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THz photonics in two dimensional materials and metamaterials: properties, devices and prospects

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Terahertz radiation refers to a broad electromagnetic spectrum range between microwave and infrared waves, which is also known as the terahertz gap due to inadequate materials and technologies for its generation and manipulation. Atomically thin two dimensional (2D) materials such as graphene, black phosphorus (BP) and transition metal dichalcogenides (TMDs) provide a powerful platform for manipulation of the propagation and detection of terahertz waves. Furthermore, hybrid metamaterials that feature the combination of artificially engineered metamaterials and 2D materials greatly facilitate the dynamic modulation or manipulation of THz radiation towards novel terahertz applications. Herein, we review recent progress in 2D materials in the terahertz domain and hybrid metamaterials with engineered functionalities through the incorporation of graphene, TMDs and BP. The emerging THz devices based on the modulation, nonlinearity, filtering, and plasmonics of 2D materials and metamaterials will be highlighted, and a brief discussion with perspectives and the remaining challenges will be concluded.

1. Introduction

2D materials, sometimes referred to as single layer materials or materials of ultrathin thickness, are crystalline materials with a monolayer of atoms. The electronic properties of 2D materials may range from insulators, semiconductors to semimetals or even metals. Benefitting from their rich electronic, chemical and physical properties, 2D materials have been employed for various applications in electronics, photonics and optoelectronics and have received tremendous attention in the last decade.[1–14] In particular, due to their broadband optical response, strong plasmon oscillation, gate-tunable conductivity, and active variable THz bandgaps, 2D materials are highly promising in THz science and technologies, especially for tunable, active and switchable THz applications.[8–10,13] One of the most heavily studied 2D materials is graphene – the first 2D atomic crystal ever and best-known to researchers.[1–3] Since its discovery in 2004,[3] graphene has drawn much attention from the scientific community.[4–14] Currently, graphene is rapidly developing in various fields such as optoelectronics, materials and physics. In addition, other 2D materials, for instance TMDs and BP, have drawn much research interest due to their rich variety of physical properties.[11–14]

The advent or origin of metamaterials consisting of artificial subwavelength resonators provides a fertile ground for achieving unconventional electromagnetic properties not occurring in natural materials, such as flat super-lens, electromagnetic cloak and giant chirality. Nevertheless, a majority of metamaterials demonstrated so far are still passive, meaning that their properties are fixed once they are readily fabricated. It is expected that the next breakthrough in metamaterials will be in the development of metamaterials with active, controllable, and tunable features. The integration of 2D materials into metamaterials should promise a powerful avenue to improve artificial design capability, particularly in the terahertz domain.[10] Herein, we will present a review on 2D materials in the terahertz domain and hybrid metamaterials with engineered functionalities through the exploitation of graphene, TMDs and BP.

2. Preparation of 2D materials

The methods for preparing 2D materials can be mainly categorized as dissection methods (top-down routes) and growth methods (bottom-up routes), in which raw materials are macroscopic three dimensional materials and microcosmic molecules, respectively. For layered materials, atoms with strong in-plane chemical bonds are vertically stacked through a weak physical electrostatic force (van der Waals interaction) to form bulk crystals. Such a weak interaction between layers paves the way for the possibility of

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top-down routes including a micromechanical exfoliation method and liquid phase exfoliation.[15] The bottom-up routes for synthesizing 2D materials are also called thin film deposition methods, for example, chemical vapor deposition (CVD), magnetron sputtering, atomic-layer deposition (ALD), molecular beam epitaxy (MBE), pulsed-laser deposition (PLD) and so on.[16–19] Among them, the CVD method is the most commonly used bottom-up route. The synthesized 2D materials through the CVD method was grown on a substrate, where the source materials may be either carried by an inert gas (*e.g.*, argon) and then deposited on the target substrates[20] or pre-deposited on the target substrates and then converted to 2D sheets.[21]

2.1. Micromechanical exfoliation method (MEM)

The MEM is a fabrication of thin sheets by simple exfoliation of layered bulk crystals with Scotch tape, thus also called the Scotch tape method. In 2004, Novoselov *et al.* used such a method to prepare graphene from graphite.[22] Since then, similar approaches for preparing other 2D materials such as MoS_2,[22] WSe_2[23] and black phosphorus[24] have been demonstrated. The Scotch tape with cleaved thin flakes is firstly adhered to a clean substrate (*e.g.*, SiO_2/Si) and then peeled off from the substrate. Finally, nanosheets attached to the substrate are obtained. The remaining Scotch tape residue can be removed by organic solvents (*e.g.*, acetone, methanol, isopropyl alcohol, and acetonitrile).[25,26] There is usually induced strain in the thin sheets after deposition onto the substrate and a variety of defects such as atomic defects, wrinkles and microscopic corrugation can be formed.[27,28] Javey *et al.* reported a chemical treatment of MoS_2 monolayers obtained by the micromechanical exfoliation method and found that the treatment dramatically eliminated defect density, leading to superior performances.[29]

The MEM is very convenient and possesses an advantage of providing high-quality[24] 2D materials which are beneficial to fundamental research[22,30,31] in association with widespread applications in electronics and optoelectronics such as diodes,[32] lasers,[33] solar cells, gas sensors and phototransistors.[34] However, low yield, poor scalability, high inhomogeneity of thicknesses and sizes of MED render it unsuitable for large-scale (*e.g.*, THz beam field) or commercial applications.

2.2. Liquid exfoliation method (LEM)

Because of the weak van der Waals force between layers of bulk materials, it is more convenient to exfoliate them into few-layer nanomaterials through MED. Similarly, layered bulk crystals dispersed in liquid media can be exfoliated into nanosheets if suitable mechanical forces have been applied. A number of different approaches based on the LEM had been proposed for synthesizing 2D nanosheets, which are divided into an acoustic wave-assisted LEM (ALEM) and a shear force-assisted LEM (SLEM).

Given appropriate conditions, little energy is required to counteract van der Waals forces in bulk media and thus exfoliation can occur, breaking the bulk crystal into few-layer sheets. Coleman *et al.* placed graphite in organic solvents such as NMP (*N*-methyl-pyrrolidone), and then applied an acoustic wave.[35] Liquid cavitation induced by sonication produced bubbles in the solution. Bulk graphite dispersed in a liquid was exfoliated into thin layers by the microjets and shock waves caused by the collapse of the bubbles. Few-layer graphite was obtained by centrifugation of the liquid after sonication for several hours. Later, they further applied the LEM (liquid exfoliation method) to various kinds of 2D crystals, offering an opportunity to investigate a series of 2D materials.[15] Under optimized conditions, the concentration of ultrathin 2D nanosheets using the ALEM can reach up to $\sim$1 mg mL^{-1}. To further increase the production rate, Coleman *et al.* used a high-shear rotor-stator mixer to exfoliate graphite.[36] The bulk is exfoliated into layers by a shearing force induced by high speed rotation in liquid. Such a method has also been used for preparing few-layer BP.[37] Compared with the ALEM, the SLEM possesses the advantages of high efficiency and energy saving ability. Theoretical and experimental analyses suggest that the similar surface energy of the dispersion agent and the bulk crystal is the main mechanism underlying the efficient exfoliation.[35,38,39] The solvents used for effective exfoliation tend to possess a high boiling point (NMP, *ca.* 204 °C; DMF, *ca.* 153 °C at 7 mm Hg), whose residues are hard to remove by elevating the temperature, especially for BP nanosheets with low stability. Such solvent residuals cover the surfaces of nanosheets and inevitably affect their intrinsic properties. Washing with liquids of lower boiling points (*e.g.*, acetone, ethanol, isopropanol), Zhang *et al.*[40] and Xia *et al.*[41] obtained free BP nanosheets based on these approaches.

Obtaining fewer and monolayer BP turns out to be more challenging and usually the yield is extremely low.[15,31,41] A previous study suggests that adding NaOH to NMP gives rise to exfoliation of BP with higher efficiency.[42] Meanwhile, by obtaining smaller thickness of 2D sheets through a higher centrifugal rate, the sheets become smaller with lower concentration, which is not favourable for practical applications. Using mechanical cleavage and an Ar^+ plasma thinning/etching process, Jin *et al.* successfully synthesized several monolayer BP slices.[43] However, a plasma-assisted LEM is difficult to control and the efficiency is extremely low. Large-scale preparation of BP nanosheets less than 3 layers is still a challenge, limiting most investigations on monolayer black phosphorus to numerical calculations.[44–46]

2.3. Chemical vapor deposition (CVD)

In plasma actuation or optical radiation, the reaction product produced by materials in gaseous or steam state deposits onto a cooler substrate and gradually forms one or more thin films. The CVD technique to fabricate few-layer graphene was proposed in the 1960s.[47] In 2009, Kong *et al.*[48] and Hong *et al.*[20] synthesized few-layer graphene with large areas on Ni substrates and successfully transferred them to arbitrary substrates. In CVD growth, many factors, including precursors, substrates, temperature, atmospheres, and catalysts, determine the structural features of the products. By tuning these parameters, graphene with a tunable layer number and lateral size can be obtained on various substrates by using different carbonaceous materials as precursors (*e.g.*, methane,[49] ethylene,[50] acetylene,[51] and SiC[52,53]) in the CVD process.[54] Many transition metals (*e.g.*, Cu,[55] Ni,[56] Fe,[57] Ru,[58] Co,[59] Rh,[60] Ir,[61] Pd,[62] Pt[63] and Au[64]), alloys (*e.g.*, Pt–Rh,[65] Cu–Ni[66]) and metallic oxide (*e.g.*, MgO[67]) substrates are found to be suitable for the CVD growth of graphene.

Although large-area graphene can be obtained through CVD, the growing rate of single-crystal graphene (less than 0.4 $\mu m\ s^{-1}$ for copper foil substrate) has been a problem for a long time. Recently, Liu *et al.* realized single-crystal graphene with a growth rate of 60 $\mu m\ s^{-1}$, faster than previously reported CVD growth rates by two orders of magnitude.[68] Before the CVD growth, an oxide substrate (Al_2O_3 or SiO_2) was placed under the copper foil with a gap (~15 μm) between them (Fig. 1a and b). During the CVD growth, the oxide substrate supplied oxygen continuously to the surface of the copper catalyst, lowering the decomposition energy barrier to the carbon feedstock and thus the growth rate was significantly improved. The rapid route to synthesise large single-crystal graphene wafers contributes to the industry.

Hofmann synthesized MoS_2 and WS_2 on various substrates by CVD growth in 1988.[71] Using WO_3 and Se as the corresponding precursors, large area monolayer WSe_2 was fabricated on a sapphire substrate by Huang *et al.*[72] With the assistance of Ar and H_2, Se and WO_3 were activated and continuous monolayer WSe_2 was obtained at a low temperature of 750 °C. However, the low growth rate was unfavorable for large-scale applications. Lou *et al.* proposed a straightforward method to grow large-area MoS_2 films with controlled nucleation and promoted the formation of large-area films formed by monolayer or few layers.[69] They used patterned substrates with the distribution of SiO_2 pillars for MoS_2 growth in the CVD process (Fig. 1c). A high density of domain nucleation occurred on the pillars and the continued growth facilitated the fast formation of large-area continuous films. However, the coalescence of neighbour grains led to the occurrence of grain boundaries which may not be desirable for fundamental investigation because of the degraded physical properties.[73,74]

The crystal domains of TMDs are to some extent smaller in comparison with SCG synthesized through the CVD route. To grow large-area single crystal TMDs, one effective solution is to decrease the nucleation density in order to produce large regions.[75,76]

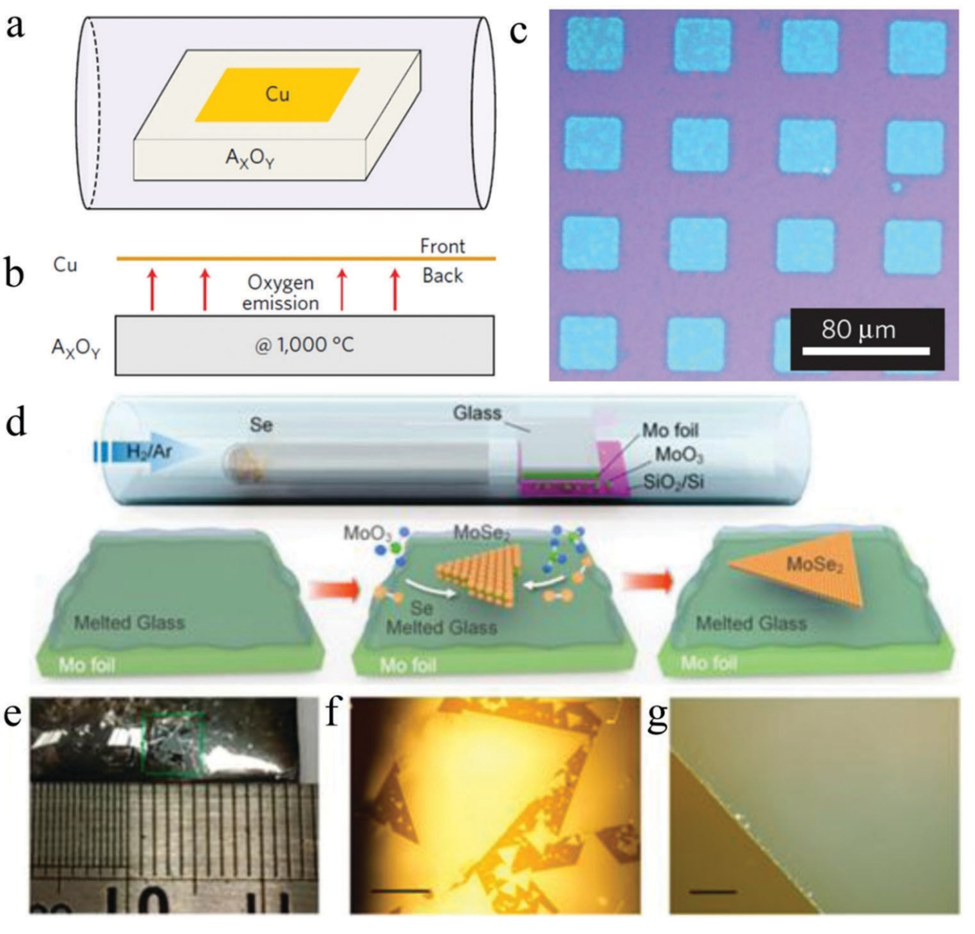

Fig. 1 Growth of graphene on copper foils assisted by a continuous oxygen supply. (a) Schematic of experimental design and (b) side view. A_XO_Y denotes the oxide. Reproduced with permission from ref. 68. (c) Optical picture of a large-area continuous MoS_2 film synthesized on substrates with rectangular-shaped patterns, between which are covered by continuous MoS_2 layers. Reproduced with permission from ref. 69. The synthesis process and morphology of $MoSe_2$ monolayers. (d) CVD process of the synthesis of $MoSe_2$ crystals on molten glass, (e) photograph of $MoSe_2$ crystals grown on molten glass, (f) and (g) optical images of $MoSe_2$ crystals grown on molten glass. Reproduced with permission from ref. 70.

Laskar *et al.* successfully prepared large single crystal MoS_2 on (0001) oriented sapphire through CVD growth.[77] However, the obtained films were relatively thick (tens of nanometers). Recently, Loh *et al.* successfully realized millimeter-sized monolayer $MoSe_2$ and MoS_2 crystals on molten glass (Fig. 1d).[70] Taking the advantage of the smooth surface generated by the melting and regeneration of glass, significantly reduced defect density was obtained, thus enabling low density nucleation for growing a large crystal domain ($\sim$2.5 mm Fig. 1e–g). Their finding demonstrates that "liquid-state" glass is a promising material for growing large-sized TMDs with good quality. In recent years, Xia *et al.* reported a scalable method for the synthesis of a large-area (up to 4 mm) BP film with a thickness of around 40 nm from red phosphorus.[78] Later, Ji *et al.* used a similar method to synthesize large area 2D BP with average areas of $>3\ \mu m^2$ and thicknesses of around four layers.[79]

Compared with other strategies to synthesize 2D materials, the CVD technique has developed into a scalable and effective method.[49,70,79–82] Because of long characteristic wavelengths in the THz spectroscopy field, it is a prerequisite to obtain large-area samples for fundamental research or applications. CVD methods provide large-area samples, which provide a possibility for investigating the properties and great potential of 2D materials in THz spectroscopy.[83] The high-quality 2D crystals grown using the CVD method turn out to be candidate materials for the next-generation THz, electronics and optoelectronics devices.[84]

3. THz photonics in 2D materials

3.1. Electrical and optical properties of graphene

Fig. 2a shows that graphene consists of one atomic monolayer of carbon in a hexagonal lattice. As a strictly 2D material, graphene offers unique features including large electron mobility, tunable conductivity and excellent optical transparency.[6,7,10] In graphene, the dispersion of energy and momentum is almost linear, therefore electrons passing through it behave as massless Dirac fermions.[4,6] Consequently, graphene shows abundant transport phenomena that are directly linked to 2D Dirac fermions, for instance, fractional and integer quantum Hall effects.[5,85–88] Valley physics is another interesting research topic for 2D materials,[89–95] introduced by a new concept of valleytronics, which is in analogy to spintronics. In valleytronics, valley features of carriers are dominant in processing information,[92] in which valley is a new internal quantum degree of freedom of charge carriers.

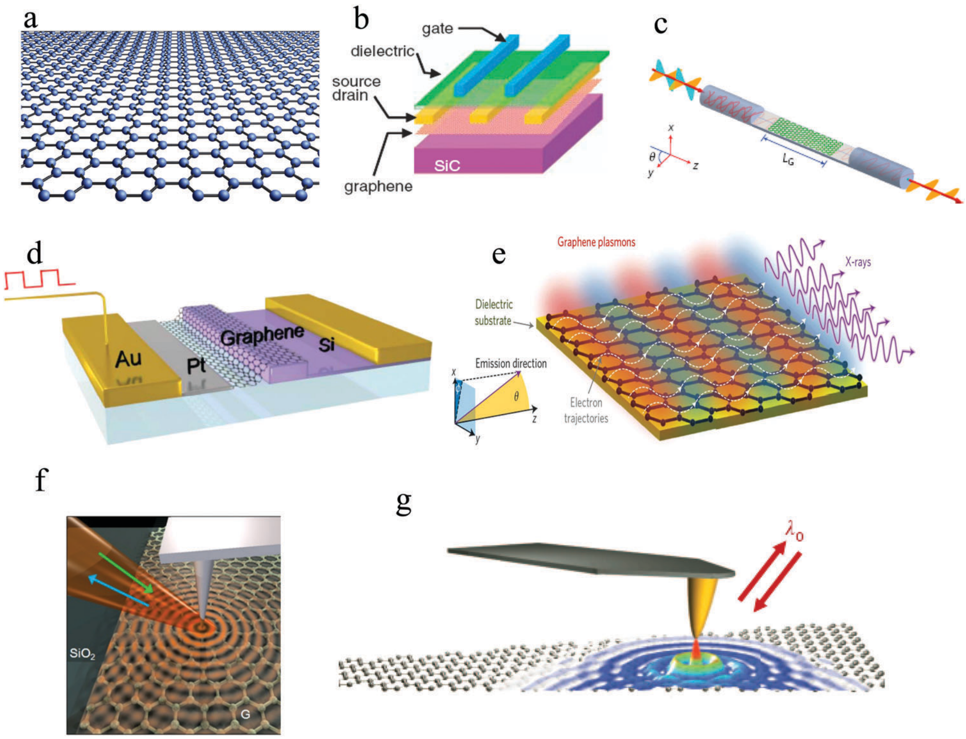

Fig. 2 Graphene and graphene-based photonic devices. (a) The atomic structure of graphene. The carbon atoms are arranged in a honeycomb lattice. Reproduced with permission from ref. 2. (b) Top view of a graphene-based field-effect transistor with top gate. Reproduced with permission from ref. 101. (c) Fiber-to-graphene coupler and polarizer. Reproduced with permission from ref. 107. (d) A graphene-based waveguide-integrated optical modulator. Reproduced with permission from ref. 108. (e) Graphene plasmon-based free-electron source with X-ray radiation. The graphene plasmon field (glowing red and blue bars) radiated by the free electrons (dotted white lines) can produce short-wavelength output radiation. Reproduced with permission from ref. 119. (f) Infrared nano-imaging diagram at the surface of graphene (G) covering a SiO_2 layer. The directions of incident and back-scattered light are denoted by green and blue arrows, respectively. Surface plasmon waves launched by the illuminated tip are illustrated by concentric red circles. Reproduced with permission from ref. 127. (g) Diagram of the imaging configuration of propagating and localized graphene plasmons utilizing scattering-type SNOM. Reproduced with permission from ref. 128.

In monolayer and bilayer graphene, various schemes have been proposed to generate valley currents by taking advantage of its unique edge modes,[89] defect lines,[91] strains[92] and the chiral state.[96] Moreover, nonlinear effects in graphene are of great significance, especially a broadband nonlinear optical response.[39,97,98] It has been demonstrated that Pauli blocking results in saturated interband absorption under strong excitation.[99] In a mode-locked fiber laser, a graphene saturable absorber was used to generate 756 fs soliton pulses in an optical communication band.[99] The graphene thickness can well engineer the modulation depth in a large range from 6.2% to 66.5%. The graphene absorber has a fast response and broadband operation that can be easily integrated into fiber lasers.[100] Graphene provides a promising platform for various important applications in diverse electronic and optoelectronic devices including transistors (Fig. 2b),[101–104] supercapacitors,[105,106] polarizers (Fig. 2c),[107] modulators (Fig. 2d),[108–111] photodetectors,[112–115] absorbers,[116,117] memory devices,[118] a short wavelength source (Fig. 2e)[119] and tunable in-line optical devices.[120]

3.2. Graphene plasmons

Plasmonics is an exciting field in optics. Surface plasmons are collective electron oscillations at metal–dielectric interfaces or nanostructures.[121] However, active and tunable manipulation of plasmonic excitations remains challenging. As an ideal candidate, graphene may facilitate the manipulation of plasmonic excitations through tuning the optical conductivity of graphene.[122–129] The intrinsic plasmons in graphene and noble metals are very distinct from each other since the conductivity of graphene can vary with external stimuli and chemical doping. Graphene plasmons exhibit extremely tight confinement, relatively long propagation distances and high tunability, being comparable to plasmons in noble metals. Graphene plasmons have already been demonstrated in optical metamaterials,[130] energy harvesting,[131] biosensing,[132] and invisible cloaking.[133] The observations of graphene plasmons have been experimentally confirmed by using an atomic force microscopy (AFM) probe (Fig. 2f and g).[127,128]

One of the most striking features in graphene is its broadband optical response.[8,9,11,13,14,98,106–108] Numerous graphene-based photonic and optoelectronic devices have been demonstrated to work at any arbitrary frequencies from the microwave to the ultraviolet regime.[11,13] In what follows, we mainly show the properties of several 2D materials including graphene, TMDs and BP in the terahertz range.

3.3. Tunable THz conductivity of graphene

THz wave between microwave and infrared frequencies has received less attention due to quite weak THz responses of natural materials, therefore this frequency range is the so-called terahertz gap and the corresponding THz technologies extremely fall behind compared to microwave and photonics. The rapid progress of graphene and other 2D materials opens a way to strengthen the responses of materials to THz radiations and control propagation of THz waves.[8,11,13,124,130]

Graphene's conductivity strongly depends on the frequency, scattering rate, temperature, and chemical potential. The carrier density dominates the chemical potential, strongly depending on chemical doping and external stimuli, for example, gating voltage, magnetic fields, and electric fields.[133] The controllable terahertz properties of graphene benefit from its conductivity tunability. The dynamics of Dirac fermions in large-area graphene has been measured by terahertz spectroscopy,[83,134,135] in which electrostatic or chemical doping had been adopted to tune the carrier density in graphene. In the measurement, the surface conductivity of graphene is frequency dependent; in other words it exhibits a strong dependence on the electron density.[135] The aforementioned characteristic can be simply understood by the Drude model. Following the first report on a transparent graphene electrode for solar cells,[136] graphene films have been demonstrated to be good candidates for transparent electrodes in THz phase shifters.[137] The observed phase shift is up to 10.8° and the saturation voltage is about 5 V with a 50 μm liquid crystal cell. The transmittance of THz waves and the conductivity of graphene are subject to the number of layers. The graphene-based phase shifter shows obvious advantages such as frequency flexibility, complete electrical tunability, and a low DC working voltage.[137] Therefore, graphene is the key enabler for novel active terahertz devices.

3.4. THz nonlinear optical response of graphene

Beyond its linear electromagnetic response, graphene with massless Dirac fermions also reveals attractive strong nonlinearity in the THz frequency range. The nonlinearity and bistability have been widely studied in various graphene configurations.[138–141] It is demonstrated that the terahertz responses at single and tripled frequencies have been greatly affected by graphene nonlinearity with measurable strength.[138] The nonlinear effects also lead to a significant enhancement of the optical activity in monolayer graphene. The nonlinear response of graphene will be of importance for developing novel THz and photonic devices. The monolayer species was shown to provide an ideal platform to exploit the nonlinear free electron response.[139] Monolayer graphene exhibited optical bistability behavior with a considerable energy level that can be measured in practice. The strong saturation absorption at the plasmon frequency was observed in patterned graphene by a terahertz pump–terahertz probe system (Fig. 3a).[141] In comparison with unpatterned graphene, the nonlinearity of patterned graphene is two orders of magnitude larger. A theoretical model was presented to support the experimental results of nonlinear absorption in graphene.[141]

3.5. THz graphene plasmonics

As mentioned above, graphene plasmonics provides great potential for designing novel THz and optical devices operating in the terahertz range, with high carrier mobility, low gate voltage, weak energy consumption and miniature size.[142–149] Surprisingly, a periodic plasmonic grating having a defect cavity was proposed to support 2D cavity plasmon modes with a deep subwavelength field confinement beyond $\lambda/1000$ (Fig. 3b). This plasmonic structure shows tremendous field enhancement factors up to a value of 10^4 that is 2 orders of magnitude larger than the value ever reported in metallic THz concentrators.

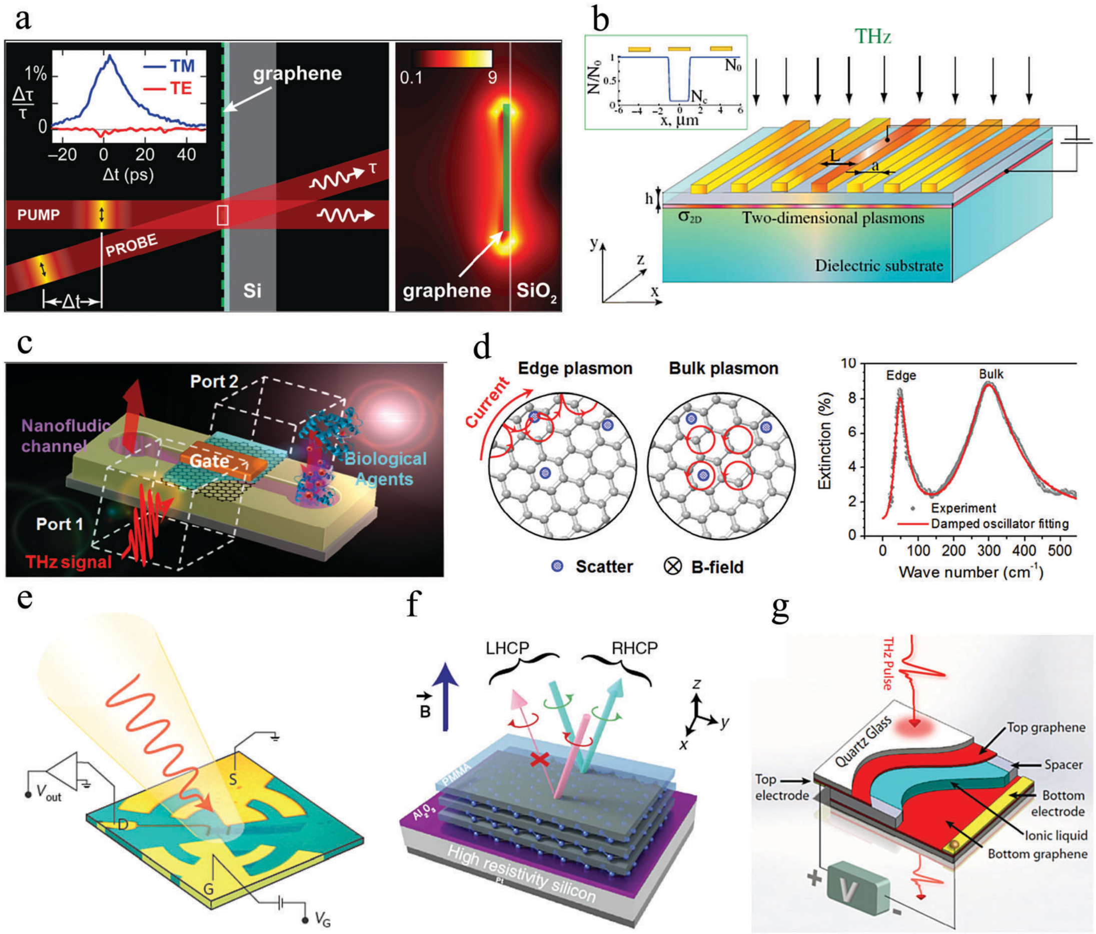

Fig. 3 THz graphene plasmonics and graphene-based THz devices. (a) Schematic of nonlinear absorption of graphene plasmons. Reproduced with permission from ref. 141. (b) Illustration of the field effect transistor with a split grating gate, in which the central gate grating is biased independently. Reproduced with permission from ref. 142. (c) Configuration of the THz nanofluidic biosensor. Reproduced with permission from ref. 146. (d) Edge and bulk plasmon modes and the corresponding extinction spectra. Reproduced with permission from ref. 150. (e) Diagram of an antenna-coupled graphene field-effect transistor-terahertz detector. Reproduced with permission from ref. 151. (f) 3D view of the graphene isolator. Reproduced with permission from ref. 154. (g) Structure of the graphene THz modulator. The sandwich configuration is composed of two graphene-coated quartz glasses, an ionic liquid, and two spacers. Reproduced with permission from ref. 162.

Further, owing to the linear dispersion of graphene, the splitting phenomenon between the edge plasmon mode and the bulk plasmon mode shows a strong dependence on chemical doping, which is quite different from conventional two-dimensional electron gas materials. This work offers a way to investigate Dirac magnetoplasmons and further establishes graphene as a strong candidate for designing tunable magneto-optical THz devices.[150]

3.6. THz graphene photonic devices

Generally, graphene is an important material for designing various THz devices including sensors (Fig. 3c),[146] magneto-optical devices (Fig. 3d),[150] detectors,[115,151–153] diodes,[33,154] couplers[155] and modulators.[13,156–167] Graphene-based THz detectors have been proposed, showing a responsivity of 150 mV/W at 0.3 THz (Fig. 3e).[151] A THz nonreciprocal isolator for circularly polarized waves has been demonstrated based on magnetostatically biased graphene, exhibiting 20 dB isolation and 7.5 dB insertion loss at about 2.9 THz (Fig. 3f).[154] An exceptionally efficient broadband graphene THz modulator enabled by intraband transitions has been realized. The modulator has an intensity modulation depth of 15% and a modulation frequency of 20 kHz, using a 570 GHz carrier at room temperature.[158] Recently, high-performance THz modulators have been experimentally demonstrated by using sandwich structures of graphene and ionic liquids (Fig. 3g).[162] The modulator can operate in a wide frequency range of 0.1–2.5 THz and its modulation depth reaches a high value of 99% when applying a gate voltage of 3 V. Thus, the emergence of graphene provides new opportunities to explore THz electronics and photonics and also develop new THz devices.

3.7. TMDs and THz properties

Bulky TMDs are indirect semiconductors with honeycomb lattices, but they were recently found to exhibit a transition between indirect and direct gaps if the thickness is reduced to a single monolayer or few layers.[13,22,30] TMDs can have wide direct bandgaps from 1.57 to 2.0 eV. Among those TMDs, molybdenum disulfide (MoS_2) and tungsten diselenide (WSe_2) have been widely studied,[11–15,168–170] which exhibit rich physics phenomena such as a direct bandgap,[22,30] strong spin–orbit coupling,[171,172] valley-selective circular dichroism,[173–176] valley Hall effect,[177,178] saturable absorption,[179,180] piezoelectricity,[181] nonlinear optical effect,[180,182] dark states,[183] photoluminescence[22,29,30,184] and two-dimensional heterostructures.[184–187] Although TMDs are suitable for novel THz devices, the performances of TMDs in the THz range have merely been investigated in a few literature studies.[188–191] With the help of time-resolved photoluminescence and THz spectroscopy, ultrafast carrier dynamics was measured in monolayer and trilayer MoS_2 and WSe_2. The measured results show that the ultrafast response time of photoconductivity and photoluminescence in the monolayer MoS_2 is 350 fs, while that in the trilayer MoS_2 and monolayer WSe_2 is 1 ps (Fig. 4a).[188] These results show the great potential of these materials that can be applied in high-speed THz devices. Based on the calculation, the maximum THz absorption of monolayer MoS_2 is approximately 5%, indicating that monolayer MoS_2 is a promising candidate for THz transparent electrodes.[190] Importantly, an optically tuned terahertz modulator has been demonstrated based on multilayer MoS_2 with an annealing treatment (Fig. 4b).[191] The annealed MoS_2 can significantly enhance the THz modulation depth of silicon under a CW pumping laser. The modulation efficiency of the device is even higher than those of graphene-based THz modulators. TMDs provide a platform for investigating the interaction between light and matter in the THz range and facilitate the progress of 2D material-based THz and photonic applications.

3.8. Black phosphorous and THz properties

In recent years, BP has been introduced as a new member into the family of 2D materials. BP is the most thermodynamically stable allotrope of three types of phosphorus (red, white and black phosphorus).[192] Single-element BP is a kind of high mobility layered semiconductor with variable bandgaps of 0.3–1.5 eV.[13,193] More importantly, as a natural material BP can appropriately cover the bandgap between graphene and MoS_2 and can be suitable for broadband practical applications especially in the near infrared and mid-infrared regimes. However, different from MoS_2 that exhibits an indirect bandgap for a large thickness, BP always manifests itself as a direct transition 2D material for any thickness, resulting in higher absorption which is good for certain optoelectronic applications.[13] BP has been extensively investigated for various exotic optical properties and applications, such as anisotropic optical properties,[193–195] a nonlinear optical response,[196] saturable absorbers,[197,198] field-effect transistors,[199–201] a photocurrent response,[202–204] p–n diodes,[205] band-gap modification[206] and a quantum effect.[207,208] Electron mobility in few-layer phosphorus was demonstrated to reach 1350 $cm^2\ V^{-1}\ s^{-1}$ and 2700 $cm^2\ V^{-1}\ s^{-1}$ at room and low temperature and moreover showed high anisotropy.[207] Such electron mobility is much faster than those in TMDs, significantly promising for applications in BP-based nanoelectronic devices.[207] However, to date BP-based THz devices have not been fully studied. For instance, the exploitation of BP for the detection of THz waves is now still at its early stage.[209,210] The first THz BP nanodetector working at

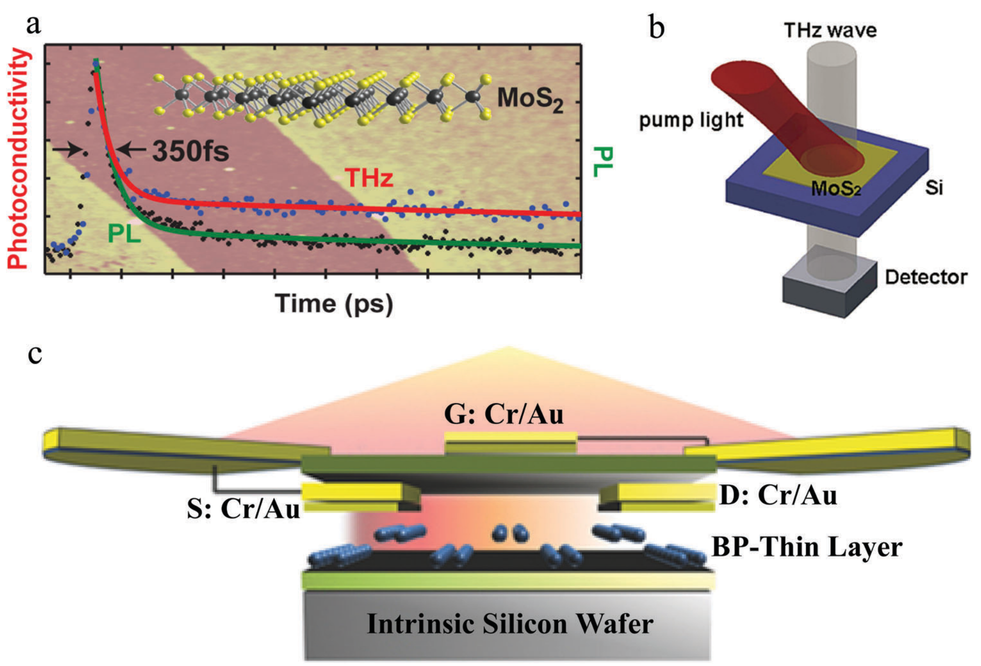

Fig. 4 Transition metal dichalcogenides (TMD)-based and black phosphorus (BP)-based THz devices. (a) Photoconductivity and photoluminescence response time of CVD-grown monolayer MoS_2. Reproduced with permission from ref. 188. The photoluminescence response time is about 350 fs. (b) The sketch map of an optically controlled THz modulator with annealed multilayer MoS_2. Reproduced with permission from ref. 191. (c) Schematic map of the first BP photodetector at room temperature. The device exploits a 10 nm-thick exfoliated crystalline BP flake for the active channel in a field-effect transistor. Reproduced with permission from ref. 209.

room temperature (Fig. 4c) has been demonstrated, in which an exfoliated crystalline BP flake with a thickness of 10 nm was utilized as the field-effect transistor's channel.[209] According to the unique in-plane electrical anisotropy of the thin BP flakes as well as in-plane thermal anisotropy, on-chip nano-transistors have been designed to efficiently detect THz radiation by using different mechanisms such as a plasma-wave, a bolometric effect and a thermoelectric effect.[210] The proposed BP detector allows selective and controllable THz detection with an acceptable responsivity and sensitivity performance. The work will be promising for novel THz applications and good to realize tunable BP-based THz devices.

4. THz photonics in 2D materials-hybrid metamaterials

4.1. General tunable THz metamaterials

Metamaterials, artificially structured media with unique engineered electromagnetic properties not available in natural materials, have been one of the most important cutting-edge fields due to their unprecedented properties such as negative refraction, invisibility, giant chirality and anomalous refraction.[211] Metamaterials open up a unique route to generate a strong engineered THz response and fill the so-called THz gap.[212–216] Many interesting phenomena have been studied in the THz regime.[212–216] Strong THz fields in metamaterials can lead to promising nonlinear as well as quantum responses for ultrafast or nonlinear THz photonics or plasmonics.[217,218] Tunable electromagnetic responses are always desirable in the THz domain. There are several approaches to design tunable and dynamic THz metamaterials. Traditionally, active tunability of electromagnetic characteristics of metamaterials can be realized by mechanically altering the size and shape of individual unit cell resonators.[219] However, this mechanical modulation introduces great complexity in fabrication, not to mention the slow tuning speed. In comparison, various hybrid metamaterials incorporating active materials have been developed, which are qualified to allow arbitrary and tunable control on the interaction between THz wave and matter. The common active materials employed in tunable metamaterials are semiconductors, liquid crystals, superconductors and phase change materials like GeSbTe (GST) and vanadium dioxide (VO_2), which show dynamic THz responses upon excitation by external stimuli *via* electric bias,[5,220,221] temperature,[222–224] photoexcitation[225–228] or MEMS.[229,230]

4.2. Hybrid graphene metamaterials in THz

At present, to our best knowledge, graphene is considered as the most popular or active material among 2D materials for achieving tunable THz phenomena and functionalities due to its dynamic conductivity.[10] Various hybrid graphene-based metamaterials or metasurfaces (generally so-called two-dimensional metamaterials) have been proposed to achieve interesting THz phenomena such as negative refraction,[231,232] tunable invisibility,[233] magnetic response,[234] enhanced THz response,[235] tunable electromagnetically induced reflection[236] and tunable plasmons.[130,237] In particular, an atomically thin mantle cloak has been realized by the nanostructured graphene metasurface in the THz spectrum (Fig. 5a), in which the metasurface was formed by periodic arrays of graphene-based subwavelength nanopatches.[233] The strong magnetic response in the graphene metamaterial with split-ring resonators (Fig. 5b) was predicted in the THz frequency range, allowing strong field confinement within a size of 2 orders of magnitude smaller than the incident wavelength.[234] Compared with gold split-ring resonators with a similar thickness, split-ring resonators of highly doped graphene reveal a much stronger induced magnetic response in the THz frequency. In a seminal work by Wang's group in 2011,[130] it was observed that the graphene micro-ribbon array supported surface plasmons excited by THz waves and the plasmon resonance in the patterned graphene could be tuned over a THz frequency range simply by changing the width of the graphene micro-ribbon and the carrier doping, as illustrated in Fig. 5c.[130] Despite the ultrathin thickness of graphene compared to the incident wavelength, THz radiation was strongly coupled to surface plasmons and consequently its absorption was measured to be higher than 13% at the plasmon resonance frequency at room temperature. The observed tunable plasmon resonances in structured graphene provide a basis for designing complex graphene-based metamaterials and offer a new route to control or manipulate THz radiation.[130]

Graphene-based metamaterials are also attractive and powerful for designing tunable THz devices such as filters,[238] absorbers[239–242] and modulators.[243] A graphene-based metamaterial has been presented to achieve a tunable THz filter, which consists of a periodic array of hybrid metal–graphene rings (Fig. 5d).[238] By controlling the tunable conductivity of graphene, the resonance frequency of the graphene structure can be modulated by 40%. Importantly, the active area in the device is less than 0.1% of the whole area of the unit cell.[238] A cross-shaped metamaterial consisting of double layer graphene wires was demonstrated for realizing a spectrally tunable polarization-independent absorber, as shown in Fig. 5e.[239] The absorption peak frequency has a tuning range of 15% depending on the controllable Fermi energy of graphene and during the modulation the perfect absorption is almost kept unchanged through controlling the bias voltage.

4.3. Graphene metamaterial THz-modulators

Remarkably, graphene metamaterial modulators have attracted increasing attention[13,93,243–257] due to their capability of modulating the amplitude,[10,93,243–251] phase,[10,252] polarization,[239,253–255] wavefront[256–258] and also refractive index of THz waves.[259] In order to enhance electronic and optical tunability in unpatterned graphene towards practical optoelectronic applications, substantial switching and linear modulation of THz radiation had been realized in an ultrathin metamaterial integrated by gated graphene (Fig. 6a).[10] The strong resonances in metamaterials can improve or enhance the interaction between THz wave in a gate-controllable graphene layer. At room temperature, monolayer thick graphene integrated into the metamaterial can tailor both the amplitude and phase of the transmitted wave, with an amplitude modulation

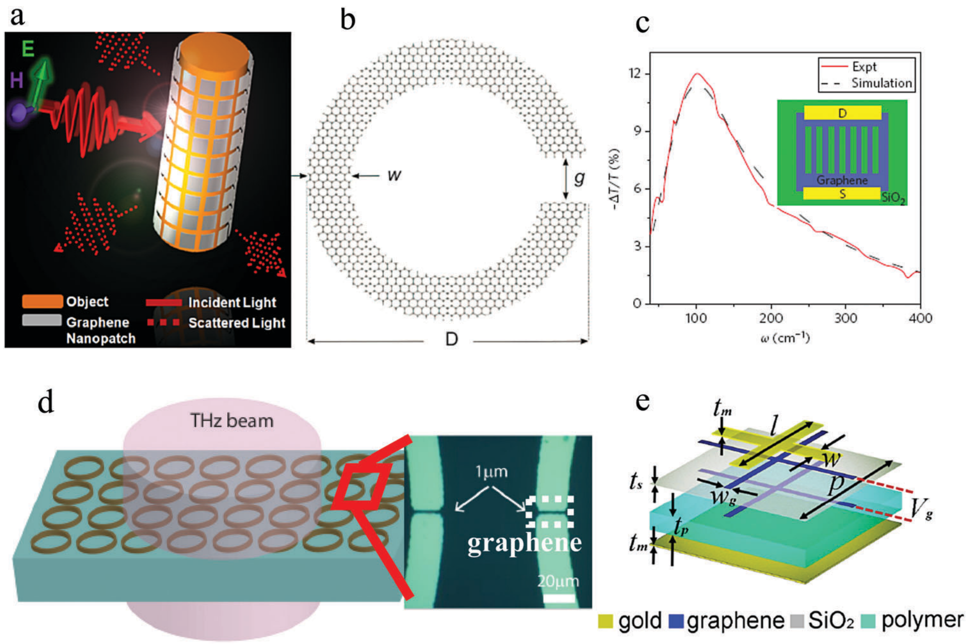

Fig. 5 Tunable THz responses of graphene-based metamaterials. (a) Schematic of graphene metasurface cloak. The dielectric cylinder covers by the graphene metasurface. Reproduced with permission from ref. 233. (b) Graphene split-ring metamaterials generating a strong magnetic response. Reproduced with permission from ref. 234. (c) Simulated and measured transmission change spectrum of graphene-based THz devices. Optical lithography and plasma etching were used to fabricate the array through transferred large-area CVD graphene. Reproduced with permission from ref. 130. (d) Tunable graphene-based micro-machined metamaterial THz filter. Reproduced with permission from ref. 238. (e) Schematic of the structure of the proposed graphene metamaterial absorber. Graphene is placed between the small gaps. The optical micrograph of the gap in the absorber is shown. Reproduced with permission from ref. 239.

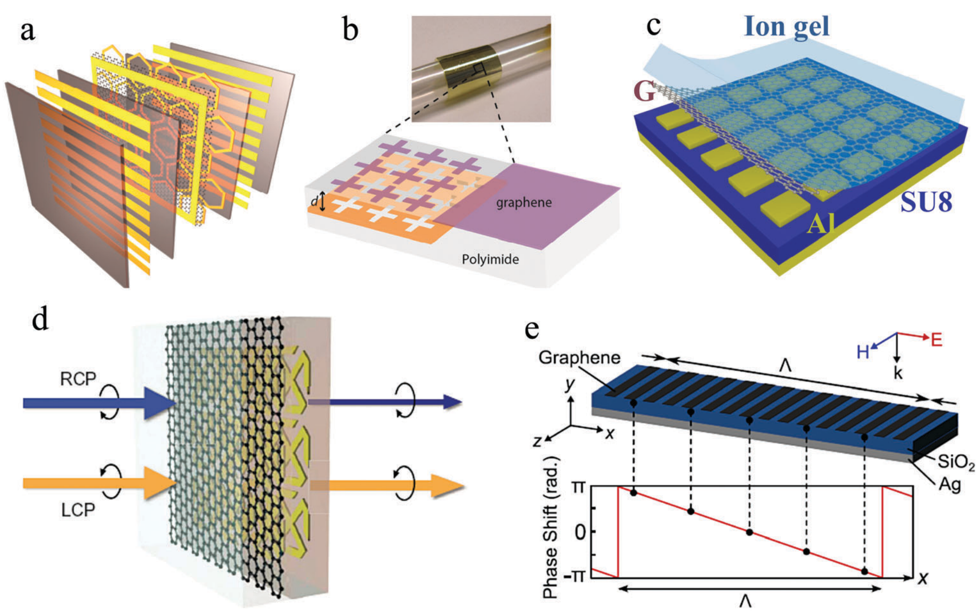

Fig. 6 Graphene-based metamaterial modulators in the THz range. (a) Diagram of an active graphene metamaterial with an electrically controlled gate. The hybrid structure consists of a monolayer graphene deposited on the hexagonal metallic meta-atom layer, with top/bottom EOT (extraordinary optical transmission) electrodes embedded in a dielectric material. Reproduced with permission from ref. 10. (b) Illustration of an exceptional graphene metamaterial modulator. The graphene metamaterial consists of graphene and a frequency selective surface embedded in a polyimide film. The nonpatterned and patterned graphene layers cover the top of the polyimide film. Reproduced with permission from ref. 251. (c) Schematic of tunable THz phase modulation based on a gate-controlled graphene metasurface. The applied electric voltage between graphene and the top gate dominates the doping level of graphene. Reproduced with permission from ref. 252. (d) Schematic of electrically controlled circular polarizations in graphene-based metamaterials with conjugated double-*Z* chiral meta-molecules. Reproduced with permission from ref. 255. (e) Schematic of a tunable graphene ribbon metasurface with a designed gradient phase. The graphene ribbons are above the silver background layer separated by a SiO_2 dielectric layer. Reproduced with permission from ref. 257.

of about 47% and a phase change of 32.2°. Actually switching THz waves can be well accomplished by a gate voltage in graphene metamaterials. The hybrid graphene metamaterial establishes a fertile ground for actively controlling the mutual interaction between THz wave and matter on the deep sub-wavelength scale and achieving various THz applications such as tunable memory devices and modulators. Another type of THz modulator has been proposed (Fig. 6b), in which a frequency selective surface is exploited to resonantly enhance the THz response in graphene.[251] By varying the geometrical structural parameters, there is an optimal trade-off value between the modulation depth, response and insertion loss in THz modulators.[251] Interestingly, another new mechanism has been presented to realize a large range of THz phase modulation on a gate-tuned ultrathin graphene metasurface (Fig. 6c), in which graphene was regarded as a tunable lossy material so as to control an underdamped to overdamped resonator transition.[252] A theoretical resonator model, verified by full-wave electromagnetic simulations, was used to interpret the underlying physics of the discovered extreme phase modulation, based on which general schemes were put forward to achieve tunable THz and optical devices. These findings open up a probability for practical applications and exploiting the mechanism of active phase manipulation. For polarization modulation, a switchable quarter-wave plate for terahertz wave has been achieved, which consists of a combination of graphene and metallic grating structures.[253] The designed polarization modulator can dynamically modulate or manipulate the polarization states of the transmitted light wave from left-handed or right-handed circular polarization to linear polarization by the electrically controlled Fermi level of the graphene grating.[253] In fact, most graphene metamaterials have been studied in theory while lack experimental realization. Remarkably, the gated graphene metamaterial and metasurface have been experimentally verified to actively manipulate the polarization state of the THz waves.[254,255] The graphene metasurface with a periodic metallic aperture has been reported to achieve an electrically controlled anomalous refraction of circularly polarized THz wave and the corresponding amplitude can be flexibly modulated by an applied bias voltage.[254] In addition, the hybrid graphene-based metamaterial with conjugated double-*Z* chiral meta-molecules has been demonstrated to exhibit electrically modulated transmission of THz waves for right-handed circular polarization while voltage-insensitive transmission of left-handed circular polarization (Fig. 6d).[255] As a result, the graphene-based chiral metamaterial shows a large modulation depth, even larger than 99% at the resonance frequency. The phase transition from the underdamped, critically damped to overdamped coupling regimes provides an effective way to achieve control of the polarization state, accompanied by a giant circular dichroism of up to 45 dB and a polarization rotation angle of up to 10°.[255] The underlying mechanism of the graphene chiral metamaterial may find many THz applications including active polarization modulators, sensors and imaging devices.

Dynamic control of the THz wavefront is also highly desirable in photonics. The reflected wavefront of THz wave can be dynamically manipulated by the graphene metasurface consisting of an array of graphene ribbons on a silver layer separated by a SiO_2 dielectric layer (Fig. 6e).[257] In graphene ribbons, localized surface plasmon resonances can also be excited with a Fermi-level dependence. An abrupt phase shift in reflection covering the whole 2π range is also introduced along the graphene metasurface. The simulated results show that the reflected anomalous beam deflects up to 53° with 60% reflection efficiency at 5 THz and the switching time of the active graphene metasurface is shorter than 0.6 ps. Wavefront manipulation of THz wave will pave a way for realizing dynamic focusing,[256,257] beam steering and beam shaping.[258]

4.4. Hybrid metamaterials with TMDs and BP

TMDs and BP have not been fully studied in the THz range, and there are few literature reports on hybrid THz metamaterials with integrated TMDs and BP. Recently, hybrid TMD and BP metamaterials have been proposed to show interesting THz applications.[260,261] The optically actuated MoS_2/metal hybrid metamaterials have been designed and experimentally investigated in the frequency range of 0.2–0.4 THz.[260] The hybrid metamaterials were composed of an array of cross-shaped metallic apertures integrated by multilayered MoS_2. The simulated results show that the hybrid THz metamaterial simultaneously has a modulation depth 2 times larger than the intrinsic modulation depth by a bare MoS_2 film and a low insertion loss of less than 3 dB. Instead of the gapless 2D material-graphene, the bandgap 2D metamaterial of MoS_2 shows several advantages, such as a reduced insertion loss, an enhanced modulation depth and a large near field enhancement. Due to intrinsic in-plane anisotropy, BP has become an active material for manipulating the polarization of waves and polarization related properties. The tunable polarization-dependent absorbers have been numerically demonstrated, and meanwhile the resonance frequencies and absorption show a strong dependence on the doping electron concentration of 2D material BP.[261] The THz absorber is constructed by an array of square BP patterns and a metallic ground mirror separated by a 2.5 μm thick insulator layer. The proposed metamaterial completely absorbs one polarization due to excitation of localized plasmons while the absorption of the other polarization is less than 10% at the same frequency, which can be well understood by the in-plane anisotropy of BP. The aforementioned results predict the promising future of TMDs and BP in THz applications and more relevant investigations of metamaterials with TMDs and BP are highly desirable.

5. Conclusion and outlook

2D materials and metamaterials are two fields that have been rapidly developed in recent years. Both of them provide alternative solutions to develop the next generation of photonics and optoelectronics, especially for novel terahertz technologies. The extraordinary electrical and optical properties of graphene in the THz range make it ideally suitable for dynamically controlling the THz waves. In combination with metamaterials, the modulation depth of graphene can be dramatically modulated or enhanced. In terahertz photonics, the tunable properties of graphene offer a new route to actively modulate or strengthen light–matter interactions. Although TMDs and BP have not been fully exploited in the THz domain, it is anticipated that further in-depth investigations will lead to the realization of many interesting terahertz phenomena and novel high-performance terahertz devices that conventional devices do not possess. The hybrid metamaterials integrated by TMDs and BP open a route to realize modulators, detectors, polarizers and absorbers. For practical applications, the response time and modulation speed of active devices with 2D materials and their energy consumption should be further addressed. In the future, the two-dimensional nanostructures are expected to be highly compatible with the current micro-manufacturing techniques and they can be easily incorporated into metamaterials. Hybrid metamaterials integrated with 2D materials provide a new paradigm for achieving tunable terahertz devices, but obtaining THz properties on demand and the trade-off between the performance and device cost are still challenging.

Conflicts of interest

There are no conflicts to declare.

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