<td>82, 115</td>
<td>8 wt.% AGO, 0.1 MPa, 25°C</td>
</tr>
<tr>
<td>Dong et al. (2016)</td>
<td>Porous RGO/Pebax MMM</td>
<td>CO₂/N₂</td>
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<td>104</td>
<td>5 wt.% Porous RGO, 0.2 MPa, 30°C</td>
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<tr>
<td>Sarfarz and Bas-Shammakh (2016a)</td>
<td>GO-ZIF-301/PSF MMM</td>
<td>CO₂/N₂</td>
<td>25</td>
<td>63</td>
<td>1 wt.% GO &amp; 30 wt.% ZIF-301, 25°C</td>
</tr>
<tr>
<td>Authors (Year)</td>
<td>MMM Composition</td>
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<td>CO₂/N₂</td>
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<td>Dong et al. (2016)</td>
<td>GO-ZIF-8/Pebax MMM</td>
<td>CO₂/N₂</td>
<td>249</td>
<td>47.6</td>
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</tr>
<tr>
<td>Dai et al. (2016)</td>
<td>Imidazole functionalized (Im) GO/Pebax MMM</td>
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<td>105.5</td>
<td>0.8 wt.% Im-GO, 0.8 MPa, 25°C</td>
</tr>
<tr>
<td>Zahri et al. (2016)</td>
<td>GO/PSF Hollow Fiber MMM</td>
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<td>21.54</td>
<td>32.14</td>
<td>0.25 wt.% GO, 0.5 MPa, 25°C</td>
</tr>
<tr>
<td>Ebrahimi et al. (2016)</td>
<td>AGO/PVA-PES</td>
<td>CO₂/CH₄</td>
<td>13</td>
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<td>10 wt.% AGO, 0.5 MPa, 30°C</td>
</tr>
<tr>
<td>Sarfraz and Ba-Shammakh (2016b)</td>
<td>GO-ZIF-302/PSF MMM</td>
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<td>123.5</td>
<td>118</td>
<td>1 wt.% GO &amp; 30 wt.% ZIF-302, 25°C</td>
</tr>
<tr>
<td>Xue et al. (2017)</td>
<td>MWCNT/GO nanoribbons/Polyimide MMM</td>
<td>CO₂/CH₄</td>
<td>17</td>
<td>25</td>
<td>1 wt.% MWCNT/GO nanoribbons, 0.1 MPa, 35°C</td>
</tr>
<tr>
<td>Dong et al. (2018)</td>
<td>Porous RGO-modified halloysite nanotube (mHNT)/Pebax MMM</td>
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<td>93</td>
<td>mHNT/Porous RGO ratio of 7.5, 0.3 MPa, 30°C</td>
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<tr>
<td>Prasad and Mandal (2018)</td>
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<td>CO₂/N₂</td>
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<td>0.5 wt.% G/54.5 wt.% Chitosan-45 wt.% silk fibroin, 0.2 MPa, 90°C</td>
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<tr>
<td>Ying et al. (2018)</td>
<td>GO-[BMIM][BF₄] ionic liquid</td>
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<td>26.5, 47.1</td>
<td>ACNT/AGO ratio of 1:1, 0.6 MPa, 30°C</td>
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<tr>
<td>Wong et al. (2019)</td>
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<td>247.5</td>
<td>107.5</td>
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<td>45.2, 80.6, 59.0</td>
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</tr>
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<td>Rea (2018)</td>
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</tr>
<tr>
<td>He et al. (2019)</td>
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<td>80.7</td>
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<td>Zhang (2019)</td>
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</tr>
<tr>
<td>Raouf et al. (2020)</td>
<td>Graphene hydroxyl (GOH)/PSF-PEG</td>
<td>$\text{CO}_2/\text{CH}_4$</td>
<td>36.50</td>
<td>22.4</td>
<td>4 wt.% GOH, PSF/10 wt.% PEG, 0.8 MPa, 35°C</td>
</tr>
<tr>
<td>Pazani and Aroujalian (2020)</td>
<td>G/Pebax MMM</td>
<td>$\text{CO}_2/\text{N}_2$</td>
<td>44.78, 55.87</td>
<td>111.95, 120.72</td>
<td>0.7 wt.% G, 0.4 MPa, 25°C 1 wt.% G, 0.4 MPa, 25°C</td>
</tr>
<tr>
<td>Yang et al. (2020)</td>
<td>N-doped G nanosheets/ Matrimid MMM</td>
<td>$\text{CO}_2/\text{N}_2$</td>
<td>2.365</td>
<td>42.23</td>
<td>0.10 wt.% N-G, 0.1 MPa, 35°C</td>
</tr>
</tbody>
</table>
high capacity and high selectivity for reducing energy-related CO₂ emissions. The advantages of graphene, such as good surface area, high solubility, conductive, and cheap source of material are some of the key merits of the application of graphene in CO₂ capture and conversion. A broad range of graphene materials have been experimentally and theoretically explored to control CO₂ emissions from fossil fuel combustion. However, this field of investigation is still at its early stage of development for translation into real-world CO₂ capture applications. Some challenges associated with graphene-based nanomaterials, such as conductivity must critically be addressed with a thorough understanding of the flow of electrons. Intensive research also needs to be conducted investigating the potential toxicity of nanomaterials and chemistry involved in the applications before they can be available commercially, with economical evaluation of nanomaterials as the next vital step for the estimation of their feasibility to be applied in industries (Mazari et al., 2021). In this sense, the approach and design in the manufacturing of graphene-based nanomaterials is crucial in the future advancement of this material.

The origin of CO₂ should also be evaluated comprehensively in terms of power plant exhausts and direct air capture, whereby integration of CO₂ capture with electrochemical conversion may further increase the efficiency and reduce the costs (Hoang et al., 2020). DFT calculations have been widely used to investigate the mechanistic understanding of the selective electrochemical reactions according to the binding energies of intermediate species with metallic nanostructured catalysts. Research involving operando and in situ approaches are the main areas that should be explored in order to gain extensive knowledge into the mechanism of relevant systems (Heidary et al., 2019; Li et al., 2020; Zhu et al., 2020). In this context, infrared and Raman are the vibrational spectroscopy that should be used to illuminate the double-layer structure, catalyst composition, identity of bound intermediates, etc. In addition, the information on local chemical environment of specific elements of interest and electronic structure should also be obtained through X-ray absorption and X-ray photoelectron spectroscopies. In situ electron microscopy and X-ray diffraction are the essential analyses which can be used to determine structural information at a single particle and combination of particles. All these analyses not only can help to close the current research gaps in the field but also can discover techniques that are time saving as well as revealing promising and uncommon catalyst formations (Zhong et al., 2020).
The following recommendations should be taken into consideration in future research for the generation of next-generation graphene-based nanomaterials for CO₂ capture and conversion (Balasubramanian & Chowdhury, 2015).

1. The maximum working capacity of graphene-based nanomaterials should be explored in order to deploy these adsorbents in industries.

2. The issues in intrinsic constraints of process advancement of graphene-based CO₂ adsorbents need to be encountered before they can be applied in a real-world CO₂ capture system.

3. The orientation of CO₂ molecules in the molecular structure of the graphene-based nanomaterials should be investigated through in situ characterization techniques for examining the correlation between the structural and chemical characteristics of an adsorbent as well as its capability of adsorption, which further help to gain the elementary perspective of the gas adsorption mechanism in designing state-of-the-art graphene-based CO₂ adsorbents.

4. A better understanding of the impact of water vapor on carbon capture would eventually assist in the rational design of more advanced water-repellent graphene-based CO₂ adsorbents.

5. Advancement of molecular models and force fields based on actual flue gas conditions is essential for screening and accessing novel graphene-based CO₂ adsorbents.

6. Evaluation of engineering economics and environmental impacts associated with graphene-based CO₂ adsorbents needs to be performed using a cradle-to-grave life cycle assessment (LCA) before the adsorbents can be applied in industries for CO₂ separation from flue gases.

**8.5 Conclusions**

Graphene-based nanomaterials have demonstrated a potential alternative technology for CO₂ capture and conversion, and also have been considered as an emerging adsorptive separation carbon material during recent years. This is due to the fact that graphene-based nanomaterials possess high specific surface area and robust surface chemical activity. Hence, the unique properties of graphene in nanomaterials have opened up new possibilities to advance in this area and allow a wide spectrum of graphene nanostructure development for the application for CO₂ capture and conversion. Although much research has been studied on graphene-based nanomaterials, there is still urgent attention required to address the maximum working capacity and large-scale production, the highly ordered structures of graphene for technology advancement in nanomaterials for industrial applications, as well as to evaluate the aspects of economics and environmental impacts that are linked for the commercial production of the graphene-based nanomaterials. Hence, this review focuses on the recent advances and development progress of graphene-based nanomaterials specifically in CO₂ conversion and conversion. Various
synthesis methods of graphene nanomaterials are also illustrated here. Additionally, an overview of different categories of graphene-based nanomaterials is presented in this chapter. Future prospects and challenges of utilizing graphene-based nanomaterials for CO₂ capture and conversion are also explored.

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Graphene-based nanomaterials for CO₂ capture and conversion


Nanomaterials for Carbon Dioxide Capture and Conversion Technologies


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NANOMATERIALS FOR CARBON DIOXIDE CAPTURE AND CONVERSION TECHNOLOGIES

Edited by Shaukat Ali Mazari, Nabisab Mujawar Mubarak and Manoj Tripathi

Key features
• Explores the theories behind CO2 capture and conversion using nanomaterials and suggests alternatives to replace traditional energy-intensive CO2 capture technologies
• Provides information on the development of a wide range of nanomaterials used for CO2 capture and conversion processes
• Assesses the major challenges for integrating nanotechnology into carbon dioxide capture and conversion systems

Currently, abundant CO2 emissions from industries and the transportation sector threaten the planet by causing climate change. Nanomaterials for Carbon Dioxide Capture and Conversion Technologies investigates development and application of nanomaterials for CO2 capture and conversion.

Nanomaterials have shown amazing catalytic and adsorption characteristics for CO2. Using nanomaterials CO2 can be converted into fuels and chemicals and can be stored. This book explores the catalytic processes, involving electro and photoreduction of CO2, hydrogenation of CO2, etc. that produce a variety of fine products and intermediates and CO2 adsorption. The book highlights synthesis, chemical, physical, and morphological characteristics of nanomaterials. Development and application of various nanomaterials such as nanofluids, waste and biomass-based nanomaterials, titanium-based nanomaterials, perovskite-based nanomaterials, graphene-based nanomaterials, carbon nanotubes, metal organic frameworks embedded with nanoparticles, nanosized zeolites, mesoporous silica nanoparticles, and ionic liquid functionalized nanomaterials are described in detail. This book also highlights environmental impact of use of nanomaterials and their techno-economic analysis for CO2 capture and conversion.

The book explores the basic principles and challenges of nanomaterials in CO2 mitigation technologies and shall be an important resource of knowledge for academicians, researchers, professionals, policymakers, and students on CO2 capture and conversion processes.

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