Chapter

The Role of Novel Composite of 2D Materials and Their Characterization, Properties, and Potential Applications in Different Fields

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Abstract

Thin layers or coating of transition metal dichalcogenides (TMDs) is a new class of two-dimensional (2D) inorganic materials with unique physical and chemical properties. This book chapter covers the recent research of thin film of 2D materials using various novel technologies to synthesize and grow monolayer 2D materials on different substrates in different fields based on the knowledge available in the literature. Thin film on substrate can be enhanced with the favorable properties. Therefore, selection of methods can play a key role in characterizing the coating. The novel coating processes on composite materials and their characterization, properties, and process and potential applications also have been discussed. The 2D materials that have been investigated created a thin film through different methods and were used to serve different biomedical purposes such as modifying drug release, improving energy efficiency and storing energy, catalysts, and so an.

Keywords: 2D materials, thin film, application, synthesize

1. Introduction

Nowadays, the potential of nanotechnology confirms us to use nanomaterials in all fields such as biotechnology, engineering, and medical; therefore, nanotechnology opens up new frontiers for innovation in these fields [1, 2]. There are diverse classes of nanomaterials in nanoscience, for example, the zero-dimensional (0D) class of quantum dots; one-dimensional (1D) class of nanoribbons, nanotubes, and nanowires; two-dimensional (2D) class of single-atom thick materials; and three-dimensional (3D) class of nanoballs and nanocones [1, 3]. Their dimensionality is important properties to distinguish these categories of nanostructure. If the same chemical elements or compounds have different dimensions, they will exhibit different properties.

Two-dimensional (2D) layered materials have attracted attention of researchers because of their unique electrical, mechanical, thermal, and optical properties [4, 5]. These types of materials include a few atoms or monomer units: thin sheets exhibiting covalent in-plane bonding and weak interlayer along with layer-substrate bonding resulting in unique chemical reactivity and several physical properties.

Graphene, hexagonal boron nitride (h-BN), and transition metal dichalcogenides (TMDs, e.g., MoS_2, $MoSe_2$, WS_2, and WSe_2) are kinds of these materials that they can exhibit high charge carrier mobilities, chemical inertness, and high mechanical strength [3, 5, 6]. In addition, 2D materials have the large specific surface area to use them in surface-active applications, for example, catalysis, sensing, separation, energy storage and conversion, and other related fields. There are various nanostructures such as metals, metal oxides, and metal chalcogenides that have established effective in reaching developed properties and creation of different purposes. Additionally, properties like atomic thickness and high anisotropy could be used to produce wearable electronic devices based on 2D materials due to their admirable mechanical flexibility and optical transparency, which these properties cause to develop 2D material-based electronic devices and wearable devices [7, 8].

In this chapter, we will mention the process of the synthesis and chemistry of synthetic elemental 2D materials and their application in different fields. Finally, we will offer perspectives and challenges for the future of this emerging field.

2. Methods of synthesis and chemistry of 2D thin film

Coating is the most widely used technology to enhance surface properties of substrates, and nanotechnology has played an important role in improving the coating action [9]. In the case of 2D materials, the monolayers can be arranged on top of one another in a selected arrangement to produce unique, heterogeneous multilayers, leading to van der Waals heterostructures [10]. Moreover, homogeneous multilayer materials, inorganic 2D materials, organic, and organometallic have also increased interest of researchers, which include 2D covalent organic frameworks and metal-organic frameworks. The structural varieties of organic ligands and the numerous linkage chemistries cause the best properties as desired composition, size, thickness, crystal phase, and surface property [7].

There are different synthetic methods based on "top-down" and "bottom-up" approaches for the synthesis of 2D materials. The "top-down" approaches contain the physical mechanical technique such as mechanical sonication, shear force, ion intercalation, and exchange. Despite a potential tool to produce large-scale single-layer or few-layer 2D materials at the ambient condition, this method has various disadvantages such as the broad distribution of sheet thickness and lateral size as well as low yield, low structure integrity, and high tendency of restacking. But, the "bottom-up" approaches, including chemical vapor deposition (CVD), physical vapor deposition (PVD), solid state reaction synthesis, and wet-chemistry synthesis, can overcome these disadvantages, and it can control the morphology and the structure of inorganic 2D materials. It also has numerous advantages such as up-scalability, solution processability, and eco-friendliness [6, 11–13].

2.1 Developed techniques of material production

Over the last decade, thin film of 2D materials such as grapheme has attracted worldwide research interest. However, there are many other materials in layered form with interlayer interactions, which made by van der Waals forces. Nowadays, these materials can be thinned with proper techniques to a few layers and even monolayers. Different methods can be used to create these layers, which are the following:

One of the main methods used to obtain monolayers is mechanical exfoliation. The process depends on the probability of cleaving the crystal of bulk materials and the bonding of metal. Therefore, only a monolayer is moved onto the desired substrate [14].

Method	Advantage	Disadvantage	Ref.
Sol-gel	Suitable to obtain high quality films up to micron thickness	To limit the use of metallic as subtracts for coating. To exhibit several drawbacks involving crack ability and thickness limits	[17]
Thermal spray (gas-flame, plasma)	To make nanocomposite coatings with a matrix of metal or alloy	High temperature	[18]
Cold spray	To allow fabrication of coatings at the lower temperatures with low porosity	High pressure	[19]
Spin coating	Preparation of polymer nanocomposite coatings. To create uniform thin films on substrates.	High speed	[20]
Electrodeposition	For the fabrication of nanocomposite coatings, which contain organic nanofillers	Formation of microcrack	[21]

Table 1.
Advantages and disadvantages of some methods.

There is a simple method for synthesizing 2D materials such as chemical vapor deposition (CVD). This method does not control the grown materials exactly and creates inhomogeneous films. Park group has recently established homogeneous, wafer-scale films like MoS_2 and WS_2 using metalorganic chemical vapor deposition (MOCVD). Therefore, they synthesized high-quality and large-area materials. Temperature, pressure, chemical reagents, and concentrations as experimental parameters can effect on the shape, size, morphology, and uniformity of the solution-grown nanostructures. Moreover, this method can control shape, size, uniformity, and layer thickness. Inappropriate conditions to produce colloidal solutions can cause agglomeration [15, 16]. Other technologies of the coating on composite materials recently concentrate great attention on researchers compared to **Table 1** with their distinct applications.

3. Characterization of 2D material coating

Coating texture, morphology, and appearance, particularly for viscosity and color, are important to characterize coating film. There are several nondestructive techniques to analyze and characterize these coatings in use, according to their film surface functionality. Extreme sensitivity and high magnification are involved due to the thin nature of films developed. In this section, to investigate morphology and texture of coating, some of the techniques are investigated. Electron microscopy techniques, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and the sensitive atomic force microscopy (AFM) can be used to evaluate morphology and texture of coating. AFM is a high-resolution imaging tool, which measures and manipulates matter at a nanoscale. It shows significant changes on the metal and coating surfaces. It offers 3D visualization, qualitative, and quantitative information on size, morphology, surface texture and roughness, statistical distribution, surface area, and volume distributions. TEM determines particle size and shape. Also, histograms of TEM images can be employed to count individual particles formed. Furthermore, TEM imaging has been employed to observe certain fabrication features between smart nanocontainers and inhibitors. SEM shows particle size and shape. Side view of the SEM images also provided dimensions of coating thickness on the brass substrate studied. UV-visible spectrophotometry is required for determining the reduction of metal ions to nanoparticles via surface plasmon resonance, which is also responsible for their unique colors upon reduction. Optical properties of the metallic nanoparticles are permissible. Fourier-transform infrared spectroscopy (FTIR) identifies possible molecules responsible for the reduction, stabilization, and capping of micro and nanoparticles coupled with coatings formed via IR absorption spectra. X-ray diffraction (XRD) determines particle crystallinity and nature of metallic particles in the coating types. Also, phase structure of metal nanoparticles was identified for some nanoparticles. Estimation of coating performance is usually employed in terms of coating degradation, corrosion kinetics, and electrochemical techniques. Scanning vibrating electrode technique (SVET) provides information on corrosion reactions initiating in small areas and also examines the inhibitor action in the coatings by monitoring both the cathodic and anodic corrosion activities through measuring current density maps over the selected surface of the sample. While GC-MS had been employed to determine the contents of encapsulated amines, micro-Raman spectroscopy determined the chemical composition and displayed the bands. Mechanical characterization is an essential aspect when characterizing a smart coat. It also determines functional recovery in self-healing coatings. Static fracture testing, fatigue testing, tear testing, microcapsule-induced toughening, microhardness test, scratch hardness test, pencil hardness test, and cross hatch adhesion test are among the relevant tests in use [17, 18, 22, 23].

4. Doping and heterostructures of 2D materials

There are different parameters that impact on properties of 2D materials. Substrate is one of them that is a new modification parameter in the synthesis of 2D materials. To produce any thin film, at any of its dimensions, typically needs a substrate. Combining novel substrates with 2D materials can make unusual properties.

Another effective way to modify properties is doping and functionalization with other atoms or molecules. If an even number of atoms is omitted, the structure will be more unstable and more chemically active due to hanging bonds. Therefore, reactive sites could subsequently be doped with foreign atoms to improve the specificity of the hanging bonds for binding other molecules.

It is important to be reminded that the "doping" here is different from the one generally being used in semiconductor physics. Replacement of heteroatom atoms in materials lattice can sometimes reach relatively high doping levels [24].

Magnetism properties of materials can be improved by using both electric field and electrostatic doping. Some researchers demonstrate that doping can control magnetism in both monolayer and bilayer [25].

Overall, the doping of materials like graphene could be roughly classified into two groups: electrical doping and chemical doping. Electrical doping is done by varying the gate voltages, and chemical doping is prepared using chemical methods that can be considered as an efficient method [25, 26].

Yang et al. demonstrated that a chloride molecular doping method decreases the contact resistance (R_c) in the few-layer WS_2 and MoS_2. This result makes high electron doping density; therefore, Schottky barrier width declines significantly. This doping method offers a highly practical technique to reduce the R_c in 2D materials and improve the performance in 2D nanoelectronic devices [27].

5. Coating of 2D materials using metal organic frameworks

Metal organic frameworks (MOFs) or porous coordination polymers (PCPs) as distinctive porous solids have attracted great attention. MOFs have a number of advantages rather than the other customary porous materials (e.g., porous carbon, mesoporous silica, and zeolite) such as high surface chemistry, structural flexibility, and variable pore size in the nanometer range. Therefore, inserting 2D nanomaterials and their hybrids in MOF materials can develop their potential applications [28, 29].

The encapsulation of other types of 2D nanomaterials and their related composites in MOF matrices to form 2D core-shell structures has been demonstrated by other researchers. For example, Huang et al. displayed the coating of numerous 2D materials counting MoS_2, graphene oxide (GO), and reduced graphene oxide (rGO) nanosheets as well as their hybrids with metal nanoparticles (i.e., Pt-MoS_2, Pt-GO, and Pt-rGO) with MOFs (i.e., ZIF-8). They have demonstrated the coating of various 2D nanomaterials such as MoS_2, GO, and rGO nanosheets and their hybrids with metal nanoparticles (i.e., Pt-GO, Pt-rGO, and Pt-MoS_2) with ZIF-8 that 2D materials as core and MOFs as shell are in these 2D core-shell structures. The TEM image of the Pt-rGO@ZIF-8 and Pt-rGO@ZIF-8 hybrid material are shown in **Figure 1a** and **b**, respectively [30].

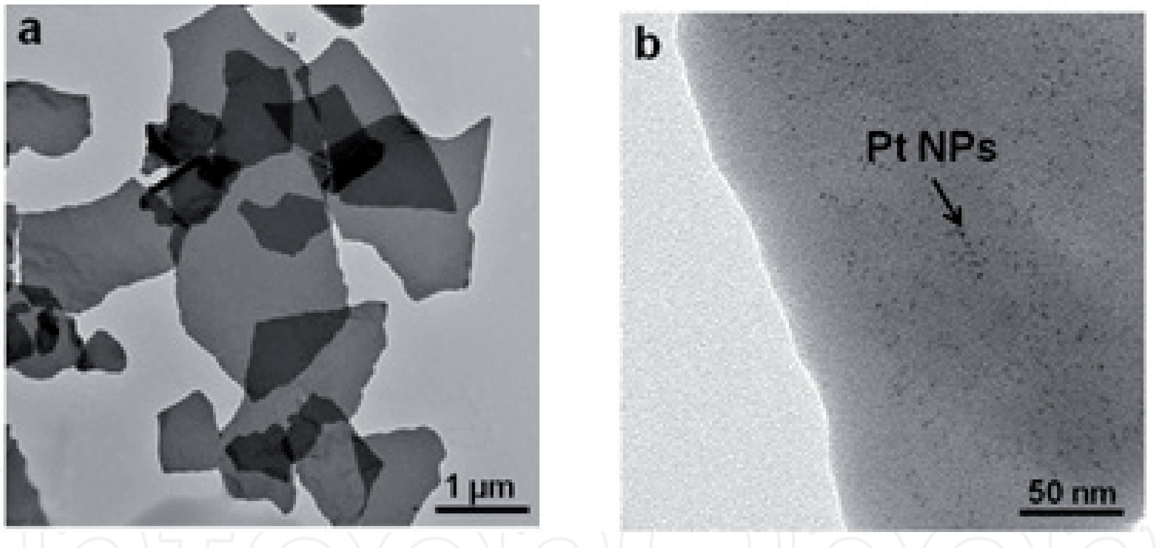

Figure 1.
(a) TEM image of Pt-rGO@ZIF-8 hybrid nanostructures. (b) Magnified TEM image of a Pt-rGO@ZIF-8 hybrid nanostructure [30].

6. Application of some thin film of 2D material

In recent years, layered transition metal dichalcogenides (TMDs) have been studied in the applications of photodetectors, photocatalysis, solar cells, optical modulators, and so on that some examples of their application will discuss in the following sections. For example, a great number of active sites could be created by the 2D-layered materials with high-specific surface areas for numerous reactions. Furthermore, nanosized 2D-layered materials could use as a support to produce different composites with a large interfacial contact. Various 2D-layered materials such as MoS_2 composed of Mo and few-layer MoS_2 nanosheet coated TiO_2 nanobelts exhibit photocatalysis activity [31].

6.1 Strong saturable absorption of 2D SnS_2 nanosheet film

SnS_2 thin film is a kind of transition metal dichalcogenide monolayers with a structure of an atomic layer of Sn between two atomic layers of S (S-Sn-S layers) as shown in **Figure 2**. The range of bandgap is from 2.1 to 2.81 eV. It has many applications such as field-effect transistors, photodetectors, and photocatalysts. The range bandgap of SnS_2 is close to the MoS_2 and WS_2. Therefore, SnS_2 thin film can have high saturable absorption property like these materials. SnS_2 can be also considered as a proper saturable absorption material with low cost. He et al. deposited SnS_2 film on transparent quartz using magnetron sputtering method by sulfuration of Sn film. The thickness of a SnS_2 thin film is measured to be 18.4 nm. The saturable absorption intensity of SnS_2 thin film was higher than other thin films that the SnS_2 thin film displayed strong saturable absorption behavior to use potential applications in mode-locked lasers for femtosecond pulse generation [32].

6.2 Water purification using 2D nanostructures

One of the global concerns is issue of the insufficient availability of drinkable water. Nowadays, pollution of water has increased. Nanoporous graphene membranes could be considered an ideal separation membrane because of its 2D nanostructures, large surface area, and transporting selected molecule properties (**Figure 3**) [33].

However, graphene is impermeable against all gases and liquids. Moreover, graphene pores were engraved with ion etching and modified with negatively charged nitrogen and fluorine and also positively charged hydrogen atoms. Therefore, pore selectivity will be improved using coupling between ions and functional groups positioned at the edge of the nanopore [34].

The passage of Li^+, Na^+, and K^+ ions is permitted by F-N-pore, and H-pore permits penetration of Cl^- and Br^- ions. Moreover, ion size has impact on the flow rate. Finally, the pore size, shape, and number of functional ligands attached can be effective on ion selectivity to enhance performance of the graphene membrane.

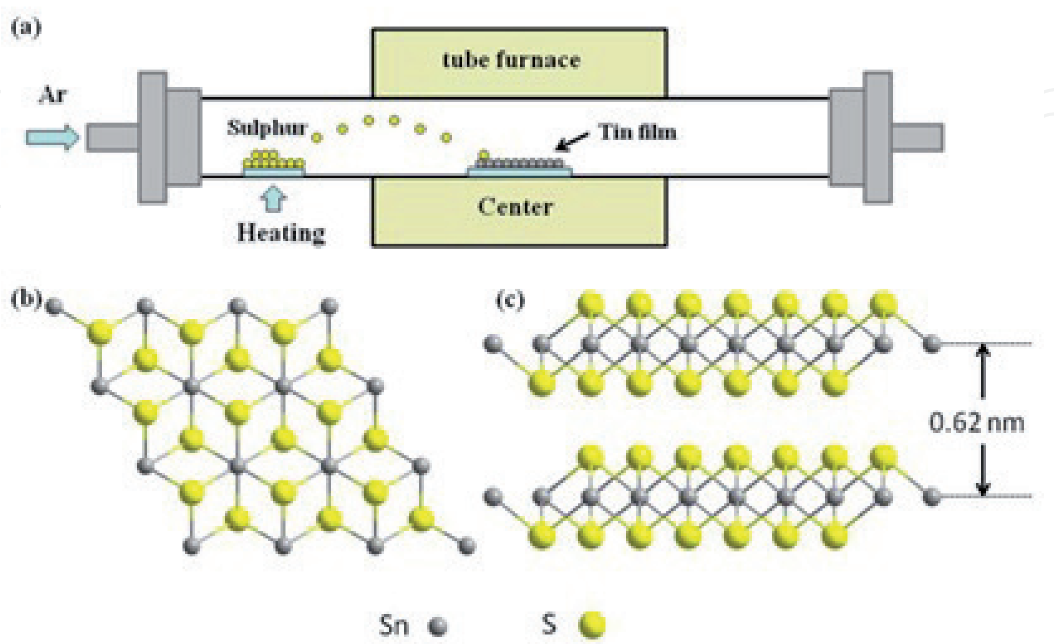

Figure 2.
(a) Schematic diagram of preparation of SnS_2 film. (b) Top view and (c) side view of the atomic structures of SnS_2 [32].

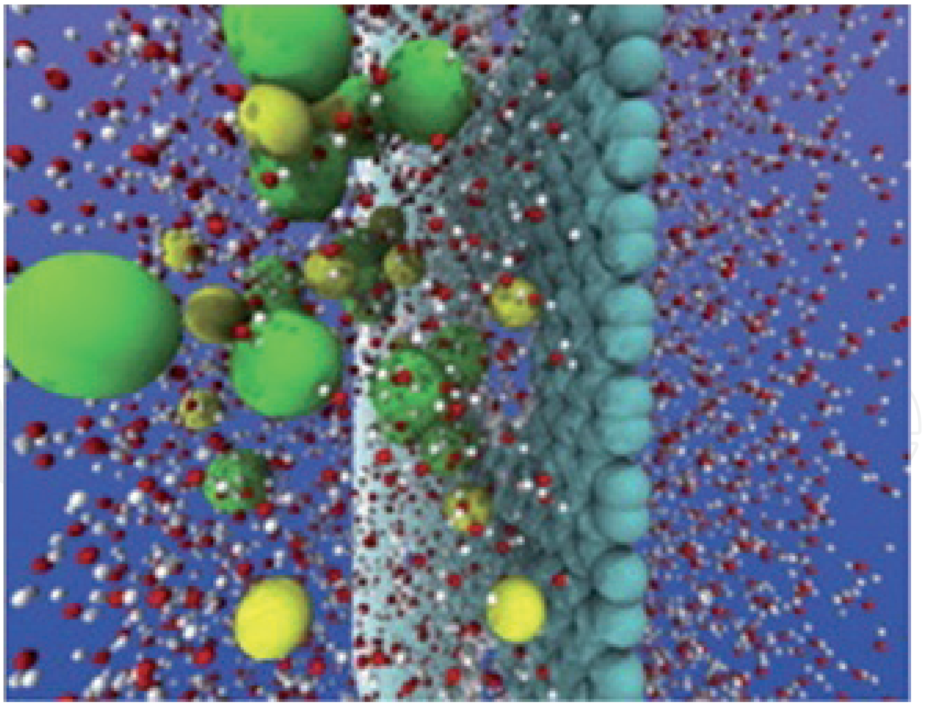

Figure 3.
Nanoporous graphene membrane for desalination [35].

Recently, use of 2D thin film materials for water treatment has attracted attention of researchers from the industry. A multilayered graphene thin film can be prepared on a support using shear force alignment to spread the viscous, uniformly arranged fluid. Multilayered graphene thin film for selective sieving can be used to charge and uncharge organic probe molecules and monovalent and divalent salts with rejection efficiency over 90%. Currently, Arvia Technology based on water and wastewater treatment uses a graphene-based thin film membrane for the treatment of toxic wastewater [35, 36].

6.3 2D materials for energy storage applications

Energy crisis is one of the critical issues in our modern society. Currently, demand for efficient, low cost, lightweight, flexible, and environmentally has increased. Therefore, use of any scale energy storage devices has raised. There are high performance energy storage devices with a high energy density at high power such as 2D materials' graphene thin film or other layered systems. Graphene has exposed excessive potential in energy storage applications as active components because of their remarkable electrochemical properties, elemental compositions, and different crystallographic structures, which can act as electrode materials for high-performance electrochemical energy storage device. Other 2D materials as layered materials of graphene analogues (GAs) refer to layered materials with a structure similar to graphene, with planar topology. This thin film can be used in energy storage. There are numerous attempts using a single-layer sheet and size to preserve their morphology to synthesize a wide range of GAs homogeneously and to control their thicknesses.

A fundamental understanding on the structures of electrodes, the electrode/electrolyte interfaces, and charge storage mechanisms plays a key role in layered material application in energy storage. Additionally, the effect of defects on the electrochemical properties of layered materials needs to be studied. The overall electrochemical performance (e.g., gravimetric energy density and power density) will improve by increasing the operating voltage and choosing an appropriate electrolyte with a high operating voltage window (organic electrolytes or ionic liquids) [37].

The lithium ion intercalation mechanisms play a key role in Li-ion batteries. **Figure 4a** shows the main power sources working for movable electronics and electric vehicles. However, lithium-ion batteries based on graphite anodes and customary cathode materials (with stable layered structures such as layered lithium metal phosphates and lithium transition metal oxides) are useful for energy storage devices with high energy density and efficiency and low cost. To develop energy storage devices with a larger capacity, higher rate ability and longer cycle life are necessary. Li-alloy-based anode materials such as silicon, tin, and tin oxide can exhibit high capacity. In recent years, extraordinary capacities in Li-ion batteries to store energy can be seen in batteries based on pure lithium metal anodes, such as nonaqueous lithium-oxygen (Li-O_2) batteries (**Figure 4b**) and lithium-sulfur (Li-S) batteries (**Figure 4c**). Li-O_2 batteries produce an insulated solid state discharge product of Li_2O_2 with high potentials. Furthermore, intermediate discharge products of lithium polysulfides were produced in Li-S batteries that are soluble and can dissolve into the electrolyte, thereby migrating to the anode side [38].

6.4 Application of 2D materials in biomedical

Recently, application of TMDCs has increased in different biomedical fields, such as drug delivery agents, therapeutics, bioimaging elements, and biosensors because of its layered structure and weak interplanar Van der Waals forces between these layers [39].

6.4.1 Photothermal therapy

Currently, there are a lot of treatments of tumors through the production of highly efficient and multifunctional nanomaterials. Photothermal therapy (PTT) has a lot of advantages such as a noninvasive, controllable, and targeted strategy to remove tumor cells. The photothermal performances can be improved using functional biomedical and bioactive nanomaterials [40]. Light is an external stimulus for cancer phototherapeutic modality. Typically, photothermal agents accumulated within tumors as internal energy absorbers can be hired by PTT to convert near-infrared (NIR) light energy into heat, producing necrosis and/or apoptosis of cancer cells. Two fundamental parameters of extinction coefficient (ε) and photothermal conversion efficiency (η) are used to determine photothermal

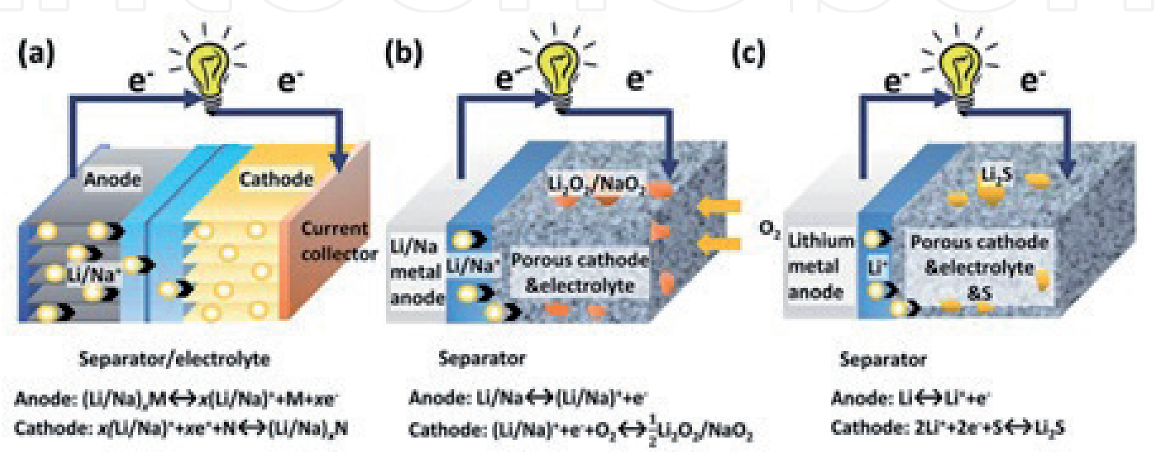

Figure 4.
Design of (a) Li/Na-ion batteries (M represents the anode material, and N represents the cathode material), (b) nonaqueous Li/Na-O_2 batteries and (c) Li-S batteries [38].

performance of a phototherapeutic agent used for photothermal conversion. 2D inorganic photothermal agents are able to increase photothermal conversion efficiency in converting the light into heat [49]. Recently, scientists have done a series of breakthroughs on exploiting ultrathin 2D transition metal carbides nanosheets (MXenes) for PTT, including effective photothermal ablation of tumors in both in vivo and in vitro as mouse model (e.g., Ti_3C_2 MXene) [41].

6.4.2 Biosensing

2D materials' thin film could also be hired as novel biosensing device for the detection of biomacromolecules and bioeffects. Recently, 2D layered molybdenum sulfide (2D MoS_2) nanosheets have displayed high potential for the development of next-generation platforms for efficient signal transduction. Opportunities to design and create highly sensitive, specific, and commercially viable sensing devices have increased through combination with DNA as a biorecognition medium and MoS_2 nanostructures. Monolayer MoS_2 nanosheets have been used as a biosensor for DNA detection, which has been confirmed to bind well with the unique transduction properties of 2D MoS_2 nanosheets. Sensors can be acted based on the principles of fluorescence, electro-chemiluminescence, and electrochemistry with many beneficial features (e.g., strong biointerfacing through various conjugation chemistries, facile sensor assembly, high stability with regard to temperature/pH, and high affinity to target) [42]. In another example, a DNA biosensor was designed based on a 2D-g-C_3N_4 nanosheet utilizing affinity changes of g-C_3N_4 to DNA probes upon their targeting of analyte and the related positron emission tomography (PET) and the fluorescence-based quenching effect. In comparison with traditional nanoparticle-based biosensors, 2D layered nanostructures have the high surface-to-volume ratio with large-area immobilization of sensing targets and the fascinating performances such as light-absorption capability and fast electron transfer fluorescence-quenching effect based on the unique physicochemical property of 2D nanosheets. Indeed, there is a continuous demand for the development of highly sensitive, selective, efficient, and cost-effective biosensing platforms [40, 42, 43].

6.4.3 Antimicrobial activity

There are different 2D layer nanostructures with potential antibacterial activities. For instance, when the Zn-Ti layered double hydroxides (LDHs) were added to bacteria suspension under visible light, the growth of microbial species such as *S. cerevisiae, S. aureus*, or *Escherichia coli* was strongly inhibited due to the effect of LDH unique properties and generation of ROS by Ti^{3+} under visible light. The antimicrobial behaviors of chemically exfoliated MoS_2 (ce-MoS_2) were investigated against *E. coli* and *Bacillus subtilis* bacterial culture and compared with other carbon-based nanostructures. In detail, the antibacterial activities of Ti_3C_2 MXenes were evaluated against *E. coli* and *B. subtilis* using bacterial growth curves and colony growth assays. Ti_3C_2 displays a higher antimicrobial activity toward both *E. coli* and *B. subtilis* in comparison with GO, a well-studied antimicrobial agent. The cytotoxicity of Ti_3C_2 MXenes can be measured by LDH release from the bacterial cells exposed. It can damage bacteria, and such significant change in the cell morphology/structure could be contributed by detachment of the cytoplasmic membrane from the bacterial cell wall [41].

6.4.4 Advances in biomedical applications

Graphene (G) is highly hydrophobic material when it is decorated using oxygen containing hydrophilic groups, and graphene oxide (GO) will be prepared. Due to unique surface chemistry, π-π stacking interactions and electrostatic interaction happen with other molecules in its area. Both physical and chemical bindings of drugs occur with the surface of G/GO for drug delivery applications [44]. In this section, we display these delivery mechanisms using G and GO in anticancer therapies among other fields. GO was chemically functionalized with amino groups and mixed with carboxymethyl cellulose as drug carriers, biomolecule sensors, and cellular imaging agents in anticancer therapies with a controlled and targeted release of the drug. Anticancer drugs can be released more slowly from G/GO composite supramolecular hydrogels than other hydrogel because of the higher binding attachment of hydrophobic drugs with G/GO in the gels, which is important to control release of drugs [45, 46].

6.5 Photocatalytic activity of self-assembly of layered double 2D nanoplates

Among many inorganic solids, high photocatalytic activity for visible light-induced generation of O_2 is exhibited by a few semiconducting layered double hydroxide (LDH) such as Zn-Cr-LDH. In addition, to enhance the photocatalytic efficiency of semiconducting materials, the control of band structure such as an increase in the lifetime of photogenerated holes and electrons is necessary.

The chemical exfoliation process of the host material can be used to synthesize the 2D nanoplates of the LDH material. Meanwhile, the exfoliated LDH 2D nanoplate owns positive surface charge; therefore, these can be easily assembled with negatively charged graphene nanosheets in terms of electrostatic attraction.

Strong electronic coupling between LDH and graphene species depends on the thickness of these 2D nanostructured components. Moreover, the formation of a mesoporous structure with an expanded surface area is extremely useful for the enhancement of the photocatalytic activity of component semiconductors. Gunjakar et al. synthesized the layer-by layer-ordered hybrid photocatalysts using the self-assembly of the 2D nanostructured photocatalyst with graphene nanosheets. For the first time, they studied mesoporous Zn-Cr-LDH-graphene nanohybrids with high photocatalytic activity for visible light-induced O_2 generation via the electrostatically derived self-assembly of positively charged Zn-Cr-LDH nanoplates with negatively charged graphene nanosheets [10, 47].

7. Conclusions

The thin films of 2D materials can be prepared using different methods that a single monolayer or multilayer as thin film can be fabricated by mechanical exfoliation or chemical techniques. In this chapter, we investigated the application of 2D thin films in different fields such as biomedical, energy storage, and water purification. Processing and applications of 2D layered nanostructures have developed, while there are several challenges in this field. The properties of 2D nanomaterials are highly sensitive to surface chemistry, underlying substrate, neighboring materials, and interfaces. Moreover, methods have major influence on the performance, reproducibility, and reliability of 2D nanomaterial heterostructure applications. Synthesis of 2D nanomaterials is important; therefore, careful consideration will be needed. There are also numerous important challenges to develop for commercialization.

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