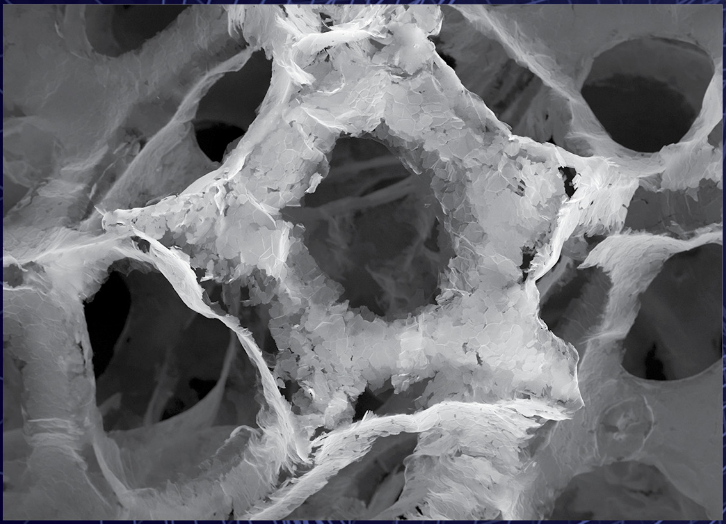
ADVANCED TWO-DIMENSIONAL NANOMATERIALS FOR ENVIRONMENTAL AND SENSING APPLICATIONS



EDITED BY

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Advanced Two-Dimensional Nanomaterials for Environmental and Sensing Applications

Advanced Two-Dimensional Nanomaterials for Environmental and Sensing Applications provides state-of-the-art progress developments in the design strategies of 2D-based nanomaterials. It covers specific focused applications in respective environmental challenges posed by pollutants such as chemical gases, bacterial and microbial, textile dyes, pharmaceutical antibiotics, agricultural pesticides, and toxic heavy metals in water and air contaminations. It elaborates the applications of 2D nanomaterials in the context of technologies such as sensing and detection to monitor pollutants, as well as photocatalysis and adsorption for the removal of pollutants.

Features:

- Elaborates the applications of 2D nanomaterials in the context of sensing and detection to monitor pollutants, as well as photocatalysis and adsorption for the removal of pollutants.
- Focuses on environmental pollutants detection, removal or remediation, and monitoring device fabrications.
- Discusses materials of specific dimension (2D).
- Covers both water and air remediation.
- Includes photocatalytic degradation and antimicrobial disinfection.

This book is aimed at graduate students and researchers in chemical and civil engineering, materials science, and nanomaterials.

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Preface

The world has over a century been undergoing industrial evolution, which is accompanied by the conversion of natural raw materials into society's needy products for their improved living standards. This has brought about a huge problem related to the generation of complex pollutants matrix entering the ecosystem. The generated pollutants at the product's production stage and also later at the end-user lifespan of the products are associated with unregulated waste disposal without measures taken to eliminate or minimize their environmental impact consequences. The untreated discharge of many pollutants such as harmful volatile organic compounds, and organic and solid wastes, is a threat to maintaining a healthy sustainable environment. The advancement of various solutions to treat and eradicate these generated wastes has relied heavily on sophisticated material design as the core integration of environmental remediation and monitoring technologies such as adsorption, advanced oxidation processes, and sensing and detection of pollutants. In the past decade, a noticeable breakthrough achievement in new materials design approaches has seen a high rise in layered two-dimensional (2D) materials that offer unique structure properties not accessible to their traditional bulk counterpart with greatly enhanced structure–activity performances. The precise control of achieving multi-stacked or single exfoliated 2D layers has shown to be pivotal in defining their superior functional performances. This book discusses comprehensively the state-of-the-art developments ranging from fundamentals to practical understanding of 2D nanomaterials synthesis, surface structure, and properties integrated with application testing in diverse environmental remediation and protection technologies. This book highlights the interplay relationship between the unique electronic, optical, mechanical, and topological properties of 2D materials manipulated by controlled synthesis approach to maximize their inherent structure effects with high functional performance in achieving efficient and economical technologies for sustainable environmental remediations. Besides, this book covers various emerging 2D materials such as metal oxide semiconductors, carbonaceous (i.e., graphene oxide, graphitic carbon nitride, and metal–organic frameworks), MXenes, layered double hydroxides, and transition metal chalcogenides, including their hybrid composites with diverse applications in sensing, electrochemical detection, photodegradation, and adsorption processes for pollutant monitoring and removal. It consists of 17 chapters written by various experts in advanced materials design and applications, which are classified into three parts. The first part consists of Chapters 1–3 focusing on the fundamental structure properties of 2D materials with extensive emphasis on design, synthesis methodologies, and characterization. The second part discusses the sensing and detection of gaseous, liquids, and solid pollutants with 2D materials covered by Chapters 4–7. The final part of the book focuses on the application of various 2D materials in the removal of volatile gaseous pollutants, radioactive toxic elements, and organic and metal ion pollutants from air, soil, and water contamination. The timely current research progress in 2D materials discussed in this book will appeal to graduate students as well as academic and industrial professionals working in advanced materials with focused applications to achieve sustainable environmental protection.

1 An Introduction to Two-Dimensional (2D) Nanomaterials

Swati Bansal, Naveen Kumar, Peter R. Makgwane, and David E. Motaung

1.1 INTRODUCTION

In the last few decades, nanomaterials had drawn the attention of researchers towards itself not only due to their distinctive features but also due to their applications in various important fields such as medicines, cosmetics, environment preservation and energy. Whenever we talk about nanomaterials, an image of size appears in our mind (i.e., size of 10^{-9}m), but nanotechnology is not just about the size of particles; it is also about how we modify and fabricate these particles to develop more advanced technologies [1]. Nanomaterials can naturally be occurred, can purposefully be prepared or can be occurred as by-products, and their physical and chemical properties are different from their bulk equivalents. The size and shape of nanomaterials affect the properties; for example, their reduced size enhances catalytic properties, while their shape increases their selectivity for catalysis [2]. Different dimensional nanomaterials exist like 0D (nanoparticles and quantum dots), 1D (nanotubes, nanorods, nanofibers and nanopillars), 2D (nanosheets, nanoplates and nanopores) and 3D (nanocomposites and complex graded structures); among which 2D nanomaterials have gained much attention after the isolation of graphene "a 2D ultrathin carbon layer" from graphite, which has exceptionally unique features such as high specific surface area, which results in greater utilization of these materials in biomedical applications such as medication, biosensing and cancer therapeutics. Graphene isolation leads to a new era in the development of 2D nanomaterials; after which various new 2D nanomaterials have been introduced having unique chemical/physical/optical properties, biodegradability and biocompatibility like high mechanical strength; good functionalization capabilities [3]; having applications in optical therapies like PTT (photothermal therapy) and PDT (photodynamic therapy) due to their quick response to external source like light [1,4–6]. Despite all these, their physiological interactions with living tissues are less understood, and hence their biocompatibility cannot be generalized because some are highly compatible in vivo and in vitro and others are not. Different compositions of 2D nanomaterials and their interaction with proteins and cell tissues are also different which will affect them in a different way. 2D nanomaterials can broadly be classified into three main groups – inorganic, organic and hybrid 2D nanomaterials.

Inorganic family includes layered double hydroxides (LDHs), Transition metal oxides (TMOs), Transition metal dichalcogenides (TMDs), Nano clays and MXenes, while covalent organic framework (COF), polymer nanosheets and sequence-defined 2D nanomaterials are associated with family of organic 2D nanomaterials, and hybrid 2D nanomaterials include MOF (metal organic framework), which are derived from both organic and inorganic species [4]. The library of 2D nanomaterials is huge, which exhibited a broad spectrum of properties ranging from conductors-to-semiconductors-to-insulators and from softest to the strongest [7].

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1.2 BULK VS 2D MATERIALS: FEATURES AND CONSEQUENCES

The physiochemical properties of 2D nanomaterials are different from their bulk equivalents, which result in greater performance of these materials due to different surface chemistry, quantum-size effect and high-aspect ratio [8]. The following aspects impart unique characteristics to 2D materials:

i. These materials have in-plane strong covalent bonds, thickness of atomic size and high flexibility, high mechanical strength and optical diaphaneity, which enables the utilization of these materials in making future flexible, transparent optoelectronic devices, as well as electrode material with high performance having great energy storage capacity and good conversion applications in batteries and fuel cells in comparison to bulk materials and other dimensional nanomaterials [9–12].
ii. Due to quantum confinement of electron in ultrathin region of 2D, specifically in single-layered material, without much interactions between inter-layers, they have enhanced optical, magnetic and electrical properties [2].
iii. Due to greater exposure of the surface atoms and high specific surface area, the 2D materials are highly desirable in various surface-active applications like photocatalysis, supercapacitors and electrocatalysis. In addition, high surface area, outstanding thermal stability and adsorption capability make 2D nanomaterials promising for constructing functional composites owing to their utilization as templates for the lithographic construction of nanostructures and as fillers to strengthen the resultant nanostructure (like 2D MT&Ds used as promising material for direct growth for noble metal nanostructures) [11,13–17].
iv. Greater fraction of surface atoms enables the easy manipulation of surface through more active-site construction to intensify the intrinsic material properties [18].
v. In comparison to other nanomaterials like nanotubes and nanowires, 2D nanomaterials exhibit tunability to somewhat greater extent due to planar surface, which makes them more compatible with fabricating techniques in device integration and scalable manufacturing [19].

1.3 UNIQUE CHARACTERISTICS OF 2D NANOMATERIALS AND PROPERTIES INFLUENCED

2D nanomaterials have specific features including high anisotropy, mechanical strength, plasmonic, electron confinement and optical properties (Figure 1.1). They have high surface-to-volume ratio, which promotes quick response and helps in the transmission of higher energy. Further, the functional properties of these materials may be tailored with ease by doping, electrodeposition, adsorption and chemical reduction, which promotes more stability, retention ability and permeability than the no-functionalized ones [20].

1.3.1 THICKNESS OF 2D MATERIALS

Thickness and size regulation of 2D materials layers have a significant effect on their chemical properties and little effect on their physical properties. As layer thickness of the material decreases, the flexibility of 2D materials is improved by decrease in flexural stiffness, which is proportional to cube of thickness of materials [21]. The layer thickness also affects the mechanical strength of some materials like in case of graphene; when the layer number is increased from 1 to 8, the strength decreases by 30% or more; but the increase in thickness doesn't affect the mechanical strength of boron nitride (h-BN) nanosheets [22]. With layer thickness reduced to atomic scale, the catalytic properties of these materials are greatly enhanced resulting from changes in electronic state as well as from the generation of in-plane defects by disordering in the structure [12,18]. The atomic-thick

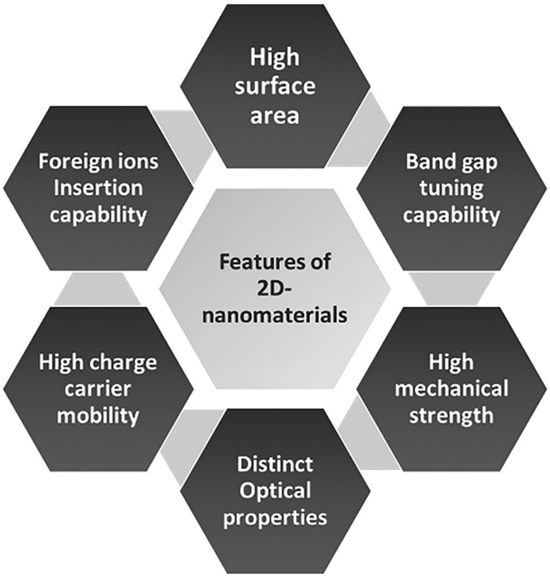

FIGURE 1.1 A representative diagram of characteristic features of 2D-nanomaterials.

Co_3O_4 has abundant active sites enabling the material to absorb CO_2 in large amount, and also due to increased and more dispersed charge density near Fermi level, the electrocatalytic efficiency enhanced to a greater amount; for example, 1.7 nm thick layer of Co_3O_4 shows 1.5 and 20 times greater electrocatalytic activity than 3.51 nm thick layer and bulk materials [23].

The specific area per gram (SAPG) value is highest for graphene among other 2D materials, but as the thickness is reduced from bulk to few layers, the SAPG value increases significantly; for example, an increase of 10–140 m^2g^{-1} is observed in the case of h-BN and 8.4–25m^2g^{-1} in the case of MoS_2. A high SAPG value and low electrical noise improve the ability to detect analyte even at low concentration [19,24–26]. On fabricating the top-gate transistor with transparent gate electrode, the MoS_2 layer has effect on photodetection ability due to the difference in band gap; for example, the device with triple MoS_2 layer (with a band gap of 1.35 eV) has good photodetection ability of red light, while the single (with a band gap of 1.8 eV) and double layer (with a band gap of 1.65 eV) have good ability in detecting green light [27,28]. Black phosphorous (a most stable allotrope of phosphorous) has a direct band gap of 0.3 eV, but as the thickness is reduced to monolayer, it increases to up to 2 eV, which open the doors for its application in optoelectronics [29].

1.3.2 HIGH SPECIFIC SURFACE AREA

2D nanomaterials with greater surface area enable them in loading and delivering therapeutic agents efficiently because of the availability of anchoring sites in larger amount [30]. Due to this feature, 2D materials have great interactions with fluorescent dyes, thus yielding greater quenching efficiency and better performance as fluorescence sensors [18]. The ultrathin nanosheets of TiO_2, ZnO, Co_3O_4 and WO_3 possess specific surface area of 298, 265, 246 and 157 m^2g^{-1}, respectively [31]. Among all the known 2D materials, graphene has the highest specific surface area of 2630 m^2g^{-1} [32], which enables its application in biomedical field like gene transfection, cancer treatment and drug delivery via the delocalized p-orbital electron, which enables this material to bind with aromatic drug molecules via π–π stacking, and the surface area of some 2D nanomaterials is presented in Table 1.1.

TABLE 1.1
Some 2D Nanomaterials with Specific Surface Area

2D Nanomaterials	Specific Surface Area Values ($m^2 g^{-1}$)	References
Graphene	2630	[32]
TiO_2	298	[31]
ZnO	265	[31]
Co_3O_4	246	[31]
WO_3	157	[31]
g-C_3N_4	306	[33]
$Ti_3C_2T_x$	5.154	[34]
In_2S_3	110	[34]

1.3.3 BAND GAP TUNABILITY

Material thickness affects the band gap of the materials significantly. By creating defects or by irradiating electron beams on the surface, the thickness of 2D materials can be reduced, i.e., from multilayer to monolayer, which changes the band gap from indirect (present in bulk state) ~1.3 eV to direct (present in monolayer) ~1.8 eV; especially in the case of TMDs (MoS_2) – due to quantum confinement of electron resulting in the better photoluminescence efficiency by a factor more than 10^4 than bulk materials [35–37]. $MoSe_2$ shows changeset in band gap from indirect (~1.41 eV) to direct (~1.58 eV) when the thickness is reduced from multilayer to monolayer resulting in greater photoluminescence efficiency and providing a route to valleytronics [38].

1.3.4 HIGH MECHANICAL STRENGTH AND FLEXIBILITY

2D materials possess a high mechanical strength, which is related to stiffness, toughness, strength and stability of materials. Due to high strength, they can bear stress to greater extent. They possess high Young's modulus; for example, monolayer graphene shows extremely high Young's modulus of 1TPa, which can bear more than 25% strain without fracturing [21,39]; monolayer TMDs (MoS_2) shows Young's modulus as high as 270 GPa which is similar to steel; Young's modulus of high crystalline tungsten nitride (WN) is about 390 GPa. Also, 2D nanomaterials possess high flexibility (which makes them to hold strain greater than 10% prior to rupture) due to which they can be used as excellent materials in making flexible sensors and electronics in comparison to traditional semiconductors and metal-based sensors, which are fragile and rigid, limiting their applications as a fruitful material in designing wearable electronics [19,40–42].

1.3.5 DISTINCTIVE OPTICAL PROPERTIES

The remarkable optical properties of 2D materials include light sensitivity, adsorption, emission and plasmonic effects resulting from their intrinsic properties such as band structure, carrier mobility and density of states [43]. The optical transparency in the visible region requires uniform and nanometer-scale thickness, and due to these characteristics, the thin films of $Ti_3C_2T_z$ exhibit optical transparency of 97%, which is almost equal to graphene (having 97.7% optical transparency) [44]. The sensitivity toward external environment and high surface-to-volume ratio enables 2D materials in making optical sensors, and further X-ray attenuation and high optical properties make these materials a successful agent in phototherapy and radiotherapy [45]. Due to the ability of graphene and its similar 2D materials as fluorescent emitters and quenchers, they can be regarded as great platforms in developing optical biosensors for detecting various biological analytes like ions, proteins, nucleic acid, small molecules and cancer biomarker targets [46].

1.3.6 High Charge Carrier Mobility

The high charge carrier mobility is the property associated with high-speed transistors [7]. 2D materials are known for fast ion and electron transport [47] and hence they have high charge carrier mobility, making them highly useful in various photoconductive applications. Additionally, high electron transport along 2D layer decreases the corrosion rate and hence gives assurance of long-time durability in aqueous electrolyte [23,48]. It was found that graphene has highest charge carrier mobility of $2 \times 10^5 \, cm^2 V^{-1} s^{-1}$, while for the TMDs ($MoX_2$, where M = Mo, W; X= S, Se, and Te), the maximum mobility was found for WS_2 with values of 0.12×10^3 and $0.21 \times 10^3 \, cm^2 V^{-1} s^{-1}$ for electron and hole along the x-direction, and for all others, it was found to be $<100 \, cm^2 V^{-1} s^{-1}$; also, as the chalcogen size increases, the mobility decreases [7]; the α-P (black phosphorous 2D format) exhibits ambipolar charge transport and a high on/off current ratio of $\sim 1 \times 10^4$ due to which they are highly useful in field-effect transistors (FETs)-based devices.

1.3.7 Intercalation of Foreign Species

Intercalation is a phenomenon in which foreign species are reversibly intercalated at the crystal gap, and 2D materials are best known for intercalating the species ranging from atoms-to-ions-to-molecules. This phenomenon is important in redesigning novel 2D-layered materials to improve their physical properties. As in the case of 2D TMDs, intercalation helps in exfoliation and tuning of various physical properties like thermoelectricity, electricity, phase changing for catalysis as well as superconductivity [49]. As in the case of MoS_2, with the thickness reduced to atomic thickness (~2–50 nm) and by intercalation of Li-ion electrochemically, the MoS_2 crystals show a drastic decrease in electrical resistance of sheet and a substantial increase in light transmission (up to 90%, in 4 nm thick lithiated MoS_2) [50]. Besides being their amazing intrinsic properties, intercalation helps in tuning the properties so as to improve the device performance drastically because it increases the doping level to maximum extent possible and is capable of changing the phase of material (ir) reversibly. The intercalation helps in increasing the charge carrier density of 2D nanomaterials (but not all) by shifting the fermi level, which increases the density of states at Fermi level. Also, the intercalated compounds are generally chemically tough as chemically inert and impermeable atomically thick layer 2D materials protect and enclose the unstable intercalants than compounds that are physically or chemically adsorbed onto the surface [51]. Superconductivity is caused by metal intercalation in bulk graphite [52]. Recently, it was found that the Li-ion intercalation in few-layer graphene increases both transmittance and conductivity simultaneously (91.7% transmittance and 3-ohm sq^{-1} sheet resistance) [53].

1.4 SYNTHESIS STRATEGIES FOR 2D NANOMATERIALS

2D nanomaterials synthesis can be broadly classified into two approaches: top-down synthesis and bottom-up synthesis. In **top-down synthesis**, the 2D materials are synthesized via mechanical exfoliation, i.e., by exfoliating the bulk materials into single- or few-layered nanosheets by eliminating weak van der Waals forces between these sheets. The driving force behind these is strong intra-plane covalent bonds and removal of weak inter-plane van der Waals forces. Top-down synthesis involves Mechanical Cleavage [54], Mechanically force assisted liquid exfoliation [55–57], Selective-etching assisted method [58] and Ion-Intercalation assisted method [59].

In **bottom-up synthesis**, the material is synthesized by direct means, i.e., by using precursors through chemical reaction at certain chemical conditions. Chemical Vapor Deposition [60] and Wet-Chemical Methods [61,62] are two typical methods of bottom-up synthesis. In the subsections below, the brief overview of frequently used synthesis methods along with emphasis on their advantages and limitations is explored.

1.4.1 Top-down Synthesis Methods

1.4.1.1 Mechanical Exfoliation

In mechanical exfoliation method, the exfoliation is done with the help of scotch tape (Figure 1.2) in which the bulk crystal is first adhered to scotch tape, and then after peeling off with the help of another adhesive, a thin layer of 2D nanomaterial is attached to tape, which is then transmitted to the targeted substrate [63]. The layer thus obtained is high in quality with little defects, have large lateral dimensions, clean surface, less destructive in nature and remains stable in ambient conditions because the layer is directly exfoliated from bulk not via any chemical reaction. Large-scale production with high quality, hardly controlled size and shape of nanosheets, and constant need for a secondary substrate to support the exfoliated nanosheets are the major issues with this method [11,28,31,64,65]. This method was originally used to exfoliate graphene from graphite, but later on was extended to other materials such as h-BN and TMDs [66].

1.4.1.2 Liquid-Assisted Exfoliation

In liquid-assisted exfoliation technique, the exfoliation of bulk sheets into thin sheets is done in a liquid medium (e.g., dimethyl formamide, N-methyl-pyrrolidone, dimethyl formamide and N-methyl pyrrolidone). The liquid exfoliation has two main means – shear force-assisted liquid exfoliation and sonication-assisted liquid exfoliation. In these, the sonication-assisted exfoliation is more practical and simpler [67]. The solvent used helps in preventing the agglomeration and stacking of resulting nanosheets, and it was found that polymer and surfactant stabilize them during the sonication process. Also, it was found that the organic liquids are highly efficient in exfoliating the sheets. As an example, direct exfoliation of MoS_2 into colloidal nanosheets was carried out in an organic solvent, i.e., dimethyl sulfoxide, and pure water as shown in Figure 1.3. To improve the dispersing ability, a surfactant (sodium cholate) was added to the solution [68]. Moreover, the efficiency can be increased if the surface tension of solvent matches that of the bulk compounds. But compared with the above-mentioned techniques, this is more efficient in preparing ultrathin 2D nanomaterial due to production at large scale and high yield at low cost [56,69]. Along with advantages, there are limitations too – such as the yield obtained of a single-layered 2D material is comparatively low, and the lateral dimension obtained is also low due to strong sonication process [55,70]. In addition, the organic solvents, which are toxic in nature, harm the sheets, and the polymer and surfactants used are also undesirable for further applications. Hence, it is necessary to optimize further the experimental conditions to obtain ultrathin sheets with large lateral dimensions and high yield. Here, in this method, the solvent used acts as an intercalating species, which weakens the force between sheets [11].

1.4.2 Bottom-up Synthesis

The bottom-up synthesis techniques are famous for obtaining high-quality nanosheets. Co-precipitation, sol–gel, chemical vapor deposition, hydrothermal/solvothermal, template-assisted

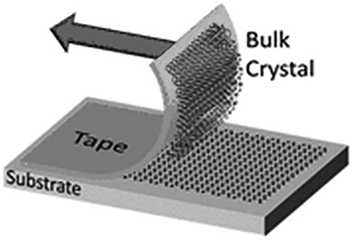

FIGURE 1.2 A representation of mechanical exfoliation via Scotch tape [19].

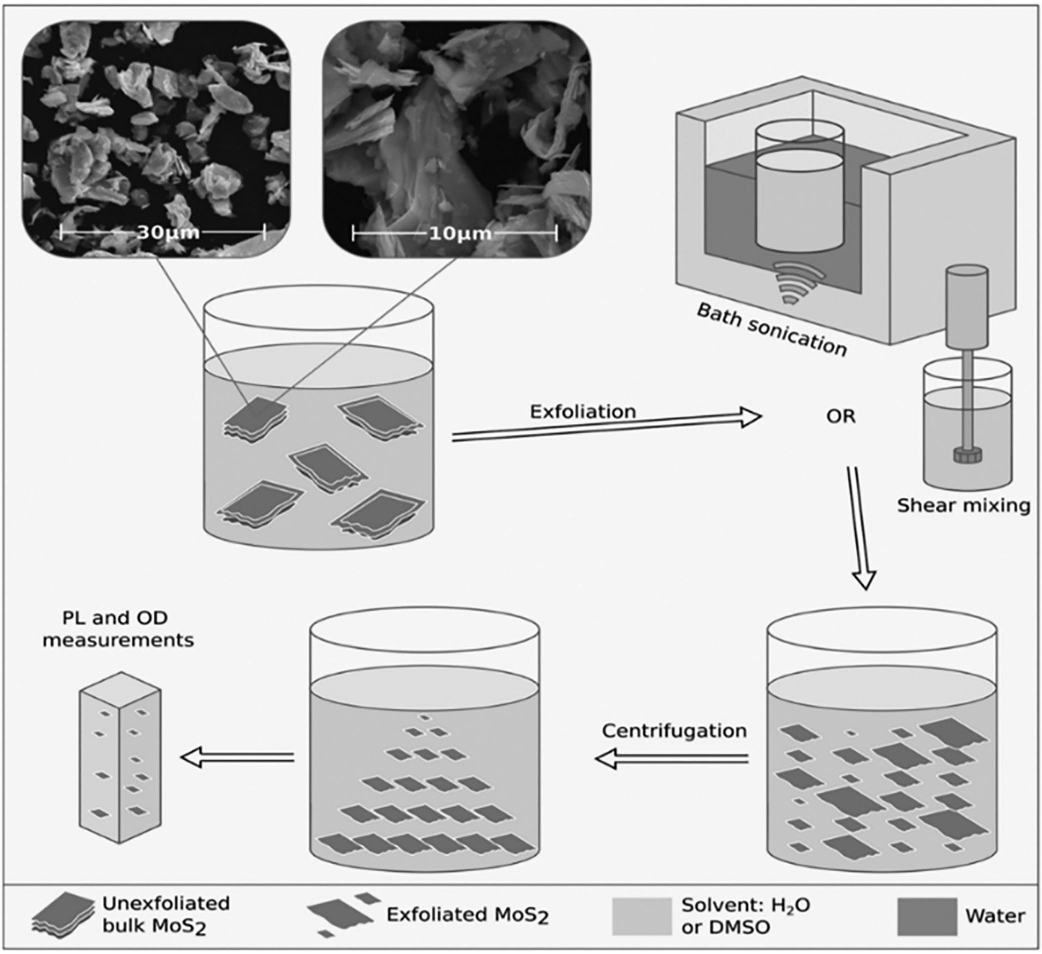

FIGURE 1.3 A representation of synthesis and characterization procedure for MoS_2 nanosheet dispersions. SEM images represent pristine nanomaterial before exfoliation procedure [68].

synthesis, polyol methods, laser ablation, plasma spraying, etc. are various bottom-up synthesis techniques [71]. But in this section, we discuss only few of them.

1.4.2.1 Chemical Vapor Deposition Method

This method is famous for synthesizing ultra-high quality with high purity, low porosity, high controllability and predictability, highly efficient with uniformity, highly stable as well 2D nanosheets onto substrate. Under high temperature and vacuum, the reactive precursors are exposed onto the substrate on which after reacting or decomposing they form a thin layer of 2D nanomaterial (Figure 1.4) [60,65,72,73]. This method is efficient in producing various 2D nanomaterials like TMDs, h-BN, metal oxides and graphene. The disadvantages of this method are high temperature requirement, poisonous gases emission as by-products and requirement of highly expensive instrumentation [65].

1.4.2.2 Wet Chemical Synthesis Technique

Wet chemical synthesis method is effective in synthesizing numerous 2D nanomaterials whether layered or non-layered such as TMDs, graphene, LDHs, MOF, COF, metal oxides, metals, polymers, metal chalcogenides, h-BN and g-C_3N_4 [75]. Co-precipitation [76], Hydrothermal [77], Solvothermal [78] and Sol–Gel are various synthesis strategies of this technique, which gain much

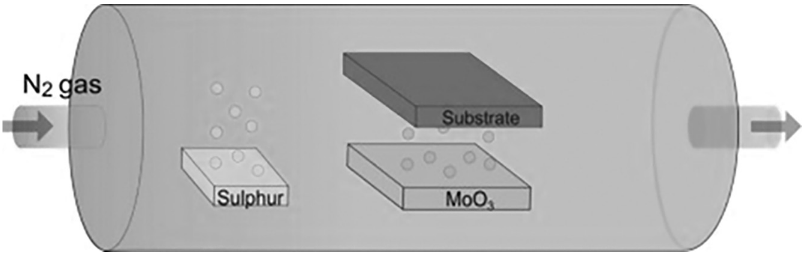

FIGURE 1.4 A typical representation of chemical vapor deposition setup for 2D transition metal dichalcogenides. (Reproduced with permission from Ref. [74], Copyright 2016, Progress in Crystal Growth and Characterization of Materials.)

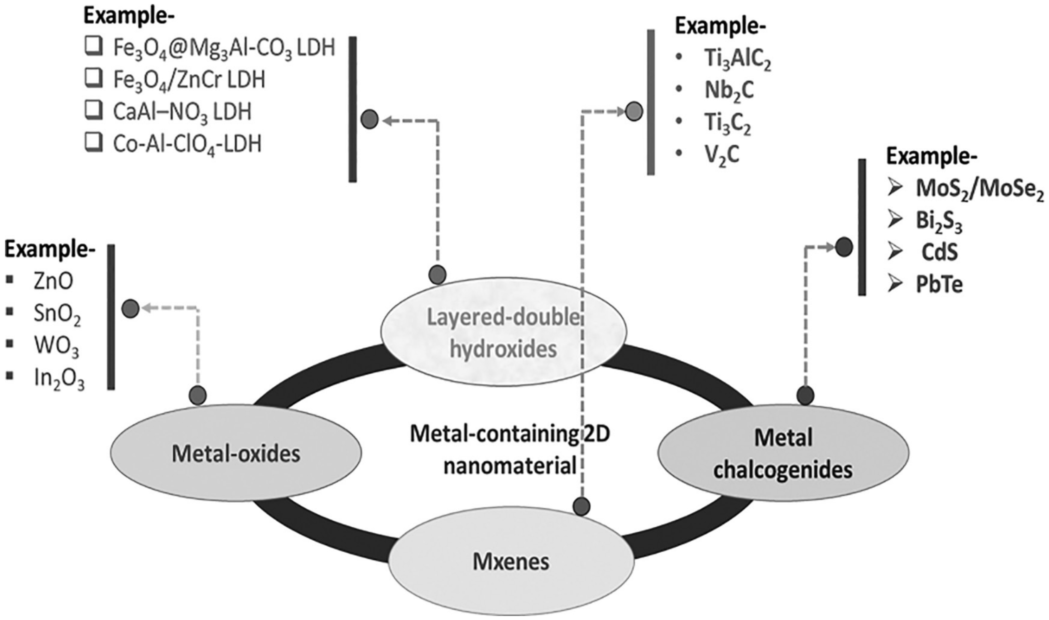

FIGURE 1.5 Various metal containing 2D-nanomaterials along with few examples.

attention due to their easy handling and operational simplicity. In this method, target material is synthesized by certain precursors through chemical reaction in solution assisted with polymers or surfactants. High yield, solution processibility and large-scale production are major advantages of this technique, while difficulty in obtaining single-layer nanosheets and the requirement of surfactants are disadvantages [75].

1.5 METAL CONTAINING 2D MATERIALS

Atomically thin 2D materials are promising materials in novel functional optoelectronic devices including modulators, photodetectors and lasers due to their novel optical and electronic properties. But, light–matter interactions in 2D materials are weak due to atomic-scale thickness, which limits the performances of these devices. Thus, to strengthen the light–matter interactions, metallic nanostructures are to be fabricated [79]. Various metal-containing 2D-nanomaterials as shown in Figure 1.5 are illustrated below.

1.5.1 Metal Oxides

Nowadays, quasi-2D metal oxides got tremendous applications in photonics, nano-sensors, etc., because of their enhanced charge carrier mobility. Also, for FETs, the 2D WO_{3-x} is gaining much importance as a semiconducting material [80] because sub-stoichiometry of this material reduces the band gap and increases the free charge carrier altogether, but after the intercalation of H^+ into this 2D WO_3 material, an increase in the carrier mobility is found by an amount exceeding 319 $cm^2 V^{-1} s^{-1}$ than 2D TMDs. So, the conclusion is that this material can be regarded as good material in making various functional FET devices [80]. The metal oxides can be regarded as ideal material in making new electronic devices because of the band gap, which allows them to be electrically conducting, insulating or semiconducting. The amorphous 2D metal oxides have many applications due to their superior performance in catalysis and energy storage [81]. Because of their disordered structure with dangling bonds, ion channels and activity sites, they have different physical and chemical properties than crystalline 2D materials; for example, amorphous 2D SnO_x and NiO have higher photocatalytic performance than their corresponding crystalline counterparts [82]. It was found that the 2D heterostructures that are formed either by van der Waals stacking or by edge covalent bonding generate many properties through synergistic effect of various 2D nanomaterials; for example, on illumination of light of 280 nm, large area heterostructure p-SnO/n-In_2O_3 shows both excellent photoresponsivity and photodetectivity due to narrow band gap at the p-n junction [83].

1.5.2 Metal Chalcogenides

TMDs are MX_2-type materials with M (representing transition metal such as Mo, W, Nb, Re, Ta, Zr, Ga and In) and X (representing chalcogens such as S, Se and Te) having three atomic-layered structure in which transition metal layer is sandwiched between two layers of chalcogens. Depending upon the metal, TMDs known to exist in many structural phases, but the two common structural phases are trigonal prismatic (2H) or octahedral (1T) [84]. The TMDs are semiconducting in nature; due to their nature and defect-free surface, thin exfoliated TMD layers can be regarded as ideal material for FET devices, and TMD-based FET devices possess remarkable electronic [85] and opto-valleytronic properties [86,87]. Recently, it was found that monolayer 2H-$NbSe_2$ has intrinsic superconductivity [88]. The superconductivity is also realized in thin films of 2H-WS_2 and 2H-$MoSe_2$, which are induced by gating [87]. The high strength makes them promising candidates for strain engineering [84].

1.5.3 MXenes

Metal carbides, nitrides and carbonitrides simply known by MXenes are the 2D nanomaterials having nanostructure composed of two or more layers of transition-metal atoms which are packed into honeycomb-like lattice in which carbon or nitrogen are intervened between these layers and occupied octahedral sites [89]. MXenes are generally synthesized by a selective etching technique from the MAX phases (having the formula $M_{n+1}AX_n$, where M represents transition metal, A represents atom from group 12 to 16, and X represents C or N) in which MX bond is stronger than MA bond; so, by the relative difference in their bond energies, the A-layer atoms are selectively etched with the help of strong acid or molten salts [90]. A large number of MAX phases, i.e., >60, are available, but from them, only few MXenes ($M_{n+1}X_nT_x$, where T represents the functional group; e.g., –OH, =O and –F) are found to have practical application [90]. Their unique mechanical, thermal and chemical stability properties make their utilization in various areas like sensors, electronics and catalysis, in electrochemical storage systems like batteries, supercapacitors and electromagnetic interference shielding and in fuel cells thereby creating an interest in researchers to develop more MXenes.

A 2D Ti_3C_2 monolayers were found to be better anode materials for Lithium-Ion Batteries than TiO_2 because of their small open circuit voltage, good electronic conductivity (metallic character) and improved Li storage capacity [91]. MXene-based nanocomposites are also utilized in photocatalytic decontamination of water; for example, $TiO_2/Ti_3C_2T_x$ shows greater adsorption and photocatalytic degradation under UV irradiation (~98% degradation of organic contaminant methyl orange within just 30 minutes) than conventional TiO_2 photocatalyst, which degrades ~77% methyl orange under same conditions [34,92].

1.5.4 Layered Double Hydroxides

LDHs have uniform interlayer galleries, and large number of hydroxyl groups are covalently bonded within the 2D host layers, making them excellent candidates for high-performance membranes [93]. These are also considered as anionic clays and have interesting properties like having intercalated ions with interlayer spacings, ability to intercalate different types of anions (organic, inorganic and biomolecules), swelling properties, high biocompatibility and delivering intercalated anions in a continuous manner [94]. Certain LDHs have more active sites for CO_2 adsorption due to high surface area [95], and the number of surface-active sites has effect on adsorption activity [96]. By increasing the interlayer distance, the more adsorption of CO_2 takes place because it helps in more CO_2 diffusion into the reaction space and thus the reaction with hydroxyl groups to create hydrogen carbonate intermediates [97,98]. This strategy is found to enhance the adsorption activity of LDH catalyst. It was found that Mg-Al LDH nanosheets with C_3N_4 photocatalyst produce more methane from photoreduction of CO_2 than with C_3N_4 alone in an aqueous solution with cocatalyst Pd [99].

1.6 METAL-FREE 2D MATERIALS

The majority of the metal-free 2D materials are composed of elements like hydrogen, nitrogen, carbon and phosphorus, which are the necessary elements in the functioning of human body. Thus, metal-free 2D nanomaterials possess higher biocompatibility and biosafety, which make them more suitable materials for biomedical application and further clinical translation [100]. Also, these materials have applications in electrocatalysis fields, which replace the employment of noble metals making the process cost-effective and favorable for large-scale production of electrocatalysts [101]. Some well-known metal-free 2D nanomaterials as shown in Figure 1.6 are illustrated in the following subsections as presented below.

1.6.1 Carbon Nitride

The graphitic carbon nitride ($g\text{-}C_3N_4$) is a unique polymeric layered 2D nanomaterial that can be considered as N-substituted graphite, but the difference is that the $g\text{-}C_3N_4$ sheets are comprised

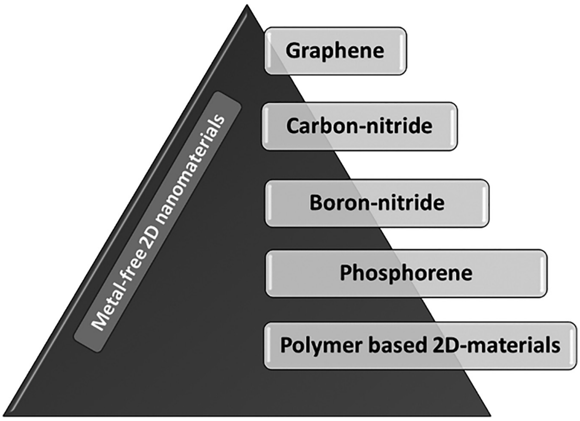

FIGURE 1.6 A graphical representation of metal-free 2D nanomaterials.

of tri-s-triazine units that are bridged by amino groups, with dangling H-atoms in the C-N layer and having periodic vacancies in lattices [33,102,103], and because of surface hydrogen atoms and surface imperfections, the g-C_3N_4 sheets have a wide range of photocatalytic applications [104]. Carbon nitride has five phases, among which g-C_3N_4 has the narrowest band and good light adsorption capability [105]. Recently, among all the known 2D materials, g-C_3N_4 is the carbon material having highest N-content and can exist as stable material in various acidic and alkaline conditions [106]. Despite this, the uniform distribution of triangular nanopores in the layers of tri-s-triazine causes strong in-plane piezoelectricity in g-C_3N_4 [107].

1.6.2 GRAPHENE

It is the single-atom thick layer 2D nanomaterial with a single layer of carbon atoms having sp^2 hybridization arranged in hexagonal pattern in which three valence electrons of carbon are involved in making strong in-plane covalent bonds, while the fourth electron remains in p-orbital for making π-bonds. Graphene shows a versatile range of chemical and physical properties such as large theoretical specific surface area ($2630\,m^2g^{-1}$) [16], high Young's modulus (~1 TPa) [39], low light absorption (~2.3%) [108] and a high carrier mobility of ~$10{,}000\,cm^2V^{-1}s^{-1}$ at room temperature [66]. It is a zero band-gap semimetal which shows exceptionally high conductivity (~5000 $Wm^{-1}\,K^{-1}$ [109]) due to the availability of highly mobile electrons, but due to zero-gap, it hinders various applications in bioimaging, optical imaging, logic circuits and FETs [17,110]. Despite the modification in the band gap, it results in degradation of its intrinsic electronic properties [111]. The graphene by itself is non-piezoelectric in nature, but it can be doped by chemical means on the basal planes, which then breaks the inversion symmetry and thus induces piezoelectricity in it [112].

The graphene oxide is an essential derivative of graphene obtained by strong oxidative agents. Various oxygen-containing functional agents like epoxy groups, hydroxy and carboxyl groups were added on the surface of graphene [16]. During the oxidation process, the hybridization changes from sp^2 to sp^3, thus making GO poorer in electrical conductivity. Despite the fact that both graphene and GO have similar structures, there is quite difference in their properties; for example, the graphene is insoluble in water, but GO is quite soluble in water because of the presence of hydrophilic oxygen-containing groups on the surface [113]. Also, graphene oxide is used in harvesting mechanical energy due to high dielectric constant and Young's modulus. The reduction of GO to reduced-GO changes the band gap from insulator to semiconductor, which depends upon the degree of reduction. Due to this, it helps in overcoming the problem of high leakage current, allowing these materials to be promising as interfacial material for triboelectric nanogenerator to increase the output voltage [114,115].

1.6.3 BORON NITRIDE

h-Boron nitride (h-BN) nanosheets, also called as "white graphene," have similar structure to graphene where it has equal number of boron and nitrogen atoms present in alternative positions in the honeycomb configuration [116] and properties as graphene, but the difference is that it has 1.8% longer lattice constant [117] and is an electric insulator due to its wide band gap than graphene [118]. Also, planar structure cleaves it into flat surface, and ionic bonding makes the surface free of dangling bonds and thus charge traps at the surface [118]. Additionally, h-BN nanosheets are stable at higher temperature than graphene. The thermal and chemical inert abilities enable this as an ideal material for corrosion protection [22]. It has also the ability to promote the photocatalytic activity of the supporting material, thus acting as a cocatalyst. In comparison to graphene on SiO_2 devices, graphene on h-BN devices showed the highest mobility, intrinsic doping, reduced roughness and chemical reactivity [119]. These sheets have wide applications in water treatment and purification because of super-high hydrophobicity power [120]. The band gap of h-BN is about 5.9 eV, and it is thermally stable up to 2000°C [121].

1.6.4 Polymer-Based 2D Materials

The combination of nanomaterials and polymers changes not only the structural and morphological features of the material but also the physiological properties in a significant manner. The addition of even a minute quantity of nanomaterials to polymers matrix enhanced the properties of polymer composites significantly; for example, it has been reported that the addition of graphene or layered silicates to polymer matrix enhances the mechanical properties up to ~200% of the polymer composites [113]. Thus, nanomaterials can be considered as "nanofillers" that bridge the gap between these two, i.e., polymer chemistry and nanotechnology. Thus, a wide variety of polymers–composites are available depending upon the 2D materials like inorganic nanomaterial and LDH, which shows insulating properties that boost the thermal and flame-retardant properties of polymers [94].

i. Graphene-based polymer composite: As graphene has highest surface area and good interaction with polymer matrix, the addition of small amount of this into the polymer matrix greatly influenced its properties like thermal conductivity, electrical conductivity, mechanical properties and dielectric properties; for example, for graphene-Poly(vinylidene fluoride) composite with 0.2 vol% of graphene, the dielectric constant reached 340 at 100 Hz, while with the 1.2 vol% of graphene, the highest dielectric constant was achieved up to 7940 at 100 Hz [122]. A small addition of graphene also increases the thermal stability (e.g., loading of 0.05 wt% of functionalized graphene sheets into polymethyl methacrylate shows an increase of glass transition temperature to 30°C [123].
ii. GO-based polymer composite: Due to rich oxidative functional groups on the surface of graphene oxide, they have good interactions with polymer matrices; thus, only a small loading greatly enhances the properties; for example, by solution mixing technique, the formed GO-Poly(vinyl alcohol) composite exhibits an increase in tensile strength by 76%, i.e., from 49.9 to 87.6 MPa, and high Young's modulus of 3.45 GPa with loading of only 0.7 wt% GO, which was 62% greater than the neat Poly(vinyl alcohol) polymer matrix [124].
iii. h-BN polymer composite: These nanocomposites are used in conditions where insulating and good thermal conducting properties are required, such as thermal interface management and electronic devices. As thermal interface management, in the h-BN-based composites, the increase of loading enhances the properties; for example, polyimide composite films achieved a thermal conductivity of 0.47 $Wm^{-1} K^{-1}$ with the loading of 30 wt% of h-BN [125]. By the loading of 30 and 60 vol% of h-BN, thermal conductivity of 3 and 7 $Wm^{-1} K^{-1}$ was shown by the same polymer composite when prepared by other methods [126].

1.6.5 Phosphorene

Also known as single- or few-layered black phosphorous, it has a puckered layer structure which makes it a promising material in biomedical applications like drug delivery, cell imaging, cancer therapy and biomedical detection. The biomedical applications are attributed to its negligible cytotoxicity and excellent biodegradability in the body. Phosphorenes possess exceptional capabilities like multiple drugs loading and maintaining the bioactivity of loading compounds. The availability of direct and tunable band gap (i.e., when the thickness is reduced from bulk to single layer, the band gap changes from 0.3 to 2 eV) makes it a promising bridging material with other 2D materials; for example, it covers the space in graphene (having zero band gap), TMDs (having large band gap), MXenes (having limited gap) and h-BN (having very large gap) [110].

1.7 CONCLUSIONS AND FUTURE OUTLOOK

The benchmarking of 2D nanomaterials makes them exceptionally different from other nanomaterials and from their bulk parts. These nanomaterials with atomic-level thickness possess distinctive optical properties, high strength, surface area and charge mobility. Along with these features, their physical properties can be enhanced with ease by modifying the band gap and including foreign species. In near future, these nanomaterials are believed to make great contribution toward practical applications in many fields. Currently, among the availability of many synthesis techniques, wet chemical synthesis technique is found to be more efficient due to solution controllability, compatibility and the synthesis of large number of 2D nanomaterials. But no synthesis technique is found to be ideal, which produces 2D nanomaterials with high yield, no defects and large dimensions, limiting their applications in industry. So, focus should be made to develop synthesis techniques which are cost-effective as well. In 2D nanomaterials, the extensive research has been conducted on graphene, TMDs (MoS_2, WS_2) and metal oxides, but similar studies are also possible for other 2D nanomaterials which may impart some better characteristics and applications. Thus, an extensive attention is needed toward 2D class of nanomaterials.

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2 Defects and Vacancies Effects on the Optoelectronic Properties of Two-Dimensional Nanomaterials

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2.1 INTRODUCTION

The sustainability and tenacity of various materials at the nanoscale are ongoing research topics. According to International Organization for Standardization (ISO), these materials typically have dimensions of 100 nm or smaller, where their distinctive characteristics allow for innovative applications. The size of a nanometer is one-billionth (10^{-9}) of a meter. The concept of nanoscience was foreseen by renowned physicist Richard Feynman in 1959 at the annual meeting of the American Physical Society (APS). In his talk titled, "There's plenty of room at the bottom – an invitation to start a new branch of physics" at the APS, he persuaded scientists that studying materials at the nanoscale would be more advantageous for various applications in the long run. Although he did not invent the word "nanotechnology," many of his projections in this field have turned out to be accurate because nanotechnology involves the use of materials and structures with dimensions between 1 and 100 nm. What is more intriguing is that it has been discovered that the chemical, physical, mechanical, clinical, and thermodynamical features of materials at the nanoscale are fundamentally and advantageously distinct from those of individual atoms and molecules or bulk matter [1,2]. These nanomaterials have been fabricated into a wide range of geometries, including wires, rods, tubes, thin films, and spheres, to obtain a high surface-to-volume ratio and mechanical strength.

Nanomaterials typically range in size approximately between 1 and 100 nm, as previously mentioned. However, these materials are categorized into different groups based on their dimensions (D), such as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) nanostructures. Materials with 0D nanostructures have dimensions no larger than 100 nm (e.g., nanospheres, nanoclusters, quantum dots, clusters, solids, and hollow nanoparticles), whereas 1D nanostructured materials are known to have two dimensions measured inside the nanoscale and one dimension outside it (e.g., carbon nanotubes, fibers, nanorods, and nanowires). Furthermore, 2D nanostructured materials are described as containing two dimensions that are not limited to the nanoscale and one dimension that is contained within the nanoscale (for example, nano-textured surfaces, nanofilms, nanolayers, and nanocoatings). Last but not least, 3D nanostructured materials—such as polycrystal nanostructures, nano/composites, pillars, and electromechanical—are thought of as compounds that have no boundaries for the nanoscale in any dimension [3,4], as shown in Figure 2.1.

Currently, 2D nanostructured materials have piqued the interest of researchers due to their degradability, biocompatibility, high specific surface area, rich structural characteristics, anisotropic chemical or physical properties, and versatile functionalities and diverse applications in drug

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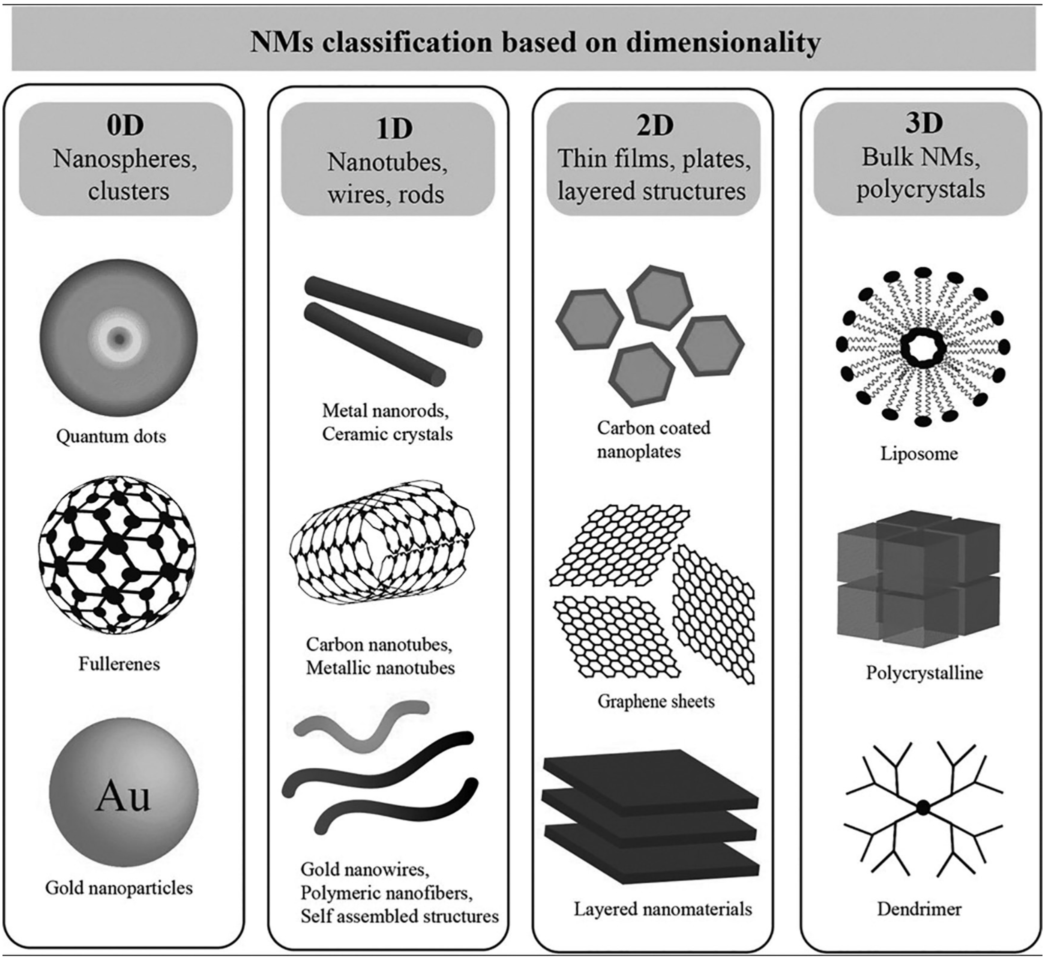

FIGURE 2.1 Classification of nanomaterial according to their dimensions. (Reprinted with permission from Ref. [5], Copyright © 2021 Elsevier.)

delivery, additive manufacturing, bio-engineering, regenerative medicine, bio-sensors, cancer therapeutics, bio-imaging, and others. Another intriguing aspect of 2D nanostructured materials is their ease of synthesis [6–9].

2D nanomaterials are layered materials composed of thin layers with a thickness of at least one atomic layer [11]. Graphene, MXenes, Monoelemental Xenes, Hexagonal boron nitride, Semiconducting transition metal dichalcogenides (STMDs), and 2D COF/MOFs are among the 2D nanomaterials families [9,11]. Figure 2.2 depicts the successful experimental fabrication of several 2D nanomaterials. Many scientists have used these 2D nanomaterials and their future markets in the above-mentioned applications. Remarkably, these 2D nanomaterials with novel physical properties represent a significant opportunity for technological innovation in the next-generation optoelectronic, electronic devices, renewable energy, storage systems, light sources, optical modulators, photodetectors, and processing modules with faster response, higher density, and smaller footprint [10,12,13]. In this context, scientists have recently expressed an interest in learning more about the optoelectronic properties of 2D nanomaterials due to their rich structures and optoelectronic properties. Arsenene, phosphorene, bismuthene, antimonene, and monoelemental materials from group-VA are classified as 2D nanomaterials with optical nonlinearity, incredible structures,

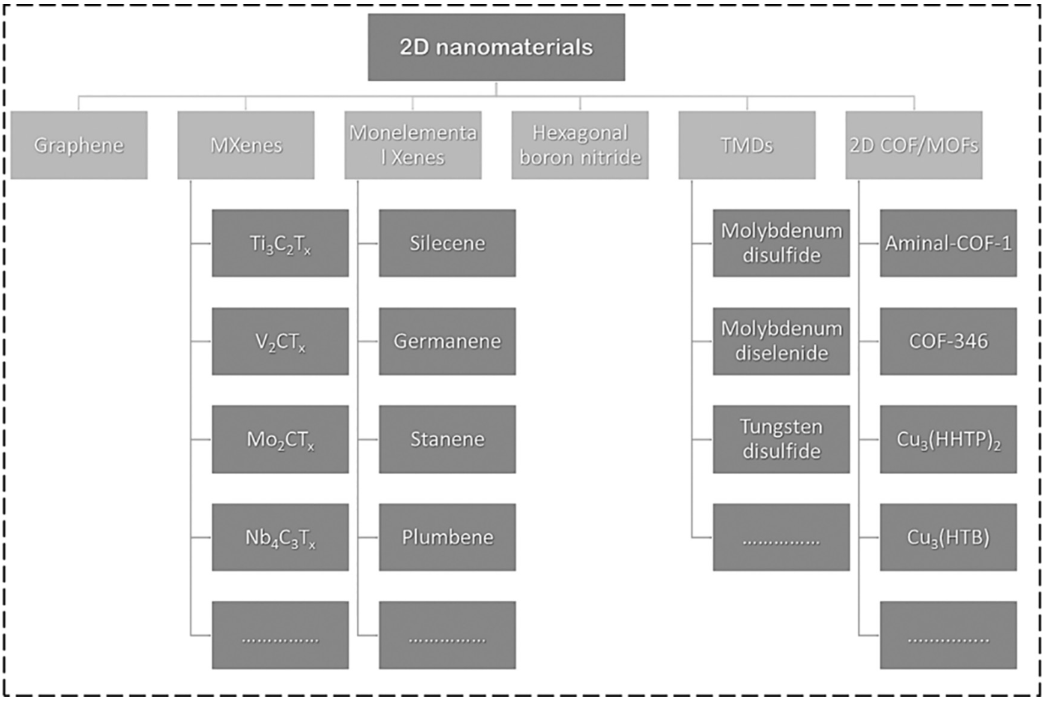

FIGURE 2.2 A diagram depicting the numerous 2D nanomaterial families. (Reprinted with permission from Ref. [10], Copyright © 2023 Elsevier.)

higher conductivity, large surface, tunable electronic structure, and anisotropic chemical/physical and optoelectronic properties [7–10,12,14]. Because of the aforementioned outstanding properties of these 2D nanomaterials, they are currently selected for a wide range of applications including hydrogen generation for energy storage, optoelectronic devices, cancer treatment, electromagnetic shielding, and water splitting. Extensive research on 2D nanomaterials revealed that some 2D nanomaterials are essential components of bulk layered van der Waals (vdW) heterostructures' crystals. However, because these 2D nanomaterials are naturally thin, they provide more chances for creating functional heterostructures, making them ideal for optoelectronic devices [7,15,16].

2D nanomaterials typically have certain lattice flaws, which vary depending on the synthesis processes used, such as the methods mentioned previously. Depending on the synthesis technique, numerous lattice defects, such as charged impurities, vacancies, grain boundaries, intrinsic defects, extrinsic defects [17], local atomic defects [15], self-interstitials, and vacancies [18], can be introduced into 2D nanomaterials either accidently or deliberately [19]. The benefits of these lattice flaws are that they are more effective in controlling the properties of 2D nanomaterials. Defect engineering is a method of modifying the properties of 2D nanomaterials by eliminating unfavorable defects and adding helpful imperfections in 2D nanomaterials for improved performance of electrical and optoelectronic devices [20]. As a result, we report on the recent effects of different flaws and vacancies on 2D nanomaterials for optoelectronics applications in this chapter.

2.2 SYNTHESIS METHODS FOR 2D NANOMATERIALS

The synthesis of nanomaterials continues to rise in prominence due to the unique optical, magnetic, electrical, mechanical, and chemical properties that nanoparticles have in contrast with bulk materials. Exploration of the distinctive characteristics and phenomena of nanoparticles in order to fully explore their potential applications in science and technology necessitates fabrication and process as main issues in the fields of nanoscience and nanotechnology. Several technical tactics and procedures have been researched to produce nanomaterials. A material's qualities determine how well it operates. The thermodynamics and kinetics of the synthesis influence the qualities in turn, which affect the atomic structure, composition, microstructure, defects, and interfaces [14]. However, the nanostructured material that was ideal for one application might be advantageous in another if it had been produced using entirely distinct processes and techniques than the one employed in the first. Similarly, how a nanomaterial is produced and created determines not just its structure but also its physical form. It is simple to produce and synthesize an amorphous nanostructured thin film using the plasma magnetron sputtering process, for example. However, due to the nature of the approach, it may be challenging to obtain a similar structure utilizing the thermal evaporation method [21]. In this context, it is necessary to address and overcome some of the barriers, such as shape control and particle size distribution (mono-dispersive: all particles of the same size), to build nanostructured materials utilizing any method for modern nanotechnology applications [14,21].

2.3 CLASSIFICATION OF SYNTHESIS METHODS OF 2D NANOMATERIALS

Top-down or bottom-up approaches are most commonly used in the synthesis of 2D nanomaterials. 2D nanostructured materials can be created by mechanically compressing bulk materials. The top-down method is extremely powerful since it is used for the manufacturing of nanomaterials, which involves the reduction of bulk material into the nano-regime and has the capacity to produce reproducible microscale products. However, when the dimensions of the structures to be targeted approach those of the nanoscale, implementation of the concept becomes increasingly problematic. Furthermore, the cost of synthesizing nanoparticles using this method is relatively high [22]. Although top-down approaches are simple to apply, they are ineffective for producing particles with irregular shapes or in extremely small sizes. As a result, the most major disadvantage of utilizing this method is how challenging it is to obtain the appropriate particle size and shape [21]. Researchers, on the other hand, are working diligently and putting out enormous effort to investigate the controlled synthesis of various types of 2D nanostructured materials and their intriguing features. To date, considerable strides have been made in the nano-scale synthesis of 2D materials with regulated compositions, shapes, and sizes with various exfoliation processes. Exfoliation methods for 2D nanomaterials include micromechanical exfoliation, liquid-phase exfoliation (LPE), and ball milling-aided exfoliation, which are all discussed extensively below [10,23,24].

2.3.1 MICROMECHANICAL EXFOLIATION

Micromechanical exfoliation is a popular approach for creating 2D nanomaterials. It is a well-known top-down technique for the simple and low-cost synthesis of 2D nanomaterials. Novoselov and Geim pioneered this strategy in 2004 with the goal of generating graphene. Because of its versatility and inexpensive cost, it has acquired broad application for the manufacturing of 2D materials since that time [25,26]. However, energy must be employed throughout the process to exfoliate the stacked material into nanosheets. Scotch tape is used in the exfoliation technique, which is presently the most common, to exfoliate stacked bulk crystals into nanosheets. The goal of applying mechanical stress/force with the use of Scotch tape is to lower the out-of-plane forces known as vdW without additionally breaking the in-plane rigid covalent bonds inside each layer, resulting in the removal of a just a single or a few layers of 2D nanomaterials. The bulk 2D substance, such as graphite, is first stuck to the adhesive area of the Scotch tape, and then the entire thing is pulled off and split into a single layer or a number of layers by sticking it onto a different sticky surface in the usual process. It is critical to repeat this process several times in order to produce the desired thickness of the 2D nanomaterials, specifically flakes. During the transfer operation, split nanoflakes over Scotch tape are stuck to the appropriate substrate and ripped off from the Scotch tape, dropping a single or several layer nanosheet on the surface of the substrate. However, the major critical challenge associated with micromechanical exfoliation is that production on a large scale is not feasible, the yield is low in comparison to other methods of synthesis that use solutions, there is no means to control the thickness, size, or shape of the nanosheets that are produced, and there is a lack of precision and reproducibility throughout the entire process because it is carried out manually. Furthermore, the purity of the material generated frequently contains remnants of the exfoliating agent. This indicates that micromechanical exfoliation may generate strain on the layer of 2D nanomaterials being formed on a substrate throughout the process. This strain may result in a variety of defects, including atomic flaws, wrinkles or ripples, and tiny corrugation. The electrical performance of optoelectronic devices may be compromised as a result of these flaws [27–31].

2.3.2 LIQUID-PHASE EXFOLIATION

The liquid-phase exfoliation (LPE) approach involves the breakdown of large layered 2D structures in liquid media into single- and/or few-layer 2D nanostructures by a range of processes such as ultrasonic treatment, electrochemical, and shear exfoliation. The aforementioned methods have demonstrated significant advancements in the production of nearly any 2D nanomaterial in enormous quantities at a reasonable cost and in a manner that is environmentally conscious. The LPE procedures are extremely promising and highly scalable technologies that are currently easily accessible and can be carried out in mild conditions to manufacture massive quantities of exfoliated 2D materials of exceptional quality in a commercially feasible manner. Direct exfoliation treatments have an added benefit of preserving the 2D materials' inherent physical and electrical properties. This may frequently result in greater quality for the exfoliated nanomaterials, with a relatively small number of flaws and functionalization by chemicals during exfoliation. Direct exfoliation procedures have additionally been shown to be more efficient than indirect exfoliation methods [32].

Figure 2.3 depicts a schematic diagram of the LPE method with (i) bulk layered material as the starting material, (ii) dispersion of layered material in a liquid medium, (iii) ultrasonication, and (iv) final dispersion after the ultracentrifugation process. The LPE process typically consists of two critical steps: dispersion of layered material in a liquid medium and purification. In such a situation, the dispersion of layered material in a liquid medium shows individual particles suspended in a liquid dispersant (Figure 2.3b). Ultracentrifugation is commonly used to separate exfoliated from unexfoliated materials (Figure 2.3c). Submerging in a liquid is one of the most efficient ways to reduce the attraction forces. As a result, the appropriate solvent balances the attractive forces exerted between the sheets of 2D nanomaterials and prevents the 2D nanomaterials from aggregating. However, the most effective solvents for dispersing 2D nanomaterials were those that minimized the amount of interfacial tension between the liquid and the 2D nanomaterials [32–35].

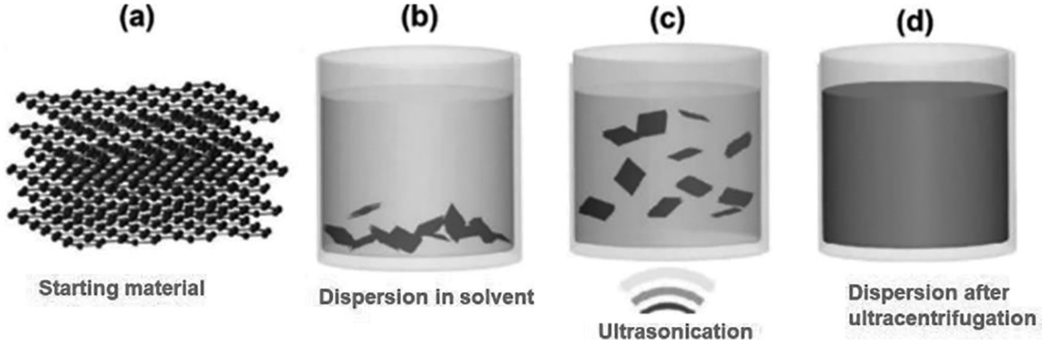

FIGURE 2.3 Schematic representation of LPE process of 2D materials. (Reprinted with permission from Ref. [35], Copyright © 2017 Royal Society of Chemistry.)

Some liquid-based exfoliation methods involve executing chemical reactions on the bulky 2D-powder that make it easier to dissolve in the fluid that is being employed. This is especially important for the processes of generating graphene oxide (GO) from bulk crushed graphite via the process of chemical oxidation, exfoliating transition metal dichalcogenides (TMD)-layered substances/materials through lithium-ion intercalation, resulting in a phase transition from semiconducting 2H to metal-based 1T phase, and preferential etching of an A-group element in layers of $M_{N+1}AX_n$ (MAX) phases to produce just one-layer MXene nanomaterials. In contrast, bulk 2D materials are exfoliated in aqueous solutions through direct liquid exfoliation, which eliminates the need for chemical interactions. If no chemical interactions occur between the 2D materials and the solvent during the exfoliation process, these methods frequently provide high-quality, faultless 2D nanomaterials with a low number of defects. The produced exfoliated 2D nanomaterials will exhibit appealing material characteristics and will substantially diffuse in the solvent present. Because of this, they can be easily dissolved with other nanomaterial solutions to generate composites and hybrid materials, and they can be cast as a thin film onto any substrate for device and coating applications [32,34,36].

2.3.3 BALL MILLING-ASSISTED EXFOLIATION

Ball milling is a type of grinding that uses lateral force to grind nanomaterials into extremely fine particles [37–39], in contrast to the sonication or Scotch tape methods of grinding, which predominantly use normal force [40]. The collision between the relatively tiny, hard balls held in a closed container generates a localized high pressure throughout the ball milling process. In many instances, porcelain, flint stones, and stainless steel are used in milling. Certain chemicals can be added to the container during the process to improve the quality of the dispersion and insert functional groups into the surface of the nanomaterial [40,41]. There are some of the elements that can influence the quality of the dispersion such as milling time frame, rotational speed, ball size, and the ratio of 2D nanomaterial to balls [38]. When utilized in the thinning process, low-energy ball milling does not cause substantial damage to the in-plane structure of 2D nanomaterials, and it also produces fewer defects and impurities. Milling at a slow speed for a lengthy period of time guarantees that shear forces dominate, which is appropriate for producing large-scale 2D nanomaterials.

Figure 2.4 depicts the basic mechanism involved in the ball milling-assisted exfoliation process. As shown in Figure 2.4, there are two possible methods for milling-assisted exfoliation: primary and secondary ways. The principal method is known as shear force, which is associated with a good mechanical process for the exfoliation process. The primary method is greatly sought for producing large-sized 2D nanomaterials, such as graphene flakes, whereas the secondary method is related with milling ball vertical impacts or collisions during rolling movements. However, in this secondary approach, huge 2D material flakes can be fractured into small flakes and occasionally even break the crystalline characteristics of structures to generate non-equilibrium or amorphous phases [39]. According to the literature, ball milling at a slow speed for a lengthy period of time reduces the amount of collision or compressive impacts, which limits the fragmentation of large flakes into smaller ones and improves the overall quality of the goods produced by ball milling [33,39]. This process has been used to generate highly curved or closed-shell carbon nanostructures from graphite, to increase the saturation of lithium composition in single-walled carbon nanotubes (SWCNTs), to modify the morphologies of cup-stacked carbon nanotubes, and to generate various carbon nanoparticles from graphitic carbon for use in hydrogen storage applications. Despite the fact that ball milling is simple to use and can be used for powder polymers or monomers, there is a risk of process-induced nanotube damage [42]. These big flakes are prone to being broken by heavy collisions, which may also alter the crystal structure, resulting in a more amorphous bulk. As a result, the number of collisions that occur during the manufacturing of high-quality nanomaterials should be reduced to a minimum [40].

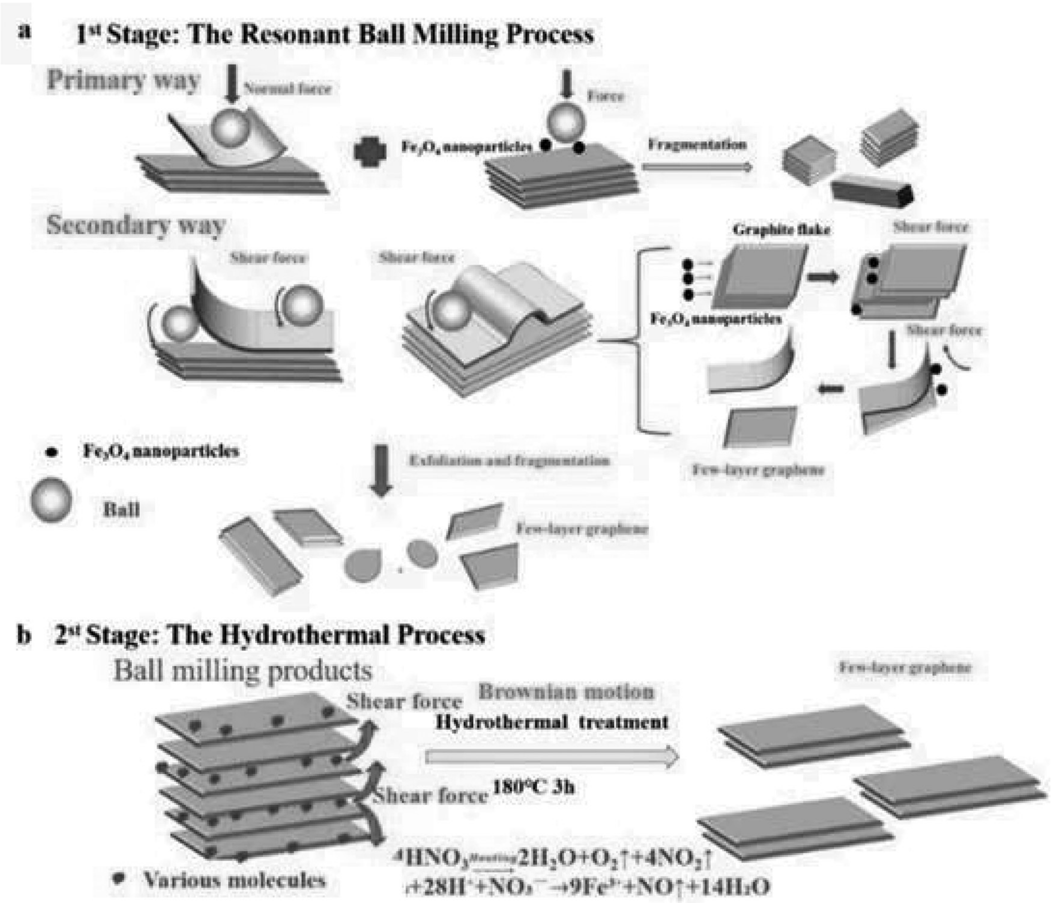

FIGURE 2.4 Schematic illustration of the preparation of 2D nanomaterials via ball milling-assisted exfoliation process. (Reprinted with permission from Ref. [39], Copyright © 2015 Royal Society of Chemistry.)

2.4 BOTTOM-UP TECHNIQUES

Bottom-up manufacturing is an efficient way for creating nanomaterials that are exceedingly thin, of high quality, and have massive lateral dimensions. It is a top-down technique option that has the ability to generate less waste and, as a result, is more cost-effective. The bottom-up technique is the process of developing a nanomaterial from individual components to the larger nanomaterial, either atom-by-atom, molecule-by-molecule, or cluster-by-cluster. Numerous well-known bottom-up methods for producing luminescent nanomaterials have been identified, including the organometallic chemical route, the revere-micelle route, the sol–gel synthesis, colloidal precipitation, hydrothermal synthesis, template-assisted sol–gel, and electrodeposition [21,43,44].

2.4.1 HYDRO/SOLVOTHERMAL PROCESS

The bottom-up methods include hydrothermal and solvothermal methods. Thus, both techniques are considered similar syntheses since they use various solvents such as water (distilled and deionized), ethylene glycol, and polyethylene glycol (PEG). In this instance, solvents are used as the reaction medium to dissolve and recrystallize typically insoluble chemical substances in a high-temperature (~100–1000°C) and high-pressure environment (~1 MPa–1 GPa) [45–48]. Figure 2.5

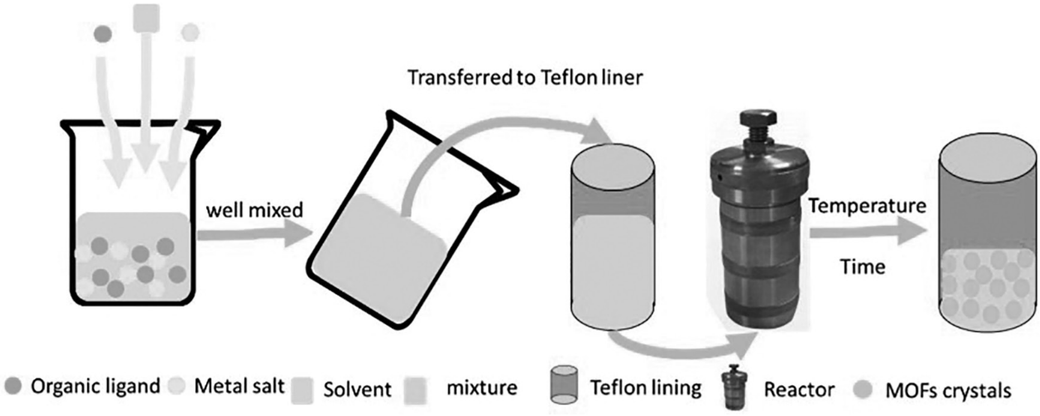

FIGURE 2.5 Schematic diagram of the hydro/solvothermal process. (Reprinted with permission from Ref. [51], Copyright © 2018 MDPI.)

depicts the fundamental mechanism of the hydro/solvothermal synthesis technique. The procedure is often carried out inside an autoclave, which is a form of steel pressure vessel in which temperatures and/or pressures are controlled to obtain the required results. The temperature is raised above the boiling point of the solvent, accomplishing vapor saturation. The hydro/solvothermal method has made a significant contribution to current science and nanotechnology due to its homogeneous precipitation, low cost, easier to synthesize materials in nanoscale, ecologically friendly nature, user-friendliness in terms of scalability, and pure small and uniform end product [21,45]. However, this method can be separated into areas such as hydrothermal synthesis, treatment, and crystal development; the treatment of organic wastes; and the manufacture of functional ceramics powders [21]. Furthermore, the hydrothermal process is separated into categories such as hydrothermal synthesis, treatment, and crystal development; organic waste treatment; and the creation of useful ceramic powder [49]. Hydrothermal methods were widely employed to manufacture several types of MXene-based nanomaterials for the removal of radioactive hazardous contaminants at high temperatures and vapor pressures. This is due to the fact that MXene-based nanomaterials are emerging as viable adsorbents for removing contaminants from the environment [50].

Precursors that match the stoichiometry of the end product are mixed in an organic solvent with reduction and template reagents during the synthesis technique depicted in Figure 2.5. After fully mixing, the ingredients are placed into an airtight autoclave and heated for a lengthy period of time at temperatures ranging from 100 °C to 250 °C. After allowing the products to cool to normal temperature, they are dried, washed, and centrifuged. One of the most prominent benefits of this technology is its capacity to manage the dimensions and form of the goods produced [52]. The hydro/solvothermal technique can also be utilized to create highly crystalline nanomaterials. On the other hand, crystal development information cannot be directly observed, and autoclaves are expensive. One of the method's major limitations is its difficulty to create a big quantity of phosphors in a single process. The comparatively small size of the autoclaves impedes industrial production of phosphors [21,53].

2.4.2 CHEMICAL VAPOR DEPOSITION PROCESS

Chemical vapor deposition (CVD) is a versatile and efficient method for creating nanomaterials. This method was an important technique in the field of microelectronics for many decades and remains one of the most appealing approaches utilized today that is capable of overcoming shortcomings provided by advancements in technology. When compared to other methods of synthesis,

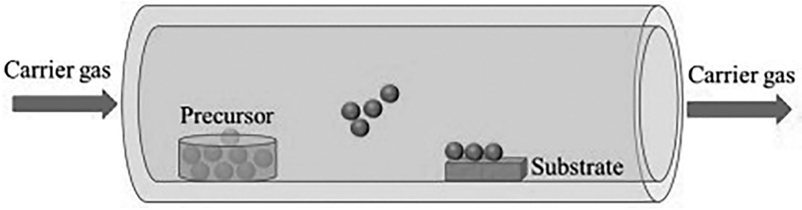

FIGURE 2.6 Schematic diagram of a CVD process setup. (Reprinted with permission from Ref. [57], Copyright © 2021 Elsevier.)

CVD provides the most control in the fabrication of 2D nanomaterials. The CVD process allows for the mass manufacturing of 2D nanomaterials with high crystal clarity, purity, and few imperfections on the substrates. However, in order to conduct additional investigation, this method always necessitates the transfer of nanomaterials from the substrates on which they were deposited. In addition, higher production costs are a disadvantage. Few precursors are hazardous in the sense that they are toxic, combustible, or explosive, and even fewer are inexpensive. The creation of highly poisonous gaseous by-products, as well as the high temperatures at which various CVD techniques deposit their ingredients, limits the substrates that can be used [21,54,55]. However, in order to perform additional examination, the nanomaterials must always be transferred from the substrates on which they were deposited. Furthermore, increasing production costs are a detriment. Few precursors are dangerous in the sense that they are toxic, combustible, or explosive, and even fewer are reasonably priced. Because of the formation of very poisonous gaseous by-products and the high temperatures at which the various CVD procedures deposit their ingredients, the substrates that can be used are limited [55,56].

In this process, the precursors, which can be gases or vapors, can react or decompose on a predetermined substrate, while the chamber is subjected to high temperatures and vacuum, as shown in Figure 2.6. The growth of 2D nanomaterials on the substrate can occur with or without the assistance of catalysts [57]. The controlled delivery of gas-phase reactants, the availability of an enclosed reaction chamber, the discharge of gases, the regulation of reaction pressure, the delivery of an energy source for chemical reactions, the cleaning of exhaust gases to safe and nontoxic levels, and automation process control to increase deposition process stability are all operational requirements for the CVD process. The 2D nanomaterial produced through the CVD method is used in a wide range of practical applications, including electronic, optoelectronic, and solar cell device applications [21].

2.4.3 PHYSICAL VAPOR DEPOSITION

Physical vapor deposition (PVD) is a vaporization coating technique that involves the transfer of material at the atomic level. This synthesis method typically requires ultra-high vacuum (UHV) settings and all-around regulated, high-purity atomic sources for the development of elemental engineering 2D materials [2]. The process is similar to CVD in several ways, except that in PVD, the precursors, i.e., the material to be deposited, begin in solid form, whereas in CVD, the precursors enter the reaction chamber in gaseous form [58]. The PVC method can be described as follows: (i) the material to be deposited is converted into a vapor by physical means (high-temperature vacuum or gaseous plasma), (ii) the vapor is transported to a low-pressure region from its source to the substrate, and (iii) the vapor condenses on the substrate to form a thin film. As a result, PVD methods are utilized to deposit films ranging in thickness from a few nanometers to thousands of nanometers. They can, however, be utilized to create multilayer coatings, graded composition deposits, extremely thick deposits, and freestanding structures [59]. Sputtering, as opposed to evaporation, is better suited for target materials that are difficult to deposit by evaporation, such as ceramics