Two-dimensional material nanophotonics

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Two-dimensional materials exhibit diverse electronic properties, ranging from insulating hexagonal boron nitride and semiconducting transition metal dichalcogenides such as molybdenum disulphide, to semimetallic graphene. In this Review, we first discuss the optical properties and applications of various two-dimensional materials, and then cover two different approaches for enhancing their interactions with light: through their integration with external photonic structures, and through intrinsic polaritonic resonances. Finally, we present a narrow-bandgap layered material — black phosphorus — that serendipitously bridges the energy gap between the zero-bandgap graphene and the relatively large-bandgap transition metal dichalcogenides. The plethora of two-dimensional materials and their heterostructures, together with the array of available approaches for enhancing the light–matter interaction, offers the promise of scientific discoveries and nanophotonics technologies across a wide range of the electromagnetic spectrum.

Many-layered materials in their bulk forms have been widely known and utilized for a long time. For example, graphite and MoS2 are used as dry lubricants owing to their layered nature, whereby atoms are strongly bonded within the same plane but only weakly attached to sheets above and below by van der Waals forces. This weak interlayer interaction makes the extraction of a single or a few layers of atoms possible, thus leading to the burgeoning research on two-dimensional (2D) materials1–15, including their photonic properties and applications. In this Review, we broadly define 2D materials to include multilayers, heterostructures and layered thin films whose total thicknesses vary from one atomic layer to tens of nanometres. 2D here implies that the thickness of the material under investigation is orders of magnitude smaller than the wavelength of light involved.

Compared with traditional 3D photonic materials such as gallium arsenide (GaAs) and silicon (Si), 2D materials exhibit many exceptional properties. First, quantum confinement in the direction perpendicular to the 2D plane leads to novel electronic and optical properties that are distinctively different from their bulk parental materials. Second, their surfaces are naturally passivated without any dangling bonds, which makes it easy to integrate 2D materials with photonic structures such as waveguides16–19 and cavities20–24. It is also possible to construct vertical heterostructures using different 2D materials without the conventional ‘lattice mismatch’ issue, as layers with different lattice constants in heterostructures are only weakly bonded by van der Waals force as in layered bulk materials. Third, despite being atomically thin, many 2D materials interact strongly with light. For example, a single layer of MoS2 absorbs around 10% of vertically incident light at excitonic resonances (615 nm and 660 nm).25 Finally, 2D materials can cover a very wide range of the electromagnetic spectrum because of their diverse electronic properties (Fig. 1a).

Graphene, being gapless and semimetallic, interacts with light from microwave to ultraviolet wavelengths27,28, thus making it a potential candidate for various light detection, modulation and manipulation applications over a wide spectral range. However, its semimetallic nature prevents the realization of efficient graphene-based light-emitting devices. In contrast, single-layer transition metal dichalcogenides (TMDCs) such as molybdenum disulﬁde (MoS2) and tungsten diselenide (WSe2) are direct-bandgap semiconductors11,12 (Fig. 1c) that exhibit encouraging light-emitting properties primarily in the near-infrared wavelength range. Here, emission is dominated by excitons and trions due to the strong Coulomb interactions arising from their low dimensionality and reduced dielectric screening. Furthermore, as will be discussed later, the breaking of inversion symmetry and strong spin-orbit coupling in TMDCs lead to valley-selective circular dichroism29–32. Different valleys can be pumped selectively using left- and right-circularly polarized light to generate carriers with different magnetic moments, leading to the emerging field known as valleytronics. Hexagonal boron nitride (hBN) is another important type of 2D material33. It has a large bandgap of around 6 eV (Fig. 1b), which makes it an excellent dielectric, and can be incorporated into various heterostructures for the electrostatic gating of other 2D materials, as the ‘lattice match’ is not necessary in these van der Waals heterostructures. Other than graphene, TMDCs and hBN, the recently rediscovered black phosphorus (BP) exhibits a direct bandgap of around 0.3 eV in its bulk form34. The bandgap of BP is expected to increase monotonically as the number of layers decreases, owing to electronic confinement in the direction perpendicular to the 2D plane, and single layer BP is estimated to reach a single-particle bandgap of around 2 eV (Fig. 1d).34, The wide range of material properties, together with the possibilities for combining 2D materials with different layer numbers and compositions, allows for the realization of various nanophotonic devices and the exploration of fundamental optical sciences, covering a wide spectral range from the microwave to the ultraviolet (Fig. 1a).

Photonic devices using 2D materials

The unique optical properties of 2D materials enable many important device applications in nanophotonics.

Photodetection mechanisms in graphene. Graphene attracts significant attention for photodetection because of its strong interaction with photons in a wide energy range27,28 and its high carrier mobility, making it a promising candidate for high-speed light detection applications in a broad wavelength range. In early studies, the photodetection mechanism in graphene was attributed to the traditional photovoltaic effect35–37 as in 3D semiconductors such as GaAs and Si, whereby photocurrent results from the separation of photogenerated electron–hole pairs by a built-in electric field.

However, subsequent investigations by Xu et al.38 revealed a more complex situation, owing to the gapless nature and reduced
multiplication electron–hole pairs with a single photon — an effect called carrier due to strong carrier–carrier interaction can also generate multiple processes, thus leading to a common quasi-Fermi level for both types and holes in the conduction and valence bands through Auger-type moelectron (PTE) effect driven by these 'hot' carriers — a phenomenon called the photo-thermoelectric (PTE) effect.

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In short, the carrier dynamics in graphene under illumination are different in many respects from those in 3D semiconductors with a significant bandgap, where photons with energies similar to the semiconductor bandgap are absorbed by the graphene Seebeck coefficient on gate biases, which governs

under zero external bias. This is fundamentally different from the multiplication effect in traditional avalanche photodetectors, in which carriers are first accelerated under a high electric field to provide them with enough energy to excite additional electrons from the valence band to the conduction band. In short, the carrier dynamics in graphene under illumination are different in many respects from those in 3D semiconductors with a significant bandgap, where photocarriers have longer lifetimes and are usually generated by photons with energies similar to the semiconductor bandgap. As a result, the photogenerated electrons and holes in traditional semiconductors are characterized by well-separated quasi-Fermi levels and the carrier temperature usually does not significantly differ from the lattice temperature.

Gabor et al. demonstrated that at a dual-gated graphene p–n junction (Fig. 2a), the photovoltage exhibits a six-fold polarity variation pattern when the top and bottom gate biases change (Fig. 2b) — a signature of the PTE effect. The changing of photocurrent polarity for multiple times is attributed to the non-monotonic dependence of the graphene Seebeck coefficient on gate biases, which governs

Figure 1 | 2D materials covering a broad spectral range. a, Electromagnetic spectrum. Applications that utilize the different spectral ranges are presented in the top portion of the panel. NIR, MIR and FIR indicate near-, mid- and far-infrared, respectively. The atomic structures of hBN, MoS₂, BP and graphene are shown in the bottom of the panel, left to right. The crystalline directions (x, y) and (z) of anisotropic BP are indicated. The possible spectral ranges covered by different materials are indicated using coloured polygons. b–e, Bandstructures of single-layer hBN (b), MoS₂ (c), BP (d) and graphene (e).
the photovoltage (or current) due to the PTE effect. On the contrary, if the traditional photovoltaic effect dominates, the polarity of the photocurrent only depends on the direction of the built-in electric field, and thus multiple polarity variations as a function of gate biases are not expected.

Freitag et al.\(^4^7\) explored photocurrents in biased graphene. Figure 2c denotes a reflection image of a graphene field-effect transistor under investigation with a channel measuring 1 μm × 6 μm. A constant source–drain bias of 1 V is applied to the device and the photocurrent is determined by comparing the source–drain current with and without light illumination. In this case, three photocurrent generation mechanisms are identified: the traditional photovoltaic effect, the PTE effect, and the bolometric effect. As shown in Fig. 2d, when the channel doping is high (but uniform), the PTE effect is negligible, as discussed above. The photovoltaic effect does exist but the bolometric effect is dominant: the total current decreases under light excitation as the increase in temperature causes a reduction in carrier mobility. When the graphene channel is intrinsic (Fig. 2e, gate bias V\(_G\) close to Dirac point voltage V\(_{\text{Dirac}}\)), the traditional photovoltaic effect dominates because the increase in carrier temperature leads to extra electrons and holes\(^4^8\), thus enhancing the total current. In intrinsic graphene, the carrier mobility is much less sensitive to temperature\(^4^9\) and so the bolometric effect can be ignored. Furthermore, although in this case a finite drain bias V\(_D\) will introduce a slightly non-uniform doping along the graphene channel, the PTE effect will reduce the total current under light illumination (Fig. 2e) and, from the polarity of the photocurrent, it is clear that the photovoltaic effect dominates in this case. Figure 2f summarizes the polarity of the photocurrent under different biasing conditions.

It has been shown experimentally by many groups that graphene photodetectors can operate at speeds greater than tens of gigahertz\(^1^7-2^0\). Photocurrents arising from the photovoltaic effect are intrinsically suitable for such high-speed operation (up to hundreds of gigahertz) owing to the high carrier mobility and high carrier saturation velocity. For the PTE effect, the maximum speed of operation depends on the carrier cooling time, which can be longer than 100 ps\(^4^6\). This relatively long carrier cooling time in graphene can still support photodetector operation in the gigahertz range. However, enhancement of photocurrent due to the PTE effect requires the suppression of cooling channels to increase the carrier temperature \(T\), which inevitably leads to a longer cooling time and thus slower speed. Effective utilization of multiple photocurrent generation mechanisms in graphene for different optical applications is an important future research topic. In addition, the carrier multiplication effect may be leveraged to further enhance the performance of graphene photodetectors.

**Light-emitting properties and circular dichroism in TMDCs.** Unlike graphene, some members of the TMDC family are true semiconductors with appreciable bandgaps. In particular, molybdenum- and tungsten-based dichalcogenides exhibit optical bandgaps in the range of 1–2 eV, which makes them suitable for near-infrared absorption and emission. Interestingly, although these materials have an indirect bandgap in the bulk and few-layer form, they become direct-gap semiconductors with strong photoluminescence at the monolayer level\(^1^1-1^2\). Bandgaps in TMDCs have also been shown to be tunable — over a range from semiconducting to near-metallic — through application of an external electric field or mechanical strain\(^1^0-1^5\), which is a useful property for engineering the optoelectronic response for specific applications. Duerloo et al. showed theoretically that mechanical deformations can switch thermodynamic stability between a semiconducting and a metallic crystal structure in Mo- and W-dichalcogenide monolayers\(^5^8\). They further identified that molybdenum telluride (MoTe\(_2\)) can be an excellent candidate for the observation of such phase transitions, which can be utilized to manipulate the optical response of the materials.

More importantly, TMDC monolayers have been shown to display unique physics hitherto unobserved in other 2D materials. In contrast with conventional semiconductors such as GaAs, the direct bandgap in TMDC monolayers occurs at the two unequalled corners (K and K') of the hexagonal Brillouin zone, thereby endowing the electrons with a valley degree of freedom\(^3^2\). It was predicted that the lack of an inversion centre in the crystal structure leads to valley-contrasting orbital magnetic moment and circular dichroism\(^3^9\), which allows selective pumping of valley carriers by controlling the circular polarization of light\(^3^6-3^2\). It is also possible, vice versa, to make polarized LEDs in TMDC monolayer p–n junctions\(^5^4-5^6\) (Fig. 3a). In
Figure 3 | Optoelectronic properties of semiconducting TMDC monolayers. a. Polarization-resolved electroluminescence spectra from a WSe$_2$ p-i-n junction. Left and right panels show the spectra dominated by $\sigma_-$ and $\sigma_+$, respectively. Also shown are the current-flowing directions and the K and K$'$ valleys. b. Derivative of the reflection contrast spectrum for a WS$_2$ monolayer. Excitonic Rydberg series (A-type excitons) are labelled using the quantum orbital terminology of 1$s$, 2$s$ and so on. AX and AX$'$ denote exciton and trion transitions, respectively. Inset: reflection contrast spectrum. Main transition peaks correspond to A, B and C excitons. c. Photoluminescence spectrum of monolayer MoSe$_2$ at 20 K. Inset: detailed view showing both exciton (X) and trion (X$'$) peaks. The binding energy of X is 30 meV. Figure reproduced with permission from: a, ref. 54, © 2014 AAAS; b, ref. 60, © 2014 APS; c, ref. 62, Nature Publishing Group.

In this case, the electric field at the junction preferably populates the carriers in one particular valley (K or K$'$), depending on the field direction. As a result, reversing the field direction switches the dominant polarization ($\sigma_-$ or $\sigma_+$) in the emitted light. Such TMDC monolayer p-i-n junctions can also be used for light detection and energy harvesting. Additionally, excitonic valley coherence has also been demonstrated. This type of dynamic control of valley index opens up the exciting possibility of valleytronics — optoelectronic devices and systems based on the manipulation of the electrons’ valley index. Furthermore, the strong spin-orbit coupling arising from transition metals locks the valley index with the electron spin, which could be useful for many optoelectronic applications. For example, the injection of carriers with specific spins through ferromagnetic contacts can create a population imbalance between the two valleys, thereby potentially providing LEDs with a dominant polarization state ($\sigma_-$ or $\sigma_+$).

Another important property of TMDC monolayers is their large exciton binding energy (0.5–1 eV) arising from the substantially reduced dielectric screening relative to the bulk. This leads to strong and long-lived excitons, thus making such devices suitable for LEDs, photomarkers and other related applications. Figure 3b shows the Rydberg excitonic series in a reflection contrast spectrum of monolayer WS$_2$. Finally, the strong Coulomb interaction also allows the observation of trions — quasiparticles comprised of two electrons and a hole (or two holes and an electron) — in doped monolayer TMDCs under optical excitation. Figure 3c shows the photoluminescence spectrum of a monolayer MoSe$_2$ at 20 K. Both exciton (X) and trion (X$'$) peaks are observed. From the energy spacing between X and X$'$, a trion bonding energy of 30 meV is determined. These quasiparticles, which are unstable in conventional semiconductors due to the screened Coulomb interaction, have binding energies an order of magnitude larger than that of GaAs quantum wells and display valley-selective properties that are similar to those of the neutral excitons. However, unlike excitons, trions, being charged quasiparticles, are amenable to manipulation by electric fields, which could allow for the exploration of charge transport by composite particles and the efficient collection of photo-generated current, rather than relying on carrier diffusion alone.

Light harvesting and detection using 2D heterostructures. Despite being atomically thin, the surface of a 2D material is self-passivated without any dangling bonds. As a result, it is possible to construct functional devices by combining different 2D materials with very different lattice constants to form heterostructures, thereby leveraging the desirable properties of each material. Britnell et al. sandwiched a thin layer of WS$_2$ within two layers of graphene to form an efficient ‘Schottky-diode-like’ solar cell. In this device, the semiconducting WS$_2$ functions as the active energy-harvesting material, whereas the metallic graphene works as a transparent electrode for the efficient collection of photogenerated carriers. Researchers demonstrated an
Enhancing the interaction using photonic integration

Many 2D materials interact strongly with light. Both graphene and single-layer MoS$_2$ have absorption coefficients of more than $5 	imes 10^3$ m$^{-1}$ in the visible range (if normalized to the corresponding atomic thickness) — this is an order of magnitude larger than the absorption coefficients of GaAs and Si. However, owing to the innate thinness of graphene and single-layer MoS$_2$, such a strong interaction must be further enhanced before it can be used in practical devices. The integration of 2D materials with external photonic structures offers a solution in this respect. In particular, integration with optical cavities allows for the significant manipulation of the local optical density of states surrounding the 2D materials, thus leading to greatly modified emission/absorption properties.

The integration of ultrathin optical materials with an optical waveguide is a classic approach for enhancing the light–matter interaction in a non-resonant manner. Liu et al. integrated wafer-scale monolayer graphene with a Si optical waveguide to produce a broadband optical modulator covering the telecommunications range of 1.3–1.6 μm (Fig. 4a). Because a single layer of graphene absorbs around 2% of vertically incident light through inter-band transitions in the near-infrared, it is only possible to modulate the transmission from 98% to 100% if graphene is used directly for light-modulation purposes. By propagating the light in the silicon optical waveguide beneath the graphene (Fig. 4a), the light absorption is no longer limited to 2% but is rather determined by the length of the waveguide. Using a 100-μm-long silicon waveguide, Liu et al. demonstrated a graphene modulator operating at a bandwidth of more than 1 GHz and a modulation depth of 10 dB. A similar concept was used independently by three groups to enhance the responsivity of graphene high-speed photodetectors for optical communications (Fig. 4b–d). A maximum responsivity of around 0.15 A W$^{-1}$ and a 3 dB bandwidth of around 20 GHz were realized in a broad wavelength range from 1.3 to 1.6 μm, enabled by the non-resonant nature of the silicon optical waveguide. However, a relatively long wavelength (tens to hundreds of micrometres) is needed to achieve high absorption in graphene, which makes the total device much longer than the operational wavelength. Because the area of the metallic contacts scales proportionally with device length, these waveguide-integrated graphene devices have a relatively large capacitance, which limits the operational bandwidth to tens of gigahertz.

In contrast, the integration of 2D materials with an optical cavity makes the realization of compact devices possible at the expense of a reduced light–matter interaction bandwidth, which is determined by the quality factor of the cavity. Furchi et al. achieved a 26-fold enhancement in graphene’s absorption by integrating a graphene photodetector with a microcavity consisting of Bragg mirrors on both sides (Fig. 4e). The limited enhancement is attributable to the relatively low quality factor of the microcavity, as the Bragg mirrors provide optical confinement only in the vertical direction. Instead, the integration of graphene with a high quality factor, silicon photonic waveguide integration, enabled by the non-resonant nature of the graphene high-speed photodetectors for optical communications

Yu et al. reported a photodetector based on a graphene–MoS$_2$–graphene heterostructure, for which they achieved an external quantum efficiency of more than 50% at a wavelength of 500 nm. In both heterostructures, because a single layer of graphene cannot screen the electric field effectively, the photoresponse can be tuned using a back gate underneath the bottom graphene contact, which offers flexibility in electrical tuning. Future research on the wafer-scale production of such graphene/TMDC vertical heterostructures may lead to practical ultrathin solar cells.

It is also possible to realize photocurrent gain by integrating graphene with other photodetection materials. Konstantatos et al. integrated lead sulfide (PbS) quantum dots with a graphene transistor to produce a phototransistor with a photoconductive gain of more than $2 	imes 10^8$. In this device, efficient light absorption is due to the PbS quantum dots; the long carrier lifetime in PbS allows the photocarriers to reach a high density, which effectively modifies the graphene channel doping. This, together with graphene's high mobility, allows a large gain to be achieved. Similar high-gain photodetection is also observed in graphene–TMDC heterostructures. In these devices, large gain usually implies a slower device response. As a result, it is essential to optimize the gain and response time simultaneously for different applications.
Plasmon–polaritons in graphene. Propagating plasmon–polariton waves in a metal–dielectric interface are often used to confine the light beyond the traditional diffraction limit by leveraging the negative permittivity of metal. The field decaying length in both dielectric ($\delta_p$) and metal ($\delta_m$) can be much smaller than the wavelength of the light. a, Atomic force micrographs of an array of graphene nanoribbons, in which localized plasmons can be excited using vertical incident light with polarization perpendicular to the ribbons. b, Relative extinction spectra due to localized plasmon resonance in ribbons with widths of 1 μm, 2 μm and 4 μm, respectively. c, Top: experimental schematic for launching plasmon–polariton waves using a scanning near-field optical microscopy tip in a graphene wedge. The tip is illuminated using infrared light and collection of the local field in graphene is also realized using the tip. Middleg: measured local field in graphene. Bottom: calculated local field in graphene. Standing waves are formed due to reflections at the edges. $\lambda_g = 9.7$ μm. e, Experimental schematic for launching phonon–polariton waves using a scanning near-field optical microscopy tip in an hBN wedge. Inset: schematic showing the relative motions of the boron and nitride atoms. $\omega_{LO}$ and $\omega_{TO}$ are longitudinal and transverse optical phonon frequencies in bulk hBN, respectively. f, Calculated phonon–polariton dispersion relations at different hBN thicknesses. g, A schematic diagram showing the coupling between the graphene plasmon and the hBN phonon. h, Transmission extinction spectrum for an array of graphene nanoribbons (300 nm wide) on a single layer of hBN on an SiO$_2$ substrate. Peaks 1 and 2 are due to the coupling of graphene plasmons and SiO$_2$ phonons, whereas peaks 3 and 4 result from the coupling of graphene plasmons and hBN phonons. Figure reproduced with permission from: b,c, ref. 76, Nature Publishing Group; d, ref. 80, Nature Publishing Group; e,f, ref. 83, © 2014 AAAS; g, ref. 85, © 2014 ACS.

Enhancing the interaction using polaritonic resonances

Another approach for enhancing the interaction of light and 2D materials is to use their intrinsic polaritonic resonances. Polaritons are quasiparticles that result from the coupling of photons with electric dipole–carrying elementary excitations such as plasmons, phonons and excitons. The wide variety of 2D materials makes the exploration of different polaritonic excitations possible.

Ju et al.\textsuperscript{76} patterned a large piece of monolayer graphene into microribbons (Fig. 5b) and observed terahertz localized plasmon resonances when the incident light polarization was perpendicular to the ribbons, as the ribbons can only be effectively polarized for plasmon excitation along the perpendicular direction. Figure 5c shows the extinction spectra for ribbons with widths of 1 μm, 2 μm and 4 μm, which together indicate the size dependence of plasmon resonance in a 2D electron gas. The plasmon resonance peak and amplitude can be tuned using a gate bias, which demonstrates the unique in situ tunability of graphene plasmons. For graphene micro- and nanodisks, localized plasmons can be excited regardless of the light polarization due to the high structural symmetry. Furthermore, utilization of multiple graphene layers effectively enhances the strength of the plasmon resonance through dipole–dipole coupling among layers, and infrared filters and polarizers have been demonstrated using such graphene stacks\textsuperscript{77}. Finally, the relativistic mass in graphene has been revealed in the exploration of plasmon resonances\textsuperscript{26–27}.

Another innovative approach for exciting plasmons in graphene is to use a scanning near-field optical microscopy tip (Fig. 5d, top)\textsuperscript{78–80}. In this configuration, the nanoscale metallic tip is illuminated with infrared light and the additional momentum required for the excitation of graphene plasmon–polaritons is provided by the tip. The tip is also used to probe the plasmon–polariton waves in graphene. The bottom two panels in Fig. 5d represent the measured and calculated light intensities, respectively, at a plasmonic resonance of 9.7 μm. Standing-wave patterns are observed due to reflections at the graphene edges.
Compared with plasmons in metals, graphene plasmons cover a relatively less-explored wavelength range of the terahertz to the mid-infrared. The unique electrical tunability of plasmons in graphene makes it possible to realize optical modulators in this wavelength range. Together with the PTE effect discussed above, graphene plasmonic resonance may also be utilized to construct high-performance tunable photodetectors covering this broad wavelength range. Furthermore, improvements in graphene quality may ultimately lead to plasmon–polariton waveguides that exhibit high confinement beyond the diffraction limit, with propagation lengths exceeding tens of polariton wavelengths. Another important research task is to extend the graphene plasmon resonance to the near-infrared by suppressing the damping pathway through the emission of its intrinsic optical phonons.

**Phonon–polaritons and plasmon–phonon–polaritons.** Similar to traditional polar substrates such as silicon oxide, 2D hexagonal boron nitride (hBN) supports phonon–polaritons, quasiparticles that result from the coupling of photons and dipole-carrying optical phonons. Dai et al. investigated phonon–polaritons at the hBN surface by employing the same scanning near-field optical microscopy technique used to probe plasmon–polaritons (Fig. 5e). The layer nature of hBN makes it possible to tune the phonon–polariton resonance in a layer-by-layer manner. Figure 5f shows the calculated dispersion relationships of phonon–polaritons at different hBN thicknesses. The phonon–polariton resonance range accessed by varying the hBN thickness may allow for the realization of tunable mid-infrared optoelectronic devices.

By placing the graphene on polar substrates such as SiO₂ or BN, plasmons in graphene and phonons in polar substrates can couple if their energies and momenta match, leading to a new mixed state known as plasmon–phonon–polaritons. Figure 5g illustrates such a coupling process and Fig. 5h shows an extinction spectrum for a graphene–hBN ribbon array on an SiO₂ substrate, with a graphene ribbon width of around 300 nm. The presence of multiple extinction peaks is due to the coupling of graphene plasmon, SiO₂ surface polar phonon and hBN phonon modes. Exploring the coupling between plasmons and phonons will not only provide useful information on the interactions of carriers and substrates, but may also further enable light detection and modulation functions, leveraging the unique properties of both plasmons and phonons.

**Bridging the bandgap using layered black phosphorus**

Researchers have extensively explored zero-gap graphene and semiconducting single-layer TMDCs such as MoS₂ and WSe₂, which have optical bandgaps greater than 1 eV. Recently rediscovered layered-material black phosphorus, which has high mobility (up to 50,000 cm² V⁻¹ s⁻¹ in bulk at 30 K) and a direct bandgap of around 0.3 eV, bridges the gap between the gapless graphene and large-bandgap TMDCs, thereby making it an interesting addition to the existing 2D material family for nanophotonics and nanoelectronics. Based on thin-film (more than ten layers) BP transistors with field-effect mobility from a few hundred to 1,000 cm² V⁻¹ s⁻¹ and photodetectors operational at 1.5 μm have recently been demonstrated. Furthermore, by reducing the number of layers, the bandgap of BP is expected to increase monotonically to around 2 eV (single-particle bandgap) in the monolayer form, thereby covering a broad energy range.

The most striking property of layered BP is probably its in-plane anisotropy. Xia et al. measured the infrared extinction spectra of thin-film (around 30 nm) BP at different incident light polarizations (Fig. 6a). Compared with graphene, puckered BP exhibits lower symmetry (Fig. 1a), which results in in-plane anisotropic properties in momentum space. The bandstructure of BP is more dispersive in the x-direction (armchair), which leads to higher carrier mobility and greater optical conductivity along this direction. Figure 6b plots the calculated thin-film BP conductivity along the x-direction at different doping levels for BP thicknesses of 4 nm and 20 nm, which reveals the great potential of BP for infrared (1–5 μm) modulation functions, in addition to its promising future for light detection. The phononic properties of BP are also highly anisotropic, and the Raman scattering spectra of thin-film BP strongly depends on the polarization of the excitation light. In addition to the traditional mid- and near-infrared emission, modulation and detection devices, its unique anisotropic electronic, photonic and phononic properties may allow for the realization of novel optical components such as polarization sensors and anisotropic plasmonic devices. More interestingly, the preferable electron and heat conduction pathways in monolayer BP...
are along the armchair and zigzag directions, respectively, which are orthogonal to each other (Fig. 6c). This unique property makes monolayer BP a promising material for thermoelectric applications with a high thermoelectric figure of merit\(^6\).

It is also possible to construct photonic devices using heterostructures comprising both narrow-bandgap BP and larger-bandgap TMDCs. Figure 6d denotes such an infrared LED. Here, the direct-bandgap BP, whose bandgap can be tuned by varying the layer number (0.3 eV being the minimum), is utilized as an active material for light emission. The injection of holes and electrons can be realized by using p-type WSe\(_2\) and n-type MoS\(_2\), respectively. The injected carriers are trapped within the BP for light emission due to the band-offset at the BP–TMDC interface. Graphene can be used to minimize the contact resistance\(^6\). Lasing might also be possible if such an LED were to be integrated with a high-quality optical cavity. Phototransistors with gain and electro-absorption modulators in the mid- and near-infrared spectral range can also be built based on this concept of vertical van der Waals heterostructures.

Outlook

The emerging field of 2D materials provides the optical community with many exciting new opportunities for exploration of sciences and technologies across a very wide electromagnetic spectral range. Gapless graphene strongly interacts with light from the terahertz to the ultraviolet. Plasmon–polaritons in graphene allow for a highly confined light field and a greatly enhanced light–matter interaction at resonance. Coupling of plasmons in graphene and phonons in a polar dielectric forms a new type of quasi-particle: plasmon–phonon–polaritons, which can be utilized to enhance and tune the interaction between light and 2D materials. Although graphene is not an optimal material for light emission, many single-layer TMDCs are direct-bandgap semiconductors and exhibit strong excitonic emission properties that are gate-tunable, which makes them promising candidates for light emission in the near-infrared. Furthermore, the breaking of inversion-symmetry accompanied by strong spin-orbit coupling in such single layers results in the unique ‘valley polarization’, which has spawned the emerging field of valleytronics.

The bandgap of BP, a recently rediscovered layered material, is around 0.3 eV in its bulk form and is expected to increase monotonically as the layer number decreases to around 2 eV in its monolayer form, thus bridging the energy gap between gapless graphene and large-bandgap TMDCs. Furthermore, it may be possible to incorporate arsenic (As) into BP, leading to layered As\(_x\)P\(_{1-x}\) with a bandgap possibly below 0.3 eV (ref. 97). The wide variety of available 2D materials, together with the approaches discussed here (through integration with external photonic structures and through intrinsic polaritonic resonances) for enhancing the light–matter interaction, may enable the discovery of new optical sciences and the realization of various light emission, detection, modulation and manipulation applications.

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Author contributions
EX. and H.W. led the project. All authors contributed significantly to the preparation of the manuscript.

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Competing financial interests
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