Review

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Two-dimensional materials for nanophotonics application

Abstract: In this article, we review the various topics on the applications of 2D materials, including both elemental and compound 2D materials, for nanophotonics application from detectors, modulators to plasmonics and light generating devices. With this review, we hope to provide an overview of the past development in this field while offering our perspectives on its future directions.

Keywords: 2D materials; nanophotonics; graphene; black phosphorus; transition metal dichalcogenides.

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1 Introduction

Since the successful isolation of graphene (Figure 1A) a decade ago, the family of two-dimensional (2D) materials has attracted tremendous interest in the research community. Graphene is the first extensively studied material with true two-dimensional nature. With its unique band structures at the limit of 2D quantum confinement, this honeycomb monolayer of carbon atoms has inspired many interesting applications in nanophotonics and nanoelectronics. The most appealing features of graphene for nanophotonic applications originate from its zero-bandgap nature with linear dispersion near the Dirac point. Due to its unique band structure, graphene offers highly sensitive responses to optical signals over a very wide spectral range through various types of light-matter interaction mechanisms. At the terahertz and mid-infrared range, graphene supports localized and propagating plasmons. Due to the controllable Fermi energy in graphene, such plasmonic responses are tunable by electro-static biasing with an external gate, a feature not available in traditional metal-based plasmonic devices. On the other hand, graphene can also be utilized to construct photodetectors and modulators for many optoelectronics applications at near-infrared, visible and ultra-violet spectrum range, leveraging its broadband absorption of light through interband transitions. However, graphene is not suitable for light generation functions due to its metallic nature, for which properties of other 2D materials needs to be explored. Besides graphene, hexagonal boron nitride (hBN), shown in Figure 1B, is also a layered material with honey-comb lattice structure. Its large bandgap (6 eV) makes it an outstanding dielectric for other 2D materials, which has enhanced the electronic and optoelectronic performance of various devices.

Recently, the research community has witnessed the rise of another family of two-dimensional materials – the single-layer transition metal dichalcogenides (TMDCs), such as molybdenum disulphide (Figure 1C) and tungsten diselenide. This rich family of mono-molecular-layer semiconductors can cover the energy range 1.5–2.5 eV and beyond, offering new opportunities to construct devices that can perform light generation functions due to its finite and direct bandgap in the monolayer form, such as light emitting diodes (LED) and lasers. In addition, the valley coherence and valley-selective circular dichroism observed in various monolayer TMDCs offer exciting opportunities for the research of novel optical phenomena.

Since the beginning of year 2014, we have also seen the arrival of the latest member of the 2D material family – black phosphorus (Figure 1D). This layered material with a moderate bandgap of 0.3 eV in its thin film form that is widely tunable to around 2.0 eV in its single-layer form bridges the energy gap between zero-bandgap graphene and relatively wide bandgap transition metal dichalcogenides. It can potentially cover a broad wavelength range.

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from mid-infrared to partial visible spectrum for light detection, modulation and generation applications.

Here, we review the various topics on the applications of 2D materials for nanophotonics application as introduced above. With this article, we hope to provide an overview of the past development in this field while offering our perspectives on its future directions.

2 Graphene photonics: photodetector, modulator, and plasmonics

2.1 Photodetectors

High speed, broad bandwidth photodetectors are essential for communication, sensing, and digital imaging. Most traditional commercial photodetectors are based on silicon or III-V semiconductors. When photons are absorbed into the photodiode’s depletion region, they excite electron-hole pairs and their separation leads to photocurrent generation. This mechanism (usually called photovoltaic effect) was also claimed to be the operational principle of graphene based photodetectors in early research [1–3]. However, more complex principles have been revealed recently. First, the lifetimes of excited carriers in graphene are found to be too short to generate efficient channel current. In addition, the slow electron-lattice relaxation in graphene results in an elevated carrier temperature under light excitation due to a thermal decoupling between the lattice and photo-generated carriers. Therefore, if graphene is doped non-uniformly, “hot” carriers will diffuse due to the electronic temperature gradient, generating a net photocurrent, which is called photo-thermoelectric effect [4]. Furthermore, due to the Auger-type processes in graphene, multiple electron-hole pairs can be generated with merely a single photon [5–7], which can potentially enhance the detection efficiency. Besides the photo-thermoelectric and photovoltaic effects, bolometric effects in graphene can also play a role in photoresponse [8]. To sum, due to the reduced dimensionality and its metallic nature, the generation of photocurrent in gapless graphene is more complex than that in traditional three-dimensional semiconductors with a sizable bandgap.

Owing to its zero bandgap nature and the interband transitions of carriers, graphene is able to absorb photons from mid-infrared to ultraviolet wavelengths [9, 10]. Unfortunately, the small optical absorption of monolayer graphene arising from its innate thinness has limited the photoresponsivity of graphene based photodetectors. The first graphene based photodetector [11] demonstrated a potential bandwidth of 500 GHz, a measured 40 GHz response without gain degradation, and a maximum photoresponsivity of ~0.5 mAW⁻¹. The effective photo-generation region in this device is as short as 0.2 μm. To extend the operation region, a metal-graphene-metal (MGM) photodetector with asymmetric electrodes (Figure 2A) has
Figure 2  Graphene photodetectors and modulators.

(A) Schematic of the metal-graphene-metal photodetector. Scale bar, 5 μm. Reproduced with permission from Ref. [12]. (B) Geometry-dependent photoresponse in antenna-graphene sandwich structure. Reproduced with permission from Ref. [13]. (C) Schematic of the graphene-microcavity photodetector. The Si₃N₄-graphene-Al₂O₃ structure is embedded within two Ag mirrors. The resonance wavelength of the cavity λ is defined by L, the thickness of the dielectric. Inset: sectional view of the device. Reproduced with permission from Ref. [14]. (D) Top: the layout of a graphene modulator; a monolayer graphene on top of a doped-silicon waveguide. Bottom: cross-section view of the device. The optical mode plot is obtained from finite element simulation. The purple curve on the right demonstrates the magnitude of the electric field. Reproduced with permission from Ref. [15]. (E) Schematic demonstration of a graphene-clad microfiber optical modulator. Reproduced with permission from Ref. [16].
been invented [17], which was able to achieve an external responsivity of 6.1 mAW⁻¹. Although graphene based photodetectors are promising for their ultra-broadband, high speed, and its compatibility to circuits. Its low photosensitivity compared with traditional semiconductor-based ones remains a major drawback. Recently, several methods have been applied to enhance the optical absorption of graphene-based photodetectors. First, combining graphene with plasmonic nanostructures is able to concentrate light using plasmonic resonances, resulting in a significantly enhanced local electric field [12, 18]. Besides the huge enhancement in quantum efficiency, multicolor detection can also be achieved through the wavelength-dependent photoresponse amplification of plasmonic nanostructures [19]. A quantum efficiency up to 20% was achieved by sandwiching plasmonics nano-antennas within two sheets of graphene monolayer [13] (Figure 2B). However, the resonance of nanostructures or nanoparticles in these systems can determine the working wavelength of the photodetectors, typically leading to a reduced operation bandwidth, which is a potential shortcoming of this type of devices.

Second, integrating quantum dots with graphene is another powerful approach to enhance responsivity of graphene photodetectors. Konstantatos et al. [20] covered graphene with colloidal quantum dots to make a hybrid photodetector with ultrahigh photodetection gain (∼10⁸ electrons/photon) and a photosensitivity of ∼10⁷ A W⁻¹. The quantum dots assist photogenerated carriers to reach graphene sheets while trap all oppositely charged carriers in quantum dot layer, resulting in a field-effect doping phenomenon. Another similar sample is the graphene-PbS quantum dots photodetector fabricated on a flexible substrate [21] with a responsivity of 10⁷ A W⁻¹, making use of the photogating effect. Graphene-quantum dot photodetectors perform tremendous responsivity, but they also suffer low operational speed, due to the long time needed to generate gain. In addition, the working bandwidth in these devices are mainly determined by the quantum dot rather than graphene.

Moreover, integrating graphene with microcavity [14, 22–24] is another useful way to increase photoresponse. In the first graphene-cavity photodetector [14], two opposite mirrors were used as a Fabry-Pérot microcavity (Figure 2C) to achieve a 20-fold enhancement of photocurrent at a given wavelength. The cavity-induced optical confinement can enhance photoresponse, but also narrows its bandwidth.

Finally, coupling graphene to various waveguide can lead to photodetectors with excellent performance [25–30]. These devices are marked by high photoresponsivity (∼0.1 A W⁻¹), ultra-wide bandwidth (from visible to infrared wavelengths), high efficiency, high speed (∼10 Gbit s⁻¹), and small footprint. In graphene-waveguide photodetectors, the waveguide convey light to graphene either by batt-coupling or evanescent coupling. The latter has been applied to many novel devices like graphene/silicon-heterostructure waveguide photodetectors [26], though integration with waveguide inevitably leads to larger device dimension [29]. The wide adsorption bandwidth of graphene-waveguide photodetectors make them advantageous over traditional photodetectors.

### 2.2 Optical modulators

Optical modulators play a crucial role in optical communications. Graphene based optical modulators are marked by their strong graphene-light interaction, ultrafast operation speed, large bandwidth, and high compatibility to silicon electronics. Despite that the absorption coefficient of graphene is large (∼5×10⁶ m⁻¹ in visible range), the ultra-thin nature of monolayer graphene has limited its absorption significantly. Hence, it is necessary to enhance graphene-photon interaction, typically by waveguide or by optical cavity, which will be discussed in this section.

Liu et al. [15] made the first graphene based modulator in 2011. In their devices, mono-layer graphene was transferred on top of a silicon waveguide, with a 7-nm-thick Al₂O₃ between them serving as a spacer (Figure 2D). A drive voltage is applied between graphene and the waveguide to tune the Fermi level. When the absolute value of Fermi level is over a transition threshold (E_g(V_D)=hv/2), interband transitions will be suppressed due to Pauli state blocking, hence graphene stays transparent. On the other hand, if a low drive voltage is applied to keep the Fermi level of graphene close to the Dirac point, optical adsorption will be enabled. Thus light transmission in graphene can be effectively modulated via tuning driving voltage. With a high working speed (1.2 GHz at 3 dB), broad operation bandwidth (1.35 mm–1.6 mm) and tiny footprint (25 µm²), this graphene-waveguide optical modulator demonstrates the potential of using graphene for modulator applications. However, the silicon back gate inevitably induces high insertion loss and degrades carrier mobility, resulting in a limited modulation depth and reduced operation speed. To solve this problem, Liu et al. [31] replaced the doped silicon layer with monolayer graphene to form a double-layer graphene optical modulator. In this modulator, two graphene layers were separated by Al₂O₃ to form a p-oxide-n junction. The modulation depth (−0.16 dB/µm) in this device is higher than that in the first
graphene-based modulator. Another similar double-layer graphene modulator was proposed by Koester et al. [32]. In their modeling, two layers of graphene separated by a thin insulator were placed on top of a silicon waveguide. The upper graphene sheet acts as a transparent electrode, while the lower one functions as a light-absorber. Their calculation revealed that the 3-dB bandwidths of this device at near-infrared bands and mid-infrared bands can reach 120 GHz and 30 GHz, respectively.

Coupling two-dimensional material to optical cavity offers an alternative way to enhance light-matter interaction. Gan et al. [33] have fabricated high-contrast, energy-efficient, and broad-band electro-optic modulators by electronically gating graphene deposited onto a HfO₂-covered silicon photonic crystal nanocavity. In this case, the Fermi energy of graphene is tuned by the electrostatic bias, resulting in tunable absorption. Once the interband transitions are Pauli blocked, graphene adsorbs less light and appears to be transparent. Therefore, the quality factor and reflectivity of the cavity can be effectively modulated by tuning the gate voltage.

The nature of gate-tunable Fermi level in graphene has led to various progresses in electro-optic modulators. However, the response time of the bias circuits typically limits the modulation bandwidth to below 1 GHz. To eliminate this “electrical bottleneck”, an all-optical modulator [16] (Figure 2E) was designed by wrapping graphene monolayer around a microfiber. This graphene-clad microfiber (GCM) can reach a response time of 2.2 picoseconds and a modulation depth of 38%, with a calculated bandwidth of 200 GHz. To tune the attenuation of weak infrared signals coupled into the GCM, a switch light is applied to excite carriers, leading to Pauli blocking-suppressed interband transitions. Thus the absorption threshold of graphene increases, lowering the attenuation of weak infrared signals. Ultrafast, flexible, and easily integrated to traditional optical devices, this all-optical modulator is promising for future fiber-optic circuits.

### 2.3 Graphene plasmonics

Because of its simultaneously high carrier mobility and high conductivity, graphene has also emerged to be a very promising candidate for terahertz to mid-infrared plasmonic devices applications. As a subfield of nanoplasmonics, plasmonics studies the excitation, propagation, and utilization of the collective oscillation of carriers. There are several types of plasmon polaritons, and for graphene, we are more interested in the surface plasmon polaritons (SPP), the collective excitations of electrons and light at the interface between a conductor and a dielectric. The field of plasmonics has attracted significant interests due to its ability to confine and manipulate light below the diffraction limit and/or produce high local field intensities. Nowadays, plasmonics has triggered a plethora of applications including optical antenna [34, 35], near-field optical microscopy [36], chemical and biological sensing [37–39] and subwavelength optics [40–42], to name a few. Despite the fact that noble metals such as silver and gold are still the predominant materials of choice for plasmonics, devices fabricated from these materials face several constraints. For example, their operating wavelengths are hardly tunable once the geometry of the structure is fixed. Moreover, they suffer from large Ohmic losses due to the limitation of carrier mobilities, surface roughness, grain microstructure and impurities. Compared to conventional plasmonic materials, graphene plasmons (GPs) presents the following unique properties: (i) Tunability. Due to the relativistic nature of carriers in graphene, the plasmon mass increases proportionally with the Fermi level. Therefore, the optical response of doped graphene strongly depends on the doping level, which can be chemically or electrostatically tuned. (ii) Strong field confinement. GPs propagate at a speed comparable to the Fermi velocity v_F, which is much smaller than the light velocity. As a result, GPs have plasmon wavelengths that are typically 1–3 orders of magnitude smaller than the light wavelength. (iii) Low losses and long lifetime. The high conductivity of graphene can be translated to a fairly long optical relaxation times (~10⁻¹⁰ s), compared to ~10⁻¹⁶ s in gold, indicating less plasmon dissipation and longer plasmon lifetime. (iv) Crystallinity. The strong carbon chemical bonds make graphene structures defect-free over several plasmon wavelengths [43]. While fabrication imperfections limit the performance of nanometallic plasmonic structures.

The strong subwavelength confinement of light is accompanied by the technical difficulty to excite plasmons experimentally. The incident light usually does not have sufficient momentum to excite plasmons directly because the free-space photons often have much longer wavelength and hence lower momentum than the plasmons. Artificially creating discontinuities in the electric permittivity of graphene enables standing localized plasmon waves confined to the metal surfaces, when the light frequency is tuned to its plasmon resonance frequency [44]. By patterning graphene, for example, into ribbons or disks, localized plasmon modes can be excited by normally incident light [45–49]. In graphene ribbons, plasmonic resonances occur when the plasmon wavevector q=(2n+1)π/W, where W is the ribbon’s width and n=0, 1, 2, which means that the plasmon half-wavelengths
should be able to fit within the ribbon width. Only plasmonic modes with odd multiples of half-wavelengths couple with light as this produces an effective charge dipole that creates the necessary restoring force for collective carrier oscillations. For incident light polarized parallel to the ribbons, the measured spectral line shape are very close to that in a continuous sheet of graphene and the response can be described by the Drude model [inset of Figure 3A]. For incident light polarized perpendicular to the ribbon, as shown in Figure 3A, distinctive absorption peaks originated from plasmon oscillation dominates the optical response are observed. A good agreement between the observed GP resonances to the damped oscillator model was found.

It is worth noting that GP resonances can be tuned in situ over a broad terahertz frequency range by varying micro-ribbon width and electrostatic doping, as shown in Figure 3A. Plasmon absorption peaks can be shifted to higher energies and gain oscillator strength with increased carrier concentration. In the experiment carried out by Ju et al., an ion gel was used for gating, and the induced carrier concentration was about $10^{13}$ cm$^{-2}$, which enabled the plasmon resonance to access the terahertz spectral range. In general, the ribbon width and carrier doping dependences of graphene plasmon frequency reveal a power-law behavior characteristic of two-dimensional massless Dirac electronsc [53]. The plasmon frequency scales like $W^{\frac{1}{2}}$, where $W$ is the width of the ribbon, and like $n^\alpha$, where $n$ is the carrier density, as predicted by the random phase approximation (RPA). Besides the tunable terahertz plasmons in graphene ribbons, plasmon hybridization in coupled graphene ribbons has been demonstrated [54] and splitting of GPs into bulk and edge modes in high magnetic fields has been achieved [55].

In addition to graphene ribbons, closely packed graphene micro/nanodisks can also support tunable localized GPs and in turn, significantly increase the light absorption at the wavelength of interest [56, 57]. In order to further increase the degree of light matter interaction and the tunability of plasmon resonance, researchers have made attempts to distribute Dirac fermions in a single layer of graphene disks into multiple layers of closely stacked graphene disks [50]. The extinction spectrum of microdisk arrays with one, two, and five graphene layers are shown in Figure 3B. In the design, the disk diameter $d$ and the lattice constant $a$ are 4.4 µm and 9 µm, respectively. The graphene disk array is patterned on 300 nm of SiO$_2$ on a highly resistive silicon substrate. As can be seen from Figure 3B, significantly increased the plasmonic resonance frequency as well as the peak intensity have been obtained. This is resulted from the Columbic interaction between adjacent layers: the in-phase collective motion of carries among layers leads to a stronger restoring force through dipole-dipole coupling [50, 58]. Interestingly, it was also found that the plasmonic frequency exhibits an $n^{\alpha}$ dependence other than $n^{\alpha}$ for the case of monolayer, which can only be explained in the context of quantum mechanics. In addition, stacked graphene disks could be used as an electromagnetic radiation shield with 97.5% effectiveness, a tunable, far-infrared notch filter with a rejection ratio of 8.2 dB and a tunable terahertz linear polarizer with an extinction ratio of 9.5 dB.

The extraordinary field confinement ($\sim 10^6$ smaller than diffraction limit) of GPs also facilitates the research of fundamentally new regimes of strong light-matter coupling or vacuum Rabi splitting (VRS) [49]. Strong light-matter coupling is one of the most intriguing fields in condensed matter physics since it has inspired the research from quantum optics such as single-atom lasing, quantum entanglement, classical regime such as non-biquitous many-atom sensing to the boundary exploration between quantum and classical physics [59–62]. VRS usually occurs when one of the oscillators consists of a two-level atom or quantum dot (QD), and the other is that of a small-volume high-quality (high-Q) cavity. When the coupling strength $g$ between two same-energy oscillators exceeds the mean of their decay rates $\frac{1}{2}(\kappa + \gamma)$, then the coupled system will have two eigen-energies. The coupling strength is measured by Purcell factor $F_p$ [63], which describes spontaneous emission modified by coupling to an optical cavity. The $F_p$ is proportional to the ratio of the $Q$ factor of the photonic or plasmonic resonance to the effective mode volume $V_{eff}$ [64]. VRS has been difficult to achieve with conventional metal plasmonics since they exhibit large Ohmic losses and are hardly tunable. Conventional optical microcavities provides an effective way to enhance light-matter coupling due to the achievement of $Q$-factor as high as even $10^8$ and is widely employed in the study of cavity quantum electrodynamics (QEDs) [65, 66]. The damping time $\tau$, i.e., $1/\gamma$, is long enough to allow the sufficient energy exchange between the emitter and the cavity. However, the reduction of $V_{eff}$ in the cavity is constrained by the diffraction limit, which limits the further enhancement of $F_p$. In addition, the technique of temperature scanning of the QD transition through the cavity resonance was usually used to map out the anticrossing, which may cause acoustic phonon broadening of the QD [62]. In comparison, graphene offers remarkable degree of confinement. Therefore, very small mode confinement compensates for the low quality factors ($Q\sim 10$) for graphene plasmons in mid-infrared regime. More importantly, the doping level tunable $E_{g}$
Plasmonics of graphene.

(A) Plasmon resonance in gated graphene microribbon arrays. Left: top and side views of a graphene microribbon array. Right: gate-dependent relative transmission spectra. Reproduced with permission from Ref. [46].

Bottom: Extinction spectra of graphene microdot arrays with various widths. A clear anti-crossing behavior is evident. Reproduced with permission from Ref. [50].

(C) Fermi- and photon-energy dependence of the extinction cross section of a combined emitter-nanodisk system. The emitter has a resonance at $\hbar \omega_0 = 0.3$ eV and is oriented parallel to the disk. Reproduced with permission from Ref. [49].

(D) Schematic of graphene nanoresonators fabricated on a monolayer h-BN sheet on a SiO$_2$ (285 nm)/Si wafer. Reproduced with permission from Ref. [51].

(E) Diagram of an infrared nano-imaging experiment at the surface of graphene on SiO$_2$. Reproduced with permission from Ref. [52].
of graphene provides an elegant approach to manipulate the coupling strength. By putting a dipole 10 nm above the center of a self-standing 100 nm graphene disk (within the decay length of localized GPs sustained by a graphene nanodisk), Koppens et al. theoretically predicted the Rabi splitting mediated by the localized GP as shown in Figure 3C. The emitter used in the calculation has an excited energy of $\hbar \omega_{0} = 0.3$ eV and natural decay rate $\Gamma_{1} = 5 \times 10^{15}$ s$^{-1}$. Importantly, the quantum mechanical strong light matter coupling of GPs and single emitter has also inspired the research of strong GP interaction with ensemble of oscillators, which can be treated classically. This may have far-reaching implications for development of the highly sensitive infrared bio/chemical sensing and molecule detection techniques [67, 68].

The electronic degrees of freedom in graphene can also couple strongly to substrate polar phonons [47] and the intrinsic IR-active phonons of bilayer graphene [69]. In these experiments, graphene devices have shown a strongly modified graphene plasmon dispersion relation caused by substrate phonons. For example, in the case of a SiO$_2$ substrate, the surface polar phonon modes at 806 cm$^{-1}$, and 1168 cm$^{-1}$ hybridize with the graphene plasmon to form the plasmon-phonon resonances [47]. Recent study by Freitag et al. has revealed that the substrate’s phonons can also affect the photocurrent generation process in graphene [70]. Besides, the high confinement of graphene plasmons even allow them to couple strongly to optical phonons in an atomically thin layer, such as monolayer hexagonal boron nitride (h-BN) sheet [51], as shown in Figure 3D. The plasmon dispersion $\omega_{pl}(q)$ of graphen/h-BN/SiO$_2$ nanoresonator was mapped out by performing measurements on graphene ribbon arrays with various widths. A clear anti-crossing behavior has been displayed, indicating the existence of hybridized plasmon-phonon mode near the surface polar phonon frequency. This hybridized mode can be phenomenologically modeled by two electromagnetically coupled oscillators [71]. The local polarization field created by lattice displacement in the h-BN applies a force on the free carriers in the graphene resonator. And in turn, the polarization due to displaced carriers in the graphene exerts a force on the h-BN lattice. As a consequence, the polarizations of the two modes cancel each other out, creating a transparency window where no absorption occurs. This phenomena, which is also denoted as phonon induced transparency (PIT) [71], is analogous to electromagnetically induced transparency (EIT) which is the result of destructive interference effect between a direct transition and an indirect transition pathway. The study of phonon-plasmon interaction offers physical insights towards plasmon dampings in graphene and serves as an important design consideration for graphene based plasmonic devices, such as waveguides, modulators and detectors in mid-infrared regime. Moreover, the realization of the EIT-like phenomenon in tunable graphene plasmonic systems opens up new opportunities for the exploration of quantum nonlinear optics [72], quantum information processing [73], and slow light [74] at room temperature without external pumps.

An alternative way of exciting GPs besides patterning graphene arrays is scattering-type near-field optical microscopy [52, 75]. A schematic picture of the experiments is shown in Figure 3E. This technique involves illuminating a sharp metallic tip with infrared light. The tip can "emit" radiation over a large span in momentum space that can be used to launch Dirac plasmons locally. These propagating plasmons will be reflected from the edge of the sample and interfere with the forward-propagating plasmon through the tip. Infrared nano-imaging revealed that the plasmon wavelength compression $\lambda_{pl}/\lambda_{sp}$ reached 40 and the plasmon in confined geometries can be tuned or switched by gating.

In general, the field of graphene plasmonics utilizes the semi-metallic nature of graphene to create plasmonic devices with their resonance frequency tunable by changing the Fermi level in graphene. This provides a new degree of freedom in the design and operation of plasmonic devices, which is not previously available in the traditional metal-based plasmonic devices. There are many promising applications of these graphene-based plasmonic devices in optical communications, sensing and imaging, especially in the strategically important mid-infrared and far-infrared region.

### 3 Photonics of TMDCs

Transition metal dichalcogenides (TMDCs) are materials with the chemical formula MX$_2$, where M stands for a transition metal element like Mo, W, Nb, Re, and X is a chalcogen (S, Se, Te). Typically one layer of TMDCs consists of an X-M-X sandwich structure. The inter-layer interaction of TMDCs is the weak Van der Waals force, while the in-plane bonding is the strong covalent bond. Thus, bulk TMDCs can be exfoliated down to few-layer films similar to graphene, extending the zoo of two-dimensional materials significantly. Some 2D TMDCs, such as molybdenum- and tungsten-based dichalcogenides, have an indirect bandgap in multi-layer forms, while become direct-bandgap-semiconductors in their monolayer forms.
Their sizable and tunable bandgap (1-2 eV) not only generates strong photoluminescence [77], but also open doors to various optoelectronic applications such as photodetectors [78–80], energy harvesting [81–83] and electroluminescence [84–87], with operational spectrum range that is different from graphene based devices. In addition, exotic optical properties such as valley coherence [88] and valley-selective circular dichroism [89] have been demonstrated in some 2D TMDCs, making these materials very promising for the discovery of new physical phenomena.

### 3.1 2D TMDCs based photodetectors

Compared to graphene based photodetectors, few-layer TMDCs based photodetectors have higher photoresponsivity, though they work mainly at the visible region. High-performance photodetectors have been made by various 2D TMDCs, such as MoS$_2$, WS$_2$, and ReSe$_2$. Lopez-Sanchez et al. [80] have made monolayer MoS$_2$ phototransistors of high sensitivity. Owning to the high gain of monolayer MoS$_2$, their devices can reach a photoresponsivity of 880 A/W at wavelength of 561 nm, with an operational range from 400 nm to 680 nm (Figure 4A). Nengjie Huo et al. [79] made a multi-layer WS$_2$ phototransistor which demonstrated a responsivity of 5.7A/W and an external quantum efficiency (EQE) of 1118% at 633 nm red light. Shengxue Yang et al. [78] have fabricated photodetector with Mo doped ReSe$_2$ nanosheets, obtaining a photoresponsivity of 55.5 A/W and an EQE of 10893% at 633 nm light in ammonia environment. Most of these detectors operate at the visible spectrum, as a result of their bandgaps being around 1.5–2.5 eV. At the visible range, these photodetectors possess much better performance than pristine graphene-based photodetectors.

![Figure 4](https://example.com/figure4.png)

**Figure 4** Photonics of TMDCs.

(A) Drain-source characteristic of the monolayer MoS$_2$ based photodetector in dark and under various incident intensities. Raising illumination intensities results in enhanced photocurrent owning to electron-hole pair generation in the direct bandgap of monolayer MoS$_2$. Reproduced with permission from Ref. [80]. (B) Schematic of the WSe$_2$ p-i-n junction formed by electric-double-layer transistors. Reproduced with permission from Ref. [84]. (C) Electroluminescence spectrum (blue) and the photoluminescence spectrum (red) of the WSe$_2$ p-n junction closely resemble each other. Reproduced with permission from Ref. [85].
3.2 2D TMDCs based LEDs

Light-emitting diodes (LED) is widely used for display, lighting, and sensing. Since monolayer TMDCs like WSe₂ are direct-bandgap semiconductors, electrons and holes can easily recombine with each other in radiative processes to generate photons. Electroluminescence localized at the contact region [90] and occurred on heavily p-doped silicon substrates [91] has been obtained in single layer MoS₂ field effect transistors. However, the optoelectronic efficiency of MoS₂ based LEDs is relatively low and drops significantly with increasing carrier injection [92]. Indeed, the difficulty to obtain hole conduction, the ineffective contacts, and the limited optical quality of monolayer MoS₂ have hindered the potential applications of MoS₂ LED.

Recently, WSe₂ monolayer lateral diodes have been demonstrated by applying multiple independent gate voltages. Through tuning electrostatic doping, both p-n and n-p diodes can be defined, leading to effective bright electroluminescence. Zhang et al. [84] have made use of the valley degrees of freedom of few-layer WSe₂ to get circularly polarized luminescence. The emitted light came from an electrostatically formed in-channel p-i-n junctions (Figure 4B). Ross et al. [85] also demonstrated a monolayer WSe₂ based LED. They made electrostatically formed p-n junctions in WSe₂ with a boron nitride film underneath served as a dielectric layer. Electrons and holes can thus be injected into channels effectively via this structure, leading to a strong electroluminescence. The total photon emission rate can reach 16 million s⁻¹ at an applied current of 35 nA. They also found that both electroluminescence and photoluminescence in this system came from the same valley excitons (Figure 4C). At this point, the research of the light emitting devices based on TMDCs are still in their early stage. More efforts are needed to further improve their efficiency and gain. Furthermore, it is still a long way from obtaining high optical gain in TMDCs and more work is still needed in exploring the possibility of achieving lasing in these materials.

4 Black phosphorus for photonics application

Few-layer black phosphorus (BP) is an emerging 2D material with a puckered orthorhombic lattice (Figure 1D). Its anisotropic in-plane lattice structure lowered its spatial symmetry, resulting in highly anisotropic electronic and optoelectronic properties. Bulk BP has a moderate bandgap of 0.3 eV [93–95], which increases monotonously with reducing number of layers, eventually reaching 2 eV [96, 97] for monolayer. Hence, for photonic applications, black phosphorus can cover a broad spectrum, from the visible to mid-infrared. The moderate and tunable direct bandgap of BP bridges the zero-bandgap graphene and relatively wide bandgap TMDCs, making BP a promising material for future electronics and optoelectronics.

Xia et al. [98] have characterized the polarization-resolved infrared relative extinction spectra of multilayer BP flakes. The incident light was polarized towards six different angles, uniformly separated by 30 degrees (Figure 5A). The relative extinction indicated a narrow bandgap of 0.3 eV. Their extinction spectra coincides with the theoretical calculation precisely [101]. Polarization-resolved Raman spectra of a BP film was also measured, indicating a polarization-dependent relative intensities of three characteristic vibration modes.

Calculations have revealed that black phosphorus has a strongly layer-dependent bandgap [102]. Bandgap of BP increases with decreased layers, due to the enhanced two-dimensional quantum confinement and reduced screenings in fewer layers. According to the calculation, the energy bandstructure of layered BP is significantly tuned by its strong many-electron effects: large self-energy corrections have contributed to enhance the bandgap of monolayer BP from 0.8eV (as calculated) to more than 2.0 eV, while a huge exciton binding energy (~0.9eV according to a recent report [103]) has lowered its first optical adsorption peak location from 2.2ev to 1.3 eV. These effects improve the tunability of the bandstructure of layered BP, making it promising for broadband device applications.

Buscema et al. [99] investigated the photorepons of few-layer BP transistors by performing electrical measurement in dark and bright environment. Their device worked from the visible region to infrared, with a response time of 1 ms (rise) and 4 ms (fall), see Figure 5B. The photoresponsivity in visible region can reach 4.8 mA/W, which decreased with incident power. Engel et al. [104] performed photocurrent measurement and high-resolution imaging with a 120 nm-thick BP. They verified that BP photodetector is capable of recording images in both the visible (532 nm) and the infrared (1500 nm) region with ultrahigh resolution. The measured responsivity is 20 mA/W at visible region and 5 mA/W at infrared region. An analysis [105] based on this experiment and related modeling revealed that photothermal effects in BP are responsible for its low bias photorespons, while the bolometric effects dominate at large bias. In addition, the photocurrent polarities, according to their analysis, originate from these two effects, rather than the photovoltaic effect.
Hong et al. demonstrated transport and optoelectronic measurement on few-layer BP based phototransistors [100]. Their work indicated that BP photoresponse near the BP-electrode interface mainly arises from the photovoltaic effect in off-state, while in on state photothermoelectric effect dominates. They also revealed that the anisotropic photoresponse should be attributed to angle-dependent absorption of BP crystals. Figure 5C is the anisotropic photoresponse measurements of a BP FET under zero source-drain bias and a back-gate voltage of 10 V. The red/blue curve demonstrates the angle dependence of the strongest positive/negative photoresponse at BP-metal interface, respectively.

Besides the advantages mentioned above, black phosphorus also has other impressive properties such as linear dichroism [96], high hole mobility [106], Large thermoelectric power factors [107], and anisotropic plasmonic excitations [108]. However, some challenges remain in BP research and application. For example, monolayer BP degrades rapidly in air, due to oxidation [109] and water.
adsorption [110]. Therefore, developing clean and efficient protection methods are necessary. Moreover, currently the fabrication of few-layer BP relies on mechanical exfoliation method [43, 111, 112], which is of rather low yield. So we need to develop large-area synthesis methods to produce wafer-scale few-layer black phosphorus. Solving these problems will push forward various novel applications of BP. Nevertheless, black phosphorus has demonstrated intriguing properties and promising potential for applications in infrared optoelectronics while its anisotropic properties may lead to the invention of conceptually new devices.

5 Future directions

Atomically thin materials such as graphene, transition metal dichalcogenides and the emerging black phosphorus are being developed as the building blocks for a wide range of optoelectronic devices. These materials offer diverse choices including metals, semimetals, and semiconductors with small or large optical gaps allowing for different and new application space even beyond what conventional bulk materials can possibly offer. To fully exploit their potentials, there is an apparent need to gain more fundamental understandings on their intrinsic and extrinsic optical behaviors, e.g., excitonics, optical non-linearity, mechanisms of photoresponse et al. Furthermore, issues involving low light absorption and short light-matter interaction length of 2D materials need to be addressed. This could open up the new areas of research into the symbiotic relation between these materials with conventional photonic elements including cavities, waveguides or plasmonic nanostructures. The potential of mid-infrared and terahertz graphene plasmons is also being realized, demonstrating very attractive features including extremely high field confinement, tunability and long lifetime, which can serve as a platform for efficient light-matter interaction in the quantum optical regime. Beyond the graphene plasmons, the extraordinary optical non-linearity and fast modulation speed of graphene are also favored for optical communication applications. One remaining challenge is to extend the operating window of tunable graphene optical response from the infrared toward other regions of the electromagnetic spectrum where it can find a larger range of applications from optical modulation, spectral light detection to sensing. To this end, the development of controllable and stable chemical doping for graphene and even other 2D materials is highly desirable. In addition to the optical properties of a material itself, the availability of hybrid heterostructures will give rise to intriguing optical properties as well as expanded device functionalities involving efficient solar cells, ultrafast optical modulators or detectors and 2D light emitting devices or lasers in the near future.

References


