

Chapter 1

1. Introduction

Nanomaterials have significantly transformed the lives of mankind in quite a short time, leading to an era of innovation and technological advancement. Since their inception, nanomaterials have considerably enhanced the healthcare sector, enabling us to target drug delivery, accurately and efficiently diagnose diseases, and develop advanced medicines. New technology is coming out daily, making electronic devices ever smaller, faster, and smarter. It has an enormous impact on the energy storage and production sector, enhancing the performance of secondary batteries and improving the efficiency and lifetime of solar cells. Nanotechnology has helped advancing technology in water remediation, food and agriculture, advanced materials, and security and defense. Nanotechnology has a transformative impact on human life, offering solutions to daily problems and paving the way for solving complex societal issues. As research and development continue, it is bound to drive society towards an enhanced quality of lifestyle. Typically, nanomaterials are characterized by extremely small dimensions, ranging from 1 to 100 nanometers¹. These can be further categorized into 0D, 1D, and 2D materials depending upon the number of dimensions in the nanometer range². Specifically, a material confined in all three dimensions by the nanoscale (1-100nm) is called 0D nanomaterial, e.g., quantum dots and nanoparticles³. These materials often exhibit unique optical and electronic properties due to the effects of quantum confinement. 1D nanomaterials have two confined dimensions, and one is outside the nanoscale regime, e.g., nanotubes and nanowires⁴. High aspect ratio and quantum confinement endow them with unique mechanical, electrical, and thermal properties. And, then, there are 2D nanomaterials, which are spatially confined in only one dimension, e.g., graphene, transition metal dichalcogenides, and nanoplates^{5,6}. These

materials offer surprisingly large surface-to-volume ratios and unique electronic, mechanical, and optical properties³. Owing to the large surface area available for reactions, these materials have found application in various fields, including but not limited to healthcare, electronics, diagnostics, energy devices, and optical devices. Compared to the bulk materials, which have all three dimensions outside the nanoscale regime, whose properties are dominated by their bulk atomic structure, these nanomaterials exhibit properties dictated by their surface effects and quantum confinement., which make them ideal for high-performance, high-precision applications in electronics, medicine, energy, and environmental remediation⁴.

Although nanotechnology as an area of research came under the limelight in the last leg of the 20th century, the use of nanomaterials has been a rather old affair. Records show the Chinese use of gold nanoparticles as red dye in their ceramic porcelains more than a thousand years ago. The beautiful colors in the glass artifacts from the Roman Empire were attributable to the metal nanoparticles present. However, the present nanotechnology research is propelled by our ability to see and manipulate matter at the nanoscale. Owing to this supernatural ability, we have been successful in developing significantly advanced techniques to fabricate, process, develop, and characterize these nanomaterials at atomic scales⁷. The theoretical understanding of the intricate working of atoms and molecules at such small scales further fueled the innovation in nanotechnology. From the crude optical usage of the past, these nanomaterials have found application in numerous industries, e.g., carbon nanotubes are added to concrete to improve its mechanical properties and durability⁸, titanium dioxide nanoparticles are applied to building materials instilling a self-cleaning property⁹, zinc oxide nanoparticles are utilized for their effective UV-protection¹⁰, iron nanoparticles are employed for removing heavy metal and other contaminants from water¹¹, perovskite solar cells have made solar cells more efficient and

cost-effective making solar energy more accessible¹², drug delivery systems based on nanoparticles are being developed for treating terminal illnesses such as cancer¹³, and graphene is used in flexible electronics^{14,15}.

1.1 Two-Dimensional Materials

Two-dimensional nanomaterials are a class of material characterized by their atomic thin planar structure bounded by weak van der Waals forces. This atomic thickness endows these materials with distinct morphology, enlarged surface area, and quantum confinement in a transverse direction, which leads to unprecedented physicochemical properties. Curiously, the existence of such 2D materials was debated as recently as the beginning of the 21st century by the physics community because such structures are not favored thermodynamically due to thermal lattice fluctuations. This changed in 2004, when two researchers from the University of Manchester, Andre Geim and Konstantin Novoselov, isolated a single graphene layer from its parent material, graphite, using the ‘scotch tape method’. Since then, a plethora of 2D materials have been suggested, designed, fabricated, and explored for their potential application in numerous fields. Specifically, researchers have poised their attention on the following 2D materials: graphene, boron nitride nanosheets, transition metal dichalcogenides (MoS₂, WSe₂, etc.), transition metal oxides (TiO₂, WO₃), and black phosphorus for their unique electronic, optical, mechanical and chemical properties, making them suitable for various applications in electronics, energy storage, catalysis, and biomedicine¹⁶⁻¹⁸.

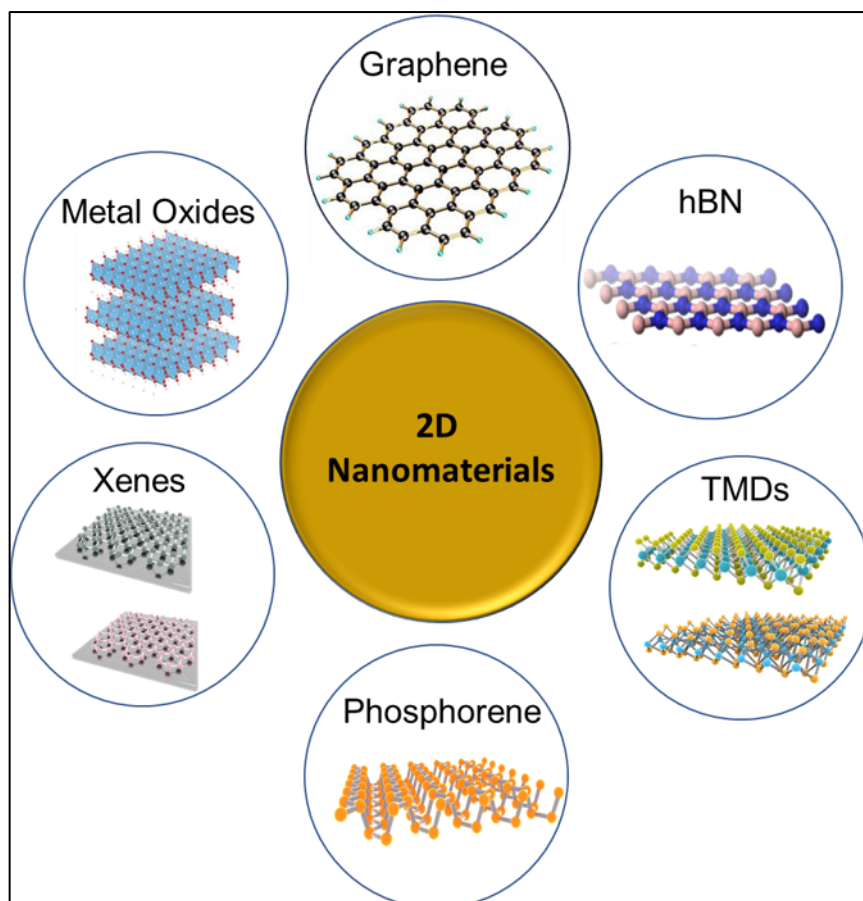


Figure 1.1 Schematic diagram of various 2D nanomaterials.

In the subsequent sections, the key 2D materials and their applications, which are central to this thesis, will be thoroughly explored. A detailed introduction will be provided for the primary nanomaterials, highlighting their unique properties and the synthesis methods employed for their fabrication. The discussion will focus primarily on layered 2D materials: graphene, hexagonal boron nitride, and boron carbon nitride. Furthermore, an in-depth analysis is conducted on the various applications for which these materials will be investigated. This includes their use in energy storage, wound healing, and electrochemical sensing. By exploring these applications, this thesis aims to demonstrate the transformative potential of 2D materials in advancing technology and addressing critical societal needs.

1.1.1 Graphene and its derivatives

Graphene is an astonishing nanomaterial that has revolutionized material science since its discovery in 2004 when Geim and Novoselov successfully isolated and studied a single layer exfoliated from bulk graphite using the ‘scotch tape method.’ This breakthrough was followed by extensive characterization of its properties, revealing its extraordinary attributes. Graphene is an allotrope of carbon comprising of single- or few-layered sp^2 -bonded carbon atoms arranged in a tightly packed honeycomb lattice¹⁹. The in-plane σ bonding between carbon atoms endows it with a rigid backbone structure, while the interaction between layers is governed by the out-of-plane π bonds, which provide it with its slippery nature. As one of the thinnest and strongest materials known to humankind, graphene exhibits remarkable mechanical strength, exceptional electrical conductivity, and superior thermal conductivity. Graphene has exhibited an extremely high tensile strength of 130 GPa and an elastic modulus of 1.0 TPa, making it 100 times stronger than steel^{20,21}. Its electric conductivity is reported to be 10^6 Sm^{-1} , with very low resistance, which is attributed to the sp^2 bonding. Furthermore, graphene has shown remarkable thermal conductivity (up to 5000 W/m.K), superior electron mobility (up to 200,000 cm^2/Vs), and an ultimate specific surface area of $2630 \text{ cm}^2 \text{ g}^{-1}$ ²²⁻²⁴. Owing to all these exceptional properties, graphene has been investigated for a wide range of applications in photonics, electronics, biomedicine, environmental remedies, and the energy sector^{14,24,25}. Over the years, several methods have been developed for synthesizing graphene and its derivatives. For any material to be commercially viable, it is of utmost importance that it is easy to synthesize, environment-friendly, and cost-effective.

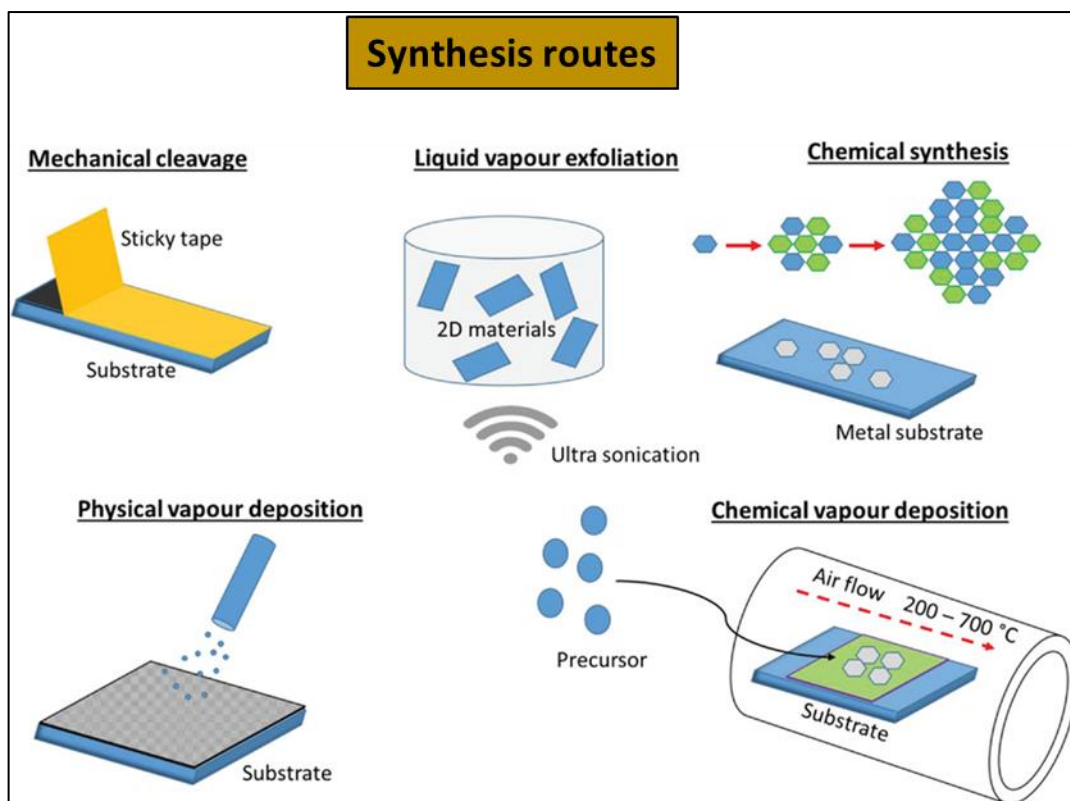


Figure 1.2 Schematic diagram showing synthesis routes for 2D nanomaterials²⁶.

The synthesis of nanomaterials can be broadly classified into top-down approaches and bottom-up approaches. Top-down methods include mechanical exfoliation, chemical exfoliation, arc discharge, carbon nanotube (CNT) unzipping, and oxidative exfoliation-reduction^{27–29}. These methods generally involve isolating or exfoliating nanoscale layers from bulk graphite and are known to produce scalable materials of good quality. However, their major drawback lies in achieving consistent properties and excess use of precursor material, leading to low yield. In contrast, bottom-up approaches involve the assembly of atoms and molecules to form desired nanostructures and include techniques such as chemical vapor deposition (CVD), template route, substrate-free gas-phase synthesis (SFGP), and organic synthesis^{28,30,31}. These techniques reportedly produce large-scale defect-free materials but involve expensive instrumentation and tedious procedures. In conclusion, each synthesis technique for graphene has its own advantages and drawbacks, and their use depends significantly on the potential application.

Despite graphene's extraordinary properties, its pristine form often lacks the surface functionalities necessary for specific applications. To overcome this limitation, researchers have explored various derivatives of graphene, such as graphene oxide (GO), reduced graphene oxide (rGO), and graphene quantum dots (GQDs). These derivatives retain many of graphene's inherent properties while offering additional functionalities through chemical modifications.

1.1.1.1 Graphene oxide

Unlike pristine graphene, which is composed of carbon atoms, graphene oxide is enriched with oxygen-containing functional groups such as hydroxyl, epoxy, carbonyl, and carboxyl groups, significantly altering its parent material's properties. The presence of these oxygen groups disrupts its pi conjugation as it converts many sp^2 hybridized bonds to sp^3 , thereby disrupting the electron mobility in the lattice. Highly oxidized forms of GO are electric insulators with bandgaps of 2.2 eV³². Contrary to graphene, the presence of oxygen functional groups renders GO hydrophilic, which makes it easy to prepare water-based suspensions. The functional groups also make GO highly reactive, allowing further modification and functionalization. The first reported synthesis of graphite oxide was performed in 1859 by B.C. Brodie, where he oxidized graphite with potassium chlorate and nitric acid³³. The acidic nature of the obtained material lends it the name 'graphic acid.' However, this method was inefficient, time-consuming, and environmentally unfriendly as it involved the release of ClO₂ gas. The most common method for synthesizing graphene oxide was devised by W.S. Hummers, which involves the oxidation of graphite with potassium permanganate (KMnO₄) in the presence of concentrated sulfuric acid, often with the addition of sodium nitrate³⁴. At the end of the reaction, hydrogen peroxide (H₂O₂) is used to neutralize the excess potassium permanganate. This method has been widely utilized for synthesizing graphene oxide due to its simplicity and effectiveness. However,

several modifications or refinements have been made to this method to improve its efficiency, yield, and, most of all, its environmental impact. Hummer's method has been modified to eliminate sodium nitrate, which is known to produce hazardous byproducts^{35,36}. In 2010, Tour³⁷ developed a novel method for synthesizing graphene oxide, which involved using phosphoric acid instead of sodium nitrate. Phosphoric acid stabilized the oxidation process and also acted as an etching agent. The stable oxidation process led to a higher yield of highly oxidized GO. Besides the chemical route, electrochemical synthesis has been utilized for the green synthesis of high-quality graphene oxide³⁸⁻⁴⁰.

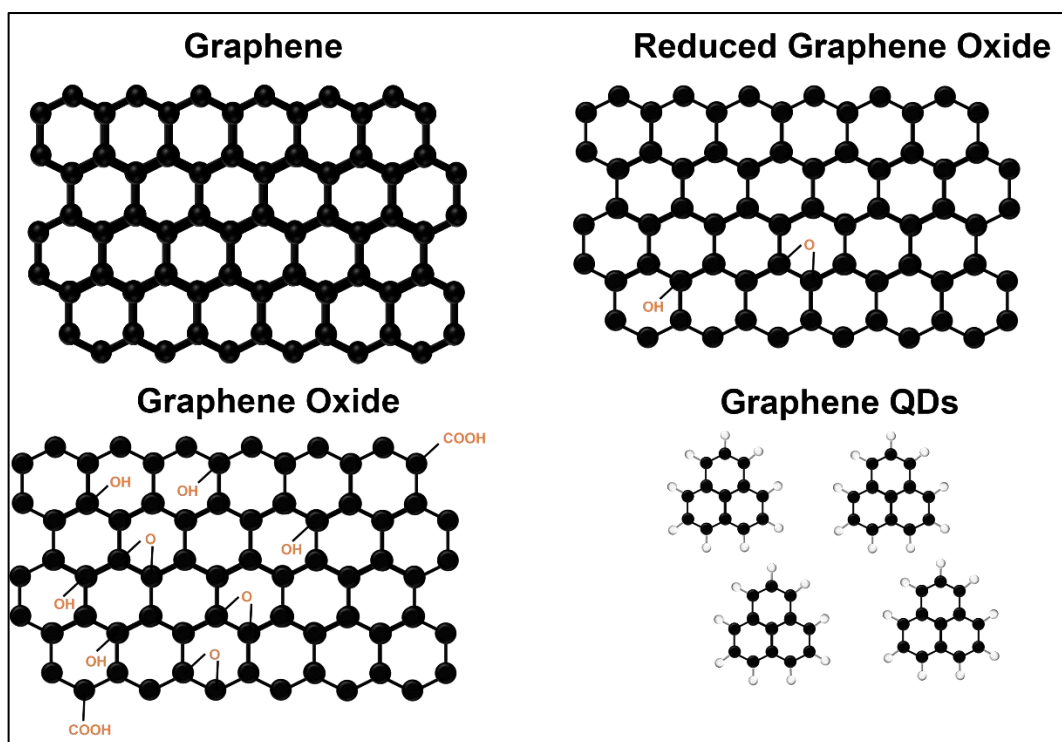


Figure 1.3 Structural representations of Graphene, graphene oxide, reduced graphene oxide, and graphene quantum dots.

1.1.1.2 Reduced Graphene Oxide

Reduced graphene oxide (rGO) is a form of graphene oxide which has undergone partial or full reduction. The reduction process leads to the restoration of the sp^2 -bonded carbon

network. Therefore, the structure of rGO consists of the graphene-like basal plane with considerably fewer oxygen groups. The partial restoration of sp^2 -network is also responsible for the conductive properties of graphene. Along with the electronic conductivity, rGO boosts enhanced mechanical properties and flexibility compared to GO, making it more suitable for use in composite materials and flexible electronics⁴¹⁻⁴³. Several methods have been developed for the synthesis of rGO from graphene oxide. Graphene oxide is chemically reduced by using chemical agents such as hydrazine, glucose, ascorbic acid, and sodium borohydride to form rGO^{42,44}. Graphene oxide can be reduced to rGO by subjecting it to high temperatures in an inert atmosphere, which removes oxygen groups by thermal decomposition⁴⁵. Furthermore, electrochemical reduction⁴⁶ and light irradiation method⁴⁷ have also been reported to reduce graphene oxide sheets. In recent years, there has been growing interest in using rGO in polymeric composites owing to the possibility of making conductive multifunctional materials with enhanced mechanical properties. The additional benefit of graphene oxide derivatives showcasing superior antibacterial properties makes them exciting candidates in forming composites for biomedical applications such as targeted drug delivery, wound healing, and tissue regeneration⁴⁸⁻⁵¹.

1.1.1.3 Graphene quantum dots (GQDs)

Consisting of quantum-sized graphene fragments, GQDs exhibit unique electronic and optical properties, making them promising candidates for a wide range of technological advancements. GQDs are characterized by their spatial confinement in all three dimensions (< 10 nm)⁵². This quantum confinement bundled with a layered graphene structure is the reason for the exotic optical and electronic properties demonstrated by GQDs. Furthermore, it offers several advantages, such as low toxicity, water-solubility, biocompatibility, and functionality, which makes it a potential candidate for biomedical applications.

Through the exploration of graphene derivatives, researchers aim to harness the full potential of graphene-based materials for diverse applications in fields ranging from electronics and energy storage to biomedical engineering and environmental remediation^{53,54}.

1.1.2 Hexagonal boron nitride

Boron nitride is a material made up of an equal number of boron (B) and nitrogen (N) atoms and has attracted significant attention from material researchers. Boron nitride exists in several crystalline forms, namely hexagonal boron nitride (hBN), which is a white slippery material with a layered structure similar to graphite, cubic boron nitride (cBN), which is isostructural to diamond, and a rare wurtzite boron nitride (wBN)⁵⁵⁻⁵⁷. Cubic boron nitride has a very high-density sp^3 -bonded structure. It has been lauded as the second most rigid material known to humankind. However, it has been facing a struggle in devising reliable and reproducible preparation methods, due to which it has not been researched that extensively⁵⁸. Hexagonal boron nitride (hBN) is the most prominent form of boron nitride, with boron and nitrogen connected with sp^2 hybridized bonds⁵⁹. For this reason, it is also known as ‘white graphite.’ It consists of layers of alternate boron and nitrogen atoms arranged in a hexagonal pattern, where adjacent atoms are strongly bonded by covalent forces, and each layer is bonded to adjacent layers by weak van der Waals force. Owing to its exceptional thermal stability, high thermal conductivity (600 W/mK), and excellent insulation properties (5.5-6.4 eV band gap), bulk hBN has been extensively employed in various industrial applications including lubricants, thermally conductive materials, composite materials, and high-temperature insulators^{60,61}. As the structure of hexagonal boron nitride is analogous to graphite structure, there were speculations about possibilities of boron nitride nanostructures similar to carbon nanostructures (such as

carbon nanotubes, graphene, carbon quantum dots). The first report of successful synthesis of BN nanotubes came in 1995⁶², followed by subsequent synthesis of nanowires, nanofibers, and nanorods⁶³. After the successful isolation and study of graphene in 2004, a similar single or few-layered structure for BN was also speculated. BN nanosheets (BNNS) came into existence as nano-mesh⁶⁴, followed by free standing nanosheets peeled off from BN crystal⁶⁵. To date, hBN nanomaterials can be considered the most important class of inorganic nanomaterials and have found applications in diverse fields. hBN nanomaterials have been widely utilized as fillers in fabricating high-performance polymer nanocomposites^{66,67}. Owing to its ultrahigh stability and softness, these nanomaterials have been used as lubricants and additives in cosmetic products⁶⁸. Although the impaired electronic conductivity impedes its usage in electrochemical sensors, researchers have devised various strategies to overcome this shortcoming and better utilize its superior chemical and thermal stability. Apart from these applications, BN nanomaterials have been widely investigated for potential applications in electrochemical energy systems⁶⁹. Nanostructured BN has been incorporated into various components of electrochemical systems such as electrolytes, separators, and electrodes to alleviate several inherent problems.

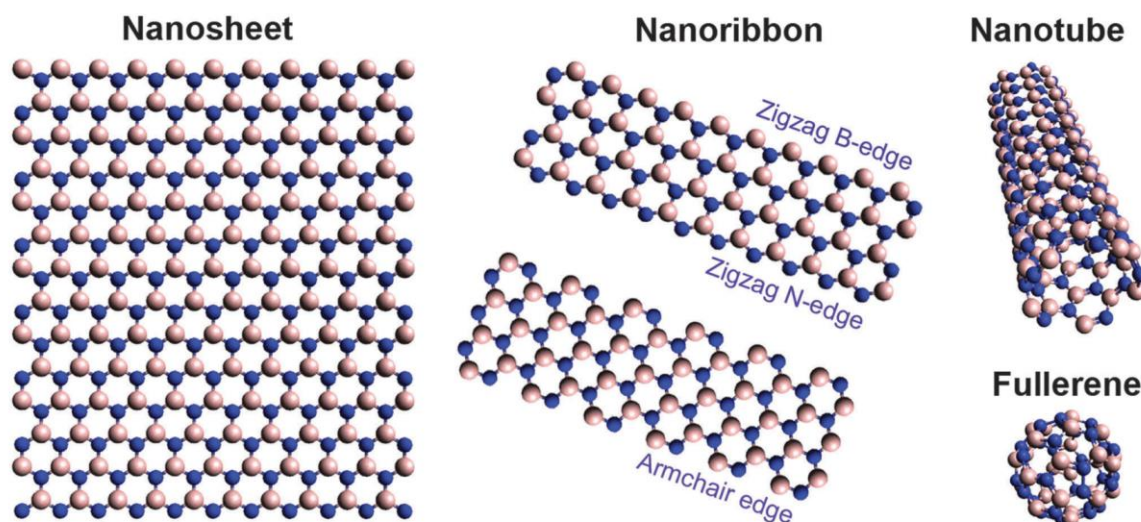


Figure 1.4 Models of 2D, 1D, and 0D structures of boron nitride⁷⁰.

1.1.2.1 Boron nitride nanosheets

BNNS are single or few-layered sheets of hexagonal BN that are isostructural to graphene. Each boron atom is covalently bonded to three nitrogen atoms and vice versa, forming a strong planar structure. This unique layout of atomically thin material provides it with specific exotic properties, namely, enhanced mechanical strength, chemical stability, extreme thermal stability, and thermal conductivity⁷¹. These nanosheets are characterized by high aspect ratios, with thickness often in the range of a few atomic layers and lateral dimensions ranging from a few nanometers to several micrometers. They possess excellent optical properties and oxidation-resistance, which makes them ideal for high-tech applications⁷². The reason for increased mechanical strength and chemical stability is attributed to the vast difference between the electronegativities of boron and nitrogen, making the bonds partially ionic. BNNSs were first synthesized by decomposing borazine in the form of nanomeshes on metal substrate⁶⁴. These can also be prepared using simple scotch tape method⁶⁵ where nanosheets are systematically exfoliated from bulk boron nitride crystal, similar to preparation of graphene sheets. BNNS have also been reported to be prepared by using liquid phase exfoliation, where BN flakes are obtained by subjecting

BN dispersion to ultrasonication^{73,74}. Other techniques utilized for BNNS synthesis include chemical vapor deposition⁷⁵, ball milling⁷⁶, and chemical exfoliation⁷⁷.

1.1.2.2 Boron nitride nanotube (BNNT)

BN nanotubes are another important hexagonal BN nanomorphology found in either single- or multi-walled structures. These have structures similar to carbon nanotubes⁷⁸. Owing to its partial ionic nature and the peculiar stacking characteristic of B-N, unlike CNTs, a single-walled structure is not typical in BNNTs. It is very challenging to obtain by usual synthesis routes⁷⁹. On the other hand, the formation of multiple layers of tubes stabilizes the whole structure, thereby making it much easier to synthesize and use. Researchers have modified the synthesis techniques used for CNT growth for BNNT synthesis, such as the arc discharge method, and CVD⁸⁰. Along with these traditional methods, several alternate methods such as plasma enhanced pulse layer deposition (PLD), substitution method, arc melting, high-temperature heating in N₂ have also been developed for BNNT synthesis⁸¹. Nonetheless, the commercial application of BNNTs is still plagued with the absence of large-scale high-quality BNNT synthesis methods.

BNNTs have a wide energy band gap, thereby showing semiconducting nature which can be tuned to narrow band n- or p- type semiconductor by either doping, external stress, and surface functionalization⁸²⁻⁸⁴. These nanotubes inherit several of its properties from their parent material, such as excellent thermal conductivity (350 W/mK), resistance to oxidation, thermal and chemical stability and strong luminescence^{62,63}. Owing to the superior stability, BNNTs have been reported for applications as protective shield for various nanomaterials such as nanowires, nanorods, and luminescence materials. It has also been used as reinforcement fillers in polymeric films and fibers. Furthermore, several researchers have reported its application in nanoelectronics, optics and photonics⁸⁵⁻⁸⁷.

1.1.3 Boron Carbon Nitride

Boron carbon nitride (BCN) ternary compounds are a fascinating and versatile material class combining elements of boron, carbon, and nitrogen into a single structure. BCN materials exhibit properties that bridge the characteristics of their constituent components, namely boron nitride (BN) and carbon-based materials such as graphene or graphite. Graphite is semi-metallic, while boron nitride exhibits insulating behavior. Consequently, hybrid BCN compounds are expected to show intermediate behavior and act as excellent semiconducting materials. This unique combination allows BCN to harness the benefits of both BN and carbon materials, leading to exceptional thermal, mechanical, and electronic properties. Initially, the dielectric properties of BCN compounds attracted significant interest from the semiconductor industry⁸⁸⁻⁹⁰. The miniaturization of integrated circuits was impeded by increased resistance and capacitance delays. To counter these effects, researchers sought low-dielectric materials to use as interlayer dielectrics (ILD) instead of SiO₂. BCN compounds emerged as a premier choice due to their superior thermal, chemical, and mechanical stability and low dielectric constant. Advancements in synthesis technology have made it possible to finely tune the composition of elements in BCN, resulting in compounds with unique properties. This innovation has garnered significant attention in research and industry, opening up various opportunities for BCN compounds in various applications. BCN has been explored for electronic applications in supercapacitors⁹¹⁻⁹³, field-effect transistors (FETs)⁹⁴, and photodetectors. In optics, BCN materials have shown promising results, such as UV detectors⁹⁵. Additionally, their mechanical strength has been utilized in making cutting tools and anti-wear protective coatings^{94,96}. Overall, BCN compounds offer a unique blend of properties from both boron nitride and carbon materials, making them highly valuable for numerous advanced technological applications.

BCN nanomaterials are among the most fascinating emerging materials due to their tunable and enhanced electrical, mechanical, and optical properties. These nanomaterials possess a graphene-like planar structure but exhibit properties distinct from graphene and boron nitride nanosheets (BNNS). One of the most prominent methods for synthesizing BCN compounds involves substituting carbon atoms in graphene with boron and nitrogen atoms. The properties of the final compound can be tailored by varying the degree and extent of this substitution, allowing for modulation of electrical properties such as conductivity, carrier mobility, and carrier concentration. BCN compounds' properties and morphology largely depend on the synthesis technique and the precursors used. Chemical vapor deposition (CVD) has become the most prominent technique for synthesizing BCN compounds. The CVD process involves the reaction of volatile precursors in a chamber to deposit the required material on a substrate. Kosolapova et al⁹⁷ first reported the synthesis of BCN by reacting carbon and boron in the presence of ammonia or nitrogen gas at high temperatures. Since then, various modifications of the CVD method have been devised for synthesizing BCN nanomaterials, such as plasma-enhanced CVD, microwave plasma-assisted CVD, low-pressure CVD, and laser CVD⁹⁸⁻¹⁰². Additionally, several other techniques have been reported for BCN synthesis, including magnetron sputtering¹⁰³, ion-beam assisted deposition¹⁰⁴, and pulsed laser deposition¹⁰⁵. Among these, the solvothermal method is an efficient synthesis technique for fabricating nanomaterials^{106,107}. This method involves dissolving precursors in a solvent and subjecting the solution to high temperatures and pressures inside a sealed vessel. High pressure facilitates chemical reactions and self-assembly that are otherwise impossible at lower temperatures. The solvothermal method effectively controls the composition and morphology of nanomaterials by adjusting reaction parameters such as temperature, pressure, solvent, and precursor concentration. This single-step synthesis route is proven efficient, environmentally friendly, cost-

effective, and high-yielding, making it suitable for the scalable synthesis of BCN nanomaterials.

Owing to their tunable electrical, mechanical, and morphological characteristics, BCN nanomaterials have attracted significant interest from researchers for application in various fields. BCN thin films have been particularly intriguing in microelectronics as their bandgap can be engineered by changing their composition and arrangement, making them suitable for specific applications¹⁰⁸. BC₅N has been reported as a working electrode for electrochemical sensing dopamine and uric acid owing to improved electrical conductivity and functionality¹⁰⁹. Like graphene and hBN, BCN can be a crucial component in hybrid materials. Research has demonstrated its potential use as UV emitters¹¹⁰. Furthermore, BCN nanosheets have been reported to display enhanced lithium storage capabilities along with outstanding cycling stability, making them highly viable materials as anode electrodes for next-generation energy storage applications¹¹¹. Karbhal et al¹¹² demonstrated the potential of BCN nanosheets as electrode material in high-performance supercapacitors. Additionally, BCN hybrid nanosheets, prepared by substituting nitrogen and boron into graphene, have demonstrated enhanced microwave absorbing properties¹¹³. Owing to outstanding surface functionality of these materials, BCN nanomaterials have also been employed in removing organic dyes from water¹¹⁴. These diverse and promising applications underscore the significant potential of BCN nanomaterials in advancing technology in electronics, energy storage, and environment remediation.

1.2 Applications of Interest

Owing to their exotic mechanical, chemical, and electrical properties, 2D materials have been investigated for potential applications in diverse fields. Here, I discuss some applications that are relevant to the work presented in this dissertation.

1.2.1 Electrochemical Sensors

Electrochemical sensors are analytical devices that measure the concentration of specific material using its electrochemical properties. These devices involve a surface where an electrochemical reaction occurs and a transducer that converts the chemical data into an electrical signal. Analytical tools such as atomic absorption spectroscopy, atomic emission spectroscopy, Raman spectroscopy, mass spectroscopy, calorimetric techniques, and UV-vis spectroscopy dominate the analysis field and are used by scientists globally. Although these instruments provide precise information about the analytes, these techniques have several drawbacks, such as costly instrumentation, long and arduous sample preparation, the need for skilled operators, and hazardous chemicals and solvents. On the other hand, electrochemical sensors provide very affordable and fast information about analytes. The sample preparation is simple, and the instrumentation is cheap and user-friendly. Furthermore, they also offer simultaneous detection of multiple analytes with significantly low LODs. Owing to these benefits, electrochemical methods have been popular candidates for analysis¹¹⁵⁻¹¹⁷.

Depending on the measurement parameters, electrochemical sensors can be categorized into three types: potentiometric sensors measure the change in potential at the working electrode compared to the reference electrode; amperometric sensors measure the current due to electrochemical reaction; and voltammetric sensors measure the current as a function of applied potential. Voltammetric sensors are interesting as they provide detailed information about the analyte through cyclic voltammetry or differential pulse voltammetry (these techniques will be discussed in the next chapter). An electrochemical sensor is comprised of three electrodes: a working electrode (WE), where the primary electrochemical reaction takes place; a reference electrode (RE), which serves as a

reference point for potential measurement; and a counter electrode (CE), which completes the circuit. The working electrode is the most crucial component of electrochemical sensors, as it is where the electrochemical reaction occurs, directly influencing the sensor's analytical properties, such as sensitivity, selectivity, and limit of detection. For this reason, significant emphasis is placed on the material from which the working electrode is made.

With the dawning age of miniaturization, electrochemical sensing has also begun distancing itself from large instruments, and there has been considerable development in small, low-cost electrode platforms. Screen-printed electrodes are such electrode platforms fabricated by depositing conductive and insulating layers onto a substrate^{118,119}. Cost-effectiveness, versatility, portability, and flexibility are some advantages that make SPEs rather exciting candidates for future electrochemical sensing platforms for providing quick and efficient analysis. Nevertheless, these miniaturized sensors face a grave challenge due to their low sensitivity and selectivity. Although several protocols have been described for this modification, such as the drop-cast and spin-coat methods, these methods have mixed results owing to unevenness and non-uniformity of deposition, material leaching into analyte sample leading to inconsistent and unreliable results¹²⁰. Our work presents a novel method for depositing 2D material onto the SPE surface through cyclic voltammetry.

1.2.2 Sodium-based batteries

With the rapid globalization, energy demands have risen considerably over the past few decades. As the world increasingly shifts towards renewable resources, there is an increasing emphasis on developing advanced energy storage systems that meet growing requirements. Electrochemical energy storage devices play a significant role in this transition. Since the emergence of lithium-ion batteries (LIB) in 1991, they have been a cornerstone of energy storage across various sectors, from electronic devices and power

tools to futuristic electric vehicles. However, this rising demand for LIBs has placed considerable strain on already exploited lithium resources, leading to a sharp rise in lithium-ion battery production's economic and ecological costs. Additionally, it is widely acknowledged that lithium batteries have reached a plateau regarding potential innovation for significantly enhancing energy density. Amid these challenges, sodium-based batteries have emerged as a promising alternative for energy storage. The relative abundance of sodium minerals and the resulting lower raw material costs pose sodium batteries as a promising candidate for next-generation energy storage systems.

Sodium-ion batteries (SIBs) are secondary rechargeable batteries where sodium ions move between the positive and negative electrodes, storing the energy in the process. During charging, sodium ions de-intercalate from the positive electrode and move to the positive electrode, storing the energy. It returns to the cathode during discharge, releasing the stored electron through an external circuit. SIBs have shown potential to address the critical limitations of LIBs. Due to the abundant availability of sodium on earth, SIBs can be produced at significantly reduced costs. SIBs are not dependent on heavy metals such as cobalt and nickel. Hence, they are less toxic, potentially reducing the environmental impact associated with their production and disposal. The reduced volatility and flammability of sodium minerals ensure enhanced performance even in extreme conditions, reducing the chances of overheating and thermal runaways, as is the case for LIBs. Another cost reduction factor in SIBs is using aluminum as a current collector. In LIBs, aluminum reacts with lithium at low potentials. Thus, copper is utilized as a current collector, which is significantly more expensive. Furthermore, as SIBs operate on chemistry similar to lithium-ion batteries for energy storage, they have a considerable advantage over emerging next-generation energy storage technologies. They can utilize the existing manufacturing and assembly infrastructure of LIBs, thereby reducing overall costs.

Although it offers several benefits over LIBs, the widespread adoption of SIBs is hindered due to several significant challenges. One of the primary issues is lower energy density compared to LIBs, which essentially means they can store less energy per unit weight, making them bulkier. This limitation is particularly problematic for applications that require lightweight, compact, and portable batteries, such as electric vehicles. Moreover, the cycling capabilities of SIBs are not on par with the well-established LIBs. These reports indicate that SIBs are still in the development phase, and further innovation and development are required to enhance their durability and efficiency over long cycles. A significant obstacle for SIBs lies in finding a suitable anode material capable of reversibly storing sodium ions. Graphite, extensively used as an anode material for LIBs, is not conducive to sodium ion hosting. Therefore, there is an urgent need to explore potential anode materials that can efficiently accommodate sodium ions for numerous cycles, ensuring stable and high-performance energy storage.

Sodium metal is a promising potential anode material, overcoming some challenges associated with other anode materials. It offers significantly high theoretical specific capacity (1166 mAh/g) and low reduction potential (-2.71 V versus SHE)^{121,122}. According to reports, the theoretical energy of a sodium-sulfur battery system is 1274 Wh/kg, which is much greater than the 387 Wh/kg density of LIBs¹²³. However, its applicability in sodium metal batteries is severely hindered by the growth of mossy and dendritic structures on subsequent charging/discharging cycles. These dendritic-growth reduce the coulombic efficiency by solid electrolyte interphase (SEI) formation, increase the internal impedance of battery and cause premature failure. Furthermore, they also threaten to pierce through the separator material and short-circuit the battery, posing a significant threat to its life cycle and safety. Although the exact phenomenon responsible for these dendritic growths in SMBs is unknown and is still under investigation, there has been efforts to mitigate this

problem and several protocols have been designed to this effect. *Liu et al* utilized a 3D carbon nanofiber layer onto sodium metal to artificially engineer an SEI layer with enhanced sodiophilicity¹²⁴. The 3D framework effectively suppressed dendrite formation by promoting controlled sodium deposition. Study by *Sun et al* confirmed that MXene containing oxygen functionalities can improve the sodiophilicity of the carbon host, reducing the overpotential and dendritic growth¹²⁵. Modification of liquid electrolyte is another strategy that has shown favorable sodium deposition without losing energy density^{126,127}. This involves the addition of certain additives in the electrolyte that promote the formation of a more stable SEI while maintaining high energy density and cyclic performance. Another effective strategy for dendrite suppression is the formation of 3D pores in the anode electrode. This method helps decrease the local current density by increasing surface area and mitigating the issue of volume expansion. The 3D pores also promote a more uniform distribution of metal ions. Separator functionalization has also been a promising strategy for reducing dendritic growth by providing uniform ion exchange channels. *Qin et al.* proposed coating PP separators with composite material comprising polydopamine and multilayer graphene. This strategy led to homogeneous sodium ion transport, suppressing the dendrite growth. The functionalized separators are reportedly mechanically more robust, have better electrolyte wettability, and sodiophilicity^{128,129}.

1.2.3 Diabetic wound healing

In India, an estimated 100 million people are diagnosed with diabetes, and nearly 136 million are prediabetic¹³⁰. These staggering numbers underscore the severity of the diabetes epidemic in our country. Among the various complications associated with diabetes mellitus, diabetic wounds, particularly diabetic foot ulcers, are notably severe.

These wounds result from a combination of factors, including neuropathy, peripheral artery disease (PAD), and impaired immune function, posing significant challenges in terms of healing and leading to high morbidity and mortality rates. Diabetic neuropathy reduces sensation in the extremities, particularly the feet, making individuals less aware of injuries or pressure sores. This lack of sensation allows minor injuries to go unnoticed and untreated, often leading to severe infections. Additionally, reduced blood flow due to PAD impairs the delivery of oxygen and nutrients essential for wound healing. This ischemia can cause wounds to become chronic and non-healing. High blood sugar levels in diabetic patients contribute to the formation of advanced glycation end products (AGEs), which impede normal cellular functions and wound healing processes. Furthermore, diabetes weakens the immune system, making it harder to fight infections that are common in diabetic wounds and can exacerbate their severity. Persistent inflammation in diabetic patients hinders the progression from the inflammatory phase to the proliferative phase of wound healing, further complicating the healing process. These factors collectively contribute to prolonged wound healing times, increased risk of infection, and a higher incidence of complications such as gangrene, often leading to amputations. Addressing the issue of diabetic wounds is therefore critical in managing diabetes and reducing the associated health burden.

Although there have been significant advancements in treating diabetic wounds, several issues and shortcomings persist in effective wound management¹³¹. Presently, wound care and debridement are key methods for treating diabetic wounds, involving removing necrotic tissue and applying dressings to maintain a moist environment conducive to healing. These methods are supplemented with advanced antimicrobial therapies, such as negative pressure wound therapy, to manage infections¹³². However, while essential, this treatment can be painful and complicated. The high costs and limited availability of

advanced dressings also pose significant challenges to effective treatment. Moreover, the overuse of antibiotics can lead to the critical issue of antibiotic resistance, along with potential side effects such as allergic reactions. Advanced therapies like stem cell therapy, growth factors, and hyperbaric oxygen therapy are expensive, require skilled personal and specialized equipment, and are often inaccessible to the majority of patients. These challenges highlight the need for the development of novel treatment routes that can provide effective, accessible, and affordable options for diabetic wound care.

Recently, Hydrogels have attracted considerable attention for potential application in wound care due to their unique properties and benefits¹³³. Composed primarily of water and hydrophilic polymers, hydrogels can be categorized into two groups: natural hydrogels, which are derived from natural polymers such as proteins and polysaccharides, and synthetic hydrogels, which are manufactured from synthetic polymers such as polyethylene glycol and polyacrylamide. The high water content in hydrogels helps rehydrate dry wounds and facilitate autolytic debridement, where the body's enzymes break down and remove necrotic tissue. This makes hydrogels particularly effective for treating wounds with minimal to moderate exudates, such as burns, pressure ulcers, and surgical wounds. One of the significant advantages of hydrogel dressings is their soothing and cooling effect, which can help reduce pain and discomfort associated with the wound. This makes them a preferred choice for patients with painful wounds. Additionally, the transparency of many hydrogel dressings allows for easy monitoring of the wound without the need to remove the dressing, thereby reducing the risk of infection and disturbance to the healing tissue. Studies have demonstrated the effectiveness of hydrogels in promoting wound repair and regeneration, evidenced by the migration of fibroblasts to the wound site in a three-dimensional type 2 diabetic human skin model. Hydrogels have also been infused with therapeutic agents, such as polydeoxyribonucleotide (PDRN), to expedite diabetic

wound healing in animal models¹³⁴. Moreover, functional hydrogels have been investigated as wound dressings to enhance healing¹³⁵. One study showcased the design of pH/glucose dual-responsive hydrogel dressings for treating diabetic foot wounds in athletes. A recent study showed the incorporation of aloe vera gel into BSA hydrogel demonstrated significant improvement in wound healing.

Hydrogels can be used in combination with other materials to enhance their functionality. For instance, they can be impregnated with antimicrobial agents to prevent infection or combined with alginates to increase absorbency for wounds with higher exudate levels¹³³. This versatility makes hydrogels suitable for a wide range of wound types and stages of healing. Consequently, hydrogels show great promise for clinical applications in treating diabetic wounds, offering an innovative and effective solution for diabetic foot ulcers.

1.3 Scope of thesis

This thesis focuses on using layered 2D materials for diverse applications. For the first application, boron carbon nitride is synthesized using the one-pot solvothermal method. Following extensive characterization, the synthesized material is used to functionalize the screen-printed electrode to enhance its sensitivity and selectivity. The functionalized surface is further tested for real-life application by estimating tryptophan concentration in test and real samples. In my second work, I investigated the potential of hBN nanomaterial as an anode material for sodium-ion batteries. For this purpose, electrodes with two morphologies of hBN are prepared and tested for electrochemical performance in coin cells. Following this work, I also investigated the potential use of hBN nanoplatelets for coating/modifying polypropylene separators for application in sodium metal batteries. The physical and chemical attributes of coated and uncoated separators are compared, followed by their application in sodium metal batteries. The electrochemical performance is tested by reversible charging/discharging cycles using sodium as an anode. The post-cycle analysis is performed to assess the effect of hBN coating on battery performance. For the next application, I prepared conductive hydrogel comprised of BSA protein and graphene oxide. The prepared hydrogel is further subjected to mild reduction by ascorbic acid to enhance its charge transfer and conductivity. The composite hydrogel is tested for its morphological, mechanical, electrical, and water retention properties. The antibacterial properties and biocompatibility of prepared hydrogel are also evaluated. Finally, the efficacy of prepared hydrogels in treating diabetic wounds is inspected by performing in-vivo studies on a murine model.

