**On recent application and advances of Two-dimensional materials**

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Directory...................................................................................................................................................................ii

Abstract ..................................................................................................................................................................iii

1. Introduction .........................................................................................................................................................5

1.1 Denfinition of Two-Dimensional Materials.......................................................................................5

1.2 Recent Advances ...............................................................................................................................5

1.3 Industrialization, transformation and application...............................................................................6

2. Theoretical Basis .................................................................................................................................................6

2.1 Superconducting Phenomenon ..............................................................................................................6

2.1.1 Discovery................................................................................................................................6

2.1.2 Properities---Thermally and Electromagnetically...................................................................6

2.1.3 BCS theory& Energy gaps......................................................................................................7

2.1.4 Higher-temperature superconductivity....................................................................................8

2.2 Topological Insulators ...........................................................................................................................9

2.2.1 Historical and General View.................................................................................................10

2.2.2 General Theories---Topological Band Theory and Topological Field Theory.....................11

3. Fantastic Properties of 2D Materials---Possible Applications ........................................................................13

3.1 Some Examples of 2D Materials..........................................................................................................13

3.1.1 Graphene against Other Two‐Dimensional Materials ...........................................................13

3.1.2 Topological Insulators............................................................................................................14

3.1.3 2D-Based Nanofluids.............................................................................................................15

3.1.4 Other Promising Competitors---Black phosphorus and Transition-Metal Sulfdes(TMDC)..16

3.2 Thermal Transport Properties of Two-Dimensional Materials.............................................................18

3.3 Mechanical Properties and Applications of Two-Dimensional Materials............................................20

3.4 Electrical Properties of Two-Dimensional Materials............................................................................23

4. Some Other Interesting Application of 2D Materials .........................................................................................26

5. Synthesis Strategies about 2D Materials .........................................................................................................28

5.1 Top-down strategy ................................................................................................................................28

5.2 Bottom-up strategy................................................................................................................................30

Bibliography............................................................................................................................................................35

i

**Contents**

ii

**Absract**

In recent years, more and more attentions have been paid to two-dimensional (2D) materials due to the excellent electrical, optical, thermal and mechanical properties. The word 2D material are once used for film materials, but are be endowed with more profound meanings today.

In the 2nd section, we will give a brief introduction to superconducting phenomenon, topological insulators and related theories in order to elaborate the advanced fundamental physical principles behind the fantastic properities and applications of 2D materials.

The 3rd section is the most exciting one, we will review some typical(and also newly found) 2D material such as graphenes, nanofluids and TMDC, including the mechanics behind their properities and some outlooks of their applications. To elaborate the theories such as phonon, we will also set forth thermal transport properties, mechanical properties and electrical properties of two-dimensional materials in this section.

Then there will be a seperate part to explore some intersting application of 2D materials, I did this because they are hard to classify and quite strange.

Finally, we will talk about synthesis strategies about 2D materials in the last chapter, such as micromechanical exfoliation and Lithium (Li) intercalation process classified as top-down strategy; Hydro/solvothermal process and chemical vapor deposition in bottom-up strategy.

**1.1 Denfinition of Two-Dimensional Materials**

**Introduction**

Traditionally, 2D materials refers to film materials, whose thickness is much smaller than the other two dimensions. Generally, the film can be divided into two types, those who are thicker than 1 micrometer are called a thick film, when it is thinner than 1 micrometer, it is a film. Semiconductor functional devices and optical coatings are the main applications of thin film technology. Long-term research has applied ferromagnetic films to computer storage devices, pharmaceuticals, thin film batteries, dye-sensitized solar cells, and so on. By applying ceramic films, the duration of knives can be increased by several orders of magnitude.

However, nowadays, 2D materials are also known as 2D topological materials or single‐layer materials, and can be defined as crystalline materials with a single layer of atoms or chemical compounds. These materials have a thickness of a few nanometres or less (one or two atoms thick).

**1.2 Recent Advances**

2D materials was thought to be unstable, until the discovery of graphene by Novoselov and Geim in 2004. It shows that it is possible to exfoliate stable single-atom sheets from van der Waals solids, and is recognized as the first 2D material. Since 2010, a large amount of research has been carried out to isolate other 2D materials due to their remarkable chemical, electronic, optical, or mechanical properties, such as ultrahigh carrier mobility at room temperature (∼10,000 cm2V −1s−1), quantum hall effect, large theoretical specific surface area (2630 m2g−1), excellent optical transparency (∼97.7%) and so on.

**1.3 Industrialization, transformation and application**

Despite great advances achieved until now, many of these materials has been used for large‐scale commercial applications with the possible exception of graphene. Their main areas of applications are electronics and optoelectronics, sensors, biological engineering, filtration (water purification), lightweight/strong composite materials, photovoltaic systems (electrodes), medicine, quantum dots, thermal management, ethanol distillation, and energy storage.

**Theoretical Basis**

The emergent phenomena such as superconductivity and topological phase transitions can be observed in strict two-dimensional (2D) crystalline matters. So it is necessary to give a brief introduction to superconducting phenomenon and topology here, some other basic condensed matter physical theory such as Valence band theory, phonon, crystal structure and some other chemical knowlege are neglected here or elaborated in related sections.

**2.1 Superconducting Phenomenon**

**2.1.1 Discovery**

Superconductivity was discovered in 1911 by the Dutch physicist Heike Kamerlingh Onnes. He found that the electrical resistivity of a mercury wire disappears suddenly when it is cooled below a temperature of about 4 K (−269 °C). He soon discovered that a superconducting material can be returned to the normal (i.e., nonsuperconducting) state either by passing a sufficiently large current through it or by applying a sufficiently strong magnetic field to it.

Hundreds of materials are known to become superconducting at low temperatures, most of them are alloys or compounds. Twenty-seven of the chemical elements, all of them metals, are superconductors in their usual crystallographic forms at low temperatures and low pressure. Bismuth and five other elements, though not superconducting in their usual crystallographic form, can be made superconducting by preparing them in a highly disordered form, which is stable at extremely low temperatures. However, superconductivity is not exhibited by any of the magnetic elements such as chromium, manganese, iron, and nickel.

In 1933, the scientists discovered that a superconductor is highly diamagnetic. (Meissner effect for one of the two men who discovered it). Its discovery made it possible to formulate: in 1934, a theory of the electromagnetic properties of superconductors that predicted the existence of an electromagnetic penetration depth. In 1950 it was clearly shown for the first time that a theory of superconductivity must take into account the fact that free electrons in a crystal are influenced by the vibrations of atoms that define the crystal structure, called the lattice vibrations. In 1953, in an analysis of the thermal conductivity of superconductors, it was recognized that the distribution of energies of the free electrons in a superconductor is not uniform but has a separation called the energy gap.

**2.1.2 BCS theory**

Dispite the success in explaining interrelationships between observed phenomena, the theories referred to above far did not explain the superconducting phenomenon as consequences of the fundamental laws of [physics](https://www.britannica.com/science/physics-science). Until in 1957, the BCS theory was introduced by US scientists John Bardeen, Leon N. Cooper, and John Robert.

In normal conductors the conduction electrons(electrons that are not bound to one atoms but are free to move through the whole material) are scattered by impurities, grain boundaries, dislocations, and lattice vibrations (phonons). In a superconductor, however, there is an ordering among the conduction electrons called Cooper pairing(BCS pair) it is a pair of electrons (or other Fermions) bound together at low temperatures in a certain manner, This pairing(attraction) is due to the electron -phonon interaction, in conventional view, the attraction between electron and the positive ions can distorts the ion lattice, moving the ions slightly toward the electron, increasing the positive charge density of the lattice in the vicinity. This positive charge can attract other electrons. At long distances, this attraction between electrons due to the displaced ions can overcome the electrons' repulsion and cause them to pair up. The energy of the pairing interaction is quite weak, of the order of 10^3 eV, and thermal energy can easily break the pairs. So only at low temperatures, in metal and other substrates, there are a significant number of the electrons in Cooper pairs.

Electrons have Spin- 1/2, so they are Fermions. However, the total spin of a Cooper pair is integer (0 or 1), which is called a composite boson. This means the Wave functions Are symmetric under particle interchange. Therefore, unlike electrons, multiple Cooper pairs are allowed to be in the same quantum state, which is responsible for the phenomena of superconductivity.

The BCS theory is also applicable to other fermion systems, such as helium-3, also, Cooper pairing is responsible for the superfluidity of helium-3 at low temperatures. It has also been recently demonstrated that a Cooper pair can comprise two bosons. Here, the pairing is supported by entanglement in an optical lattice. It has also been useful in understanding electromagnetic properties, including the fact that any internal magnetic flux in superconductors exists only in discrete amounts (instead of in a continuous spectrum of values), an effect called the [quantization of magnetic flux](https://www.britannica.com/science/quantization-of-magnetic-flux).

**2.1.3 Higher-temperature superconductivity**

The majority of the classical superconductors have transition between 1 K and 10 K. But since 1986 many compounds have been found to have extraordinarily high transition temperatures(Tc, below which a substance is superconducting). The properties of these high-Tc compounds are quite different.

The high-Tc superconductors are type II superconductors, which exhibit zero resistance, the Meissner effect, an energy gap for the superconducting electrons, and so on. Specifically, they have a characteristic temperature dependence of the specific thermal conductivity.

Therefore, it is clear that the conduction electrons in these materials form the Cooper pairs as in the BCS theory, which demonstrated its central deduction. But it is unlikely that these interactions are strong enough to explain transition temperatures as high as 90 K. So it is believed that interactions among the electrons are responsible for high-temperature superconductivity. Moreover, because the motions of the electrons are strongly correlated with each other, thus magnetic phenomena play an important part in determining the microscopic properties of these materials.

**2.2 Topological Insulators(TI)**

**2.2.1 Topology and its physical application**

Topology is a newly developed concept in mathematics. It can be refered as the continuous deformation of geometric objects. As shown in Figure2.2.1, with a certain constant(such as the number of 'hole' through a object), topology is insensitive to detail and continuous variation: despite other different properties of oranges and bowls, bagels and teacups, they have the same topology. This concept is extended to materials science, the physical quantity or quantum state of a material can be made to determines its topological characteristics, and through the acquisition of these topological features, physical properties that are insensutive to detais such as the defects, impurities of the material.

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Figure2.2.1 Just like teacups and bowls, although they belong to the same category, ceramics, but because of the difference in the number of holes, it is refered to as a different topology.

More specifically, in the study of quantum Hall effect, when the two-dimensional conductive layer at the heterojunction interface of the semiconductor is placed under low temperature and strong magnetic field, the Hall resistance deviates from its normal linear relationship with the magnetic field intensity, indicating a stepped shape(in Figure 2.2.2).And the resistance value corresponding to each step platform is exactly , (where v is an integer). In the figure we can see that the vertical resistance is zero on each of the corresponding platforms, which means that the electrons can move resistance-freely. The topological features of the quantum Hall system is determined by the number of charged Landau levels(v), and the Hall resistance of the sample is determined by its topological characteristics and the quantization constant , which is independent of the specific material, or the purity of the sample.

In the quantum Hall effect we need to introduce magnetic fields of a few Tesla strong. However, there are difficulties in realizing the application, so the scientists set their eye towards the spin quantum Hall effect. It relies no external magnetic field, the particals couple with each other via their own spin-orbit, and strong spin-orbit coupling will lead to valance band reversal. After the turned over, a pair of edge states will be generated in the valance gap, and the two edge states have opposite spin.

In the spin quantum Hall effect, the electron is protected under time inversion symmetry, which allows them to go in two directions in the edge state.In addition, the number of electrons in opposite directions is equal, so no current is generated. But there will be a spin current at the edge of the surface. And the current generated by the upper and lower spin electrons propagates in opposite directions.

**2.2.2 General View about TI**

Electronic bands in crystals are described by an ensemble of Bloch wave functions indexed by momenta deﬁned in the ﬁrst Brillouin Zone, and their associated energies. In an insulator, an energy gap around the chemical potential separates valence bands from conduction bands. Therefore, a band insulator is a material which has a well-deﬁned set of valence bands separated by an energy gap from a well-deﬁned set of conduction bands. The object of interest in the study of topological order in insulators is the ensemble of valence bands, which is unambiguously well deﬁned for an insulator. The ensemble of valence bands can possess non-trivial or twisted topological properties. In the case of a twisted topology, the insulator is called a topological insulator.

The question underlying the topological classiﬁcation of insulators is whether all insulating phases are equivalent to each other, i.e. whether their ensemble of valence bands can be continuously transformed into each other without closing the gap.

Topological insulators correspond to insulating materials whose valence bands possess non-standard topological properties. Related to their classiﬁcation is the determination of topological indices which will differentiate standard insulators from the different types of topological insulators. A canonical example of such a topological index is the Euler–Poincaré characteristic of a two-dimensional manifold(this is also shown in the example in 2.2.1) . This index counts the number of ''holes'' in the manifold. Two manifolds with the same Euler characteristic can be continuously deformed into each other, which is not possible for manifolds with different Euler characteristics.

For TI, a consequence of a nontrivial bulk topology is the existence of gapless edge or surfacestates; in otherwords, the surface of the topological insulator isnecessarily metallic. As mentioned before, this kind of topological phase ordering ﬁrst arose in condensed matter in the context of the integer quantum Hall effect. From this point of view the robustness of the phase manifested in the high precision of the Hall conductivity plateau is an expression of the topological nature of the related order, which by deﬁnition is insensitive to perturbations. The existence of robust edge states is another manifestation of this topological ordering. The quantized Hall conductivity can be alternatively accounted for by the ballistic transport properties of the edge states.

In 2008, Zhang Shoucheng's research group predicted a two-dimensional topological insulator material AlSb/InAs/GaSb/AlSb based on traditional III-V semiconductors. (In this material, AlSb is a barrier layer composed of wide-gap semiconductors. In As and GaSb are narrow-gap semiconductors. In this structure, GaSb and InAs layers are both limited by each other and the AlSb layer, resulting in the highest energy hole quantum well sub-band formed in GaSb being on the lowest energy electron quantum well sub-band formed in InAs, which is reversed. This leads to the non-trivial nature of the system topology. After that, the theoretical physicist predicted that single or several layers of Bi, Si, Ge, Sn and other elements of the near two-dimensional honeycomb structure are two-dimensional topological insulators. And some materials have been experimentally confirmed to have the properties of two-dimensional topological insulators.

**Fantastic Properties of 2D Materials---Possible Applications**

**3.1 Some Examples of 2D Materials**

**3.1.1** **Graphene**

Graphene, a two-dimensional form of crystalline carbon, either a single layer of carbon atoms forming a honeycomb (hexagonal) lattice or several coupled layers of this structure, is the most researched 2D material till now.

Graphene is a parent form of all graphitic structures of carbon: graphite, which is a three-dimensional crystal consisting of relatively weakly coupled graphene layers; nanotubes, which may be represented as scrolls of graphene; and buckyballs, spherical molecules made from graphene with some hexagonal rings replaced by pentagonal rings.

The theoretical study of graphene was started in 1947 by physicist Philip R. Wallace as a first step to understanding the electronic structure of graphite. By applying a gate voltage or using chemical doping by adsorbed atoms and molecules, one can create either electron or hole. Conductivity in graphene that is similar to the conductivity created in semiconductors. However, in most semiconductors there are certain energy levels where electrons and holes do not have allowed quantum states, and, because electrons and holes cannot occupy these levels, for certain gate voltages and types of chemical doping, the semiconductor acts as an insulator. Graphene, on the other hand, does not have an insulator state, and conductivity remains finite at any doping, including zero doping.

Due to the zero band gap of graphene, which results in its low on/off ratio, and disqualifies it to be applied to FETs(Field Effect Transistor) for applications in digital circuits. Thus, graphene has been chemically modified into different versions such as graphane, graphone, graphyne, graphdiyne, fluorographene or graphXene. Graphyne is better than graphene in directional electronic properties and charge carriers. Graphone (partially hydrogenated) and graphane (100% hydrogenation of graphene with stoichiometry CH) have applications in nanoelectronics and spintronics due to the presence of band gap and magnetic properties.When interact with Group IA and Group VIIA elements, it can form graphXenes. These materials present a range of band gap between 0 and 6.4 eV. Therefore, metallic, semiconducting, and insulating behaviours are presented. Such properities are obtained through a mixture of sp2/sp3 systems, for example, Graphone with hydrogen coverage of 8% reaches a band gap of ∼1.0 eV due to the rehybridization from sp2 to sp3.

Modern electronics (e.g., integrated circuits in computer chips) are basically two-dimensional in that they use mainly the surface of semiconducting materials. Therefore, graphene and other two-dimensional materials are considered very promising for many such applications. More importantly, because of its relative simplicity, Graphene can be considered as a model system for studying two-dimensional physics and chemistry in general. Other two-dimensional crystals besides graphene can be derived by exfoliation from other multilayer crystals (e.g., hexagonal boron nitride, molybdenum disulfide, or tungsten disulfide) or by chemical modification of graphene. (e.g., graphane, hydrogenated graphene, or fluorinated graphene).

**3.1.2 Topological Insulators**

Topological insulators behave as an [Insulator](https://translate.baiducontent.com/transpage?cb=translateCallback&ie=utf8&source=url&query=%2Fwiki%2FInsulator_(electrical)&from=zh&to=en&token=&monLang=zh) In its interior but their surface contains [Conducting](https://translate.baiducontent.com/transpage?cb=translateCallback&ie=utf8&source=url&query=%2Fwiki%2FElectrical_conductivity&from=zh&to=en&token=&monLang=zh) States, in other words, electrons can only move along the surface. What is special about topological insulators is that they have [non-trivial](https://translate.baiducontent.com/transpage?cb=translateCallback&ie=utf8&source=url&query=%2Fwiki%2FNon-trivial&from=zh&to=en&token=&monLang=zh) [symmetry-protected topological order](https://translate.baiducontent.com/transpage?cb=translateCallback&ie=utf8&source=url&query=%2Fwiki%2FSymmetry-protected_topological_order&from=zh&to=en&token=&monLang=zh) and their surface states are symmetry protected by particle number conservation and [Time-reversal symmetry](https://translate.baiducontent.com/transpage?cb=translateCallback&ie=utf8&source=url&query=%2Fwiki%2FTime-reversal_symmetry&from=zh&to=en&token=&monLang=zh).

In the bulk of a non-interacting topological insulator, the [Electronic band structure](https://translate.baiducontent.com/transpage?cb=translateCallback&ie=utf8&source=url&query=%2Fwiki%2FElectronic_band_structure&from=zh&to=en&token=&monLang=zh) resembles an ordinary band insulator, with the [Fermi level](https://translate.baiducontent.com/transpage?cb=translateCallback&ie=utf8&source=url&query=%2Fwiki%2FFermi_level&from=zh&to=en&token=&monLang=zh) falling between the conduction and valence bands. On the surface of a topological insulator there are special states that fall within the bulk energy gap and allow surface metallic conduction.

The most promising applications of topological insulators are spintronic devices and dissipationless transistors for quantum computers based on the quantum spin Hall effect and quantum anomalous Hall effect.

**3.1.3** **2D-Based Nanofluids**

Energy management becomes crucial for meeting the rising needs of mankind, thus, in recent years, the prevention of heat dissipation has become a hot topic. Among other processes, there is a high demand for successful heat management and energy-efficient fluid-based heat transfer systems, with aid of reinforced materials.

Conventionally, many devices use inexpensive heat transfer fluids to intensify heat dissipation, such as water, ethylene-glycol (EG), oils, and other lubricants. However, the inherent limitation of these fluids is the relatively low thermal conductivity; water, for instance, is roughly three orders of magnitude less conductive than copper or aluminum. What these conventional fluids lack in thermal conductivity, however, is compensated by their ability to flow. Still, if the thermal conductivity of conventional fluids were enhanced, it would be much more effective. Hence, since the solid materials possess several orders higher thermal conductivity compared with that of conventional fluids, an idea to introduce conducting particles to fluids was consider.

Most early studies used suspensions of millimeter- or micrometer-sized particles, which led to countless problems, such as a tendency to settle too rapidly, forming sludge sediment which increases the thermal resistance. In addition, flow rate increased to avoid deposit also increases erosion of pipelines; outstanding thermal conductivity enhancement is based on high particle concentration, which leads to apparent increase in viscosity. Furthermore, fluids of this scale size could have considerably larger pressure drops, thus making flow through smaller channels much more difficult.

However, nanofluids are a new class of stable heat transfer liquid suspensions which are engineered containing homogeneously dispersed solid nanofillers. Compared to micro- or milli-fluids, nanofluids tend to be more stable, since nanofillers possess unique properties, such as large surface area to volume ratio, as well as dimension-dependent physical properties, which make nanostructures better and more stably dispersed within conventional fluids.

Nanofillers size has positive effect on conventional fluids performance, making flow through small channels much more easier. Moreover, nanofluids are promising for practical application without clogging, sediment or such. Nanofluids will keep the fluidic properties of the conventional fluids, behave almost like conventional fluids, and incur in little or no extra penalty of pressure drop.

Some nanofluids are currently expensive, partly due to the difficulty in manufacturing. However, mass production of nanostructures could further decrease the cost, also low filler fraction is necessary to make nanofluids more affordable before they will witness wider applications.

**3.1.4 Other Promising Competitors---Black phosphorus and Transition-Metal Sulfdes(TMDC).**

Phosphorene is the 2D crystalline allotrope of phosphorus consisting of a single layer of atoms as graphene, which possesses a non‐zero band gap (∼0.1 eV) while displaying high electron mobility. These qualities make it a better electronic material than graphene. Phosphorene is a p‐type semiconducting material, and presents photoluminescence in the visible optical range. Besides, phosphorene has a high specific capacity, superb stability, and high electrical conductivity. These capacities allow its use in FETs, batteries, radio receivers, and gas sensors.

Transition metal chalcogenides (TMCs) are thin‐layered semiconducting structures of the type MX2, where M is a transition metal atom (Mo, W, etc.) and X is a chalcogen atom (S, Se, or Te). One layer of M atoms is sandwiched between two layers of X atoms. These materials have layered structures of the form chalcogen‐metal‐chalcogen, with the chalcogen atoms in two hexagonal planes separated by a plane of metal atoms. MoS2 is one of the most typical TMDs; it has a direct band gap of 1.8 eV in monolayer, which can be tuned in different ways. A MoS2 monolayer has a thickness of 6.5 Å, and it has been used in chemical and gas sensors. MoS2‐based sensors have been implemented to detect NH3 down to 400 ppb. Besides, MoS2 has applications in fields such as flexible electronics, energy storage and harvesting as well as electrochemical catalysis

2D TMDs are also exciting materials for future applications in nanoelectronics, nanophotonics, and sensing. TMDs monolayers such as MoS2, MoSe2, MoTe2, WS2, and WSe2 have a direct band gap and thus can be used in electronics as FETs and in optoelectronics as emitters (light‐emitting diodes) and optical detectors (photodetectors).

**3.2** **Thermal Transport Properties of Two-Dimensional Materials**

In addition to issues regarding scrap materials, maintenance, and components wear among others, a hot topic in industry is the heat dissipation. Avoiding or reducing the use of resources for cooling equipment, there is a high demand for successful heat management and energy-efficient heat transfer systems, with aid of reinforced materials. This is particularly important in electronics industry, since with the chips are becoming more and more meticulous, heat dissipation becomes a problem.

**3.2.1 Phonon**

To further our study in thermal properties of 2D material, we need to introduce the concept of phonon. In solid crystals, the atoms behave as if they are connected by tiny springs, their own thermal energy or outside forces make the lattice (crystal) vibrate. This generates mechanical waves that carry heat and sound through the material. It has a definite energy and momentum. So, just as a photon carrying a quantum of electromagnetic energy in optics, via quantum mechanical view, the waves can be treated as a particle, called a phonon. Whereas electrons are responsible for the electrical properties of materials, phonons determine the thermal conductivity of materials. Through figure 3.2.1, we can see that in materials with different thermal transport properties the phonon dispersion curve also differs.

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Figure 3.2.1 The phonon dispersion curves along the path passing through the main high-symmetry k-points in the irreducible Brillouin zone of graphene, silicene, and phosphorene. Three acoustic phonon modes (LA, TA, and FA) are labeled.

**3.2.2 Graphene**

Experiments have shown that the thermal conductivity of graphene reaches as high as about 3000 W/mK, which makes graphene very promising for thermal management applications such as heat dissipation in electronics. In addition to the heat dissipation applications, due to its extremely high electrical conductivity, graphene has also been explored to be used as thermoelectric material by largely reducing its thermal conductivity by varieties of functionalization, such as constructing graphene nanoribbons, hydrogenation, defects, and doping.

There have been a long time for an intriguing open question on the phonon transport in materials has three polarization branches, including longitudinal acoustic (LA) and transverse acoustic (TA) phonons, out-of-plane flexural acoustic (FA)

As for graphene, because of the reflectional symmetry of the structure, the phonon scattering processes involving odd number of FA modes are not allowed, which restricts the phase space for phonon-phonon scattering. The suppression of scattering of FA leads to its extremely low scattering rate, which is equivalent to a very large phonon lifetime, which results in the huge contribution to thermal conductivity from FA modes. The selection rule can be broken by placing graphene on any substrate or due to the presence of nanoscale corrugations. Therefore, it is intuitive to see that thermal conductivity of supported graphene is dramatically reduced.

**3.2.3 Silicene**

Silicene is the silicon counterpart of graphene. Compared to graphene, silicene is more compatible with silicon-based semiconductor devices and technologies. In particular, in terms of thermoelectric application, silicene is even more exciting than graphene as the charge carrier of silicene is massless fermion, and the electrical conductivity of silicene is as high as that of graphene.

However, the thermal conductivity of silicene is expected to be much lower than that of graphene. Several numerical simulations have predicted the thermal conductivity of silicene and the results at 300 K range from 5 to 69 W/mK. This is due to its buckled atomic structureWhat's more, in nanoelectronics application, the buckled atomic structure breaks the symmetry of the silicene, making it possible to open a band gap by applying electric field.

**3.3 Mechanical Properties and Applications of Two-Dimensional Materials**

Many 2D materials possess fantastic mechanical properties such as ultralow weight, high Young’s modulus, and high strength. What's more, many reports have found that the breaking stress of 2D materials can reach the theoretical upper limit, this is due to the low disorder and impurities in the characterized 2D materials. However, 2D materials possess high anisotropy between the in-plane and out-of plane mechanical properties. In pristine-layered 2D materials, the nearby atoms in the same plane are bonded covalently, resulting in strong in-plane mechanical properties. But the interlayers are not so strong, since they are stacked together via weak van der Waals interactions.

**3.3.1 Factors affecting mechanical properities**

The mechanical properities are greatly affected by the bond type and the crystal structure. With strong in-plane covalent carbon–carbon bonds, Pristine monolayer graphene is reported to have a Young’s modulus of approximately 1 Tpa. Another example is 2D TMDCs with the same crystal type, a smaller Young’s modulus of WSe2 has been observed compared with MoS2 and WS2; this is due to a decrease in the charge transfer and an increase in the lattice constant, resulting in a weakened binding between the metal and chalcogen, as M changes from Mo to W and X changes from S to Se.

Meanwhile, the Young’s modulus of some 2D materials (e.g., MoS2, BP, and h-BN have been found to decrease with an increase in their thickness , which is caused mainly by interlayer stacking errors. The occurrence of interlayer sliding in multilayer 2D materials during indentation is also a factor for underestimating the intrinsic Young’s modulus. However, the Young’s modulus of WSe2 remains unchanged statistically with increasing number of layers, which possibly results from the strong interlayer interaction in WSe2.

In addition, the mechanical properties of 2D materials largely depend on the density of crystal defects. For instance, the larger number of vacancy defects in the GO-reduced graphene and the existence of voids at the grain boundaries, together with wrinkles in polycrystalline graphene prepared by the CVD method, the weaker mechanical properties they may prosess.

**3.3.2 Applications**

With the combination of high breaking strain, low thickness, and versatile electronic properties, 2D materials can be applied in some new area such as flexible transistor, strain sensor and nanogenerator.

For example, because of the semiconducting properties, certain TMDCs (such as MoS2, WS2, and WSe2) and BP can be used as channel materials in flexible transistors. Some 2D materials like MoS2 undergo band structure change under applied strain(a piezoresistive effect). Combined with the high breaking strain, it enable 2D material to produce wearable strain sensors for human motion detection.

Moreover, we can make use of the piezoresistive effect to produce the so-called nanogeneraters. Odd-layer TMDCs possess piezoelectric property due to the absence of inversion symmetry. Figure 11(a) shows a flexible device with the monolayer MoS2 flake outlined with black dashed line. When the substrate is bent, the MoS2 flake will be stretched, and piezoelectric polarization charges will be induced at the zigzag edges of the MoS2 flake which can drive the flow of electrons in an external circuit. When the substrate is released, electrons flow back. Through this method, mechanical energy is converted into electricity. Experiment shows that A 5.08% mechanical-to-electrical energy conversion efficiency can be achieved, together with the mechanical flexibility 2D materials, 2D materials are promising in wearable power-generated nanodevices.

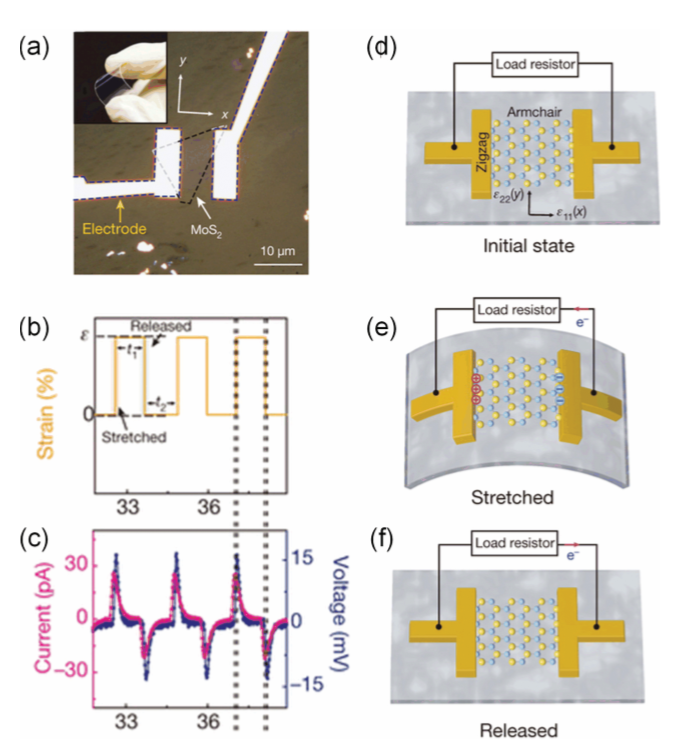


Figure 3.3.2 (a) A flexible device with a monolayer MoS2 flake and metal electrodes at its zigzag edges. (b) Applied periodic strain as a function of time. (c) Corresponding piezoelectric outputs when strain is applied along the armchair direction. Operation of the MoS2-based piezoelectric device in initial state (d), stretched state (e), and released state (f)

**3.4 Electrical Properties of Two-Dimensional Materials**

A few decades ago, the potential of the electronics industry depended entirely on silicon. Howver, new materials such as carbon allotropes of the groups III, IV and V elements are being introduced assubstitutes to increase efficiency, specific capacity, and speed of information processing. Actually, in electronics, 2D materials are used in the manufacture of supercapacitors, batteries, field‐effect transistors (FETs), solar cells, light‐emitting diodes, transparent electrodes, coatings for electrostatic dissipation, and so on. The use of 2D materials in the electronic industry will be extended in the design of new electronic devices being applied either individually or as a component within a composite, hybrid, or functional material.

**3.4.1 Overview**

Optical and electronic properties of the 2D materials are completely different from those of the bulk materials due to confinement of electrons and absence of interlayer interactions, which play an important role in the band structure presented in these materials . On the other hand, mechanical and chemical properties are obtained thanks to geometric effects (chirality, dilution, defects, etc.) and to the high surface‐volume ratio (it trends to infinity in the thinnest materials)

While dichalcogenides and buckled nanomaterials have sizeable band gaps, graphene has zero band gap and they also become semiconducting or metallic materials. With different gap energy, 2D materials have different conductivity, and can be classified into3 types, those with metallic behaviour (Table 1), with semiconducting behaviour (Table 2), and with electrical insulator behaviour (Table 3).

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The electrical properity are very sensitive to the number of layers, ranging from indirect band‐gap semiconductor in the bulk phase to direct band‐gap semiconductor in monolayers. 2D materials are leading to ubiquitous flexible and transparent electronic systems for applications in integrated circuits, solar cells, and storage energy.

**3.4.2 Optoelectronic**

2D materials have interesting properties for photonics and optoelectronics compared with other materials. Electrons in 2D crystals possess a valley degree of freedom (DOF) in addition to charge and spin. 2D materials exhibit an anomalous Hall effect whose sign depends on the valley index effect (VHE). It implies that circularly polarized light excites electrons into a specific valley in the structure band, causing a finite anomalous Hall voltage whose sign is controlled by the helicity of the light.

2D materials enables charge carrier generation by light absorption over a very wide energy spectrum, which present the photovoltaic effect, the photo‐thermoelectric effect, the bolometric effect, the photogating effect and the plasma‐wave‐assisted mechanism. Moreover, 2D materials have ultrafast carrier dynamics, wavelength‐independent absorption, tunable optical properties via electrostatic doping, low dissipation rates and high mobility, and ability to confine electromagnetic energy in small volumes.

By far many applications have been developed using 2D materials. For example, graphene layers are used as electrodes with tunable work function, while TMDs are applied as photoactive material due to the strong light‐matter interaction and photon absorption. Other applications such as transparent electrodes in displays, photovoltaic modules, photodetectors, optical modulators, plasmonic devices, and ultrafast lasers are also developed. 2D TMDs exploit their primary figure of merit and low room‐temperature photoluminescence quantum yield (QY) for applications such as light‐emitting diodes, lasers, and solar cells based on MoS2

**Some Other Interesting Application of 2D Materials**

**4.1 Graphenes and High-energy physics**

The simple geometrical arrangement leads to the appearance that the electrons and holes in graphene have an unusual degree of internal freedom, usually called pseudospin, which mimics the spin, or internal angular momentum, of subatomic particles. Similarly electrons and holes in graphene can be regarded as particles and antiparticles in quantum electrodynamics. At the same time, however, the velocity of the electrons and holes is only about 1/300 the speed of light. This makes graphene a test bed for high-energy physics: some quantum relativistic effects that are hardly reachable in experiments with subatomic particles using particle accelerators have clear analogs in the physics of electrons and holes in graphene, which can be measured and studied more easily because of their lower velocity. An example is the Klein paradox, in which ultra-relativistic quantum particles, contrary to intuition, penetrate easily through very high and broad energy barriers. Thus, graphene provides a bridge between materials science and some areas of fundamental physics, such as relativistic quantum mechanics.

**4.2 Biomimicry**

Biomimicry refers to the design of bioinspired functional materials with tailored properties for actuation, sensing, electronics, and communication and so on, it enables synthetic devices to mimic natural behavior. Polymer materials have previously been dominant in fabricating such functional biomimetic devices(such as artificial muscle and electronic skin) owing to their soft nature. However, recently, versatile and highperformance two-dimensional (2D) materials such as graphene and its derivatives have been studied and proven as promising alternatives in this area.

Take the largest organ in the human body, skin, as an example, it is self-healing and can provide a variable degree of touch sensitivity. Mimicking the functions of natural skins is widely accepted to be very important in the future for robots application.

A novel reduced graphene oxide foam (rGOF) shows temperature sensitivity based on thermoelectric effects in the graphene with assistance of its good electrical properties. The rGOF can respond rapidly to finger pressure owing to the finger heating effects. To inmitate more complex functions,a device shown in Figure 4.2 make use of various functional components including piezoelectric and electrically conductive layers as well as a healing substrate. Poly(N,N-dimethylacrylamide), poly(vinyl alcohol), rGO, and polyvinylidene difluoride are employed in this hybrid device.

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Figure 4.2 (a) Schematic of the hybrid e-skin and its pressure sensitivity.(b–e) Cross-sectional FESEM images of the hybrid e-skin showing microscopic structures and the boundary between functional layers. Scale bars are 30 μm, 5 μm, 3 μm, and 500 nm, respectively.(f)Photographs of the hybrid e-skin. Scale bar is 2 cm [59].

**Synthesis Strategies about 2D Materials**

Scientists have witnessed many fantastic properities of 2D materials, however, studying them in lab is one thing, while mass manufacturing is another. Progress depends not only on the basic science but also on the development of new ways to produce graphene on an industrial scale. In order to integrate them into a multitude of applications, it is essential to explore the reliable syntheses of single and few-layer 2D materials. The challlenges in the quest for methods of producing 2D materials mainly lies in how to syntheses them with controlled thickness and lateral size, which may be caused by the anisotropic crystal growth and strong chemical bonds in crystal structure.

Regardless of the challenges, by far, many strategies, such as micromechanical exfoliation, ultrasonic exfoliation, hydrothermal method, topochemical transformation, chemical vapor deposition method and so on, have been developed to synthesize high-quality nanosheets.

According to the principle of generating two-dimensional materials, we can divide theses synthetic strategies into top-down and bottom-up strategies. In the former approach, scientists carves nanoscale structures by controlled removal of materials from larger solids. While in the later approach, nanoscale materials are constructed from atomic or molecular precursors that can self-assemble into more complex structures.

**5.1 Top-down strategy**

This strategy applies physical-based or through chemical-based process to exfoliate layers from larger van der Waals solids. The physical top-down approach employs the use of mechanical force (which is used by Novoselov and Geim)or ultrasonic wave, whereas the chemical top-down strategy relies on chemical reaction.

**5.1.1 Micromechanical exfoliation**

Those that applies mechanical force are called micromechanical exfoliation, it is both versatile and economical, but the metod is impossible to scale up for industrial production. What's more, this method is applicable only for layered van der Waals solids, and several other factors (stoichiometry and stacking orders) also play the key roles in the successful fabrication of monolayer nanostructures.

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Figure 5.1.1 (a) An illustrative procedure of sonication-assisted exfoliation. The layered crystal is sonicated in a solvent, resulting in exfoliation and nanosheet formation

**5.1.2 Ultrasonic exfoliation**

To get higher efficiency and productivity, we can apply ultrasonic exfoliation, the details are shown in Figure 5.1.1 (a). Ultrasonic can provide the energy needed to break van der Waals bond, and with appropriate surface energies, suitable solvents can stabilize the exfoliated nanosheets against reaggregation.

**5.1.3 Lithium (Li) intercalation process**

Ultrasonic exfoliation is incapable of peeling off a single layer of 2D nanostructure; thus, lithium (Li) intercalation process is introduced. As is shown in Figure 5.1.2 (a), via electrochemical method, we can insert Li atom into layered materials, forming LixXS2(X represents transition metals) compound. After electrochemical process, the product is washed with organic solvent to remove residual electrolyte, followed by exfoliation and ultrasonication. The yield of this strategy for obtaining single-layer transition metal dichalcogenide(such as MoS2) is nearly 100%, however, the lithium intercalation must be controlled carefully, while preventing the formation of metal nanoparticles and precipitation of Li+.

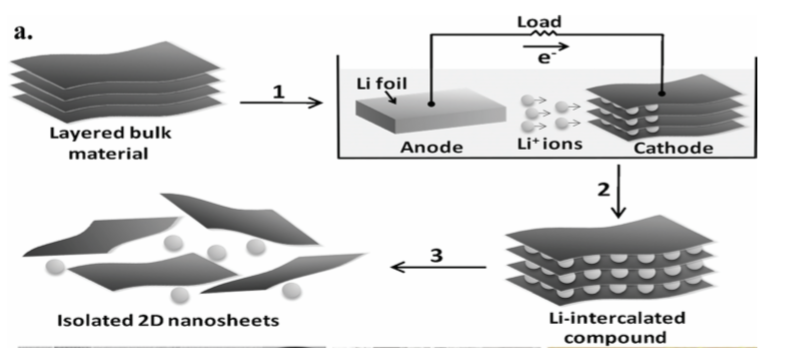


Figure 5.1.2 (a) Electrochemical lithiation process for the fabrication of 2D nanosheets from the layered bulk material

**5.1.4 Ion-change exfoliation**

Similarly, a method called ion-change exfoliation can be applied to exfoliate layered ionic solids such as LiCoO2 or LDHs, which have strong ionic bonds in the layers. The details are shown in Figure 5.1.3(a)

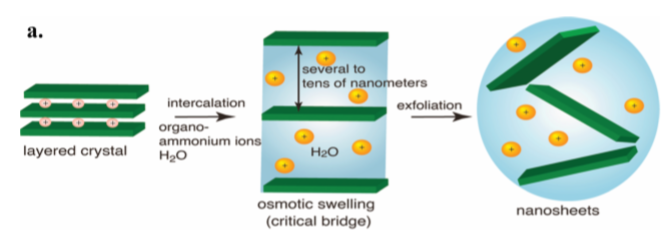


Figure 5.1.3(a) Schematic illustration of the osmotic swelling to exfoliation process

**5.2 Bottom-up strategy**

All exfoliation methods as mentioned above are only suitable to those materials whose crystals are layered, thus, for other 2D materials, we must constructed them from atomic or molecular precursors. It is also useful in preparing ultrathin and high-quality nanosheets with large lateral size.

Wet chemical strategy refers to chemical analysis using specific resolvent. It is a big kind of synthesis method, which includes hydro/solvothermal synthesis and template synthesis.

**5.2.1 Hydro/solvothermal strategy**

Hydro/solvothermal method is a common strategy for the synthesis of inorganic materials. It doesn't require high temperature and it is convenient to adjust reaction conditions. A typical procedure of hydro/solvothermal synthesis is to dissolve precursors in certain solvent, then the mixture is stirred for reaction and then transferred, dried under vacuum.

**5.2.2 Template strategy**

Template method includes complicating morphology of template by growing crystal confined in specific dimension and then removing template through high temperature or adjusting pH. By this way, nearly all types of nanostructure including quantum dot (0D), nanowire (1D) and nanosheets (2D) can be prepared. And many nonlayered structure 2D nanomaterials can be synthesized using the as-prepared 2D nanomaterials as the template, such as Fe2O3, Au, CuInS2 and so on.

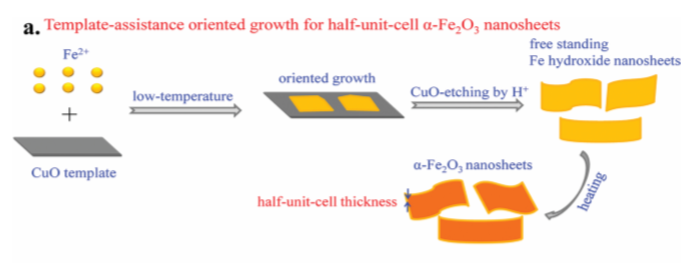


Figure 5.2.1 (a) Schematic of synthesis strategy of α-Fe2O3 nanosheets.

**5.2.3 Microwave-assisted strategy**

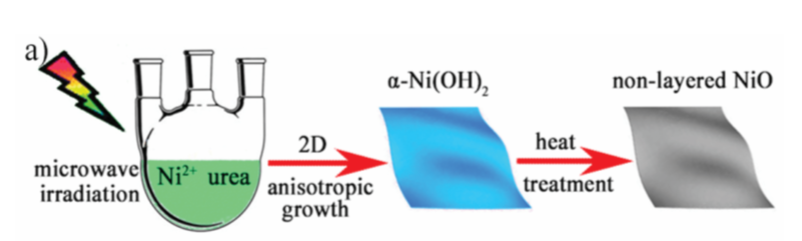
In recent years, microwave-assisted chemical synthesis strategy has been developed to promote and enhance chemical reactions. The main advantages of this method are represented by much shorter reaction time (generally in only a few minutes) and higher energy efficiency when comparing to other conventional strategies. For detailed steps, it resembles the traditional Hydro/solvothermal syntheses, but microwave-assisted liquid-phase growth can shorten the reaction time to less than 20 min.

Figure 5.2.2 (a) Schematic illustration for the synthesis of nanosheets.

**5.2.4 Topochemistry**

Topological conversion is also a new strategy, in which the product’s morphology is inherited from their precursor through nucleation and growth inside the precursors. For example, as illustrated in Figure 8a, the thickness of (001)-oriented few layered α-Co(OH)2 is closer to the thickness of (111)-oriented Co3O4 nanosheets. More specifically, the discrepancies between α-Co(OH)2 {100} (d=2.76 Å) and Co3O4 {220} (d=2.84 Å) are calculated to be below 3%. Moreover, Co2+ atomic arrangement in α-Co(OH)2 (001) plane and Co3O4 (111) plane is very closer (Figure 8b). These features enable atomically thick Co3O4 nanosheets to preserve the thickness of the precursor possible.

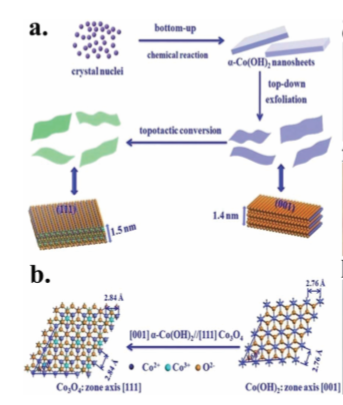


Figure 8. (a) Schematic illustration of the preparation of ATCNs. (b) Schematic model of the top-view illustrating the topochemical transformation from α-Co(OH)2 (001) plane to Co3O4 (111) plane.

**5.2.5 Chemical vapor deposition**

Chemical vapor deposition (CVD) technique has also shown promise to generate high-quality TM(transition-metal dichalcogenide) layers. CVD is a hightemperature chemical synthesis process by which a desired material is deposited on substrates. The detailed scheme of CVD method is shown in Figure 5.2.3. The precursor vapor is introduced from outside or generated inside the tube furnace. The main advantages of CVD synthesis process are represented by the accesses to high quality, high purity 2D nanomaterials with controlled properties, which allow one to control the morphology, crystallinity and defects of 2D nanostructures by tuning the process parameters . Due to these advantages, some 2D nanomaterals have been prepared by this way conveniently, such as graphene, MoS2, h-BN.图片包含 屏幕截图

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Figure 5.2.3 (a) Schematic illustration of experimental setup for the 2D materials synthesis by a noncatalytic vapor deposition process.

**Summary**

In summary, synthetic strategies, such as top-down and bottom-up method, have been employed for synthesizing two-dimensional materials. The top-down strategy, including micromechanical exfoliation, ultrasonic exfoliation, lithium-intercalated and exfoliation and ionchange exfoliation, is able to obtain high-quality and large-size two-dimensional crystal conveniently. Even so, this method is only appropriate for those materials whose crystals are layered. Comparatively, bottom-up strategy could overcome this shortage, which is composed of wet chemical method, microwave-assisted chemical, topological conversion strategy and chemical vapor deposition method. All these strategies present different features for manufacturing two-dimensional materials.

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iii