Review

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Fabrication, optical properties, and applications of twisted two-dimensional materials

https://doi.org/10.1515/nanoph-2020-0024
Received January 13, 2020; revised February 13, 2020; accepted February 14, 2020

Abstract: Two-dimensional (2D) materials such as graphene, black phosphorus, and transition metal dichalcogenides have attracted significant research attention due to their novel properties and wide range of applications in electronic and optoelectronic devices. In particular, investigation of twist-controlled 2D materials has attracted tremendous attention due to their excellent properties such as smooth heterointerfaces, highly gate-tunable bandgaps, and ultrafast carrier transport. Twist-controlled 2D materials combined with their fascinating electronic structures have also indicated their outstanding potential in electronic and optoelectronic applications. In this review, the recent developments in twisted 2D materials are summarized, covering aspects related to their fabrication, twist angle-dependent optical properties, and optoelectronic applications. The photodetectors and orientation-dependent van der Waals junctions are introduced and discussed systematically. Finally, we deliver a summary and outlook to provide a guideline for the future development of this rapidly growing field.

Keywords: twisted two-dimensional materials; optical properties; optoelectronics; twist angle; anisotropic properties.

1 Introduction

Properties of materials change dramatically with the change in the dimensions of material, as exemplified by the form transition from bulk graphite to two-dimensional (2D) graphene. Theorists predicted that, at room temperature, the physical reality of free-standing graphene was impossible due to the minimization of its surface energy [1, 2]. This speculation was overthrown after the discovery of graphene in 2004 by Novoselov et al. [3]. The discovery of graphene has inspired the development of many novel 2D materials. 2D materials, such as transition metal dichalcogenides (TMDs), hexagonal boron nitride (h-BN), and black phosphorus (BP), have become a major focus in the field of materials science [4–7]. Besides, many newly-emerging 2D materials have also attracted tremendous attention from researchers [8–13]. Based on different properties, 2D materials can be classified as, semiconductors, insulators, ferromagnetic semiconductors, topological insulators, metals, and ferromagnetic metals. Owing to their outstanding properties, 2D materials have a wide range of applications in fields such as electronic and optoelectronic devices [14–17].

The concept of heterostructures originated in the 1950s, when the hypothesis was to combine two different semiconductors to obtain different types of electrical devices. In 1963, Steele [18] presented a theoretical analysis of the van der Waals heterostructures (vdWHs) based on 2D materials. However, limited by the availability of the methods of fabrication, the possibility of physically adsorbing a single layer sample on the surface of the heterostructure was only theoretically analyzed.
In 2010, Hone et al. [19] explored the optoelectronic properties of the graphene-h-BN heterostructure, thus increasing the photoelectric performance of graphene by more than 10 times. Since then, researchers have acquired a variety of heterostructures by using progressively improved 2D material transfer techniques. This phenomenon thus inspires researchers to be so enthusiastic about the field to discover versatile ideas governing the fundamental phenomena in nature. Figure 1 displays schematic illustration of twisted 2D materials (T2DM). The T2DM introduced in this review include not only heterostructures, but also the stacking of the same type of 2D materials. The T2DM emphasize changes in energy bands, optical properties, and electrical properties caused by twisted angles. Compared with 2D materials, the T2MD not only have the properties of them, but research can modulate their properties by changing the twist angle, which has a tremendous significance in the applications of novel electronics and optoelectronics. In 2013, Geim and Grigorieva [20] systematically introduced and prospected T2DM for the first time. The interlayer coupling in T2DM was found to be weak at the interface, which not only induces new properties, such as bandgap opening in graphene [21], semiconductor band alignment [22], charge transfer [23] and new optical absorption [24], but also preserves the intrinsic properties of corresponding 2D materials. T2DM with these new properties can be effectively used to fabricate devices with novel electronic and optoelectronic applications, such as solar cells [25–30], field-effect transistors [19, 31–34], PN junctions [35, 36], PN diodes, and photodetectors [37–45]. For most T2DM, two different 2D materials are typically stacked. In fact, the stacking of the same type of 2D materials has also attracted tremendous attention of researchers. In 2018, Cao et al. [46] reported the realization of intrinsic unconventional superconductivity in a 2D superlattice created by stacking two sheets of graphene that were twisted relative to each other by a small angle. They found that the twisted bilayer graphene is a precisely tunable, purely carbon-based, 2D superconductor. It is therefore an ideal material for investigation of strongly correlated phenomena, which could lead to insights into the physics of high-critical-temperature superconductors and quantum spin liquids [46, 47]. In this review, after an elaborate introduction of synthesis of T2DM, their optical properties (including Raman spectroscopy, optical anisotropy, optical rotation, photoluminescence [PL], optoelectronic properties and other properties) are discussed (Figure 1), and the relationship between the structure and electronic properties is also reviewed. In the last part, we not only summarize recent progress in electronic and optoelectronic applications of T2DM, but also propose the future prospects of T2DM and provide an outline for prospective researches.

2 Fabrication methods

Herein, the recent development of various methods for preparing T2DM is reviewed. This section introduces isotropic 2D materials, such as graphene, molybdenum disulfide (MoS₂), and anisotropic BP. A convenient way to prepare twisted graphene samples is the thermal decomposition of the hexagonal faces of SiC single crystals. In 2008, Varchon et al. [48] unintentionally discovered the Moiré patterns when studying the multilayer graphene synthesized by this method. The area of the Moiré patterns is tiny, thus it can only be observed by scanning tunneling microscopy technology [49, 50]. However, the twisted graphene prepared by this method generally has a relatively large number of layers, and the size of the prepared sample is also quite small. Therefore, it can only be used for measurements by scanning tunneling microscopy, and it is difficult to meet the requirements of practical applications.

Graphene prepared by mechanical exfoliation technology has very high quality and has always been...
the preferential choice for researchers to study the properties of graphene. Notably, in the process of preparing graphene by mechanical exfoliation, there is a certain probability of folding [51–53]. In 2014, Wu et al. [54] found that the folded region forms a twisted multilayer graphene structure. The size of twisted graphene prepared by this method is generally between several micrometers and 10 micrometers, which can basically meet the needs of measurement such as Raman spectroscopy [55, 56]. The disadvantage of this technique is the low yield, and there is generally only one rotation angle on each sample, which is not conducive to systematically study the angle-dependent performance of the twisted graphene.

In recent years, with the continuous improvement of the chemical vapor deposition (CVD) technique, this technique has been successfully used in the preparation of a variety of T2DM [57, 58]. In 2013, by controlling the gas flow and pressure, Lu et al. [59] successfully synthesized twisted graphene at different rotation angles on copper substrate for the first time. In 2016, Kardynał et al. successfully processed the graphene-MoS$_2$ heterostructure and large-area twisted MoS$_2$ on the surface of the patterned silicon wafer. The overlap area of twisted graphene is generally several micrometers to several tens of micrometers [60]. All these studies laid the foundation for the CVD technique as an effective approach to fabricate other kinds of T2DM. Compared to other techniques, CVD has the advantage of high yield and can satisfy the requirements of T2DM for various stacking angles in experiments. Nonetheless, compared to the mechanical exfoliation technique, the quality of graphene prepared by CVD is much inferior, and CVD is currently suitable for fabricating only twisted bilayer graphene. Moreover, the CVD technique cannot precisely control the rotation angle between graphene. All these defects severely limit the application of the CVD technique in the preparation of T2DM. In summary, the relative twist angle of graphene is random when fabricated by these existing methods, and numerous samples must be fabricated to select one with the designated angle. Whereas, distribution of small twists with sizes as small as 0.1° is sufficient to generate a completely new property, thus the lack of the capability to control the twist angle seriously limits the general applications of these methods.

Based on femtosecond laser micromachining and a specific transfer technique, Chen et al. [61] developed a new method that could be used to fabricate twisted bilayer graphene and double twisted trilayer graphene with the designated twist angles, as illustrated in Figure 2A. Femtosecond laser is widely used in micromachining, because its machining precision is much higher than that of long pulse lasers. A single-crystal graphene is cut into two pieces by a femtosecond laser, with a pair of straight and parallel edges. Further, these parallel “cutting lines” play a key role for the control of the twist angles. Electrical devices always have regular shapes, such as the hall-bar structure, which benefits the measurement. This method also has the capability to fabricate twisted bilayer graphene with specific patterns. Graphene flakes are first cut into the required patterns by a femtosecond laser, and then the cutting-rotation-stacking (CRS) procedure is performed. Compared to other techniques, the CRS technique provides a method to investigate the angle-dependent electrical and optical properties of twisted multilayer graphene. Moreover, the most important contribution of the CRS technique is that double twisted trilayer graphene with arbitrary twist angles can be successfully fabricated by this method, which is an important breakthrough in the experimental research of twisted trilayer graphene.

In 2019, Lu et al. [47] developed a step-by-step stacking process for the preparation of twisted bilayer graphene with a graphite bottom gate (Figure 2B). Monolayer graphene, thin graphite and h-BN flakes (around 10-nm thick) were first exfoliated on SiO$_2$/Si substrate, followed by the “tear and stack” technique with a polycarbonate/polydimethylsiloxane stamp to obtain the final h-BN/twisted bilayer graphene/h-BN/graphite stack. Separated graphene pieces were rotated manually by a twist angle of around 1.2–1.3°. In order to increase the structural homogeneity, a mechanical cleaning process was further carried out to squeeze out the trapped blister and release the local strain. In order to avoid the uncertainty induced by thermal expansion of the transfer stage, all the stacking processes were carried out at a fixed temperature of 100°C, except that the final stacks were released at 180°C. The technique can not only be used for the preparation of heterostructures with highly accurate rotation alignment, but also has the potential to be scaled up using large area graphene single crystals, or TMDs, and it can also enable the function of various functional vdWHs.

For 2D materials with translational asymmetry, Yin et al. [62] observed 1D nonlinear optical edge states of a single atomic membrane of MoS$_2$. The electronic structure changes at the edges of the 2D crystal resulted in strong resonant nonlinear optical susceptibilities, allowing direct optical imaging of the atomic edges and boundaries of a 2D material [62]. By using the symmetry of the nonlinear optical responses, a nonlinear optical imaging technique was developed that allows for the rapid and all-optical determination of the crystal orientations of the 2D material at a large scale. Figure 2C shows the nonlinear optical images of a continuous monolayer MoS$_2$ membrane epitaxially grown by CVD. The second harmonic generation
(SHG) image revealed the polycrystalline nature of the uniform monolayer, and the average grain size was in the range from 20 mm to 40 mm. Although the grain boundaries were only a few atom sites in width, the crystal boundaries were clearly observed. Moreover, the nonlinear generation not only reveals the symmetry properties of the crystal, but also allows for the rapid mapping of crystal orientations (Figure 2D, E). Then, the preparation process of twisted anisotropic 2D materials was introduced. Anisotropic 2D materials, such as BP and rhenium disulfide (ReS$_2$), possess intrinsically in-plane anisotropic properties that can be tuned for advanced applications, such as in
thin-film polarizers or polarization-sensitive photodetectors [65–70]. Noteworthy, the crystal orientations should be accurately determined before these materials are applied. Current methods for measuring the crystal orientation such as reflection and transmission spectra, photothermal detection (PTD), and polarized Raman-related techniques enable accurate determination of crystal orientation [71–74]. However, these techniques suffer from inevitable defects. For example, reflection and transmission spectra, and polarized Raman-related techniques suffer from significant uncertainty and unreliability because of complex interference, sample thickness, and background signals, which can be particularly strong on transparent substrates. Moreover, the PTD technique is limited by complicated and challenging sample preparation procedures. Concerning BP, one additional difficulty comes from its chemical instability under ambient conditions, which leads to the rapid loss of the device performance. Therefore, the development of a rapid, simple, and accurate method for accurate determination of the crystal orientation is extremely important. In 2015, Mao et al. [63] developed a polarized imaging technique that could be used not only to investigate the optical constants of BP, but also to determine the crystal orientation of anisotropic 2D materials. Figure 2F displays the experimental setup of the polarized optical microscope measurement system to facilitate the rapid detection of the orientation of BP samples. The light (mercury lamp) passes through a dichroic mirror, a focusing lens, and then illuminates the BP sample normally. Next, the reflected light passes through the dichroic mirror, the focusing lens, a polarizing film, and finally is detected by a charge coupled device. Then, via rotating the sample clockwise and analyzing the brightness of the reflected light through the charge coupled device, the optical anisotropy of BP can be observed accurately. As displayed in Figure 2G, H, Xin et al. [64] utilized a polarized optical microscope to determine the crystal orientation accurately, and then the stacking system was used to prepare twisted BP samples. More importantly, the techniques described above are not only suitable for the preparation of twisted BP samples, but also for other types of anisotropic 2D materials.

3 Optical properties

3.1 Optical absorption

The optical absorption of graphene is related to the stacking pattern between the layers of graphene. For single-layer graphene and Bernal stacked bilayer graphene, the optical absorption in the visible range is independent of frequency and the optical absorption of single-layer graphene is 2.3% [75, 76]. In contrast, for twisted bilayer graphene, the change of the band structure leads to the appearance of the van Hove singularities (vHSs) on the state density. The photoconductivity of twisted bilayer graphene is proportional to the density of states (DOSs) [77, 78], which also leads to the appearance of sharp peaks in the absorption spectrum. Moreover, the relationship between the band structure and the twist angle also gives rise to the change of corresponding optical absorption of twisted bilayer graphene. Figure 3A, B illustrates the relationship between the optical absorption and the twist angle [79]. Similar to the DOSs, the peaks of optical conductivity can be divided into three categories. During the process of increasing the rotation angle from 0° to 30°, the peak (i) evolves toward high energy and the peak (ii) moves toward low energy, while peak (iii) remains unchanged. These three types of absorption peaks have been successfully observed experimentally [57, 77, 80, 81]. For the peak (i), when the stacking angle is large, the absorption peak is located in the visible range. Moreover, with the decrease in angle, the absorption peak gradually moves toward the mid-infrared (IR) wavelengths. Furthermore, the photoconductivity of the twisted graphene in the ultraviolet band and terahertz bands has also been studied. It was found that although the twist angle significantly influences the optical conductivity of the bilayer graphene, the relative position between two layers does not influence the photoconductivity. In other words, the relative translation of the two layers does not affect the optical absorption of incident beams when the twist angle remains invariant.

To date, the basic optical properties of the twisted graphene such as band structure, absorption spectrum, and Raman spectroscopy have been mainly focused upon. Further study of advanced optoelectronic devices using twisted graphene is limited by sample preparation techniques. Based on the preparation of twisted graphene by the CRS method, the application of twisted graphene in optoelectronics was systematically studied by Chen et al. in 2015 [61]. The vHSs caused by the stacking angle of the twisted graphene result in the appearance of new absorption peaks in the absorption spectrum. By modulating the twist angle, these new absorption peaks can be continuously changed in the spectrum. The optical absorption of ordinary Bernal stacking bilayer graphene in the visible range is only about 4.6%. The development of graphene-based optoelectronic devices is limited by the weak interaction between graphene and incident beams. Chen et al. [61] proposed a total internal reflection (TIR)
method to enhance the interaction between incident beams and graphene. The absorption of graphene and twisted bilayer graphene was significantly enhanced by this technique. Figure 3C exhibits the preparation of the twisted bilayer graphene with stacking angles of 10° and 13° on SiO₂ substrate by the CRS technique. For comparison, a monolayer graphene and a Bernal stacking bilayer graphene were processed into the same pattern by using a femtosecond laser. Then, the optical absorption scanning imaging technique was performed on different graphene samples. Four different types of graphene samples were integrated on the same SiO₂ substrate: twisted bilayer graphene with rotation angles of 10° and 13°, Bernal stacking bilayer graphene, and monolayer graphene. Different samples were investigated at 514 nm and 633 nm, and the corresponding results are displayed in Figure 3E, F. The phenomenon that twisted graphene with different stacking angles of 13° and 10° is significantly different from other types of graphene under the excitation of different wavelengths indicates that absorption enhancement of twisted graphene is obviously amplified. In order to observe enhancement in the absorption of twisted bilayer graphene under the TIR, a linear scanning technique was utilized to characterize different graphene samples. As displayed in Figure 3D, compared to Bernal stacking bilayer graphene, the optical absorption of twisted graphene gets enhanced by about 35%. Owing to the enhanced optical absorption of graphene under TIR, the absorption peak of graphene due to the twist angle can be observed clearly, thus the stacking angle of the bilayer graphene can be resolved by TIR absorption imaging. In order to verify the angular resolution of absorption imaging for irregular patterns, Chen et al. [61] performed absorption imaging experiments on irregular samples with different rotation angles. The consequences indicated that the monolayer graphene, Bernal stacking bilayer graphene, and twisted graphene with different stacking angles could be distinguished by optical absorption under TIR mode. Therefore, this technique is capable of distinguishing the twist angles of graphene.
3.2 Raman spectroscopy

Raman spectroscopy is a commonly employed technique for characterizing 2D materials and it is used to efficiently explore all phonon modes of these materials. The crystal structure, lattice symmetry, and the presence of defects and impurities can be obtained based on the investigation of the modes of phonon [82–86]. Raman spectroscopy also provides key information for comprehensive understanding of the mechanical, thermal, electrical, and optical properties of 2D materials. In this section, we review recent progress of Raman spectroscopy of T2DM. The difference between twisted bilayer and the ordinary Bernal stacked graphene is that twisted graphene has a twist angle, which makes it exhibit characteristics different from those of single-layer graphene and bilayer graphene [51, 53, 87, 88]. In the vicinity of the Fermi level, the electron band of single-layer graphene is linear, while that of Bernal stacked double-layer graphene is a quadratic curve. Figure 4A illustrates that for twisted bilayer graphene, the Brillouin

![Diagram](51x150 to 533x567)

Figure 4: Electronic band structure and twist angle-dependent Raman spectroscopy of twisted bilayer graphene. (A) Brillouin zone of twisted bilayer graphene misoriented by \( \theta \). The distance between two near-by Dirac cones is \( \Delta k \) [89]. (B) Schematic illustration of band structure of twisted bilayer graphene [79]. (C) The twist angle-dependent Raman spectroscopy of twist bilayer graphene [89]. (D), (E) The relationship between the strength of Raman mode \( R' \) and the twist angle when measured with wavelengths of 1.96 eV and 2.41 eV [59]. (F) Raman spectra of chemical vapor deposition (CVD) grown twisted bilayer graphene with different twist angles on Si/SiO\(_2\) substrates. The color of the curve represents the different energy of incident beams: 1.96 eV for red, 2.41 eV for green, and 2.54 eV for blue [90].
zone of the top and bottom layers of graphene rotates, the Dirac cone is coupled, and the band structure of the overlap region changes, which leads to the band structure exhibiting a linear distribution in the vicinity of the Fermi level [89]. Figure 4B displays the schematic illustration of band structures of twisted bilayer graphene along the line \( K'^{(1)} - K'^{(2)} - K^{(2)} - K^{(1)} \) in the extended zone scheme. Herein, dashed and solid dispersions represent the energy bands of the top and bottom layers, respectively. The interlayer coupling results in band anticrossing at the intersection, and the resultant energy band is characterized by saddle points accompanied by the vHSs in the DOSs. These saddle points can be classified into the following three types: (i) and (ii) caused by the band intersection between different layers, and (iii) derived from the band structure of original single layer graphene [79]. Similar to its electron band structure and optical absorption, the strength of the Raman spectrum depends on the stacking angle. Figure 4C, E displays the variation of Raman spectroscopy of twisted graphene with the change in the stacking angle [59, 89]. When the twist angle is smaller than 8°, a new characteristic mode appears in the Raman spectrum due to the strong coupling, and when the twist angle is greater than 13°, the Raman spectrum of twisted bilayer graphene becomes similar to that of the single layer graphene. Figure 4F displays the new Raman mode induced by a twisted graphene superlattice, which is marked by \(*\), and the frequency of this Raman mode changes with the twist angle. The Raman mode \( K' \) located on the right side of the G peak is generated by the double resonance Raman scattering in the valley [90]. Figure 4D, E indicates that the Raman mode only appears when the twist angle is quite small; besides, the twist angle corresponding to the maximum value of the signal is related to the energy of the incident beam.

The Raman modes of graphene, such as G and 2D bands, also change with the variation in the twist angle in Raman spectroscopy of twisted bilayer graphene [89]. The Raman mode of G peaks for single-layer and twisted bilayer graphene with different stacking angles is displayed in Figure 5A. Compared to single layer graphene, the G peak of twisted graphene has a slightly larger full width at half maximum (FWHM) while the center location shows a slight shift towards red. Figure 5B illustrates that unlike its width and peak position, the G mode intensity at a laser wavelength of 633 nm is, however, extremely angle-dependent. The consequence indicates more than a 30-fold increase of G peak intensity at 10° and 11°, compared to that at other angles, where the intensity is largely angle-independent. Figure 5C displays that G peak enhancement occurs at higher angles (13°) with a larger laser excitation energy of 2.41 eV. The inset of Figure 5C shows a linear relationship between the experimental laser energy and the rotational angle at which G peak enhancement is observed. Figure 5D–G displays the effect of the stacking angle on the intensity, position, and FWHM of 2D mode in twisted bilayer graphene. It should be emphasized that the Raman 2D peak of the twisted bilayer graphene is a single peak, rather than splitting into four peaks such as in the case of the Bernal stacking graphene.

In 2017, Mao et al. [91] explored the Raman spectroscopy of the BP-Bi\(_2\)Se\(_3\) heterostructure. Taking advantage of polarized Raman spectroscopy, they demonstrated that layered BP with a nanometer thickness could remarkably alter the polarization state of a linearly-polarized laser and behave as an ultrathin optical polarization element in a BP-Bi\(_2\)Se\(_3\) stacking structure, by inducing exceptionally polarized Raman scattering of isotropic Bi\(_2\)Se\(_3\). The BP-Bi\(_2\)Se\(_3\) stacking structure is schematically illustrated in Figure 5H. The results indicated that the polarization of the incident beam passing through the thin BP layer and interacting with Bi\(_2\)Se\(_3\) was different from that of the incident light on the BP surface. Figure 5I illustrates that the Raman spectrum of the BP-Bi\(_2\)Se\(_3\) stacking structure in the overlapped region is comprised of the Raman modes from both crystals. The typical Raman modes \( A_{1g}^1 \) (72 cm\(^{-1}\)), \( E_{2g}^2 \) (130 cm\(^{-1}\)), and \( A_{1g}^2 \) (173 cm\(^{-1}\)) belonging to Bi\(_2\)Se\(_3\) are observed in Figure 5I. The inset shows the corresponding atomic displacements of these modes. In addition, the other three strong Raman peaks (marked in purple) originated from the \( A_{1g}^1 \) (362 cm\(^{-1}\)), \( B_{2g} \) (440 cm\(^{-1}\)), and \( A_{2g}^2 \) (366 cm\(^{-1}\)) modes of BP. Figure 5J demonstrates that the Raman modes of the Bi\(_2\)Se\(_3\) crystal under BP exhibit periodic variation features under parallel polarization due to the optical anisotropy of the BP sample. These findings clearly reveal a promising way to design novel optical polarization elements with nanoscale thickness based on 2D anisotropic crystals, which can be directly integrated in photonic and optoelectronic devices for polarization modulation.

### 3.3 Photoluminescence

In this section, we detail and review the recent reports in PL of 2D materials and T2DM. Due to the charge confinement and reduced dielectric screening effect, the existing forms of carriers in 2D materials have significantly different characteristics from bulk materials. Carriers are mostly in the form of excitons in 2D materials due to the strong Coulomb effect, and the exciton properties can be analyzed accurately by observing the variations of the PL spectrum.
of the materials [92]. Recently, several research groups have revealed the properties of excitons by PL measurement in different 2D materials, and even the features of many-body phenomena have also been discussed [93–97]. For example, in 2016 Lee et al. [97] studied the exciton, trion, and biexciton properties of MoS$_2$ monolayers at room temperature. In the experiment they observed that as the excitation laser power enhances the position of the PL peak and the FWHM will change. This indicates that, under the optical doping, the internal environment of the MoS$_2$ monolayer varies, which in turn causes the change of the biexciton population, as shown in Figure 6A, B. Similar experimental results are also reflected in chemical doping materials. In 2013, Mouri et al. [101] demonstrated the tunability of the PL properties of monolayer MoS$_2$ [101]. The PL intensity was drastically enhanced by the adsorption of p-type dopants with high electron affinity; however, it was reduced by the adsorption of n-type dopants. This PL modulation results from switching between exciton PL and trion PL depending on carrier density in the MoS$_2$ monolayer.

Figure 5: The Raman spectroscopy of twisted bilayer graphene and BP-Bi$_2$Se$_3$ stacking structure. (A–C) Change in the strength of Raman mode G with twist angle at different wavelengths. (D–G) The twist angle-dependent intensity of Raman mode 2D peak, position, and full width at half maximum [89]. (H) Schematic illustration of the BP-Bi$_2$Se$_3$ stacking structure. (I) Raman characterization of the BP-Bi$_2$Se$_3$ stacking structure on SiO$_2$/Si substrate. Insets show the A$_{1g}$ (72 cm$^{-1}$), E$_1$ (130 cm$^{-1}$), and A$_{2g}$ (173 cm$^{-1}$) Raman modes in Bi$_2$Se$_3$. (J) Polar plots of the angle-resolved polarized Raman intensities for the A$_{1g}$ mode with 514.5 nm (red dots) and 632.8 nm (green dots) excitations [91].
The above results indicate that the carrier transport characteristics in a 2D material are greatly affected by the environment. With the rising research of the vdW stacking system, it has also been found that the types of materials and stacking formations have had a significant influence on the exciton properties [102]. This provides a new degree of freedom for the modulation of exciton performance in 2D materials. In 2014, Fang et al. experimentally observed the electronic structure and optical properties of TMD heterostructures for the first time [98]. They fabricated some WSe2/MoS2 heterobilayers on Si substrate and then compared the PL spectrum at different positions on the samples, either on the monolayer samples or at their overlapping locations. The measurement results are shown in Figure 6C. Because of the strong interlayer coupling of charge carriers at the overlapping, a Stokes-like shift between the PL and absorbance peaks was observed. This exhibits an approximate relationship between the donors and acceptors in organic semiconductor heterostructures, suggesting a typical spatially direct to indirect transition in a type II band structure, including sometimes showing new peaks related to the interlayer exciton and strong quenching phenomena at the junction area (Figure 6D) [35, 103, 104]. Further time-resolved PL results present that the lifetimes of the interlayer excitons can be an order of magnitude longer than those of the excitons in monolayers [104]. Moreover, the thermal annealing operation also has a great influence on the interlayer coupling of carriers, which is identified by the appearance of new peaks or the shift of peak positions in the PL spectrum [105].

Although many works mentioned above have found the key role of interlayer excitons in the heterostructures,
most of them have not considered the system properties changes caused by such as precise stacking or misaligned lattice in the same material system, which has obviously been shown to have a significant influence [102]. For example, in 2014 Liu et al. [106] conducted a detailed analysis of the relationship between the twist angles and the interlayer coupling in MoS2 bilayers (MoS2/MoS2). The PL results show that with the change of the twist angle, the peak related to the monolayer Brillouin zone remains, but the peak related to the interlayer electronic coupling has been significantly shifted. At 0 and 60 degrees of twisting, the FWHM of this peak is the broadest. By using the \textit{ab initio} calculations, they found that the steric effects resulting from the different interlayer separations between play a key role here. Afterwards, the researchers on the evolution of interlayer coupling with twist angles in different T2DM systems are detailed [99, 107, 108]. For example, Kunstmann et al. [99] researched the system composed of different 2D materials (MoS2/WSe2) for this problem. Figure 6E shows the PL results. They found that as the angle changes, the interlayer exciton becomes more important in energy shift than an exciton and trion. Through the density functional theory calculations, they found that the process of \Gamma – K interlayer transitions matched the experimental results well. At the same time, they also found that the energy shift is closely related to the mean layer separation between material layers, as shown in Figure 6F, G. When there is a twisted angle between layers rather than the AA or AB stacking formation, the interlayer exciton transition energies will be enhanced because of the incommensurability and lattice mismatch. With the continuous development of these works, people are aware of the importance of property changes of the T2DM system caused by the twist angle [46, 109]. So, with the introduction of some important work in 2019, a new concept—moiré exciton—is being mentioned more and more [100, 110–112]. The relative rotation between layers in T2DM will form superlattice marked as moiré patterns, which will further form a periodic moiré potential in the material system to affect the interlayer electronic coupling. This potential will periodically regulate the carrier transition and lead to new physical phenomena. Alexeev et al. [100] studied the exciton hybridization of the MoSe2/WS2 system in detail in 2019. Because of the near-degeneracy at their conduction-band edges, the materials mentioned above are ideal for studying the problems of moiré excitons. For example, due to the spin-orbit splitting, sub-bands at the conduction and valence band states in both materials will be created, which lays the foundation for interlayer hybridization of excitons, as shown in Figure 6H, I. The PL measurements of this system have shown that the peaks of the PL spectrum are periodically shifted, which directly proves the role of moiré excitons in the interlayer coupling process, as shown in Figure 6J. The above research shows that the PL measurement is a very reliable means to study the exciton transition. As developed, many potential applications of the T2DM system may be revealed. More detailed information can be seen in Section 4.3.

### 3.4 SHG

Recently, research on the nonlinear optical effect on the 2D materials has indicated that these materials exhibit a large nonlinear optical response compared to the traditional nonlinear materials. For example, second-order optical nonlinear coefficients of MoS2, WS2, and WSe2 are two to three orders larger than those of the commonly used nonlinear crystals [113–120]. This large nonlinear coefficient can also be tuned by the hot carriers and electric field, and enhanced by the excitonic resonance. Owing to these characteristics, these 2D materials are desirable for on-chip frequency conversions such as SHG and terahertz generation for integrable devices [121–125]. The ability to control the stacking structure in layered materials could provide an exciting approach to tuning their optical and electronic properties. Owing to the lower symmetry of each constituent monolayer, h-BN allows more structural variations in multiple layers than graphene. However, the relationship between structure and property in this system remains largely unexplored. In 2013, Kim et al. [126] reported a strong correlation between the interlayer stacking structures and optical and topological properties in chemically grown h-BN bilayers, measured mainly by using dark-field transmission electron microscopy and optical SHG mapping. They discovered that there existed two distinct h-BN bilayer structures with different interlayer symmetries that gave rise to a distinct difference in their SHG intensities. In particular, the SHG signal in h-BN bilayers was observed only for structures with broken inversion symmetry, with intensity much larger than that of the single layer h-BN. Figure 7A displays the dark-field transmission electron microscopy image of a region containing both AB and AA’ stacking configurations with similar electron diffraction patterns. Figure 7B shows an image of SHG intensity measured for the same region. Notably, the strong signal observed only from the AB stacking region clearly arises from a nonlinear two-photon SHG process, as the signal increases quadratically with the incident laser intensity. Furthermore, a polar plot of the parallel component of the SHG signal (inset, Figure 7B)
measured as a function of the relative angle between the in-plane polarization of the incident laser and the sample exhibits a clear six-fold symmetry. Moreover, it also shows its minimum (maximum) values when the incident laser polarization is parallel to the zigzag (armchair) orientations of h-BN. Figure 7C displays the broadband absorption spectra measured from monolayer and bilayer h-BN in two different stacking regions. The dominant absorption peaks appear at 6.1 eV for all three regions with no observable difference between AB and AA' stacking regions in the peak amplitude. These findings thus confirm that the strong SHG intensity variation in h-BN bilayers is mainly caused by the difference in the local lattice symmetry. In 2014, Hsu et al. [127] explored the SHG from homo- and
heterostructural TMDs bilayers formed by artificial stacking with an arbitrary stacking angle. The SHG from the twisted bilayers is due to a coherent superposition of the SH fields from the individual layers, with a phase difference depending on the stacking angle. A proof-of-concept demonstration of using the SHG to probe the domain boundary and crystal polarity of mirror twins formed in chemically grown TMDs was also presented. All these findings clearly indicate that the SHG is an efficient, sensitive, and nondestructive characterization technique for determining the stacking orientation, crystal polarity, and domain boundary of vdWHs.

Figure 7D displays a particular bilayer with a stacking angle of 25° between flakes 1 and 2. Figure 7E indicates that the SHG experiment was performed in a back-reflection geometry using a pump laser normally incident on the sample. The SH light from the stacking region also shows a six-petalization pattern, but with petals lying along a direction between the two nearest perpendicular bisectors of flakes 1 and 2. This result clearly indicates that the SHG from the stacking region is not contributed independently from individual flakes. The polarization-resolved SHG of individual flakes (measured under the parallel polarization configuration) exhibits a six-petal pattern, with petals lying along the perpendicular bisectors of each flake. This also agrees with the transmission electron microscopy analysis, which indicates that the perpendicular edges of the MoS2 triangles are aligned with the armchair (zigzag) directions. Interestingly, the SH light from the stacking region also shows a six-petalization pattern (Figure 7F), but with petals lying along a direction between the two nearest perpendicular bisectors of flakes 1 and 2. This clearly reveals that the SHG from the stacking region is not contributed independently from individual flakes. More importantly, light-frequency conversion based on 2D materials is of great importance for modern integrated photonics.

In 2019, He et al. [128] explored both the intrinsic and extrinsic second-order nonlinear coefficient tensor from graphene/WX, vdWHs by first-principles calculations. The enhanced nonlinear optical response in the IR band could be achieved in graphene/WS, vdWHs, resulting from the interlayer charge transfer between graphene and WS2. The value of the intrinsic second-order nonlinear coefficients of graphene/WSe2 vdWHs was found to be 1.5 times larger than that of pure monolayer WSe2 at the bandgap energy of the WSe2 monolayer. This is attributed to the enhanced carrier generation after the heterostructure formation. Different from pure monolayer WX, azimuthal angle-dependent SHG from graphene/WX, vdWHs exhibits extraordinary rotational symmetry at different photon energies, which can be utilized to deduce the extrinsic second-order nonlinear coefficient. All these findings pave the way for the design of the nonlinear optical coefficient based on 2D heterostructures for nonlinear nanophotonics and integrated devices. Figure 7G shows that the nonlinear coefficients (d15 and d24) in graphene/WS2 heterostructures are enhanced within the IR region. The nonlinear coefficient d15 of graphene/WS2 heterostructures within the IR region is about two orders of magnitude greater than that of famous nonlinear crystals. In order to better understand the enhancement of second-order nonlinear coefficients, a schematic illustration of carrier generation within the IR band for graphene/WS2 is displayed in Figure 7H and the enhanced carrier generation at K point for graphene/WSe2 is presented in Figure 7I. Figure 7H demonstrates that the charge density differences of graphene/WSe2 vdWHs reveal that some of the conduction bands and valence bands in graphene/WSe2 rely on both graphene and WSe2. This indicates that the wave function mixing is higher in graphene/WSe2 with a stronger interlayer interaction in the heterostructures. As such, more photogenerated carriers can be shared between graphene and WSe2 after photoexcitation with 0.88 eV or 1.76 eV at the Γ point from graphene/WSe2, as shown in Figure 7I. These results clearly reveal that electronic band engineering by heterostructures could be used to control second-order nonlinear optical responses.

3.5 Other properties

It is well known that the chiral materials possess left- and right-handed counterparts linked by mirror symmetry. These materials are widely used in advanced applications of polarization optics, spintronics, and optoelectronics [129–133]. In particular, the realization of spatially uniform chiral films with atomic-scale control of their handedness could provide a powerful means for developing nanodevices with novel chiral properties. However, previous approaches based on natural or grown films or arrays of fabricated building blocks, could not offer a direct way to program the intrinsic chiral properties of the film on the atomic scale [134–138]. Furthermore, 2D materials can be used to fabricate the chiral materials due to their atomic thickness and novel properties. In 2016, Kim et al. [139] developed a chiral stacking approach, where 2D materials were positioned layer-by-layer with precise control of the interlayer rotation and polarity, which eventually resulted in tunable chiral properties of the final stack. The left- and right-handed twisted bilayer graphene samples
were fabricated by this method. This twisted graphene displayed one of the highest intrinsic ellipticity values (6.5 deg μm⁻¹) ever reported, and a remarkably strong circular dichroism (CD) with the peak energy and sign tuned by the stacking angle and polarity. They found that these chiral properties originated from the large in-plane magnetic moment associated with the interlayer optical transition. Furthermore, the chiral properties of atomically thin films were programmed layer-by-layer by producing three-layer graphene films with structurally controlled CD spectra. Figure 8A illustrates the approach for generating chiral twisted bilayer graphene with a precisely controlled interlayer structure. First, a monolayer graphene with a uniform crystalline orientation is grown. Then, the graphene is cut into multiple pieces and is stacked layer by layer with a controlled twist angle based on the known crystalline orientation, while rotating anticlockwise or clockwise to form left- or right-handed films, respectively, that are connected by a mirror plane. The chiral twisted bilayer graphene films were prepared by this method, where twist angle and handedness were controlled uniformly over several millimeters with a high yield of interlayer coupling. Figure 8B shows the electronic band structures (top images) and the cross-sectional schematics (bottom images) of left- and right-handed twisted bilayer graphene with spiral atomic arrangements of opposite handedness. Regardless of the handedness, the electronic band structure and the electrical and optical properties of twisted bilayer graphene could be tuned using the twist angle. However, the intrinsic chiral properties of bilayer graphene have not been explored yet. Figure 8C exhibits that the twisted bilayer graphene shows strong CD and absorbs left and right circularly polarized light by different amounts. The ellipticity (Ψ) spectra (or CD spectra) were measured from the left-handed (red) and right-handed (blue) twisted bilayer graphene samples with an

Figure 8: Chirality and birefringence of two-dimensional (2D) materials. (A) Schematic representation of chiral stacking process for generating left- and right-handed twisted bilayer graphene. (B) Electronic band structures (top images) and cross-sectional schematics with spiral atomic arrangements (bottom images) of left- and right-handed twisted bilayer graphene. (C) Ellipticity (Ψ) spectra, or circular dichroism (CD) spectra, measured from a pair of chiral twisted bilayer graphene films with an angle of 16.5° (red: left-handed, blue: right-handed) and single-layer graphene (gray) [139]. (D) Transmitted light intensity as a function of black phosphorus (BP) rotation angle under crossed polarization illumination. The red line depicts the fitting result. (E) Measured light ellipticity and its fitting as a function of rotation angle after the light propagates through a ~45 nm BP flake at different wavelengths. (F) Phase retardance as a function of BP flake thickness [140].
angle of 16.5°, and single-layer graphene (gray). It can thus be observed that unlike the CD spectra of single-layer graphene, which show negligible values over the entire measurement photon energy range, the CD spectra of left- and right-handed twisted bilayer graphene show two strong peaks, one with a positive sign and the other with a negative sign. Besides, Ψ measured from twisted bilayer graphene flips its sign depending on the handedness of the twisted bilayer graphene, whereas the two CD peak energies are similar to those of the interlayer transitions, indicating the direct correlation between the CD spectra and the structure of twisted bilayer graphene. All these findings clearly indicate that this fabrication process and tunable chiral properties can be extended from graphene to other 2D layered materials to form chiral atomically thin films. Besides, this technique could enable the production of multi-functional integrated circuits based on ultrathin devices with advanced electrical, optoelectronic, spintronic, and chemical sensing functionalities.

Noteworthy, birefringence is an inherent optical property of anisotropic materials introduced by the anisotropic confinement in their crystal structures. It enables easy manipulation of light propagation properties for various photonic and optoelectronic applications, including waveplates and liquid crystal displays. Furthermore, 2D layered materials with high anisotropy are currently gaining an increasing interest in research for polarization-integrated nanodevice applications, which advances the research on birefringent materials [141–147]. In 2017, Yang et al. [140] investigated the optical birefringence of three anisotropic 2D layered materials including BP. They observed a polarization-plane rotation of 0.05° per atomic layer at 520 nm. All these findings showed that the relatively large birefringence of anisotropic 2D layered materials can enable accurate manipulation of light polarization with atomically controlled device thickness for various applications where integrated, nanoscale polarization-controllers are required.

Figure 8D demonstrates that the transmitted intensity changes periodically with the flake rotation angle with a period of 90°. Further, the transmitted intensity is the lowest when the BP flake is rotated by 0° and 90° with respect to the incident light polarization. All these results indicate strong birefringence of the BP samples. Figure 8E presents the ellipticity change as a function of the flake rotation angle with respect to incident light polarization after the light passes through a 45 nm thick BP flake at three different wavelengths. The results indicate that the ellipticity is the highest when the flake rotation angle is either 0° or 90°. This is expected as no phase retardance occurs. By contrast, when rotation angle lies between 0° and 90°, the value of ellipticity decreases rapidly and this is attributed to the birefringence. Figure 8F illustrates the relationship between phase retardance and sample thickness at different wavelengths. These findings highlight that the relatively large birefringence of anisotropic 2D layered materials, such as BP, can facilitate accurate manipulation of light polarization with atomically controlled device thickness for various applications where integrated polarization-controllers at the nanoscale are required.

The absorption of graphene has been experimentally observed to have a universal value (2.3%) for incident beam in the visible spectral range [75, 148]. Graphene-based photonic and optoelectronic devices remain affected by the problem that most incident light does not interact with graphene for its atomic thickness. To date, several methods have been employed to enhance light-graphene coupling, including periodically patterned graphene, coverage of plasmonic nanostructures on graphene, and twisted graphene [149–153]. In 2013, Ye et al. [154] discovered that graphene exhibits strong polarization-dependent optical absorption under TIR. Compared to universal absorption of 2.3%, more absorption was observed for the s-polarized incident beam under TIR. They found that the polarization-dependent absorption optical properties of graphene were significantly affected by the angle of incidence and the layers of graphene. Based on the polarization-sensitive absorption effect, Wang et al. [155] proposed a method to accurately count the number of layers for both exfoliated and CVD graphene samples on a transparent substrate. The atomic thickness and strong broadband absorption of graphene caused it to exhibit very different reflectivity for s- and p-polarized incident beams in the context of a TIR structure, which was found to be sensitive to the media in contact with the graphene.

In 2012, Xing et al. [156] developed a novel optical sensor combining graphene and a microfluidic structure to achieve sensitive real-time monitoring of refractive indexes. The sensitive and real-time monitoring of the refractive index was demonstrated using a graphene-based optical sensor, with a broad dynamic refractive index range from 1.0 to 1.438, a fast response time of 10 ms, a high sensitivity of 10^7 RIU^-1, and excellent stability [156]. In 2014, based on the polarization-dependent absorption of graphene under TIR, Xing et al. [157] designed a graphene-based optical refractive index sensor with high resolution of 1.7 × 10^-8 and a sensitivity of 4.3 × 10^7 mV/RIU, as well as an extensive dynamic range. This highly sensitive graphene optical sensor enables label-free, live-cell, and highly accurate detection of a small quantity of cancer cells among normal
cells at the single-cell level. Furthermore, this also enables the simultaneous detection and distinction of two cell lines without separation [157]. It provides an accurate statistical distribution of normal and cancer cells with fewer cells. Moreover, the ultrahigh resolution and sensitivity of the sensor to refractive index measurements can be extended to other areas, such as drug discovery, environmental monitoring, and gas- and liquid-phase chemical sensing [158–161]. Manipulation of the polarization of light at the nanoscale is essential for the development of nano-optical devices. Owing to their anisotropy properties and structure, 2D layered BP, ReS$_2$ and ReSe$_2$ exhibit outstanding in-plane optical anisotropy with distinct linear dichroism and optical birefringence in the visible region, which are superior characteristics for ultrathin polarizing optics. In 2019, Xin et al. [162] studied the reflectance of few-layered BP in the TIR mode in detail. They demonstrated that its optical anisotropy can be changed on a large scale by varying the incident angles, polarization states, and in-plane rotation angles of the BP samples. All these findings pave the way to understanding the properties of BP more comprehensively, and providing guidance for developing new optoelectronic applications, in particular when BP and other atom-thick biaxial crystals are integrated with TIR devices. Figure 9A illustrates the process of measuring the optical anisotropy of the BP samples in the TIR condition. Figure 9B shows the reflectance of the BP after s- and p-polarized irradiation under the two conditions. A huge difference in reflectance intensities can be observed regardless of whether the sample is fixed to rotate the polarization states or fixed polarization is achieved to rotate the sample. The variation trend is shown in Figure 9C. This phenomenon is unusual in the reflectance measurement of isotropic 2D materials; nonetheless, it is common and interesting for testing the BP regardless of its thickness. In 2018, using the polarization-dependent optical absorption of 2D materials under TIR and a modulated pump beam, Gao et al. [72, 163, 164] developed the PTD technique to characterize the photothermal anisotropy of 2D materials and identify the crystal orientation. PTD is a refractive index sensing optical technique, in which a pump beam modulated by an acoustic-optic modulator (AOM) is absorbed by BP or ReS$_2$, which leads to thermal diffusion and a local change in the refractive index of the photothermal medium. The propagation of the probe beam at different wavelengths is modified by the produced periodical change of the refractive index in the photothermal medium. Figure 9D, E shows the experimental setup of the PTD system. The linearly-polarized pump laser (at 532 nm) polarization angle is varied using a half-wave plate, and then the heating beam enters an AOM operated at 1 kHz. A wave generator provided an intensity modulation signal for the AOM and reference lock-in amplifier. The circularly-polarized probe laser beam (at 632.8 nm) is adjusted using a polarized and quarter-wave plate and focused at the center of 2D materials. The adopted balanced detector, consisting of two well-matched photodetectors, is used to detect the local changes of the refractive index in the photothermal medium. The 2D materials not only act as a heat source for the photothermal medium, but also allow the detection of minor photothermal signals as sensing layers. Figure 9F, G demonstrates the exploration of the relationship between the polarization angle of the pump beam and the intensity of the photothermal signal, for evaluating the photothermal anisotropy of BP and ReSe$_2$. It was demonstrated that layered BP with different thicknesses could remarkably change the photothermal contrast. In contrast, the photothermal contrast of ReSe$_2$ did not change with the variation in the thickness of the samples. Furthermore, the photothermal anisotropies of BP/ReSe$_2$ heterostructures were also explored. The photothermal contrasts of samples were observed to change with different stacking angles, indicating that the photothermal anisotropy of heterostructures is dependent on the stacking angle. It was believed that this phenomenon is caused by the linear superposition of two different degrees of optical anisotropy. These findings indicate a promising way to design novel optical in-plane anisotropy elements with 2D anisotropic materials, which can be directly integrated into photonic and optoelectronic devices for anisotropy modulation. Besides, the PTD technique has been used to identify the crystalline orientation of anisotropic 2D materials. Compared to other techniques, the PTD technique has the following advantages. First, the photothermal signal is background-free as it relies on the signal issued from the sample absorption, which then thermally diffuses to the surroundings, thus inducing an increase in the contrast when compared with the transmission/reflectance spectroscopy technique. Then, the low intensity of the pump and probe beams used in the experiments would not harm the samples, overcoming the limitations of the weak Raman signals when the BP samples are exfoliated on the transparent substrates. Besides, the PTD technique is robust, as it is independent of the probe and pump laser wavelength and the sample thickness. Moreover, this technique could be applied to all anisotropic materials, which can significantly facilitate the study of anisotropic 2D materials.
4 Optical applications

4.1 Photodetector

Since graphene has been proven to be a light-harvesting material, photodetectors based on different 2D materials have been reported endlessly [165]. To solve the inherent problem of weak photoabsorption of 2D materials, different architectures have been optimized to improve the light response [166–168]. One of the methods involves the preparation of the vdWHs as the light-harvesting material [169]. Although most researches focus on the effect of p-n or Schottky barriers at the 2D material interface, some studies have also been reported on the application of strong coupling in twisted materials for an enhanced photoresponse.

As previously reported, the energy band structure of twisted bilayer graphene can be regarded as the shift and overlap of energy bands of two monolayer graphene in Figure 9:

Figure 9: Photothermal properties of twisted two-dimensional materials (T2DM). (A) Schematic representation of the optical anisotropy of few-layered black phosphorus (BP) under total internal reflection (TIR). (B) The reflectance of BP under the s- and p-polarized irradiation under two special conditions. (C) Top: the changing process of reflectance with the change in the rotation angle of the sample, corresponding to the trend shown in Figure 8B (dashed arrows). Bottom: the polarization-dependent reflectance when the position of BP is fixed, corresponding to the solid arrows indicated in Figure 9B [162]. (D) Schematic illustration of the photothermal detection experiment setup including the mirror (M), the acoustic-optical modulator (AOM), the dichroic mirror (DM), the polarization beam splitter (PBS), the balanced detector (BD), the half-wave plate (l/2), the lock-in amplifier, and the data acquisition system. (E) Schematic representation of the essential parts, which consist of a coverslip, polydimethylsiloxane (PDMS) channel, BP or rhenium disulfide (ReS₂) and a prism [72]. (F, G) Photothermal detection of BP/ReSe₂ heterostructures [163].
k space (Figure 10A). Strong interlayer coupling results in two saddles and a minigap at the M points on both sides of the Dirac point. Correspondingly, there exist two VHSs in the DOSs, the positions of which are determined by the twist angle \[\theta\] [172]. The theory predicts that an approximately linear relationship exists between the singularity energy difference (E\text{VHS}) and the twist angle \[\theta\], which has been confirmed by the micro angle-resolved photoemission spectroscopy, as shown in Figure 10B, C [170]. When the energy difference and the incident photons energy match each other, the enhanced photoresponse can be generated. Based on this idea, in 2016 Yin et al. [170] and Tan et al. [173] applied the CVD twisted bilayer graphene for photodetection for the first time. They grew the twisted bilayer graphene domains with different twist angles on copper substrates, and selected two unique samples with twist angles of 13° and 10.5° to transfer to the heavily doped Si substrate (90 nm SiO\textsubscript{2}) for device fabrication. Figure 10D shows the schematic structure of the device. The incident-photon dependent photocurrent measurements show that the different samples have different light-sensitive wavelength regions, which is in good agreement with previously reported photoabsorption theories (Figure 10E). Using this photodetector, they exhibited a 6.6-fold photocurrent enhancement. By combining with metal plasmon nanostructures, they further demonstrated that the photoresponse could be enhanced by about 80 times (Figure 10F).

Interestingly, similar results were also reported by other groups at about the same time. Chen et al. [61] first measured the photoresponse of twisted bilayer graphene samples in a TIR mode. They found that photocurrent has significant polarization-dependent properties, and the phenomenon is more obvious at the interface between the gold electrodes and graphene (Figure 10G). Soon afterwards, Xin et al. [171] conducted a more detailed study on a traditional Kretschmann configuration system. They fabricated different graphene samples (monolayer, bilayer, trilayer, 10.0° and 12.0° twisted bilayer graphene) as
light-harvesting materials in the typical metal-grapheneformal architecture photodetectors. The detailed comparison results show that it is indeed the strong interlayer coupling in twisted bilayer graphene rather than the pure thickness that plays a greater role in the photoresponse enhancement. In addition, by employing Maxwell’s equations for theoretical analysis in a multilayer material model, they found that the surface plasmon resonance of the gold electrode aided in the determination of the polarization-dependent characteristics of the device. That is why the photoresponse produced by the transverse magnetic (TM) mode is about 1.8 times larger than that produced by the transverse electric (TE) mode. By operating this device in the TIR mode, they achieved up to seven times enhancement in photovoltage. Figure 10H–J shows the schematic illustration of the structure of the sample, the polarization-dependent photoresponse, and the simulated photoabsorption of TM and TE incident light, respectively.

4.2 Orientation-induced photodiode

Unlike conventional in-plane isotropic 2D materials, anisotropic 2D materials provide the possibility for unidirectional modulation of carriers’ properties in a low-dimensional space, which gives them great potential in the application of new micro/nano optoelectronic devices [174–176]. However, the system stacking anisotropic materials together for applications of interface coupling has rarely been reported. As one of the important members of anisotropic 2D materials, BP was first studied in recent years [65]. Moreover, in 2016 the electronic structure and optical transitions of a bilayer BP system with an interlayer twist angle of 90° were also studied first in the anisotropic vdWHs structure (Figure 11A) [177]. Cao et al. [177] employed a supercell approach and carried out a detailed theoretical analysis of the band structure of this architecture. They found that the bilayer system presented astonishing in-plane isotropic properties although any one of layers was anisotropic (Figure 11B), which is greatly distinct from that of a naturally stacked bilayer. They further applied an out-of-plane electric displacement field (0.2 and −0.2 V/Å) to the structure. Under the Stark effect, the band splitting leads to tunable polarization-dependent photoabsorption (Figure 11C).

The abovementioned phenomenon is mainly attributed to the architecture of only bilayer materials. With the increase in the thickness of the sample, the role of anisotropy in interface coupling is highlighted. For example, when the charge-transport condition is changed rapidly in low-dimensional anisotropic material, a new “orientation barrier” (OB) that may further affect the characteristics of the carrier is formed (Figure 11D). In 2018, Xin et al. [64] predicted and verified this phenomenon for the first time. Through the first-principles calculations and experimental analysis, they believed that an OB as small as 0.05 eV would exist in a 90°-twist stack few-layer BP system (Figure 11E). Affected by this barrier, the carrier exhibited unidirectional transportation. In order to prove this assumption, they constructed three devices with different architectures. Each of them exhibited obvious electrical rectifications with ratios of 6.8, 22, and 115, respectively. Figure 11F presents the typical rectified features, which can also be modulated by gate voltage. When the samples were exposed under light illumination, an enhanced photoresponse could be observed (Figure 11G). This is mainly attributed to the fact that the OB can cause a built-in electric field at the interface, and it further changes the carrier transmission characteristics under light exposure. Soon afterwards, they also performed scanning photocurrent imaging experiments focusing on different samples. These results not only verified the credibility of the existence of OB, but also demonstrated the sensitivity of the architectures to the polarization state of incident light (Figure 11H) [178, 180]. Unlike this work, Li et al. [179] prepared the twisted structures using different kinds of 2D anisotropic materials, for instance BP-ReS₂ (Figure 11I, J). Although type II band structures have been established, they are more concerned with the key role played by the crystal lattice here. Experiments show that under similar external conditions, the change of the crystal orientation of the materials may cause the intensity of the photoresponse to change by more than an order of magnitude. This also shows that the crystal lattice of the material has a great effect on the interlayer coupling effect when preparing the 2D heterostructure. With the abovementioned perspectives for only considering the coupling between materials, new potential orientation-induced micro/nano devices may be prepared. This can allow simplification of the experimental process, thus avoiding some complex operations such as the chemical doping technique.

4.3 Interlayer exciton laser

Changes in the dimensions of materials lead to variations in the exciton binding energy and band structure. Considering the effects of charge confinement and reduced dielectric screening, carriers in 2D materials mainly exist as excitons, which are bound states of electron-hole pairs
attracted to each other by electrostatic Coulomb forces [92]. The behavior of the excitons dominates the optical characteristics of the materials. Moreover, because of the strong interlayer electronic coupling in the T2DM, lateral confinement imposed by the deep moiré potential constrains the novel moiré excitons [181]. For example, Figure 12A shows a typical moiré superlattice formed by an MoSe\textsubscript{2}/WSe\textsubscript{2} heterobilayer with a small twist angle $\theta$ [182]. The theory predicts that the formation of a superlattice results in periodic topological phase transitions in the local phase space, which further leads to the spatially periodic modulation of excitons limited by different valley optical selection rules [184, 185]. This indicates that the interlayer excitons are moiré-trapped, as shown in Figure 12B. Subsequently, different groups have reported many experimental results for the detection of moiré excitons [99, 110, 111]. Seyler et al. [182] compared the PL spectra between a 2°-twist MoSe\textsubscript{2}/WSe\textsubscript{2} heterobilayer and two analogues with large twist angles (20° and 57°). Under low temperature (30 K) and excitation power (20 nW), a few narrow peaks close to the free interlayer exciton energy could be observed at around 1.33 eV in every sample. The difference is that, excited by the circular polarization laser, the dominant excitation component gets reversed with the increase in the twisted angle. At the same time, when a gradient out-of-plane magnetic field is applied to the samples, the Zeeman splitting of trapped interlayer excitons, which varies linearly with magnetic field intensity from −3 to 3 T, was obvious, as shown in Figure 12C. Similar phenomena have also been observed in other WSe\textsubscript{2}/WS\textsubscript{2} bilayers. Compared to the large-twist-angle system, the WSe\textsubscript{2} A exciton state in PL spectra splits into three peaks (I, II and III in Figure 12E). This also provides the evidence for moiré excitons in the sample with a near zero twist angle (0.5° ± 0.3°). The behavior could be tuned by applied gate voltages (Figure 12F). Recently, another exciting study reported by Paik et al. [183] pushed the application value of strong coupling of interlayer excitons to a new level. By integrating a heterobilayer WSe\textsubscript{2}/MoSe\textsubscript{2} material in a silicon nitride (SiN) grating resonator, for the first time, they fabricated an exciton laser with excellent temporal and spatial coherence performance. Figure 12G
shows the schematic diagram of the laser device. The heterobilayer WSe$_2$/MoSe$_2$ with interlayer twist angle of precisely 0° was used as a gain medium. Under the excitation of a weak light source over the threshold (633 nm, 20 μW), the population inversion density in the medium was realized, which further led to a strong exciton emission in PL measurements (Figure 12H). The type II band alignment was considered to play a key role (Figure 12H insert). Compared with the TM mode, the emission of the TE mode is stronger with a higher quality factor (Q-factor) around 2000. Besides, Figure 12I shows that with the enhancement of input pump power, the photon occupancy ($I_p$) of the TE emission increases along with a diminished and stable linewidth around 2 meV, implying a further enhancement of temporal coherence. Furthermore, they performed the first-order spatial coherence measurements by using a retro-reflector Michelson interferometer setup. Obvious interference fringes were observed (Figure 12J). After calculation, the coherence length was stable at about 5 μm above the threshold. All these works laid the foundation and provided exciting platforms to design and modulate the novel interlayer exciton-based devices.

5 Conclusions and outlook

In summary, we have reviewed the recent progress in synthesis methods, optical properties, and optoelectronic applications of T2DM. The last few years have witnessed a dramatic increase in research efforts both at the fundamental level and in technological applications...
of thin layered T2DM. Combining different kinds of 2D materials into vdWHs is an emerging research area. The distinct advantages of optical transparency and unique electronic properties make 2D materials attractive for the next generation of technologies; advantages include low cost and low power electronics, flexible and transparent solar cells, and displays or wearable computing devices. Although tremendous theoretical efforts have been devoted to this emerging field of T2DM over the past several years, there are undeniably still several significant issues that are required to be addressed and explored.

The first challenge is that practical difficulties in creating pure forms of layered 2D materials with precise angles of rotation limit the field. It is still necessary to develop new methods to prepare T2DM with larger areas and higher quality. The second challenge is that theoretically proposed 2D twisted materials always consist of ideal 2D materials, which are difficult to fabricate via experiments. This is attributed to the presence of grain boundaries, dislocations and folds in 2D materials synthesized in experiments, resulting in new properties but complex structural properties, which are difficult to study using theoretical simulations. The third challenge is that more experimental characterizations and theoretical simulations on accurate structural properties of T2DM are expected in future research. For example, the twist angle-dependent PL and SHG still remain unexplored. In addition, newly emerging 2D materials are worth exploring systematically. Another issue is that multilayer T2DM consist of multilayer 2D materials or more types of 2D materials. Multilayer T2DM have more complex properties and structures, which are also difficult to simulate in theory. Further methods and tools should be developed to study such multilayer T2DM. Besides, T2DM exhibit different quantum mechanisms to traditional heterostructures, which indicates that most of their properties are different. We can expect totally different behaviors in future T2DM-based integrated circuits, which should provide countless possibilities for the next revolution of modern nanoelectronics.

Acknowledgement: This work was supported by the National Natural Science Foundation of China (11774184, Funder Id: http://dx.doi.org/10.13039/501100001809, 11974190, 11804334), the Natural Science Foundation of Shanxi Province (201901D211071, Funder Id: http://dx.doi.org/10.13039/501100004480), and the National Science Foundation of Tianjin (18JCZDJC30400).

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