Materials Horizons: From Nature to Nanomaterials

Subhash Singh
Kartikey Verma
Chander Prakash *Editors*

Advanced Applications of 2D Nanostructures

Emerging Research and Opportunities

Springer

Materials Horizons: From Nature to Nanomaterials

Series Editor

Vijay Kumar Thakur, School of Aerospace, Transport and Manufacturing, Cranfield University, Cranfield, UK

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Series Editor's Preface

In an attempt to cover the span of research interests, the book entitled "Advanced Applications of 2D Nanostructures: Emerging Research and Opportunities" encompasses a thorough investigation on two-dimensional materials. The authors included a range of topics from the history, evolution of 2D materials, the recent advancements as well as the future prospects associated with them. The most captivating part is the simplicity with which the book is written and the spectrum of topics discussed. For scientific researchers, this book provides a platform to brush up and enhance their knowledge on the topics of two-dimensional materials, inspiring them for new discoveries in the field. For the non-scientists, this book serves as an encyclopaedia providing them with all the fundamentals, applications and the advances pertaining to two-dimensional materials. The material in the book has been clearly illustrated through written text and pictures. This book can stimulate interest in undergraduates, postgraduates and budding researchers. It is a compilation of explanatory notes on molecular structures, synthesis techniques and developments. Additionally, limitations can help students unleash the existing research opportunities by overcoming the barriers associated with them. Thus, it can be understood by pupils of any level of education. Lastly, this book gives a bird's eye view on 2D nanostructures, its wide applications in the area of supercapacitors, solar cells and biosensors, etc.

I am immensely proud of Dr. Subhash Singh and Dr. Kartikey Verma for their endeavours to compile information on this trending topic. This book is an illustration of their hard work which will be a brick in the future evolution of many intellect minds pouring across the world in this line of research. I also appreciate all the authors who made their valuable contributions to the individual chapters. I sincerely wish them the very best for their future endeavours.

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Preface

The editors are delighted to present the high-quality research content of book series *Materials Horizons: From Nature to Nanomaterials* in first edition book *Advanced Applications of 2D Nanostructures: Emerging Research and Opportunities*. Book title was chosen as it converges upcoming technologies in all science and engineering disciplines for the next decade. This book will be one of the biggest breakthroughs to bring together the researchers, scientists, engineers, scholar and students from all areas of engineering and sciences science exclusively dedicated to nanostructured 2D materials and nanocomposites. We hope that this book will be extremely useful to researchers and students working in this diversified field. Basically, this book emphasizes the current advancement in interdisciplinary research on introduction, origin, processing, morphology, structure and noble properties of nanostructured 2D materials and nanocomposites and their applications in various fields of engineering and sciences. We try our best in bringing together a panel of highly accomplished experts in the field of nanostructured 2D materials and their nanocomposites in formulation of this manuscript.

Since the exfoliation of graphene in the year 2004, a new material class comprising of sheet-like structure has come into existence. They earned their name as two-dimension (2D) materials precisely due to this structure with thickness equal to that of a single atom. The unique properties exhibited by them have garnered the attention of researchers across the world. The tremendous scope for exploitation of these characteristics has enforced rapid advancements in the field of 2D materials. The discovery of graphene (2D material having single atomic layer of carbon) opens up the possibility of other layered materials and structures. An exceptional characteristic of layered materials is their ability to accommodate various ions and molecules between their layers, a phenomenon known as intercalation. Intercalation compounds of inorganic hosts (graphite, clays, dichalcogenides and others) have also gained renewed interest owing to their unique chemical and physical properties. De-intercalation of those compounds under certain conditions (such as thermal shock) as well as sonication or volume expansion reactions in the interlayer space led to the formation of widely used exfoliated graphite and two-dimensional (2D) materials with unusual electronic properties. Recently, a large family of 2D materials, labelled MXenes, was produced by the extraction of the A-element from the layered ternary carbides, such as Ti_3AlC_2 and other MAX phases. For developing these multifunctional materials for energy storage/generation, some renewed synthesis techniques and characterization efforts required. Further, exploration of alternative sustainable energy resources such as solar energy, geothermal power, biomass/biofuel and hydrogen energy is extremely important for the sustainable development of human civilization. Hydrogen is considered as one of the efficient and most likely future fuels, and there have been continued efforts to develop a hydrogen-based energy economy. However, the current hydrogen production mainly depends on the steam reforming technique, which is not a sustainable route, owing to the high energy involved in the process, in addition to CO_2 being the by-product. Hence, it has become extremely important to come up with breakthrough discoveries in the area of solar photovoltaics, especially on the development of highly efficient and low-cost electrocatalysts to replace the state-of-the-art precious metals—based hydrogen evolution reaction (HER) catalysts. Nanostructures of layered transition metal carbides and nitrides show promising electrocatalytic activity towards energy storage and hydrogen evolution reaction. Keeping this as the central theme, the editors/authors are proposing to explore several topics related to energy generation, conversion and storage with novel atomically thin 2D materials and their hetero-structures.

An early transition 2D nanomaterial, MXene, has recently come into the existence after graphene with so many exorbitant properties mainly related to energy storage-type material. Several scientists across the globe are working with 2D materials. This carbide belongs to the MAX phases which have a chemical formula $M_{n+1}AX_n$ where M is an early transition metal, A is an A-group element, and X is carbon or nitrogen. The crystal structure of MAX phases can be described as octahedral ternary metal carbide and/or nitride sandwiched by close-packed layers of A-element. One of the most widely studying and a promising members of this family is Ti_3AlC_2 among 70 MAX phases those are currently known. MXenes are expected to be applied extensively in many such promising anode materials for lithium-ion battery, hydrogen storage materials, high capacitors electrode materials and lead adsorption material.

The chapters included in this book highlight impactful research in the field of nanostructured 2D materials. Chapter 1 focuses on the initial developments leading to the discovery of 2D materials. A detailed description providing insights into the nature of 2D materials is broadly discussed. The classification of this new material class is listed. Moreover, the nature of growing interests in this field and the reasons behind this are reported. The research on 2D materials is still in the initial stages. Therefore, it is essential to understand the challenges and limitations in this field. A section in this chapter focuses on various prospects and challenges faced which provides the researches an idea before entering into the analytics of 2D materials. Overall, the entire chapter gives an overview on 2D materials, and it acquaints the readers to this new generation materials. Chapter 2 covers different types and intense classification of 2D materials in detail. An account of their various properties, synthesis methods, functionalization methods and applications will be given in this chapter. These materials possess unique optical, electrical and catalytic activity.

These properties have been exploited in various applications such as sensing, catalysis and in energy generation. 2D materials encompass a large family of materials which includes graphene family, oxide family and metal dichalcogenides.

In present scenario, 2D materials are attaining significant attraction from both technological and fundamental science aspect owing to their chemical, physical, magnetic and electronic characteristic differences over conventional bulk material. In Chap. 3, the author critically discussed different methods for production of 2D materials. Methods are broadly classified as mechanical and chemical exfoliation methods. The mechanical exfoliation provides versatility and low cost, whereas chemical exfoliation provides chemical homogeneity and molecular-level mixing. The synthesis and fabrication processes control the morphology and size of product which further improves the performance of 2D NSMs in different applications.

Sensors have wide application in various fields. Chapter 4 is based on the research developments regarding the synthetic background, physicochemical studies and applications in the field of sensor and catalysis. The synthetic pathway generally follows the improved hummers method and further chemical modifications as per requirement for the target applications. ^{13}C-NMR, IR, AFM, TEM, RAMAN, XPS and BET studies reveal about structure, surface topology, chemical and elemental composition of graphene oxide. The applications broadly focused in this chapter are sensing of ascorbic acid, pesticide detection and detection of diseases affected DNA. Further, its usage as a reusable heterogenous catalyst for the synthesizing important biological molecules and catalytic degradation of organic dyes.

The significance of nanocoatings is that they form a protective barrier between the material and the atmosphere serving both the aesthetics as well as preserving the material properties (chemical, mechanical and tribological). Hence, nanocoatings and thin films have a spectrum of applications in the manufacturing sector, tooling, electronics, biomedical, etc. Chapter 5 briefly explains the coating techniques entailing the properties of 2D materials correlating the relevance of 2D materials as nanocoatings and thin films.

There is a new buzz in the scientific community about a novel two-dimensional material called Mxene, which after graphene has attracted many a minds due to its unique mechanical, electrical and primarily electrochemical properties, thus predicting its widespread utility in next-generation highly efficient electrochemical devices for energy storage and delivery which are the need of the hour due to our increasing dependence on small-scale portable electronic devices, medium-scale utility in electric vehicles and large-scale standalone or grid-connected power storage units. Chapter 6 highlights these aspects of MXene for next-generation energy storage materials for batteries and supercapacitors, whereas transparent conductive electrodes have been a crucial element in interactive devices like touch panels and smart phones. MXene TCEs can be the best material for high-performance supercapacitors and transparent conductive electrodes explained in Chap. 7.

Chapter 8 emphasizes on gas detection capabilities of metal oxide (MO) species embedded in thin films engaged in the phenomena of absorption, chemical reaction and desorption of analyte gases at elevated temperatures, could confirm the importance of the nanostructured species existing at the reaction sites. For better sensitivity of the gas detection, it became a normal practice of increasing the surface area of interaction by making the sensing film as porous as practically possible. Simultaneously, the developments of 2D material families including graphene and the related nanomaterials along with a large variety of layered metal oxide nanosheets (MO-NSs) were also found extremely useful in using them as such or in the nanocomposite forms to replace the above-mentioned species. A large variety of synthesized single-/multiple-layered MO-NS films conjugated with different types of inorganic and organic molecules have been exhibiting additional advantages due to their programmable physicochemical properties in comparison with their nanoparticulate and one-dimensional counterparts.

Chapter 9 "Modeling and Simulation of Nano-Structured 2D Materials" entails typical simulation techniques which can be used for assessing different carbonous and non-carbonous nanomaterials. It will also enable to understand the various possibilities for surface modification and evaluation of properties of the characteristic nanomaterials. The use of different molecular dynamic simulation techniques simplified the validation of possible nanostructures and evaluation of their mechanical, physical and chemical *properties.* Chapter 10 specifically focuses on corrosive nature of some nanostructured 2D materials for advanced applications in the form of nanocoatings and thin films. Fundamental strategies for corrosion protection have been briefly reviewed, followed by exploration on role of protective coatings for corrosion prevention. Keeping in view different functional requirements, essential characteristics for an ideal anti-corrosion coating have been chalked out.

Chapter 11 entitled "Nanostructured 2D materials for Biomedical, Nano Bioengineering, and Nanomechanical Devices" addresses the recent renovations and the existing studies of 2D materials for biosensing, drug/gene delivery, antimicrobial activity, bioimaging and other multimode therapeutic applications. We would put special emphasis on the extensive flexibility of various rational combinations of 2D materials superior properties for the design and construction of assorted forms of reagents or devices with highly effective simultaneous diagnostic and therapeutic functions.

In continuation to biomedical application of 2D nanomaterials, one of the most important applications is the therapeutic application through proper understanding of the toxicity profile of the material can be utilized in vitro and in vivo experimentation as explained in Chap. 12. Also, another future biomedical application is in vivo gene transformation. Various researchers found that 2D nanomaterials could serve like in vitro gene transformation vector. An application in biomolecules detection and drug delivery could be development of a latest and scalable training procedure for inerratic nanomaterials synthesis.

"Mechanical performance of 2D Nanomaterials-Based Advanced Composites" Chap. 13 highlights results associated with the mechanical properties of 2D nanomaterials and their composites for advanced structural applications. The 2D nanomaterials thus produced are extra light in weight and high in strength and stiffness. This is why these nanomaterials find application in the area of aerospace and construction works.

The book's content is multifaceted and multidisciplinary having 2D nanostructures as central theme of the book. The variety of models presented in the book are up to date and potentiality valuable to researchers, scientist, scholars in all engineering and science disciplines, such as the areas of chemical engineering, nanotechnology, mechanical engineering and medical science, electronics engineering, chemistry and physics. We are sure that everyone will be benefited with information provided in this book.

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We express our heartfelt gratitude to *Springer Nature Singapore* and the editorial team for their aspiring guidance and support during the preparation of this book. We are sincerely grateful to reviewers for their suggestions and illuminating views on research content presented in this book *Advanced Applications of 2D Nanostructures: Emerging Research and Opportunities*.

We are thankful to Prof. Karunesh Kumar Shukla, Director, National Institute of Technology, Jamshedpur, and Prof. S. B. Prasad, Head, Department of Production and Industrial Engineering, National Institute of Technology, Jamshedpur, for encouragement and their support. Our sincere thanks to Prof. Vijay Kumar Thakur, Enhanced Composites and Structures Centre, School of Aerospace, Transport and Manufacturing, Cranfield University, Cranfield, UK, for guiding us at different stages of this project. Our gratitude to Prof. Raju Kumar Gupta, Associate Professor, Department of Chemical Engineering, Indian Institute of Technology, Kanpur, Uttar Pradesh, India, for encouragement and support throughout working on this book. Our sincere thanks to Prof. Kaushik Pal, Department of Mechanical and Industrial Engineering, Joint Faculty Centre of Nanotechnology, Indian Institute of Technology, Roorkee, Uttarakhand, India, for providing constant ideas of innovation for chapters. Special thanks to Dr. Ashwani Kumar, Department of Technical Education (Ministry of Technical Education) Government of Uttar Pradesh, India, for sharing his research experience and views on final draft of this book project.

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Introduction

In the present era of modern science and engineering, when technology is discussed, the roots go back to the understanding of material systems. It is often debated that properties of materials are based on what the material is made of. However, it is not only the composition but also the size and dimensionality of the materials that decides its behaviour. This is substantially true for some materials when their dimensions are reduced to nano-scale; i.e., their size can be expressed in nanometres. In the prevailing times of nanotechnology, materials can be easily engineered in the nano-scale. The analysis on materials is done by having at least one of the dimensions at nano-scale. The materials synthesised at nano-scale may be classified based on their dimensionality restraint on one of the dimensions produces a 2D material with sheet structure. Restraining two dimensions in terms of their size, 1D material is obtained, and when all the dimensions are restrained to nano-scales, 0D materials are produced. Structures with nano-metric dimensions shaped into zero-, one- or two- dimensional materials have radically different properties. Hence, it can be authoritatively established that apart from a material's atomic structure its material characteristics are also influenced by its dimensions.

In this context, it can be said that the nanostructures of carbon are an integral and a vital part of nanotechnology. It is the initially discovered carbon nanotubes (CNTs) and fullerene that enforced research development in the direction of 2D materials. It is post this discovery that attempts have been made to isolate the two-dimensional materials of graphite. Finally, in the year 2004, the attempts paved way and a breakthrough was achieved in successfully isolating graphene. Graphene possessed distinctive characteristics which initially elicited unmatched attention towards its two-dimensional sheet like structure and characterizations. Subsequently, research on remaining non-carbon-based elements grew. Therefore, the 2D materials gathered much interest within the recent past rendering outstanding electronic, mechanical and optical properties for various practical applications. Their unique features with emerging prospects in various engineering fields have inclined the interests of researchers across the world towards 2D materials. This eventually guided to the isolation of many 2D materials in the span of a decade.

The research advancements extended the discovery of 2D materials in carbides and nitrides. Rare characteristics (physical) are observable in the nanostructured 2D materials when charge and heat transmission are established to one single plane. Hence, the structure of 2D materials is extensively reviewed. It is in the field of electronics that 2D materials exhibit encouraging prospects. It is deemed that 2D materials are capable enough to replace silicon in various photonics, electronics and nano-electromechanical systems in the coming years. This is due to the fact that 2D materials unveil an exceptional range of optical, thermal as well as electronic characteristics. A whole new system of electronic devices can be generated through the 2D materials.

This book focuses on the initial developments leading to the discovery of 2D materials. A detailed description providing insights into the nature of 2D materials is broadly discussed. The classification of this new material class is listed. Moreover, the nature of growing interests in this field and the reasons behind this are reported. Therefore, it is essential to understand the challenges and limitations in this field. A section in this book focuses on various prospects and challenges faced which provides the researcher an idea before entering into the analytics of 2D materials. The applications of 2D materials have gained popularity in electronics, biomedicine, biosensors, water purification, energy storage devices and electrochemical sensors, etc. Overall, the entire book gives an in-depth knowledge on 2D materials and their applications which acquaint the readers to this new generation materials.

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Dr. Subhash Singh is currently working as Assistant Professor in Department of Production & Industrial Engineering, NIT Jamshedpur. He completed his PhD from Indian Institute of Technology Roorkee in 2017. He has over 8 years of teaching experience in various institutions/universities. He specializes in the areas of modification of nano materials, thin coating, Synthesis of nanocrystalline spinel, metal matrix composites (MMCs), synthesis of 2D materials, friction stir processing (FSP), and unconventional machining of biodegradable materials. He has over twenty research publications in various prestigious international journals and authored eight book chapters. Currently, two research projects are running under his supervision funded by SERB (DST) and IUSSTF.

Dr. Kartikey Verma has been working as Young Scientist Fellow (DST Young Scientist Fellow) in Department of Chemical Engineering at Indian Institute of Technology, Kanpur, India. He received his Ph.D. in Physics from University of Lucknow, Lucknow, Uttar Pradesh, India. His research interests include processing and characterization of thin films, polymer matrix composites, nanocomposites, bio-based polymers and carbon based materials for barrier properties, packaging and energy storage material. He has published more than 20 research papers in several international journals, along with more than 25 publications in proceedings of international/national conferences.

Dr. Chander Prakash is Associate Professor in the School of Mechanical Engineering, Lovely Professional University, Jalandhar, India. His area of research is biomaterials, rapid prototyping & 3-D printing, advanced manufacturing, modeling, simulation, and optimization. He has more than 12 years of teaching experience and 6 years research experience. He authored 60 research papers and 25 book chapters. He has written more than 150 research articles for various journals and conferences. He has edited 19 Books for Springer, Elsevier, and CRC Press. He has authored 1 book with World Scientific Publisher. He is also the series editor of "Sustainable Manufacturing Technologies: Additive, Subtractive, and Hybrid" with CRC Press.

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Chapter 1
Introduction, History, and Origin of Two Dimensional (2D) Materials

S. V. Satya Prasad, Raghvendra Kumar Mishra, Swati Gupta, S. B. Prasad, and Subhash Singh

1 Introduction

In the present era of modern science and engineering, when technology is discussed, the roots go back to the understanding of material systems. It is often debated that properties of materials are based on what the material is made of. However, it is not only the composition but also the size and dimensionality of the materials that decide its behaviour. This is substantially true for some materials when their dimensions are reduced to nanoscale, i.e., their size can be expressed in nanometres. In the prevailing times of nanotechnology, materials can be easily engineered in the nano-scale. The analysis of materials is done by having at least one of the dimensions at nano-scale. The materials synthesized at nanoscale may be classified based on their dimensionality (Gupta et al., 2015). This categorization is tabulated in Table 1. A restraint on one of the dimensions produces a 2D material with sheet structure. Restraining 2 dimensions in terms of their size, 1D material is obtained and when all the dimensions are restrained to nano-scales 0D materials are produced (Ozin et al., 2008). Structures with nanometric dimensions shaped into zero- one- or two- dimensional materials have radically different properties. Hence, it can be authoritatively established that apart from a material's atomic structure, its material characteristics are also influenced by its dimensions.

In this context it can be said that the nano-structures of carbon are an integral and a vital part of nanotechnology. It is the initially discovered CNTs (carbon nanotubes) and fullerene that enforced research development in the direction of 2D materials.

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Table 1 Dimensional categorization of materials

Dimensional category	Examples
Zero Dimensional (0D)	Fullerene, Quantum Dots
One Dimensional (1D)	Nanotubes, nanowires and nanoribbons
Two Dimensional(2D)	Materials with thickness of a single atom
Three Dimensional (3D)	Nanocones and nanoballs

Gupta et al., (2015)

It posted this discovery that attempts have been made to isolate the two dimensional materials of graphite. Finally, in the year 2004 the attempts paved way and a breakthrough was achieved in successfully isolating graphene. Graphene possessed distinctive characteristics which initially elicited unmatched attention towards its two-dimensional, sheet-like structure and characterizations. Subsequently, research on remaining non-carbon-based elements grew. Therefore, the 2D materials gathered much interest within the recent past rendering outstanding electronic, mechanical, and optical properties for various practical applications. Their unique features with emerging prospects in various engineering fields have inclined the interests of researchers across the world towards 2D materials. This eventually guided to the isolation of many 2D materials in the span of a decade.

The research advancements extended the discovery of 2D materials in carbides and nitrides. Rare characteristics (physical) are observable in the nanostructured 2D materials when charge and heat transmission are established to one single plane. Hence, the structure of 2D materials is extensively reviewed. It is in the field of electronics that 2D materials exhibit encouraging prospects. It is deemed that 2D materials are capable enough to replace silicon in various photonics, electronics and nano-electromechanical systems in the coming years. This is due to the fact that 2D materials unveil an exceptional range of optical, thermal as well as electronic characteristics. A whole new system of electronic devices can be generated through the 2D materials.

Presently, apart from the materials of carbon, the family of 2D materials is inclusive of metal oxides (layered) and TMDs (transition metal dichalcogenides). The entire family of 2D materials is represented in Fig. 1 (Geim & Grigorieva, 2013; Huang et al., 2014). One of the most crucial aspects of 2D materials is their stability. Among the existing 2D materials, monolayers of the graphene family, Micas, BSCCO and the TMDs (MoS_2, WS_2, $MoSe_2$, and WSe_2) under atmospheric conditions are stable. Stability may be observed in case of MoO_3, WO_3, the semiconducting dichalcogenides and the layered oxides of copper in atmospheric conditions. But the stability of layered semiconductors and metallic dichalcogenides is only possible in inert conditions. Though the exfoliation of 2D perovskite oxides and hydroxides is complete, not much data is available on these.

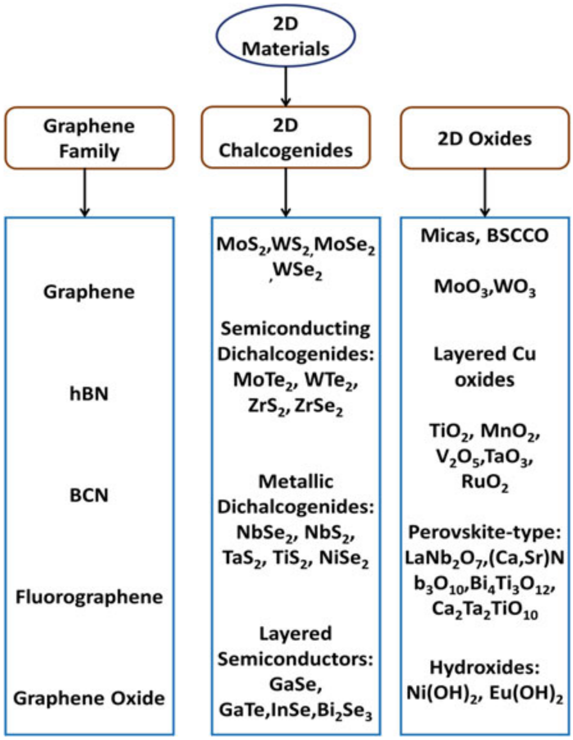

Fig. 1 The family of 2D materials (Geim & Grigorieva, 2013; Huang, 2014)

2 Evolution of 2D Materials

Many years ago, scientists believed that the two-dimensional materials cannot exist in nature due to their environmental instability. But presently, the theoretically recognized number of stable 2D materials is around 700. Although some of them are yet to be synthesized. The initial analyses on the electronic as well as the atomic structures of germanene and silicene were carried out in the year 1994, i.e. 10 years prior to the discovery of graphene. In the year 1962, Boehm coined the suffix "ene" to the foils of carbon with one layer. When the various discoveries related to carbon are studied in a sequential manner, it will be surprising to know that Graphite is quite familiar among the researchers for a very long time (specifically dating back to sixteenth century). The industrial applications of graphite also have been widespread especially in making steel or as dry lubricants and brake linings. But only when the fullerenes were discovered in 1985, the existence of many other allotropes of carbon came into limelight (Kroto, 1985). This also established the presence of carbon nanotubes of one-dimensional structure. The findings related to nanotubes of carbon were initially reported in the year 1991 (Iijima, 1991). These findings fuelled huge quantities of research encouraging the researchers to produce one-dimensional nanoribbons or isolate the two-dimensional materials of graphite from the two-dimensional crystals

(Gupta et al., 2015). Considering graphite (solitary layered) to be the initial material, multiple reports on fullerenes, graphite and nanotubes were presented since then. But only in the year 2004, the isolation of monolayer sheet of graphene was possible as an initiative (Novoselov, 2004). This was a great leap forward to a new class of materials. The solitary graphite layers obtained from graphite (in bulk form) post isolation were termed as graphene.

The graphene sheet is the primitive 2D material (thickness equal to single atom) that has been isolated. Multiple endeavours in the last 50 years have been towards achieving the sheets of graphene. This is to envisage the characteristics of single-atom thick, closely packed layer consisting of sp^2 carbon. The success achieved for previous attempts was modest and the nature of work till 1990s was intercalation of graphitic compounds. The process involves the atom to be sandwiched amid the layers of graphite due to which the inter-planar forces become weak and expedite the layer separation (Mas-Ballesté, 2011). Moreover, expandable graphite was extensively used which has the ability to expand in terms of its volume when heated quickly. The success in obtaining outstanding results was limited (about 10–50 layers). This trend was prevalent in 1960s. In the subsequent years, multiple attempts were made with various other complex processes with no much success. At last, success befriended the Andre Geim's group in 2004 that successfully isolated the solitary graphite layers at Manchester University (Novoselov et al., 2005). The scotch tape process was employed in which layers of graphene were pulled and transmitted to SiO_2 (thin layer) over silicon wafer (Novoselov et al., 2004). The new material obtained was extremely thin compared to a paper and had strength higher than that of a diamond with an electrical conductance much higher than Cu.

Now, the researchers have developed many methods for the preparation of graphene. Thus, graphene was the first modern carbon-based 2D material and its success revealed that stable, single and few-atom-thick layers materials are possible exhibiting exceptional technologically useful properties. The discovery of graphene also made researchers to switch to study and synthesis of non-carbon-based 2D materials. Since then there have been many other 2D materials that are identified. Among the entire family of two-dimensional materials, the initial and extended lineage that evoked research interests is the TMDs (Choi, 2017). The world's attention has been gathered by TMDs due to their exceptional electronic characteristics. They have good flexibility, are extremely thin and exhibit transparency. Due to their semiconductor nature, TMDs find their applications in memory devices, transistors, photovoltaic devices, photo detectors, Li-ion batteries and catalysis of HE (H_2 evolution). The TMDs structure is different to that of graphene, as TMDs possess sandwich structure with two chalcogens sandwiching the transition layer of metal. In contrast, graphene possesses carbon layer of sole-atom thickness (Lv, 2015). The transition metals include Mo, Nb, W whereas the chalcogens include elements like S, Te, Se, etc. TMDs possess strong covalent bonds within the plane and weak interlayer non-covalent bonds. Hence, either of the chemical/physical exfoliation methods can be employed to isolate TMDs 2D structures. The isolating methods include Li intercalation, exfoliation by adhesive tape, chemical or solvent aided exfoliation (Nicolosi, 2013; Zeng, 2011, 2012).

Thereafter, first MXene, generalized as $M_{n+1}X_nT_x$ was discovered at Drexel University in 2011 by selectively etching MAX phases (Naguib, 2011). The first reported Mxene was $Ti_3C_2T_x$. Within few months, many other 2-D materials were obtained through exfoliated compounds like Ta_4AlC_3,Ti_2AlC, $(V_{0.5}Cr_{0.5})_3AlC_2$, Ti_3AlCN and $(Ti_{0.5}Nb_{0.5})_2AlC$ (Naguib et al., 2012). So far more than 30 variations of Mxenes are fabricated. Many more have been theoretically predicted, making it one of the fastest-growing 2D material families (Anasori et al., 2017).

Later in 2012, Silicene, a 2D allotrope of silicone was discovered on a silver (111) single crystal in prevailing situations of ultrahigh vacuum through the process of molecular beam epitaxy (MBE) (Vogt, 2012). The fabrication of silicene triggered a concentrated search for similar 2D materials fabricated using equivalent techniques like the MBE. The characteristics of silicine are largely contrasting to that of graphene. The only similarity lies in their two-dimensional structure. These elements do not naturally exist nor do they have parental crystal having a 3D layer. Therefore, the possibility of exfoliation is eliminated and chemical fabrication is the available option. The fabrication may also be carried on a substrate by the process of epitaxial growth. Hence, the electronic and structural characteristics may be dependent on substrate.

After generation of silicene, researchers estimated that borophene can be achieved on similar lines by utilizing support extended by metal surface. Finally, in 2015, successful synthesis of three different borophene phases was achieved on the surfaces of silver (111) surfaces in the prevailing surroundings of ultrahigh-vacuum (Mannix, 2015). This 2D boron structure is metallic in nature despite its bulk boron being semiconductor (Wu, 2012).

Further in 2014, germanene (2D germanium) was reported by an international team of researchers led by Guy Le Lay at France's Aix-Marseille University (Dávila, 2014). In 2016, 2D tin known as stanene was discovered (Zhu, 2015). Survey of the 3D materials that can be exfoliated has shown that there may be many 2D materials that are yet to be discovered. Among the new system researchers have worked with hexagonal boron nitride, different transition metals chalcogenide.

3 Growing Interest in 2D Materials

The emerging field of 2D materials has become an area of great interest both in the field of fundamental science and technological aspect and without any doubt it could be presumed that over the next few years this field will lead to many new and exciting discoveries. The 2D materials maybe considered as the suitable section of emerging materials for engineering applications. The sheet-like structure possessed by 2D materials allows the flexibility to customize its characteristics through the surface treatments like chemical functionalization (Xu, 2009). Moreover, it is an extremely effortless process to get the 2D materials as dispersed nano-flakes (Hernandez, 2008). The characteristics of 2D materials include high strength, extreme lightweight nature,

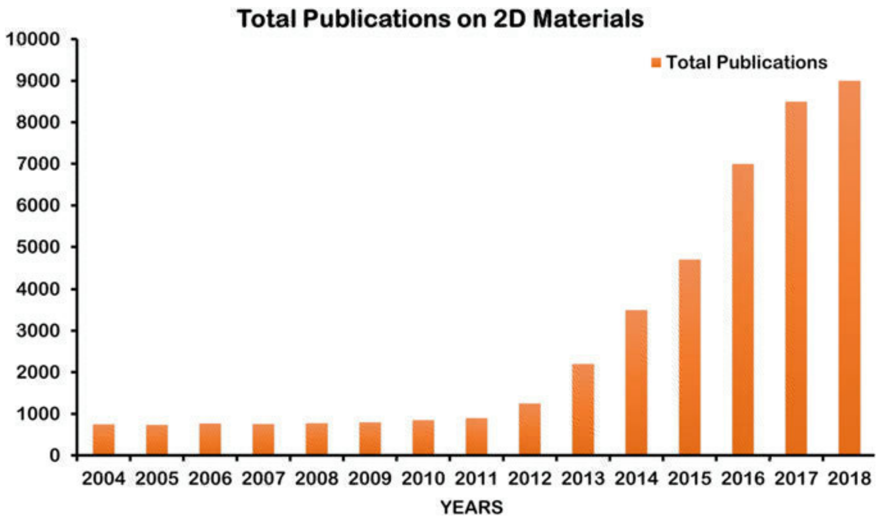

Fig. 2 Increasing trend of the total 2D material publications per year (Choi et al., 2017; Donarelli & Ottaviano, 2018)

good mobility of carriers, great modulus of elasticity, high optical, high UV adsorption, and superconductivity. These distinctive characteristics are restored. Hence, these may be thoroughly exploited in the fabrication of high-performance composites (Coleman, 2011). Also, the electronic band structures of these materials are a field of attention. Their zero band gap allows absorption of wide light span within the region of electromagnetic band (Reina, 2009). Among various reasons, the prime reason for the extreme growth in 2D material research is due to the unmatchable characteristics spotted in them. An appealing fact is that there is an increasing trend in the documentation of 2D material research every year as represented in Fig. 2. Approximately there are over 150 sheet structured materials that can be synthesized at nano levels. The list incorporates graphene family, 2D chalcogenides, 2D oxides as well as 2D carbides or nitrides (Choi et al., 2017).

The sheet structured materials are ideal for electronic applications since they are accessible to charge carriers enabling extraordinary mobility of carriers in all atmospheric conditions. Also, they possess excellent thermal conductivity. The strength (breaking) possessed by 2D materials (like graphene) is abnormally high because in comparison to steel their strength is greater by 200 fold (Lee, 2008). They also exhibit exceptional flexibility apart from the strength. The extremely thin membrane and its stretchable nature have the ability to overcome elastic deformation over 20%. These properties make 2D materials desirable prospects for lightweight applications. They are added to light weight polymers to enhance mechanical characteristics. The 2D materials have a slight disadvantage that they are brittle in nature and crack at higher strains. The 2D structured materials are an attractive prospect for mechanical applications in terms of the strength of their chemical bond. There is a possibility of modifying sheet structured elements chemically. The mechanical characteristics can be altered due to the existence of functional compounds (Yazyev & Louie, 2010). The best illustration of this is converting metals into insulators by the process of functionalization (Gierz, 2008). These functional characteristics can be produced in local regions and facilitate the fabrication of 2D material gadgets with multiple characteristics in different areas. Therefore, the 2D materials are the most sought after for their extraordinary range of exhibited properties which may be exploited for various applications (Gao, 2015).

4 Challenges and Opportunities

Currently, the research interest on 2D materials other than graphene is extremely high in the field of nanomaterials. The pursuit of other 2D materials signifies the characteristic similarities with graphene. But it is essential to thoroughly comprehend the behavioural aspects under testing conditions before they are applied for everyday use. For instance, the electronic characteristics of TMDs layers are known based on academic reports but the remaining mechanical, thermal and chemical characteristics are yet to be learnt. The research analysis on TMDs is currently limited. Hence, many endeavours are to be put in towards the analysis on how reliable the sheet structured materials are. Their performance needs to be evaluated to identify longevity under thermal or electrical stress examinations. The sheet-like structure of 2D materials is bound with issues like surface passivation especially for electronic applications. Moreover, only techniques like exfoliation or flake transmission are the commonly employed for bulk production. This is feasible to graphene or BN. As such no proper methods are available which would yield high productivity. Hence it is of top-most priority to discover advanced techniques which would be suitable for large-scale production of 2D nanomaterials. If not the applications of other 2D-based materials shall be extremely difficult and expensive for practical aspects.

Similar issues are persistent with active materials like silicene/germanene. The theoretical findings stress upon resemblance of their properties (electronic) with graphene but practical investigations are still inadequate. The layers of silicene/germanene currently are formed on substrates that are metals. But in the production of electronic devices these substrates are inappropriate. Hence, endeavours towards generation of silicene/germanene on substrates that are insulators or non-metallic are indispensable.

The research on sheet structured materials is taking baby steps but developing at an extremely rapid rate. It is the unmatched characteristics exhibited by 2D materials that stimulate the researchers to take interest in this briskly progressing field. Large advancement scopes are available in terms of formulating newer techniques for producing 2D materials on mass scale. It is also essential to achieve superiority in the structural development of existing layers. Further research is required in determining physiochemical characteristics of multi/single-layered nano-sheets. Material characteristic advancements through doping, functionalization and strain effect can be done as a part of forthcoming research. Additionally, the possibility of fabricating newer 2D materials with enhanced properties is always present which can further broaden the scope of these unique materials.

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