Optical modulators with 2D layered materials

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Light modulation is an essential operation in photonics and optoelectronics. With existing and emerging technologies increasingly demanding compact, efficient, fast and broadband optical modulators, high-performance light modulation solutions are becoming indispensable. The recent realization that 2D layered materials could modulate light with superior performance has prompted intense research and significant advances, paving the way for realistic applications. In this Review, we cover the state of the art of optical modulators based on 2D materials, including graphene, transition metal dichalcogenides and black phosphorus. We discuss recent advances employing hybrid structures, such as 2D heterostructures, plasmonic structures, and silicon and fibre integrated structures. We also take a look at the future perspectives and discuss the potential of yet relatively unexplored mechanisms, such as magneto-optic and acousto-optic modulation.

Optical modulation is one of the most crucial operations in photonics. It is ubiquitous in photonics and optoelectronics applications, such as optical interconnect, environmental monitoring, biosensing, medicine and security applications. We are amid the era of information, where Internet applications (for example, media streaming, cloud computing and the Internet of Things) continue to develop at an extremely fast pace. This is generating an exponential increase in the number of network data interconnections, which include traditional data network and intra- and interchip data connections. The dominant electronic interconnection approach (for example, copper cables) suffers from issues of bandwidth and loss due to its performance restrictions in terms of speed, energy consumption, dispersion and cross-talking. This leads to an urgent need for alternative interconnect methods with better performance. Optical solutions offer intrinsic advantages in terms of higher bandwidth and lower loss. Therefore, intense research efforts are being directed towards light modulation with the aim to develop compact, cost-effective, efficient, fast and broadband optical modulators for high-performance optical interconnects. This will also greatly impact other applications, such as fibre-to-the-home, environmental monitoring, astronomical, biosensing and medical applications.

In recent years, graphene and other 2D layered materials (for example, transition metal dichalcogenides (TMDs) and black phosphorus) have attracted increasing attention for applications in electronics, photonics and optoelectronics, due to their unusual electrical and optical properties. Two-dimensional layered materials can exhibit a rich variety of physical behaviours, ranging from that of a wideband insulator to a narrow-gap semiconductor to a semimetal or metal. They provide exciting opportunities for diverse photonic and optoelectronic functions enabling new conceptual photonic devices, fundamentally different from those based on traditional bulk materials2–4. For example, graphene, the best-known 2D material, has been widely used for numerous photonic and optoelectronic devices, operating at an extremely broad spectral range extending from the ultraviolet, visible and near-infrared to the mid-infrared, far-infrared and even to the terahertz and microwave regions due to its unique linear energy–momentum dispersion relation2–4. The demonstrated devices include transparent electrodes in displays, solar cells, optical modulators and photodetectors2–4.

Apart from graphene, monolayer TMDs (such as MoS2 (refs 5,6) and WS2) and black phosphorus7 are direct-bandgap semiconductors, offering properties complementary to graphene. Different atomically thin 2D materials can be readily stacked together by van der Waals forces to make 2D heterostructures without the conventional ‘lattice mismatch’ issue, offering a flexible and easy approach to design desired physical properties8. Two-dimensional materials have been demonstrated to be compatible with different photonic structures, such as well-developed fibre9–12 and silicon13–15 devices. In particular, 2D materials offer potential for large-scale (for example, up to wafer-scale photodetectors16) and low-cost integration into the current dominant optical fibre network and silicon complementary metal-oxide–semiconductor (CMOS) technology.

Compared with traditional bulk semiconductors, 2D materials also provide additional values, such as mechanical flexibility, easy fabrication and integration, and robustness17. Furthermore, previous demonstrations of graphene and other 2D materials suggest that almost all functions required for integrated photonic circuits (for example, generation, modulation, detection and propagation of photons) can be accomplished by 2D materials17. Such versatility of operation combined with their unique electronic properties (that is, high mobility and bandgap tunability) may enable the integration of 2D material-based electronic and photonic devices to achieve multifunction integrated photonic and electronic circuits.

Optical modulation effects in 2D layered materials are among the most extensively studied research topics over the past few years. Prominently, this has led to massive prototype demonstrations of optical modulators with different modulation mechanisms (for example, all-optical, electro-optic and thermo-optic modulations; Box 1), showing competitive performance. For example, the most distinctive performance in reported graphene optical modulators is its extremely broad operation bandwidth, which can cover from the visible to microwave regions18–21. These demonstrated 2D material-based optical modulators have already been effectively used in numerous applications. For instance, graphene, other 2D materials and their heterostructure-based saturable absorbers (an all-optical passive modulator) have been successfully implemented for ultrafast pulse generation in a variety of lasers, demonstrating superior performance22–24. This greatly

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encourages commercialization interest for various laser applications, including high-repetition-rate ultrafast laser sources for optical interconnections\textsuperscript{13,23}. Graphene-enabled nonlinear wavelength modulators\textsuperscript{25} and electro-optic amplitude modulators\textsuperscript{13,15} also have been tested for high-speed data transmission experiments at speeds up to 22 Gbit s\textsuperscript{-1} (ref. 15), promising for high-speed light modulation in optical interconnections.

In this Review, we present the state of the art of optical modulators based on 2D materials, including graphene, TMDs and black phosphorus. We also cover recent advances employing their hybrid structures, such as 2D heterostructures, plasmonic modulators, and silicon and fibre integrated modulator devices. Finally, we conclude with a comprehensive discussion on the future perspectives of 2D layered materials and their applications.

**Electronic and optical properties**

In 2D layered materials with single-unit-cell thickness, new electronic and optical properties can emerge due to quantum confinement, enhanced electron–electron interactions, reduced symmetry

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**Box 1 | Fundamentals of optical modulators.**

Optical modulators can be categorized in different ways. For example, depending on the attribute of light that is modulated (panel a), optical modulators can be classified into amplitude modulators, phase modulators, polarization modulators, wavelength modulators and so on. Depending on the principle of operation (panel b), optical modulators can be classified into all-optical, electro-optic, thermo-optic, magneto-optic, acousto-optic, mechano-optic modulators and so on. Depending on the optical property of the material changed for light modulation, primary modulators can be categorized as absorptive modulators or refractive modulators. For absorptive modulators, the absorption coefficient of the material (that is, the imaginary part of its refractive index) is controlled by an absorption-related effect, such as saturable absorption, electro-absorption, the Franz–Keldysh effect and the quantum-confined Stark effect. In refractive modulators, light modulation is generally realized by effects correlated with the change of the real part of the refractive index, such as the Kerr effect, the Pockels effect, thermal modulation of the refractive index, and change of the refractive index with sound waves (that is, acoustic waves).

The key figures of merit used to characterize a modulator are modulation speed, modulation depth, operation wavelength range, energy consumption and insertion loss\textsuperscript{1}. Modulation speed is a critical parameter for optical modulators. It is typically defined by the operation frequency when modulation is reduced to half of its maximum value. Fast modulation is generally needed for most data transmission applications (for example network interconnects), where the modulation speed is normally measured by its ability to modulate optical signals at a certain data transmission rate (for example, bit s\textsuperscript{-1}). The modulation depth is often measured by the extinction ratio, that is, the ratio between the maximum and minimum transmittance \((\frac{T_{\text{max}}}{T_{\text{min}}})\) in transmission-type devices (or the ratio between the maximum and minimum reflectance \(R_{\text{max}}/R_{\text{min}}\) in reflection-type devices). The decibel unit is widely used for its simplicity in engineering. As a result, the modulation depth is typically given by \(10 \times \log(\frac{T_{\text{max}}}{T_{\text{min}}})\) (or \(10 \times \log(\frac{R_{\text{max}}}{R_{\text{min}}})\)). High modulation depth (>7 dB) is preferable for most applications (for example, high data-rate interconnects and high-sensitivity sensing); however, <4 dB modulation depth can be adequate for certain applications (for example, passive mode-locking and short-distance data transmission)\textsuperscript{3}. Another important parameter of a modulator is its operation wavelength range. For optical data transmission systems, modulators are typically required to operate at one or more of the three major telecom windows (that is, ~0.85, 1.3 and 1.5 μm), or at the visible range for emerging visible light wireless (Li-Fi) communications. For some applications, such as data centres and high-performance computing, energy efficiency is now a critical requirement. The targeted energy consumption for future energy-efficient optical modulators is estimated to be around a few fJ bit\textsuperscript{-1} for on-chip connections (about two orders of magnitude below the current power consumption level)\textsuperscript{20}. Optical devices and systems, including modulators, have the potential to outperform their electronic counterparts in terms of lower energy consumption and higher data connection speed. Insertion loss of a modulator is also of practical significance as it directly relates to the system energy efficiency. In addition, other considerations, such as stability (for example, thermoopticity), compatibility (for example, waveguides; panel b), footprint and cost, are also essential for evaluating any potential trade-offs between the performance metrics discussed above for practical applications.
and proximity effects. In addition, unprecedented control of these properties can be achieved through a large range of methods for light modulation, such as electrostatic gating\textsuperscript{24,25}, mechanical strain\textsuperscript{26} and substrate engineering\textsuperscript{27}. Next, we briefly review the unique fundamental electronic and optical properties of the most widely studied 2D materials, including graphene, TMDs, black phosphorus, as well as layered heterostructures.

**Graphene.** Graphene, a single atomic layer of a hexagonal carbon lattice, has been extensively studied due to its unique mechanical, thermal, electronic and optical properties. It has an electronic structure characterized by two linear Dirac cones at the K and K’ points of the Brillouin zone (Fig. 1a). Electrons in graphene behave as massless Dirac fermions with forbidden backscattering, and exhibit the highest mobility at room temperature. Photons across a wide range of the electromagnetic spectrum interact strongly with graphene. Optically, the linear dispersion of electrons leads to a strong and universal absorption of \( \alpha \) in pristine graphene across the whole infrared to visible spectral range, where \( \alpha = e^2/\hbar c \) is the fine-structure constant\textsuperscript{28,29}. Here \( e \) is the electron charge, \( \hbar \) is the reduced Planck constant, and \( c \) is the speed of light. Remarkably, the strong and broadband light–matter interaction in graphene can be controlled effectively by tuning the Fermi energy, \( E_F \), of graphene with electrostatic gating. On the one hand, interband transitions with energy below \( 2E_F \) become forbidden due to Pauli blocking\textsuperscript{24,25}. Consequently, graphene becomes essentially transparent for photons with energies up to \( 2E_F \) (refs 24,25). On the other hand, intraband transitions from free carriers increase dramatically on gating, leading to strong Drude-like absorption peaks in the infrared\textsuperscript{30,31}. In addition, this free-carrier response of graphene supports the 2D plasmon mode, which exhibits unusually strong confinement and a distinctive dependence on carrier concentration\textsuperscript{20,32}. The ability to control broadband graphene absorption and plasmon excitation through electrostatic gating has enabled many electro-optic modulator designs based on graphene that function at the terahertz to visible wavelengths\textsuperscript{13,14,17-20}.

**Transition metal dichalcogenides.** Layered TMDs — in which the \( d \)-orbital electron interactions lead to a rich variety of physical properties ranging from semiconductors to charge density waves and superconductors — offer a rich platform to explore novel 2D phenomena. Semiconducting TMDs (such as MoS\textsubscript{2}, MoSe\textsubscript{2}, WS\textsubscript{2}, and WSe\textsubscript{2}) are particularly interesting for optoelectronic applications. These semiconducting TMDs are indirect semiconductors in bulk. However, they exhibit an indirect- to direct-bandgap transition when thinned to monolayers\textsuperscript{33,34} (Fig. 1b), with a direct bandgap ranging from 1.57 to 2.0 eV for different TMDs. As a result, photoluminescence in monolayer TMDs can be orders of magnitude stronger than that in their bulk counterparts, even though the amount of material in monolayer TMDs is much less\textsuperscript{35}. The strength of photoluminescence can also differ strongly (by more than one order of magnitude) depending on the monolayer TMD. Optical absorption in monolayer semiconducting TMDs is remarkably strong, reaching >10% at bandgap resonances\textsuperscript{8}. Theoretical and experimental studies show that these optical resonances are dominated by excitonic transitions in semiconductor TMDs, where the exciton binding energy can be at hundreds of millielectronvolts due to dramatically enhanced electron–electron interactions in 2D monolayers\textsuperscript{33,34}. In addition, a pair of degenerate exciton transitions are present at the K and the K’ valley in the momentum space of TMD monolayers with broken inversion symmetry, giving rise to a unique valley degree of freedom that is analogous to electron spin\textsuperscript{15}. Polarization-resolved photoluminescence studies show that the valley pseudospin in TMDs can couple directly to the helicity of excitation photons, raising the intriguing prospect of valleytronics that exploits the valley degree of freedom\textsuperscript{35}. Electrically, field-effect transistors with a high on/off ratio have been realized using TMD monolayers, owing to the large semiconductor bandgap. The electron mobility in TMDs is relatively low, typically limited to 0.1–100 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} at room temperature\textsuperscript{16}.

**Black phosphorus.** This is another single-element layered material. Monolayer and few-layer phosphorene are theoretically predicted to bridge the bandgap range from 0.3 to 1.5 eV (ref. 37), between
the zero bandgap of graphene and bandgaps higher than 1.57 eV in semiconducting TMDs (Fig. 1c). Inside monolayer phosphorene, each phosphorus atom is covalently bonded with three adjacent phosphorus atoms to form a puckered, honeycomb structure. The three bonds take up all three valence electrons of phosphorus, so unlike graphene, monolayer phosphorene is a semiconductor with a predicted direct optical bandgap of ~1.5 eV at the Γ point of the Brillouin zone. The bandgap in few-layer phosphorene can be strongly modified by interlayer interactions, which leads to a bandgap that decreases with phosphorene thickness, eventually reaching 0.3 eV in the bulk limit. Unlike TMDs, the bandgap in few-layer phosphorene remains direct for all sample thicknesses. This makes black phosphorus an attractive material for mid- and near-infrared optoelectronics. The puckered structure of black phosphorus breaks the three-fold rotational symmetry of a flat honeycomb lattice, and leads to anisotropic physical properties (for example, electronic, optical and phononic properties). For example, it was shown that optical absorption and photoluminescence in black phosphorus are highly anisotropic36-38, enabling unique photonic applications (for example, a polarization-sensitive photodetector39 and a multifunctional polarizer and saturable absorber40). Field-effect transistors based on few-layer black phosphorus exhibit a reasonably high on/off ratio of 105 at room temperature, which is between the values achieved in graphene- and TMD-based transistors. Electron mobility of few-layer phosphorus is highly anisotropic, reaching 1,500 cm2 V−1 s−1 along the x direction and 800 cm2 V−1 s−1 along the y direction at low temperature41. This mobility is significantly higher than that in TMDs. One material challenge facing black phosphorus is its sensitivity to oxygen and humidity: monolayer and few-layer phosphorus degrade quickly in ambient conditions, and hermetic sealing will be required for any black phosphorus-based devices.

Layered material heterostructures. Atomicsmly thin 2D layers with wide-ranging properties can be prepared separately and then stacked together to form van der Waals-bonded heterostructures, in which each layer can be engineered separately. Details on the fabrication and characterization procedures of 2D heterostructures can be found in ref. 8. There have been tremendous efforts to explore different 2D heterostructures, including but not limited to graphene–hexagonal boron nitride (hBN), graphene–black phosphorus, TMD–hBN, TMD–phosphorene and TMD–TMD combinations. The graphene–hBN heterostructures are characterized by fascinating moiré superlattice physics that gives rise to mini-Dirac points42 and a Hofstadter butterfly pattern43,44. Heterostructures including TMDs are particularly exciting for optoelectronic and light-harvesting applications, because many TMD monolayers are direct-bandgap semiconductors with remarkably strong light-matter interactions. For example, TMD–graphene heterostructures have enabled novel memory devices45 and ultrathin photodetectors46,47. TMD–TMD heterostructures with different 2D materials, on the other hand, form type-II heterojunctions (Fig. 1d). Such TMD–TMD heterostructures allow efficient separation of photoexcited electrons and holes, where ultrafast charge transfer between MoS2 and WS2 at the femtosecond timescale has been observed48,49. In addition, atomically thin p–n junctions have been realized based on MoS2–WSe2 heterostructures50. The freedom of combining a rich variety of different materials in van der Waals heterostructures is likely to lead to even more exciting discoveries of novel electronic and optical properties.

State of the art of optical modulators

Research on optical modulators with 2D materials has attracted huge interest, and this has translated into tremendous progress over the past few years. In this section, we review the state of the art of various optical modulators based on 2D materials, including all-optical, electro-optic, thermo-optic and other less-explored modulators.

All-optical modulators. All-optical light modulation using 2D layered materials has been extensively studied as it allows the signal processing to be realized fully in the photonic domain. Thus, modulation can be done directly in an optical fibre or other waveguide (for example, silicon waveguide) system, allowing ultrafast, low-loss and broadband optical signal processing in simple configurations. Demonstrated all-optical modulators with 2D materials include saturable absorbers51-53, wavelength converters54, optical limiters55 and polarization controllers56. The majority of these devices exploit the strong nonlinear optical response of 2D materials (mainly the third-order susceptibility), their broad bandwidth, fast response and miniature size for compact, integrated all-optical operation. For example, the imaginary part of the third-order nonlinearity Im(χ(3)) is responsible for saturable absorption, a mechanism employed for passive mode-locking and Q-switching of lasers. The real part Re(χ(3)) is responsible for nonlinear processes, such as four-wave mixing and third-harmonic generation.

Driven by the growing need for ultrafast lasers, 2D material-based saturable absorbers are among the earliest and most successful photonic devices utilizing 2D materials. Here, the 2D material operates as a passive self-amplitude modulator that enables ultrafast pulse generation57-59. As discussed, graphene's band structure ensures the existence of electron–hole pair excitations in resonance with any incoming photon from the visible to the far-infrared. The interaction between charge carriers and ultrafast optical pulses produces a non-equilibrium carrier population in the valence and conduction bands, which relaxes on an ultrafast timescale60. This guarantees wideband and ultrafast saturable absorption from Pauli blocking. In practice, however, a relatively large saturation fluence at wavelengths shorter than the near-infrared spectral region has hindered graphene's applicability at that end of the spectrum61. Unlike graphene, TMDs52,56,62 and black phosphorus57 exhibit finite bandgaps for resonant light absorption. For example, TMDs52,56,62 typically have resonant absorption in the visible, and black phosphorus63,64 shows resonant absorption in the near- and mid-infrared. This offers a suitable alternative to graphene saturable absorbers at those wavelengths. For example, TMD-based (that is, WS2, MoS2 and MoSe2) saturable absorbers for all-fibre pulsed lasers in the visible regime have been reported (Fig. 2a)65, demonstrating the potential for future pulse fibre laser sources in the visible (even ultraviolet) range. An additional interesting feature of TMDs is that they can work as saturable absorbers at wavelengths below the bandgap56,61, possibly due to sub-bandgap absorption from crystallographic defects and edge states62 in 2D TMD flakes64.

Intensive research effort on 2D material saturable absorbers, particularly for ultrafast pulse generation, has led to a steady performance improvement62,66. For example, most laser formats (for example, fibre (Fig. 2a,b), waveguide, solid-state and semiconductor lasers62,67) have been successfully modulated for ultrafast pulse generation, delivering pulse repetition rates up to 10 GHz (Fig. 2b)68, pulse widths down to sub-100 fs (ref. 22) and broad wavelength coverage69 from the visible (for example, 635 nm (ref. 10)) to the mid-infrared (for example, 2.9 μm (ref. 9)) range. External cavity optical processing (for example, amplification, frequency conversion and pulse compression) also has been demonstrated as a convenient way to push the output performance60,62, for example, the wavelength accessibility, the pulse duration, and the output power and pulse energy. A particularly innovative approach is currently undergoing development to improve the ultrafast laser performance with a combined active and passive modulation function in 2D materials56,66. Figure 2c proposes a high-performance ultrafast laser enabled with a 2D material-based

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Figure 2 | Two-dimensional material-based all-optical modulators. a, Photograph of a transition metal dichalcogenide (TMD)-based saturable absorber modulated visible fibre laser. Bottom: Schematic of the laser set-up. LD, laser diode; L1, L2 and L3, lens; M1 and M2, mirror; PD, photodetector; Pr:ZBLAN, praseodymium-doped ZBLAN fibre; PVA, poly(vinyl alcohol). b, Photograph of a high-repetition-rate graphene mode-locked fibre laser. c, Schematic of a high-performance ultrafast laser enabled with a 2D material-based photonic integrated circuit. This laser can be realized by integrating a modulator and photodetector into a waveguide or fibre laser system. The modulation part can provide active and passive mode-locking and laser stabilization, while the detection part can provide feedback for laser stabilization. d, Schematic of a graphene-clad microfibre all-optical modulator. e, All-fibre experimental set-up of four-wave-mixing-based wavelength conversion in graphene. ECL1 and ECL2, external cavity laser; EDFA, erbium-doped fibre amplifier; OSA, optical spectrum analyser. f, Graphene-clad silicon photonic crystal nanostructure for enhanced nonlinear frequency conversion. Scale bar, 500 nm. Inset: Simulated optical confinement in the cavity. a is the lattice constant. Figure adapted with permission from: a, ref. 10, RSC; b, ref. 11, AIP Publishing LLC; d, ref. 12, American Chemical Society; e, ref. 23, IEEE; f, ref. 72, Nature Publishing Group.
photonics integrated circuit. Such a concept potentially could lead to compact, reliable, low-noise and cost-effective ultrafast lasers, by which various emergent applications (for example, in telecommunications and metrology) will be underpinnned.

Borrowing the concept of pump–probe spectroscopy that is widely used to study carrier dynamics in nanomaterials (including 2D materials26, all-optical active modulation has been realized by exploiting different mechanisms (for example, Pauli blocking27 and optical doping28). In this case, light transmission through 2D materials at the signal’s wavelength is modulated (or switched) by another light beam with photon energy higher than the signal29,30. An all-optical modulator with a single-mode microfiber wrapped with graphene has been demonstrated (Fig. 2d)31, achieving 38% modulation depth and ~2.2 ps response time, which is limited by the ultrafast carrier lifetime in graphene. This approach is in principle suitable for ultrafast signal processing with a modulation rate of >200 GHz (ref. 12). In free-space set-ups, wideband (from ~0.2 to 2.0 THz) terahertz light modulation has been demonstrated with a maximum modulation depth of 99% in a graphene–silicon structure by exploiting the optical doping effect32. In principle, other 2D materials beyond graphene (for example, TMDs) can also be effective for all-optical active modulation when the excitation wavelength is resonant to the bandgap (for example, visible light modulation with TMDs and mid-infrared light modulation with black phosphorus).

Experimental studies on the coherent nonlinear optical response of graphene have confirmed its very large third-order susceptibility using four-wave mixing33 and, more recently, using third-harmonic generation34. This shows the possibility of atomic-scale nonlinear optics-based wavelength modulators for ultrafast all-optical information processing (for example, all-optical wavelength conversion35) due to the fast response (typically in femtosecond region) of the third-order nonlinear susceptibility. An early study demonstrated wavelength conversion of a 10 Gbit s−1 non-return-to-zero signal in an all-fibre configuration using graphene deposited on a fibre end (Fig. 2e)36. The device had a conversion efficiency of ~27 dB and a wavelength detuning of 12 nm. However, various previous studies on graphene and other 2D materials also evidenced that, to fully harness the potential of the strong nonlinearity of 2D materials at the atomic scale, it is necessary to circumvent the issues of inefficient light–matter interaction due to 2D materials’ subnanometre thickness as well as optical damage due to the high optical excitation power required. Several approaches (for example, stacking multiple monolayers37, evanescent mode integration38, doping39, interference effects40, coherent control41, microcavities (Fig. 2f)42 and slow-light waveguides43) have demonstrated the possibility of enhancing light–matter nonlinear optical interaction in 2D materials in recent years. For example, by placing graphene in a high Q-factor silicon photonic crystal microcavity (Fig. 2f), resonant optical bistability, temporal regenerative oscillations and cavity-enhanced four-wave mixing in graphene have been demonstrated at light intensities as low as a few femtowatt44. Two-dimensional material-based heterostructures (for example, MoS2–WS2 (refs 48,49) and MoS2–WSe2 (refs 49,50)) have also been proposed for novel linear and nonlinear optical device designs with tunable optical properties (for example, reflectance45 and carrier dynamics46), but the full potential of 2D heterostructures for nonlinear optics still deserves further exploration.

To date, most practical all-optical photonic devices using 2D materials rely on third-order nonlinear processes. Graphene is centrosymmetric, so it only exhibits weak second-harmonic generation47. Other 2D materials with broken symmetry, however, can exhibit strong second-order nonlinearity. This has been demonstrated on several 2D materials (for example, MoS2 (refs 64,75,76), hBN (ref. 76), WS2 (ref. 77) and WSe2 (refs 77,78)), where samples with an odd number of layers exhibit second-order nonlinearity orders of magnitude higher than that with an even number of layers. The strength of the generated second harmonic can be electrically controlled with exciton related effects48, and is strongly dependent on the crystallographic orientation of the crystal49. Consequently, second-harmonic generation has proven very useful for the characterization of the number of layers and orientation50 of TMDs. Furthermore, the nonlinear frequency conversion process (including four-wave mixing and the reverse process of harmonic generation) is the dominant method to achieve quantum light sources. High optical nonlinearity in 2D materials (for example, graphene, TMDs and black phosphorus) may make high-purity quantum emitters and quantum optical switches51 possible for integrated quantum circuits with atomic thickness.

**Electro-optic modulators.** These exploit electro-optic effects to electrically control the light properties. They are particularly desirable for data communication link applications. Thus far, 2D material-based electro-optic modulators have been demonstrated mainly by utilizing the gate-tunable electro-absorption effect in graphene77,78. Recently, the tunability of the refractive index of graphene has also been experimentally demonstrated by gating59,60, indicating the possibility of using 2D materials for electro-refractive phase modulators. Other electro-optic effects in 2D materials, such as the Franz–Keldysh effect1 and the quantum-confined Stark effect1, are also possible for light modulation, but have not yet been experimentally addressed.

Early results on 2D material-based electro-optic modulators revealed the significant advantages of using 2D materials owing to their broad operation bandwidth, compactness, low operation voltage, ultrafast modulation speed and CMOS compatibility10. In contrast to the conventional semiconductor materials, where absorption is limited by their bandgap, graphene absorbs light across a broad electromagnetic spectral range from the ultraviolet to the terahertz. This enables light modulation with a much broader operation wavelength range. Indeed, light modulation with graphene has been demonstrated, covering the visible17, infrared13,38,62–84 and terahertz19,31,85–88 range.

The intrinsic speed of electro-optic modulators, one of the most crucial figures of merit of modulators, is typically limited by its RC time constant. Supplementary Table 1 lists a performance comparison between high-speed electro–optic modulators with 2D materials and the current state-of-the-art silicon technology. Typical modulation speeds of graphene electro-absorption modulators at the visible and near-infrared range are on the order of gigahertz (for example, ~1 GHz (refs 13,14,82) and 30 GHz (ref. 15)). However, theoretical predications have shown that modulation speeds far beyond 100 GHz (refs 15,89) are feasible and such speeds are comparable to state-of-the-art high-speed 2D material electronics2.
graphene\textsuperscript{82} devices), reflection mode\textsuperscript{84}, patterned structure\textsuperscript{90}, interference enhancement\textsuperscript{84}, evanescent-mode coupling\textsuperscript{83} and cavities\textsuperscript{91}.

For silicon integrated photonics, the current leading candidate technology for short-reach optical interconnects\textsuperscript{1}, the issue of the low modulation depth of 2D material-based devices has mainly been addressed by using evanescent-mode coupling in different formats, including non-resonance waveguides\textsuperscript{13,82,92} (Fig. 3a), interferometers\textsuperscript{83} and cavity-enhancement approaches\textsuperscript{91} (Fig. 3b,c). A graphene–hBN heterostructure-based electro-optic modulator integrated with a silicon photonic crystal cavity has been demonstrated (Fig. 3b)\textsuperscript{14}, achieving operation frequency up to 1.2 GHz with a modulation depth of 3.2 dB. Similarly, silicon-based micro-ring resonators can provide efficient light modulation with various advantages, such as small footprint, large modulation depth and small energy consumption, which have also been used for 2D material-based silicon modulators\textsuperscript{94,95} (Fig. 3c). A graphene electro-optic micro-ring silicon nitride modulator with critical coupling effect has been demonstrated\textsuperscript{15}, whereby an increase in loss of a coupled micro-ring resonator increases the device transmission by changing the resonance coupling condition. This offers considerable improvement in the performance, such as a 30 GHz bandwidth with a modulation efficiency of 15 dB per 10 V driving voltage\textsuperscript{15}. It must be noted that resonant structure approaches can have drawbacks, such as a relatively narrow operation wavelength range and high sensitivity to fabrication tolerance and temperature variation. To date, experimental demonstrations of 2D material integrated modulators have shown impressive performance (>15 dB modulation depth\textsuperscript{15,92}, ~100 fJ bit\textsuperscript{−1} energy consumption\textsuperscript{15,91} and 30 GHz speed\textsuperscript{15} (Fig. 3d)), already comparable with current semiconductor modulation technologies (for example, silicon)\textsuperscript{1} (Supplementary Table 1).

Further down the line, theoretical calculations predict that by using high-quality 2D materials and optimizing the device structure and fabrication\textsuperscript{13,89}, the performance could reach operation speeds in excess of 100 GHz\textsuperscript{89} and energy consumption levels below 1 fJ bit\textsuperscript{−1} (ref. 89).

Terahertz research has been one of the most investigated research fields in the past decade. There is a great demand for components in this spectral range for numerous applications extending from health and environmental to security applications, but conventional optical components have been challenged in this spectral range. Graphene modulators working at the terahertz region\textsuperscript{19,31,85–88} (Fig. 4a,b) have been demonstrated through modulation of the intraband absorption, giving good modulation performance, such as >94% modulation depth\textsuperscript{86}. The operation...
Thermo-optic effects are also used for light modulation. The most common type is based on refractive index associated with variations in the temperature. Unsurprisingly, thermo-optic modulators are rather slow (~MHz) due to the intrinsically slow thermal diffusivity. Therefore, thermo-optic modulators...
These modulators employing graphene plasmonic waveguides (Fig. 5a) have been used to deliver localized heat for light modulation in a disk resonator and silicon ring resonator. The Faraday rotation have been experimentally reported in graphene at the far-infrared range, indicating the possibility of graphene-based magneto-optic modulators for various non-reciprocal applications. A Faraday rotation of up to 0.1 rad (~6°) at a magnetic field of 7 T (Fig. 5d) has been demonstrated in the far-infrared range, originating from the excitation of the cyclotron resonance. This is an attractive property for various thermal applications, such as flexible heat conductors.

High thermal conductivity in 2D materials (for example, graphene) combined with the easy fabrication and integration, makes them a suitable and cost-effective solution for applications not requiring ultrafast modulation speed (for example, short-distance optical communication and sensing).

**Magneto-optic modulators.** These modulators employing magneto-optic effects (for example, the Faraday effect or magneto-optic Kerr effect) for light modulation are yet to receive as much attention as all-optical or electro-optic modulators. This is partly because of the operation simplicity of the all-optical and electrical approaches. However, a unique non-reciprocal property in magneto-optic modulators offers the opportunity to create various devices with special functions that are not feasible with other modulators. In particular, magneto-optic modulators may find applications such as optical isolators, circulators, polarization controllers, and electric- and magnetic-field sensors.

**Figure 5 | Two-dimensional material-based thermo-optic and magneto-optic modulators.** a, Schematic of a thermo-optic modulator based on a graphene heater. Thermally induced inhomogeneous refractive-index distribution of the cladding polymer controllably attenuates the graphene-based long-range surface plasmon waveguide for light modulation. The red tube depicts the incoming light, which is modulated by the applied electric current (yellow line). b, Schematic of a thermo-optic modulator based on a graphene heat conductor, BOX, buried oxide; L, length. c, d, Schematic of a graphene-based Faraday rotator (c) and its Faraday-rotation response at different magnetic fields, B (d). The polarization plane of the linearly polarized incoming beam is rotated by the Faraday angle θ after passing through graphene on a SiC substrate in a perpendicular magnetic field. Simultaneously, the polarization acquires a certain ellipticity. The red and green arrows indicate polarization and propagation directions of the optical beam, respectively. Figure adapted with permission from: a, ref. 106, OSA; b, ref. 108, AIP Publishing LLC; c, d, ref. 111, Nature Publishing Group.
extremely large Faraday rotation, if we consider that this is achieved with a graphene monolayer with single-atom thickness, but practical applications will require significant improvements in performance, such as reducing the required magnetic field and pushing its operation towards shorter wavelengths. The magneto-optic response (for example, Faraday rotation and cyclotron resonance) can be enhanced using cavities, magnetoplasmons and metastructures. In other 2D materials, such as TMDs and black phosphorus, various magneto-optic effects (for example, Faraday rotation, the Zeeman effect and magneto-optic Kerr effect) have also recently been addressed, offering new opportunities to use these nanomaterials for magneto-optic modulators at the nanoscale for future applications, such as isolators, circulators and magnetic measurements.

Acousto-optic modulators. These modulators mainly use acoustic waves to change the refractive index of a material for light diffraction and frequency changing. Acousto-optic modulators have been widely used for pulse generation (for example, Q-switching) and signal modulation in optical telecommunications and displays. Graphene and other 2D materials (for example, MoS$_2$ (ref. 117)) are attracting growing interest from the field of optoelectronics. These 2D materials are being considered for the generation, propagation, amplification and detection of surface acoustic waves. This indicates that it is technically feasible to conceive 2D material-based acousto-optic modulators. In addition, periodic diffraction gratings generated in graphene with a sound wave have been theoretically proposed to enable efficient excitation of surface plasmon polaritons, demonstrating a simple way to realize plasmonic light modulation with surface acoustic waves. Owing to their large surface area and unique properties (for example, high frequency sensitivity to absorbed molecules), 2D material-based acousto-optic modulators can potentially be used to miniaturize the current bulk acousto-optic modulators for specific applications, such as gas sensing and displays.

Other modulation approaches. Graphene and other 2D materials have unique mechanical properties, including high Young’s modulus combined with a low mass, suggesting they are promising materials for optomechanics (that is, mechno-optical modulators). For example, graphene membranes can be actuated up to high mechanical vibration frequencies (>few hundred MHz), which can be accommodated for modulation of microwave photons. Stress-induced physical property changes in 2D materials can also be used for mechanooptical modulators. In addition to the aforementioned physical methods (for example, optical, electrical and thermal), which provide simple and effective ways for light modulation with 2D layered materials, other approaches, such as chemical or biological means, can also be utilized to modify the properties of 2D materials for light modulation. This capability gives 2D material-based optical modulators the potential for a wide range of applications in biomedical instrumentation, chemical analysis, environmental sensing and surgery.

Perspectives

For practical applications, superior performance is always advantageous. In this Review, we have discussed the substantial improvements in the performance of 2D material-based optical modulators. For example, the modulation speed of graphene electro-optic modulators has seen a 30-fold improvement over the past four years, from 1 GHz (ref. 13) to 30 GHz (ref. 15). Nonetheless, there is still a significant need for performance improvement to compete with the well-developed traditional technologies, for example, on modulation speed and energy consumption for optical interconnection applications.

Two-dimensional materials can enable various functions (for example, electronics, energy storage and conversion, sensors, photonic and optoelectronic functions) due to their diverse physical properties. For example, multifunctional optical modulators (such as a multifunctional modulator and photodetector and a multifunctional modulator and plasmon waveguide) have been demonstrated with 2D materials. This not only offers a significant benefit for electronics and photonics in terms of integration with an ‘all-in-one’ solution, but also enables new devices with superior performance (for example, simultaneous modulation and detection). However, the trade-off between performance and cost might make the commercial success of all-2D material systems challenging in the short term. A more realistic success for 2D materials in the short term would build on the well-developed photonic technology platforms of silicon photonics and fibre optics, where the bulk of research on 2D material-based modulators is conducted. In this case, excellent integration capabilities and competitive performance have been achieved, showing that 2D materials are ready to become a complementary technology to empower the traditional photonic platforms (for example, fibre optics and silicon photonics).

Furthermore, intense research on 2D material-based modulators has already revealed several distinct advantages of 2D material modulation technology (for example, broad operation bandwidth from the visible to terahertz range, small footprint, low cost, easy integration and large flexibility). And these characteristics have led to an enormous range of new photonic devices, such as, tunable notch filters, spatial light modulators, modulator integrated surface-emitting lasers, tunable photonic memories and tunable adaptive cloaking, just to name a few. Given the extremely fast pace at which 2D materials are being studied, the large variety of available 2D materials, their heterostructures and hybrid systems may continue to introduce new modulation concepts based on their unique physical properties, and more importantly, performance improvements to outperform competing technologies. Therefore, if production of large-scale and high-quality 2D materials is successful, it is anticipated that 2D material-based optical modulators might create a completely new market to address ongoing challenges and emerging applications (for example, visible wireless communication, mid-infrared and terahertz biosensing and pharmaceutical applications, and wearable and bendable photonic applications), potentially revolutionizing current photonics.

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References

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Author contributions
Z.S. led the project. All authors made significant contributions to the preparation of this manuscript.

Additional information
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Competing financial interests
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