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Two-Dimensional Nanomaterials

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Abstract

Two-dimensional (2D) nanomaterials are composed of thin layers that may have a thickness of at least one atomic layer. Contrary to bulk materials, these nanomaterials have a high aspect ratio (surface-area-to-volume ratio) and therefore have many atoms on their surface. These atoms have a different function than internal atoms, and so the increase in the number of surface atoms leads to a change in the behavior of 2D nanomaterials. Graphene, as one of the most widely used and most important 2D materials, has unique properties that result in its widespread use in various industries. After successful performance of graphene in many applications and industry, it is expected that other two-dimensional materials will also have this capability. However, the use of other two-dimensional materials requires more time and effort.

Keywords: two-dimensional, nanomaterial, graphene, hexagonal boron nitride, chalcogenide

1. Introduction

Dimensional classification is one of the methods for classifying nanomaterials: the same chemical compounds can exhibit extraordinary different properties when they are configured in a zero (0D)-, one (1D)-, two (2D)-, and three (3D)-dimensional crystal structure [1]. In spite of the fact that there have been plenty of scientific reports on 0D [2], 1D [3–5] and, of course, 3D [6, 7], however, a limited number of researches on 2D nanomaterials are published.

2D nanomaterials are considered to be the thinnest nanomaterials due to their thickness and dimensions on macroscale/nanoscale. These nanomaterials have a layered structure with strong in-plane bonds and weak van der Waals (vdW) between layers. These ultrathin nanomaterials can be produced from laminated precursors described in the following sections. Although the ideal state is a single layer, but often these nanosheets are composed of few layers (less than ten layers). In recent years, 2D nanomaterials such as graphene, hexagonal boron nitride (hBN), and metal dichalcogenides (MX_2) have attracted a lot of attention due to their satisfactory properties and widespread uses in the electronics, optoelectronics, catalysts, energy storage facilities, sensors, solar cells, lithium batteries, composites, etc.

The schematic structure of graphene, boron nitride nanosheets, and tungsten diselenide (WSe_2) as a dichalcogenide has been illustrated in **Figure 1**. As shown, these compounds are configured in honeycomb structure, but the arrangement of the neighboring atoms in the upper and lower layers of 2D nanomaterials is

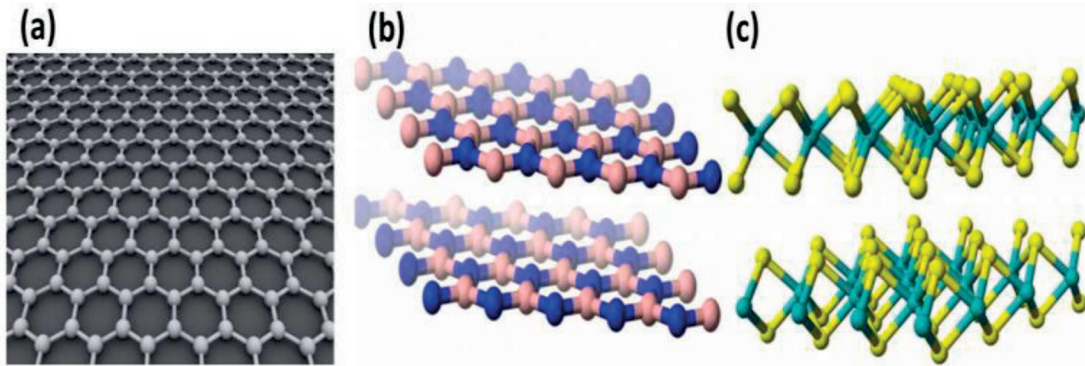


Figure 1.

The structure of (a) single layer of graphene with a lattice of carbon atoms, (b) boron nitride nanosheets with B in blue and N in pink, and (c) tungsten diselenide (WSe_2) with W in blue and Se in yellow [8].

different. In graphene, each carbon atom is next to another carbon atom in its upper and lower layers, while in the structure of BNNSs, each atom is located in the center of the benzene ring on the upper and lower layers. In the structure of dichalcogenides, each atomic layer of metal is sandwiched between two atomic layers of X.

In this chapter, the recent developments in the synthesis, properties of 2D nanomaterials especially graphene, and boron nitride nanosheets (BNNSs) are discussed. A comprehensive understanding of the properties and physics of these materials can be very effective in finding their application in the industry that is discussed in this chapter. The reported virtues and novelties of these nanomaterials are highlighted, and the current problems in their developing process are clarified.

2. Introduction of graphene

There are some well-known nanosheet materials with strong bonding on surface and poor bonding between layers such as graphene, BNNSs, and MX_2 . Due to their specific structures, researchers have made great efforts to produce 2D nanosheets by exfoliating these layered compounds into distinct layers. A transmission electron microscopy image of crumpled monolayer of graphene is shown in **Figure 2**.

Graphene is the most famous of 2D nanosheets that is composed of carbon atoms in a hexagonal (honeycomb) configuration with sp^2 -hybridized atoms

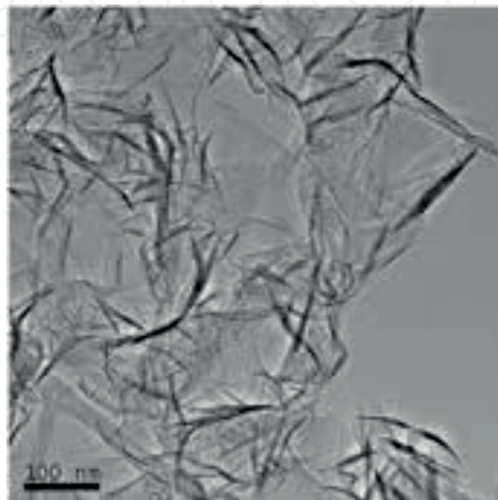


Figure 2.

The transmission electron microscope image of a crumpled graphene [9].

[10, 11]. Graphene is also the most important member of the multidimensional carbon material family that is formed by putting together carbon atoms and which included fullerene as the zero-dimensional nanomaterial (0D), carbon nanotubes as a one-dimensional nanomaterial (1D), and graphite as a three-dimensional nanomaterial (3D) (**Figure 3**) [12].

Graphene has a very weak absorption coefficient of 2.3% of white light, and so it's seen as a white powder. The surface area of graphene is $2630 \text{ m}^2/\text{gr}$, which is twice as much as carbon nanotubes with a surface area of $1315 \text{ m}^2/\text{gr}$. The legendary discovery of this compound in 2004 attracted a lot of attention and led to the discovery of great electronic properties, electron transfer capabilities, unprecedented impermeability, and high mechanical strength, excellent thermal, and electrical conduction.

Single-layer graphene is a substructure for the construction of carbon structures, which if placed on each other, produce 3D graphite. The attractive force between layers is van der Waals (vdW) force with a gap of 0.335 nm [14]. If single-layer graphene is rotated around the axis of the tube, the 1D carbon nanotube, and if they are wrapped spherically, it forms the 0D fullerene.

2.1 The synthesis of graphene

The numerous chemical and physical methods have been proposed for the production of different types of graphene (from single layer to few layer) based on top-down and bottom-up approaches. Chemical vapor deposition (CVD) and epitaxial growth [15, 16], plasma-enhanced chemical vapor deposition (PECVD) [15], mechanical cleavage [14, 17], Scotch® tape technique [17], chemical synthesis [18], liquid exfoliation [19, 20], etc. have been widely used to produce graphene.

2.2 Graphene properties

Considering the attention of scientists to graphene and the hope for its various applications in the near future, many research efforts have been devoted to understanding the structure and properties of graphene. Graphene is expected to

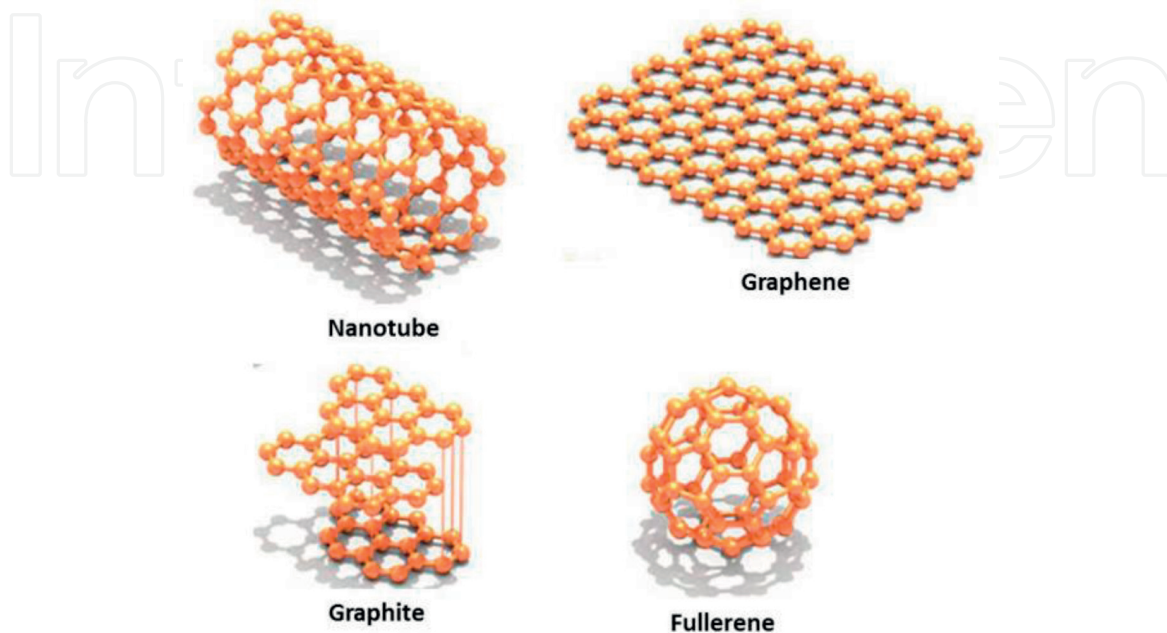


Figure 3.
Different forms of graphitic carbon [13].

consist of only single layer, but there is a significant attractive force to bind layers and to form two-layer or few-layer graphene. Two- and few-layer graphene consist of two and three to ten layers of these 2D nanosheets, respectively. The graphene structure, which contains more than ten of these 2D sheets, is considered to be “thick graphene” and is less of a concern for scientists. The status of graphene has changed from an unknown to a superstar in various fields of science and technology [21]. This is due to graphene’s exceptional characteristics including high current density, ballistic transport, chemical inertness, high thermal conductivity, optical transmittance, and superficial hydrophobicity on a nanometer scale [14].

Single-layer graphene, as previously discussed in this chapter, is defined as a 2D nanosheet of carbon atoms that are arranged in a hexagonal network. Each sp^2 -hybridized carbon atom is bonded to three other atoms with strong covalent bond (σ) that are configured in the hexagonal structure and also has a π orbital perpendicular to the sheet that forms π bond out of plane. These bonds can control the interaction between different layers of graphene in few-layer graphene [21].

Graphene is a semimetal or a semiconductor with a bandgap of zero and also has very high electron mobility at room temperature. Single-layer graphene has an unexpected high degree of transparency so that it absorbs $\pi\alpha \approx 2.3\%$ the incident white light, in which α is a substructure factor [7]. Single-layer graphene is also considered as one of the strongest materials. Given these mechanical properties, more applications in nanocomposite and coating industries are expected to be opened [21].

Graphene nanosheets are demonstrated to exhibit high transparency in UV-Vis and IR radiation and could be used to produce transparent electrode in solar cells [22]. Graphene has a good ability to functionalize with different functional groups in the form of covalent and noncovalent which leads to its solubility in different solvents. On the other hand, the high surface area of graphene provides a lot of area for loading of functional groups, which leads to reach a higher-level loading of targeting group in the surface, so graphene is considered as a suitable agent for drug delivery. In addition, the high surface area of graphene allow for development of targeted drug delivery systems [23].

2.3 Graphene applications

Different types of graphene, single-layer and few-layer, have potential applications in various fields. As stated above, graphene is the hardest and thinnest substance ever produced by human beings. Despite the fact that it has a dense structure, due to its very thin thickness, which is equal to the thickness of a carbon atom, it allows light to pass through and is highly transparent; it is also conductive, even more conductive than copper. Its ability to pass through heat and electricity makes it a new option for using on optical screens and computers.

It is 200–300 times stronger than steel and is even harder than diamond; however, it is very light and flexible. In addition, one of its properties is the great ability to move charge carriers. Electrons move relatively freely throughout graphene. With these features, graphene could be called supermassive, and it is expected that this material will create a revolution in the electronic, transistor, composite, coating, and sensor industries. Some examples of graphene applications can be:

- As reinforcement in composites instead of carbon fiber, this results in the creation of lighter and stronger aerocrafts and satellites.
- Used instead of semiconductor silicones in transistors due to superb conductivity properties. In this case, electrons can move 100 times faster than the

electrons present in silicon, which is why potentially graphene have many applications in the electronics industry. This material is currently the main competitor of silicon [24].

- Embedding graphene in plastics to enable them to conduct electricity [25, 26].
- To increase the durability of batteries using graphene dust [27].
- Used in optical electronics [28].
- Make harder, stronger, and lighter plastics [29].
- As conductive transparent coating for solar cells and screens [30].
- Producing stronger implants (medical) [31].
- Create supercapacitors [32].
- Application in flexible touch screens and displays [33].
- Application in liquid crystal display (LCD) [34].
- Applications in light-emitting diodes (LEDs) and organic light-emitting diodes (OLEDs) [35].
- Making conductive inks for coating [36].

3. Introduction of hexagonal boron nitride

hBN is structurally similar to graphite and has hardness comparable to graphite. Since hBN is the isoelectric analog of graphite structure and shares very similar structural characteristics and many physical properties, is so-called white graphite. It is not present in nature and is synthesized.

Due to its unique properties, including high resistance to oxidation, high thermal conductivity, good thermal insulation, chemical inertness, excellent lubrication, non-toxicity, and environmental friendliness, hBN has diverse industrial applications in surface coatings, composites, lubricants, and insulators. Due to the impressive properties of nanoscale materials and the development of the application of nanomaterials in the industry, ongoing research is carried to develop new methods for synthesis of nanomaterials. However, until now, there is no ensured large-scale and high yield method to achieve a significant amount of boron nitride nanosheets (BNNSs).

Although researches on 2D nanomaterials have been began several decades ago, the wave of interest and attention to these materials get started in 2004 when Novoselov discovered single-layer graphene with superb electronic properties [1]. Many efforts have been made to achieve 2D materials including graphene, boron nitride, and several dichalcogenides. Boron nitride (BN) is one of the most promising systems ever to be the lightest compound of the three and four groups in the periodic table. BN is composed of equal numbers of N and B atoms, which are configured in hexagonal arrange, similar to carbon atoms in graphene. For naming, the term “single-layer BN” is used for monolayer of BN, and in the case of multilayers, is called BNNSs.

As shown in **Figure 4**, single-layer BN has honeycomb structure consisting of isoelectric borazine rings and benzene structures. B—N bonds have a covalent nature, but due to the electronegativity difference, these bonds have ionic properties with a length of 1.45 Å. The distance between the two centers of the borazine rings is 2.54 Å (compared with 2.46 Å for graphene). The edges of the plates could be zigzagged (boron or nitrogen on the edges) or armchair (nitrogen-boron on the edge) [37].

The lateral dimension of BNNSs is in range from several hundred nanometers to several 10 micrometers [39, 40]. The dimensions of the nanosheets are different depending on the synthesis method. **Figure 5** shows a transmission electron microscopy (TEM) micrograph possessing boron nitride plates, with a lateral dimension of 600 nm.

The single layers of BN can be placed on each other to form few-layer BNNSs. The vdW interaction between layers holds BN layers together, so that the distance between these sheets is 0.333 nm, while the layer's distance in carbon structures is about 0.337 nm [37].

The inorganic analog of graphene, sometimes assigned white graphene, is isoelectronic similar to graphene. However, due to electronegativity differences between the boron and the nitrogen atoms, π electrons are shifted into nitrogen atomic centers, forming the insulating materials [42, 43].

The arrangement of atomic layers in BN and its nanosheets differs with graphite and graphene. The arrangement in the graphene is called AB stacking mode, so that each carbon atom is located at the top of the center of the neighboring layer benzene ring. While in the layers of BN, the stacking mode is AA, and each atom at the upper and lower layers has nitrogen atoms due to polar-polar or electrostatic interactions [6]. Although the AA stacking mode is always observed in nanosheets obtained from the top-down approaches, this order is not always seen in bottom-up synthetic techniques [39, 40]. In addition, the calculations show that the B—N layers have relative displacement from AA to AB stacking mode, along the favorable energy [44].

Duo to the difference in electronegativity, B—N bonds have ionic characteristic which is compared to covalent C—C bonds in graphene. This can lead to lip-lip interactions between the layers, i.e., chemical interactions as bridges or spot-welds. This phenomenon helps to reduce energy and then stabilize the formation

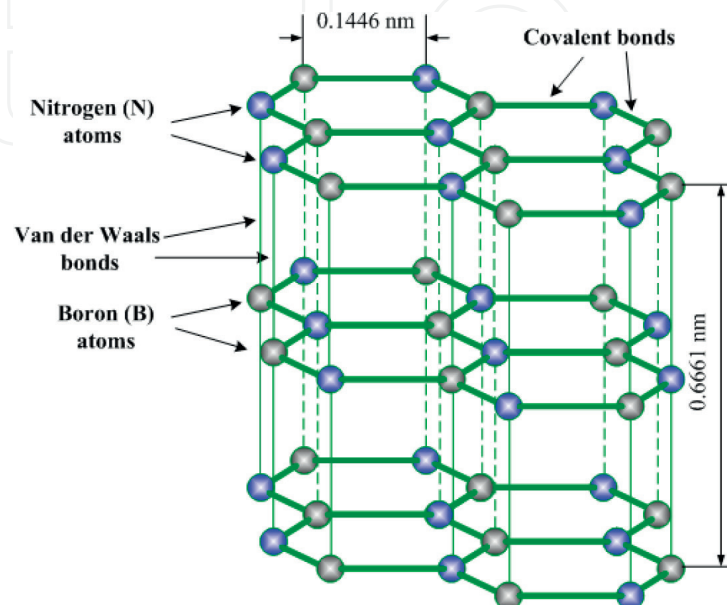


Figure 4.
Structural view of 2D BNNSs [38].

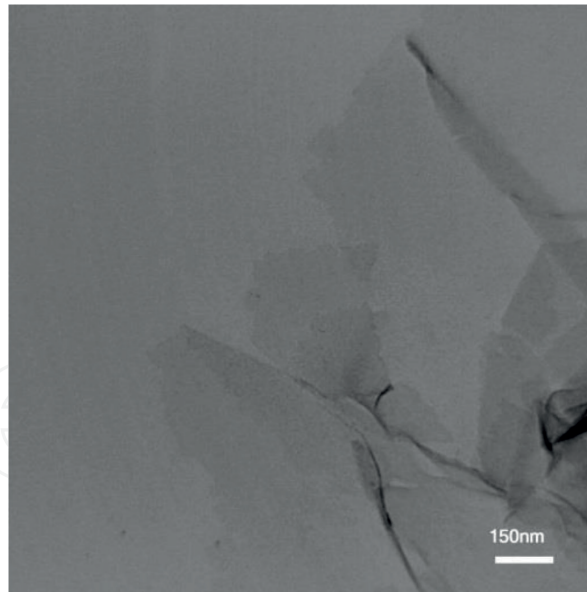


Figure 5.
The transmission electron microscope image of two relatively large BNNSs, which have been overlapped in the middle [41].

of few-layered BNNSs by reducing the number of dangling bonds at the edges, as well as reduction of frustration effect (forming B—B and N—N bonds instead of favorable B—N bonds) [45, 46]. Interestingly, such a strong interaction has only a negligible effect on the distance between the BN layers compared to graphene [6].

3.1 The preparation of BNNSs

2D nanosheets can be synthesized with two bottom-up and top-down approaches that relate to the synthesis of sheets from boron and nitrogen precursor [47, 48] and also the separation of layers. Chemical reaction [49] and CVD [39, 40, 50] are based on the former and micromechanical cleavage [51, 52], high-energy electron beam [53, 54], ball milling [55], and chemical [49, 56, 57]/liquid exfoliation [58–61] are based on the later approach.

Each technique has unique advantages for a specific application; however, there are always disadvantages in any way. In synthesis processes, a great amount of effort was put into preventing the formation of a strong chemical bond between the substrate and nanosheets. The crystallization process time, the nucleation on the substrate and the low density of critical nuclei are the important factors in synthetic methods. On the other hand, in the top-down view, exfoliation of layers is used. Nanosheets obtained from exfoliation usually have a higher crystallinity, but their lateral dimensions are limited by the material used. Also, due to lip-lip interactions between sheets, exfoliation of layers to isolate them is difficult. Therefore, the production of single layer is associated with a lot of problems. But in the bottom-up approach, there is a lot of control over the supply of thin nanosheets with high lateral dimensions. However, the crystallinity of obtained nanosheets is less than the exfoliation process.

3.2 The properties and applications of BNNSs

hBN has attracted many attentions due to its low density, high thermal conductivity, electrical insulation, high resistance to oxidation, low chemical efficiency, and low refractive index. BNNSs also inherit these properties, and in addition, they also have special properties due to high surface area.

3.2.1 Optical properties of BNNSs

BNNSs have not any absorption in the visible region but have absorption spectroscopy in the ultraviolet region [62]. Its commercial powders are white and its single crystal is transparent. Thin films obtained from chemical exfoliation or CVD also have high transparency [39, 40]. BNNS dispersion is often transparent at low concentrations and shows the Tyndall effect (the path of visible light inside the dispersion with laser light); at higher concentrations, the laser light is diffracted; and the dispersion is seen milky because of the lateral dimensions of nanosheets that are larger than the wavelength of laser light. Due to diffraction, there is any peak in the visible area. The measured extinction coefficient for absorption and diffraction of nanosheets is much smaller than that of graphene. The smaller lateral dimensions and more defects often influence on the optical bandgap, which is attributed to the absorption of the small distribution bandgap at the fermi surfaces and is produced due to the presence of defects [57]. However, hBN has two peaks in the 4 and 5.7 eVs: the first one related to the bandgap energy of BN, as a direct-gap semiconductor, and the latter is related to impurities and vacancy defects [63]. The lateral dimensions and number of layers affect the bandgap energy of nanosheets. For example, Rafiei-Sarmazdeh et al. [58] reported the absorption spectra of as-obtained BNNSs (2-nm-thick layer) at 204 nm (6.08 eV) that are related to the intrinsic excitement of BN structure and which is consistent with the reported results in other previous literatures [64, 65] and is also close to the bandgap energy predicted by theoretical calculus (6.0 eV) [66].

3.2.2 Thermal conductivity

The thermal conductivity for BNNSs is in range 300–2000 W/mK, which is comparable to graphene (1500–2500 W/mK). The difference in the conductivity may be due to the soft phonon modes of carbon sheets and the mass difference between boron and nitrogen [67]. Single BN layers have higher conductivity than multilayers, as the number of layer decreases and the phonon diffraction between layers reduces. As the number of layers increases, the conductivity decreases and converges to the conductivity of hBN. Although hBN has high conductivity and thermal capacity, recent studies have shown that its strong phonon diffraction leads to lower thermal conductivity than graphite. Therefore, the reduction of diffraction in BNNS leads to a significant increase in the conductivity (at room temperature > 600 W/mK) [68].

3.2.3 Mechanical properties

The hardness for BNNS and graphene is 267 and 335 TPa, respectively [69]. Hence, BNNSs can be used as reinforcement for polymer composites. It has been shown that modulus and tensile strength for nanosheets (thickness of 1–2 nm) are in the range of 220–510 and 8–16 TPa [39]. For multilayer, it is expected that the main values are somewhat less than these values.

3.2.4 Lubricant properties

Another interesting case with BN materials is frictional properties. hBN and graphite are used as lubricants for many years. The lubricating properties result from the application of the external shear force on the weak forces between the layers and sliding. At the level of atomic layers, friction force microscopy (FFM) studies show that the friction properties of these nanosheets depend on their thickness.

Thin nanosheets show more friction due to increased out-of-plane deformation. More studies have shown that reversible dynamic wrinkling on the top surface of most layers is created by frictional force [70]. Then, BNNSs and graphene could be used as lubricating additive.

3.2.5 The neutron absorption

Boron is introduced as one of the most important neutron absorbers due to its high neutron absorption cross section. The compounds containing boron are good neutron absorber. In the middle, hBN and, of course, BNNSs are better absorbers due to layer structure and larger surface area that is exposed to neutron beam than other BN structures (such as nanotube, nanoparticle, etc.). They are used in nuclear shielding [71] and boron neutron therapy [72].

4. Introduction of metal dichalcogenides

In recent years, metal dichalcogenides (MX_2) have attracted a lot of attention, like other 2D materials where M is transition metals and X_s are S, Se, and Te such as WSe_2 , molybdenum disulfide (MoS_2), tellurium disulfide (TeS_2), etc. MX_2 can be a semiconductor or metal depending on the oxidation state of their metal atoms. As graphene-like compounds, they have similarities to graphene, resulting in new opportunities for detecting and building sensors, lithium batteries, optoelectronics, and energy storage. Many researchers have shown that the exfoliated layers of MX_2 have large energy of bandgap and are semiconductors. In addition, they have the properties of fluorescence and photoluminescence [73].

There are currently only a limited number of reports on single-layer and few-layer group IV–VI and III–VI layered compounds. Therefore, the 2D properties of these materials are largely unknown. However, MX_2 shows a variety of electrical and optical properties that are suitable for catalysts, nanotribology, optoelectronics, and lithium-ion batteries. These materials are expected to exhibit extraordinary properties after reaching a thickness to single layer or multilayer [74].

4.1 The synthesis of TMD

The synthesis routes to MX_2 are similar to other 2D nanomaterials that are based on two top-down and bottom-up approaches. Methods such as chemical synthesis, CVD, mechanical cleavage, and liquid exfoliation are performed to produce of these nanomaterials [75].

4.2 The application of TMD

These layered compounds, like other 2D nanomaterials, have interesting optical, electrical, photovoltaic, and catalytic properties. These compounds are considered as the next generation of flexible and ultrathin photoelectric devices. Also, MX_2 has a suitable photovoltaic response to laser excitation and also used as catalyst in the hydrogen evolution reactions (HER).

5. Future outlook

One of the major problems with 2D nanostructures is to achieve a large-scale synthesis method for producing high quality, large surface area, high crystallinity,

and free from any impurity nanosheets. Different methods have been reported to synthesize these nanosheets so far, which generally suffer from problems such as impurities, low crystallinity, low lateral dimension, and little yield, which limit the use of these 2D nanosheets in the industry. At present, many studies focus on improving the synthesis methods of these nanosheets.

6. Conclusions

This chapter is an attempt to better realize 2D nanostructures, especially graphene and boron nitride, and getting to know the synthesis methods and the application of these materials in various fields. Recently, there have been advances in the production and application of 2D nanostructures, especially graphene and boron nitride.

In general, the properties and applications of nanostructures are determined by their structure and morphology. The large surface area, high aspect ratio, and much number of atoms on the surface provide the special properties to these 2D nanomaterials, such as thermal and electric conductivity, lubricating, mechanical characteristic, etc. These impressive properties allow them to be used in fields such as coatings, electrical and optoelectronic devices, composites, etc. However, the low efficiency of the synthesis methods, especially boron nitride, which has an ionic nature, creates some of the limitations that researchers are trying to overcome.

Conflict of interest

The authors declare that they have no conflict of interest.

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