2D NANOMATERIALS

Synthesis, Properties and Applications

Edited by
Subhendu Chakroborty and Kaushik Pal

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Preface

In recent years, 2D nanomaterials have emerged as a remarkable cornerstone in the field of advanced materials research, with their unique properties and versatile applications captivating the attention of scientists and engineers worldwide. This book is a testament to the ever-growing interest and importance of 2D nanomaterials in the realm of material science, nanotechnology, pharmaceuticals, and a myriad of engineering specializations. This book provides a comprehensive overview of the synthesis, modification, characterization, and application of 2D nanomaterials. Since the topic is vast, spanning a wide range of scientific disciplines and technological advancements, it is important to acknowledge that no single book can encompass the entirety of this field. However, this diverse collection of chapters covers essential themes and materials, focusing particularly on the synthesis strategies and potential applications of 2D nanomaterials.

The book is structured into three sections, each delving into different aspects of 2D nanomaterials. The first section explores the synthesis of these materials, providing an overview of both top-down and bottom-up strategies. Understanding the methods by which these materials can be synthesized is crucial for advancing their potential applications. Additionally, this section delves into the structural characterization of 2D nanomaterials, shedding light on their intricate compositions and properties.

The second section examines the diverse characteristics exhibited by 2D nanomaterials. From their magnetic and mechanical properties to their electrical, plasmonic, and optical behaviors, these materials possess an array of intriguing attributes that make them highly attractive for a wide range of applications. This section of the book provides a comprehensive understanding of these properties, enabling readers to appreciate the unique potential of 2D nanomaterials.

The final section focuses on the applications of 2D nanomaterials, highlighting their use in various fields such as energy, water purification, biomedical applications, multimodal tumor therapy, and supercapacitor technology. By showcasing the breadth of their applications, we hope to inspire readers to explore further and unlock the immense possibilities that lie within these materials.

The editors would like to express sincere gratitude to all the authors and co-authors who contributed their exceptional research to this book. Their expertise and dedication have enriched its content, ensuring its relevance and significance. Furthermore, we extend our heartfelt appreciation to the Wiley-Scrivener publishing team for their unwavering support throughout the challenging process of bringing this book to fruition. Their professionalism and commitment have been invaluable in making this project a reality.

As editors, we firmly believe that this book will serve as a valuable resource for students, researchers, and professionals in material science and related fields. It will spark new ideas, ignite curiosity, and pave the way for groundbreaking discoveries in the realm of 2D nanomaterials. We are confident that this book will find its rightful place in university and institute libraries across the globe and will be a source of inspiration for future research and innovation.

Once again, we extend our deepest gratitude to all who have contributed to this book. We are honored to present this collection of knowledge and discoveries, and we eagerly anticipate witnessing the impact it will have on the ever-evolving landscape of 2D nanomaterial research.

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January 2024

Part I

SYNTHESIS OF 2D NANOMATERIALS

1

Top-Down Strategies Synthesis of 2D Nanomaterial

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Abstract
The nanotechnology field originated in the 21st century. Especially 2D-based nanomaterials have received a lot of attention since they are easily affordable, non-toxic, and have excellent electrical, optical, thermal, and mechanical properties. Moreover, it is simple to synthesize and can be applied to a wide range of applications. The present chapter mainly focuses on various types of synthesis methods for 2D nanomaterials using top-down strategies. Many top-down strategies have been developed to synthesize 2D nanomaterials, such as etching, mechanical milling, sputtering, and laser ablation. In all methods, we would introduce their synthesis parameters, advantages, disadvantages, and applications. Moreover, its characterization and toxicity were briefly introduced.

Keywords: Nanomaterials, synthesis, 2D nanomaterials, top-down strategy, application of nanomaterials

1.1 Introduction

Nowadays, nanomaterials (NMs) are diverging materials among all research fields [1–4]. Nanomaterials are tiny-sized materials with external diameters up to 100 nm. The nanomaterials are primarily used to make the tubes, rods, and fibers. In addition, the nanoparticles found their physical existence in nature [5]. Nanomaterials possess different physical properties

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as well as chemical properties to form the bulk of their counterparts. As the size of the nanomaterials is too tiny, they cannot be seen with the naked eye. These nanomaterials are added to different materials, such as cloth, cement, and other materials. The tiny size of these materials also makes them useful in electronics, environmental remediation, and neutralizing toxins. The emergent properties of nanomaterials make them beneficial and impart great impacts in electronics, medicine, and other fields [6–8]. The chemical and physical properties of NMs highly depend on the surface atoms. As per the applications, NM size can be controlled by various techniques, such as modification of surface and micelle concentration [9, 10]. Dimensionally, NMs are divided into zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three dimensional (3D). In 0D, all three dimensions merge into a nanoscale range. A schematic diagram of dimension-based NMs is provided in Figure 1.1. In this category, nanospheres, quantum dots, and nanoclusters are included. In 1D, two dimensions merge into one. In this category, nanotubes and nanorods are included. In the 2D category, one dimension is at the nanoscale and the other dimension is outside [11]. In this category, nanofilms and nanolayers are included. 3D NMs are bulk NMs with diameters greater than the nanoscale (1–100 nm). The building blocks for 3D NMs are 0D, 1D, and 2D NMs. Core shells, nanowire bundles, nanotube bundles, and multi-nanolayers are included in this category [12].

Among these, more and more attention has been paid to two-dimensional (2D) NMs due to their unique properties, such as excellent

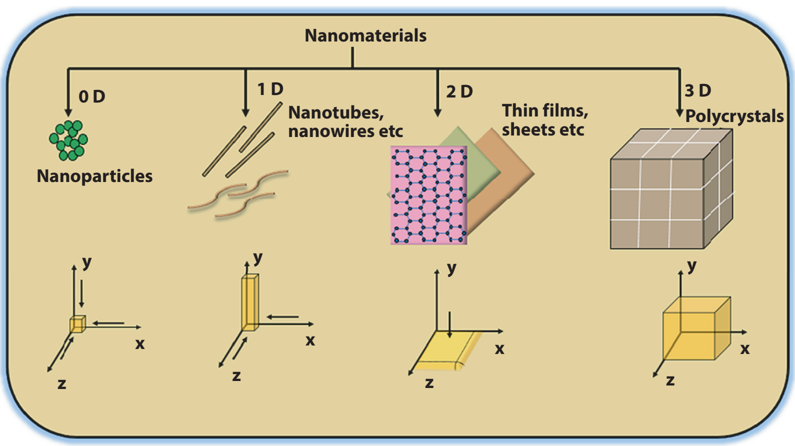

Figure 1.1 NM classification based on dimensions [13].

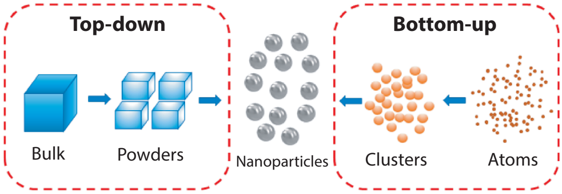

Figure 1.2 Nanoparticle's production strategies [23].

electrical, optical, thermal, and mechanical properties [14–17]. Many strategies have been developed to synthesize it for a specific application. These synthesis methods are broadly divided into two types of strategies: top-down and bottom-up approaches. Figure 1.2 displays an illustration of NM top-down and bottom-up strategies. The distinction between these two general classifications is based on the processes involved in the creation of nanometer-sized structures, and the choice of method depends on the specific requirements of the desired end product and the available techniques and technologies [18]. In the bottom-up approach, nanoscale materials are constructed from atomic or molecular precursors that are allowed to react, grow in size, or self-assemble into more complex structures [19]. By contrast, the top-down approach carves nanoscale structures by controlling the removal of materials from larger or bulk solids [20]. Each strategy has its own advantages and disadvantages [21]. In bottom-up strategies, nanoshells, ultrafine nanoparticles, and even nanotubes can be produced with a size of 1–20 nm. However, massive production is not possible, and synthesized nanomaterials need chemical purification. In a top-down strategy, nanomaterials can be produced massively, and purification is not needed. However, with this strategy, it is difficult to optimize the synthesized parameters [22]. This strategy is also not cost-effective.

In this chapter, we mainly emphasize the synthesis of 2D nanomaterials using a top-down strategy. In this strategy, we introduce the synthesis parameters, advantages, disadvantages, and applications for all methods. Eventually, the characterization and toxicity of 2D materials will be proposed.

1.2 Top-Down Strategy Synthesis Method

In a top-down strategy, bulk material is first converted into powder-based materials, which are then converted into nanomaterials [20]. There are mainly four methods available in this strategy (Figure 1.3), such as etching,

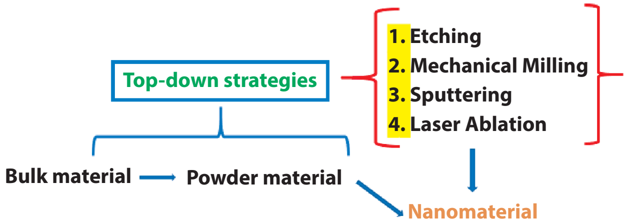

Figure 1.3 Top-down synthesis method of 2D nanomaterials.

mechanical milling, sputtering, and laser ablation. Each method's advantages, disadvantages, and own perspectives on applications are critically discussed. A summary of 2D NMs is listed in Table 1.1 using different top-down strategy methods.

Table 1.1 Synthesis of 2D NMs by different methods of top-down strategy.

NMs	Method	Parameters	Size	Applications	Ref.
GO	Mechanical milling	Ball size 5 nm; rotation speed 600 rpm, time (6, 16, and 24 h)	5 nm	Dye removal	[33]
GO	Mechanical milling	Ball size 3 mm, rotation speed 200 rpm, time 12 h	40 nm	Drug delivery	[34]
MoO_3	Laser ablation	Argon emission lines, Oxygen supplied	NA	Cancer therapy	[42]
GO-nano ribbon	Laser ablation	NA	NA	Optical	[43]
WS_2	Sputtering	Pulsing frequency of 20 kHz, DC power supply	>100	NA	[44]
MoS_2	Sputtering	Working distance 6 mm, a base pressure 2×10^{-6} Torr prior, 60 W	721	Supercapacitor	[45]

(Continued)

Table 1.1 Synthesis of 2D NMs by different methods of top-down strategy. (*Continued*)

NMs	Method	Parameters	Size	Applications	Ref.
MoO_2	Electro explosion	Surfactant, Thickness, temperatures, and current density	18.2	Antibacterial activity	[46]
MoS_2	Etching	Cl_2 plasma and Ar plasma	NA	Nanodevices	[47]
Hexagonal BN	Etching	O_2 and N_2 plasma (10 W); pressure: 1 Torr	NA	NA	[48]

1.2.1 Etching

In this method, the 2D NM surface is modified for enhanced physical and chemical properties. Mainly, this method of obtaining materials is applicable to the semiconductor industry. In this approach, a bulk material is treated with an etchant that selectively removes or dissolves certain layers or regions, leaving behind thin layers or flakes with desired 2D NM properties. This method has been used to synthesize 2D NMs such as graphene oxide (GO), transition metal dichalcogenides (TMDs), and boron nitride by selectively oxidizing or etching away layers from their respective bulk materials [24]. In this method, it is necessary to understand growth mechanisms [25]. Etching can be used to create patterns, structures, or features on the nanoscale, and it is a crucial step in the fabrication of various nanodevices and nanosystems [26]. Depending on the material and the desired outcome, several etching techniques can be used for 2D nanomaterials. Here are some commonly used etching techniques for 2D nanomaterials:

Wet etching: Wet etching involves the use of liquid chemicals to dissolve or remove material from a substrate selectively. For 2D nanomaterials, wet etching can be performed by immersing the substrate containing the nanomaterial in a chemical solution that selectively reacts with the material to be etched while leaving other parts of the substrate untouched [27]. Wet etching is relatively simple and can be used for a wide range of 2D NMs, including graphene, transition metal dichalcogenides (TMDs), MoS_2, and WS_2.

Dry etching: Dry etching, also known as plasma etching, involves using reactive gases and plasma to remove material from a substrate. Dry etching can be used for 2D NMs by exposing the substrate to a reactive gas, typically in a plasma chamber, which reacts with the material being etched and removed [28]. Dry etching offers higher precision and control over the etching process than wet etching, but it may require more complex equipment and processing conditions. Standard dry etching techniques for 2D NMs include reactive ion etching (RIE) and plasma etching.

Chemical vapor etching: Chemical vapor etching involves using reactive gases that are deposited onto the substrate as a vapor, which then reacts with the material to be etched. Chemical vapor etching can be used for 2D NMs by exposing the substrate to the reactive gases in a controlled environment, such as a vacuum chamber, and allowing the gases to react with the material to be etched [29]. Chemical vapor etching offers high control over the etching process and can be used for selective and precise material removal from 2D nanomaterials.

Atomic layer etching: atomic layer etching (ALE) is a specialized technique that offers precise control over the etching process at the atomic scale. ALE involves using sequential, self-limiting reactions to remove material from a substrate, layer by layer, selectively [30]. ALE can be used for 2D nanomaterials by controlling the exposure of the substrate to the reactive gases in a cyclic manner, which allows for highly controlled etching with atomic-level precision.

It is important to note that the choice of etching technique depends on the specific material properties of the 2D nanomaterial, the desired outcome, and the equipment and facilities available for the fabrication process. Careful consideration of the material properties, etching parameters, and safety precautions is necessary to ensure the successful etching of 2D NMs.

1.2.2 Mechanical Milling

Mechanical milling is the simplest top-down strategy. Mechanical milling, also known as mechanical alloying or ball milling, is a technique used to synthesize and process materials at the nanoscale through mechanical means. In this method, NMs are produced by the collision of rigid balls and bulk materials [31]. The whole system works under high pressure and is conducted through a sealed container. Usually, containers are made of ceramic and steel-based materials. The final product size depends upon many factors, such as ball size, milling time, milling duration, rotating speed, amount of bulky raw materials, and milling environment. The milling process is more effective when the ball-to-powder ratio is higher [32]. The milling process have many more advantages such as easy to handle, safety, high capacity, and long term maintained, even sometime no need solvent [32]. Despite this, disadvantages include disordering the crystal structure, requiring a lot of energy, the chance of contamination, and noise. It has been widely used to fabricate 2D nanomaterials, which exhibit unique properties due to their thickness being limited to the nanometer scale. The process of mechanical milling for 2D nanomaterials typically involves the following steps:

Material selection: Suitable precursor materials, typically in the form of powders, are chosen based on the desired properties of the final 2D nanomaterial.

Ball milling: The precursor materials are loaded into a ball mill and milling balls are usually made of a hard material such as stainless steel or tungsten carbide. The ball mill is then rotated at high speeds, causing the milling balls to collide with the precursor materials, leading to mechanical deformation, grinding, and mixing.

Milling parameter optimization: Various milling parameters, such as milling time, milling speed, and ball-to-powder ratio, are optimized to control the size, shape, and properties of the resulting 2D nanomaterials. These parameters can be adjusted to achieve the desired nanoscale features and properties of the 2D nanomaterial.

Post-milling treatment: Additional post-milling treatments such as annealing, doping, or functionalization may be employed to tailor the properties of the 2D nanomaterials further.

In this method, various types of 2D nanomaterials are synthesized and listed in Table 1.1 with different parameters. Recently, Mahmoud and his co-workers synthesized graphene oxide (GO) MPs through the ball milling method [33]. The obtained NM size was 5 nm. Authors set different parameters such as rotating speed (600 rpm), milling time, ball size, etc. Further authors characterize it using various sophisticated techniques such as BET, UV, XRD, TEM, and Raman. Moreover, synthesized materials are applicable for methylene blue dye removal. Further, Caicedo *et al.* fabricated GO from graphite using this method. The obtained GO NM size was 40 nm in a 12 h processing time and is applicable in drug delivery systems. From the graphite precursor, GO was produced [34]. The main mechanism is the oxidation process.

1.2.3 Sputtering

Sputtering is a well-known synthesis method in the category of top-down strategies. Sputtering is a versatile and widely used technique for synthesizing 2D nanomaterials due to its ability to produce thin films with precise control over their thickness, composition, and properties [35]. It has been employed to synthesize various types of 2D NMs and 2D layered materials, with applications in areas such as electronics, optoelectronics, energy storage, and sensors [36]. Generally, in this method, thin films are fabricated on a substrate through bombardment of the target with energetic ions [37]. In practice, there are several types of sputtering, such as DC diodes, RF-diodes, magnetron diodes, and ion beam sputtering. In this method, thin films are commonly produced on the substrate. For the production films, an ultra-high vacuum system was needed [38]. The sputtering process for the synthesis of 2D nanomaterials typically involves the following steps:

Target preparation: A solid target material, which is the source of the atoms or ions to be deposited, is selected and prepared. The target material can be a pure element or a compound, depending on the desired composition of the 2D nanomaterial.

Substrate preparation: A substrate, which is a flat surface onto which the atoms or ions will be deposited to form the 2D nanomaterial, is prepared. The substrate can be made of various materials, such as silicon, glass, or a flexible polymer, depending on the intended application of the 2D nanomaterial.

Sputtering process: The target material is bombarded with high-energy ions, which dislodge atoms or ions from the target surface. These atoms or ions are then deposited onto the substrate surface, where they can form a thin film with a thickness in the nanometer range. The substrate is typically placed in close proximity to the target material, and the sputtering process is carried out in a vacuum chamber to minimize contamination and promote uniform deposition.

Control of deposition parameters: Various parameters, such as the sputtering power, gas pressure, and deposition time, can be adjusted to control the thickness, composition, and morphology of the deposited 2D nanomaterial. These parameters can be optimized to achieve the desired properties of the final nanomaterial.

Post-deposition treatments: After the deposition, the 2D nanomaterial may undergo additional treatments, such as annealing or etching, to further modify its properties, such as crystal structure, electrical conductivity, or surface morphology.

1.3 Laser Ablation

The laser concept was first introduced by Einstein. Laser ablation is a straightforward process. Using this process, lasers are the main source for