Review

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All-optical modulation with 2D layered materials: status and prospects

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Abstract: Optical modulation technique plays a crucial role in photonics technologies, and there is an ever-increasing demand for broadband and ultrafast optical modulation in the era of artificial intelligence. All-optical modulation is known to be able to operate in an ultrafast way and has a broadband response, showing great potential in applications for ultrafast information processing and photonic computing. Two-dimensional (2D) materials with exotic optoelectronic properties bring tremendous new opportunities for all-optical modulators with excellent performance, which have attracted lots of attention recently. In this review, we cover the state-of-art all-optical modulation based on 2D materials, including graphene, transitional metal dichalcogenides, phosphorus, and other novel 2D materials. We present the operations mechanism of different types of all-optical modulators with various configurations, such as fiber-integrated and free-space ones. We also discuss the challenges and opportunities faced by all-optical modulation, as well as offer some future perspectives for the development of all-optical modulation based on 2D materials.

Keywords: all-optical; 2D layered materials; modulation.

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1 Introduction

"Photonics will be in the twenty-first century what electronics was in the 20th century," John S. Mayo, the previous president of AT & T Bell Labs, who devoted his lifelong career into computing and telecommunications, summed up this thesis. Indeed, the scope and influence of photonics have been staggering in the recent years, with the so-called Moore's law that drives the progress of the semiconductor chips face grant challenges [1]. Especially in the era of big data and artificial intelligence, there is increasing demand for faster and more efficient photonic devices for information processing and storage, and photonic is playing a more and more important role [2]. Among these photonic technologies, optical modulation that modulates the propagation states of the signal light is one of the most basic and critical operations, which is ubiquitous in photonic and optoelectronic applications [3, 4]. Optical modulators, including electric-optic and thermo-optic ones, have been widely used in optical communications networks. However, with the increasing demand for modulation speed and bandwidth, current optical modulators face great challenges, and new approaches and methods are being sought. All-optical modulation, a scheme that the propagation of light is controlled by another light beam analogous to its counterparts of electronic modulation, has attracted tremendous attention recently [2] because it allows ultrafast, low-loss, and broadband optical signal processing in simple configurations, which is essential for future optical communication networks, optical computing system, and quantum information processing chips [5, 6].

The discovery and experimental study of graphene truly opens the door to a gorgeous world of two-dimensional (2D) materials in the early 21st century, although the theoretical exploration had gone through for over 150 years [7–9]. Graphene shows lots of exitonic properties and is even named as "miracle" material. Inspired by graphene, a great deal of 2D materials have been successfully isolated and studied, including transition metal dichalcogenides (TMDs) [10] and black phosphorus [11]. These materials, consisting of only one or a few atomic layers, show excitonic and distinct electronic and optical properties compared to their three-dimensional counterparts, which have brought tremendous new opportunities for nanoscale electronics and photonics [12–16]. Among these emerging possibilities, all-optical modulation based on 2D materials has shown great potential for optoelectronic applications.

The aim of light modulation research is to develop compact, fast, efficient, cost-effective, and broadband optical modulators for high-performance interconnects and signal processing. 2D materials offer some distinguished advantages compared with bulk materials. First, 2D materials interact strongly with light despite being atomically thin. For example, a monolayer graphene of 0.3 nm thickness absorbs 2.3% incident light [17], and a monolayer MoS_2 can absorb up to 10% light in the resonant regime [10]. The strong light-matter interaction in 2D materials induces highly optical nonlinearity, thus making it possible to achieve ultrafast light modulation on the nanometer scale [18, 19]. Second, thanks to their diverse electronic structures, the optical response of 2D materials covers an extremely wide range of spectra from ultraviolet to terahertz, or even to the microwave regions [13]. Third, since 2D materials are mechanically robust with passivated interface, they can be firmly integrated onto various photonic structures such as optical waveguides, photonic crystal cavities, and optical fibers, without the "lattice mismatch" issues that are usually faced by bulk materials [12]. Especially, for silicon photonics, the integration of 2D materials might offer great feasibility to enable various on-chip passive and active devices, such as optical modulators, photodetectors, and lasers [20, 21]. And last, but not the least, the electronic and optical properties of 2D materials can be tuned in a large scale by electric gating [22, 23], strain [24], optical excitation [25, 26] or chemical doping [27], offering lots of capabilities to build high-performance electronic and photonic devices based on 2D materials. We notice that there have been several review articles on 2D materials-based optical modulators [5, 28, 29] or generally all-optical modulation [2], which have provided a prompt review on materials, operation mechanisms, and devices on 2D materials-related modulation. As the research moves forward, it is interesting to give an overview of the development in all-optical modulation based on 2D layered materials.

In this paper, we review the state-of-art development of all-optical modulation based on 2D materials. A brief introduction of typical 2D materials is presented in section 2, followed by the principles of all-optical modulation based on 2D materials in section 3. In section 4, we present the up-to-date all-optical modulation applications with 2D layered materials, categorized by their types and configurations. Future challenges and opportunities with regard to all-optical modulation based on 2D materials are discussed in section 5.

2 Fundamentals of 2D materials

2D materials usually refer to crystalline materials consisting one or few layers of atoms, showing distinguished properties compared to their bulk forms, and the thickness varies from subnanometer to more than ten nanometers [13, 30]. So far, a great deal of 2D materials with various exotic properties have been fabricated and studied. In this section, we focus on the introduction of basic optoelectronic properties of typical 2D materials, including graphene, TMDs, and black phosphorus. Some emerging materials will be discussed briefly as well.

2.1 Graphene

Graphene, the best known 2D material, which consists of a single layer of carbon atom forming a hexagonal lattice, shows lots of extraordinary electrical and optical properties. The charge carriers inside graphene can be described as massless Dirac fermions; thus, the conduction electrons at low energies have a light-like linear dispersion and behave like massless, which brings a platform to study the abundance of novel physical phenomena [31, 32]. This kind of electronic spectrum also leads to many novel optical properties. Graphene interacts strongly with photons across a wide range of spectra spanning from the whole infrared to the visible parts (Figure 1), with absorption coefficient as $\pi\alpha$, where $\alpha = e2/\hbar c$ is the fine-structure constant [17]. In addition, graphene can also interact strongly with terahertz wave due to intraband transition, which makes it promising for the detection, generation,

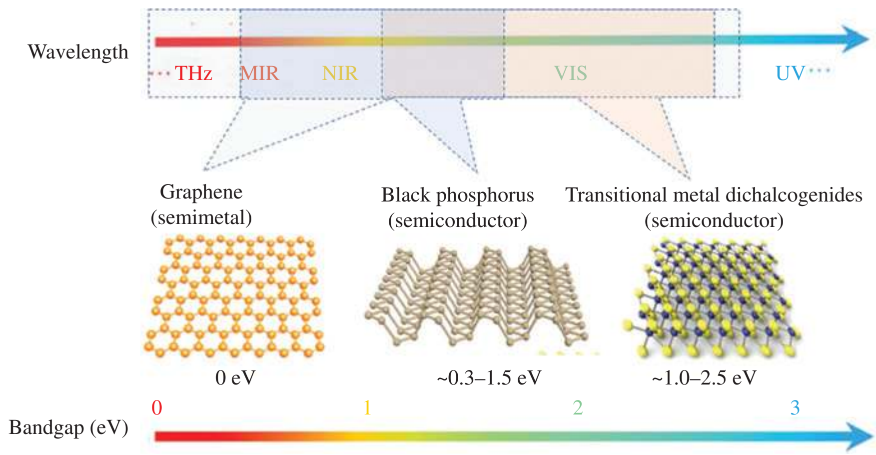

Figure 1: Optical response and electronic bandgaps of typical 2D materials.
Intrinsic graphene is a zero-bandgap semimetal with optical response covering from THz to visible parts. TMDs have layer-dependent bandgap ranging from 0.3 eV to 1.5 eV. Black phosphorus shows direct bandgap of 1.0 eV to 2.5 eV depending on the thickness. Adapted from [13], Reproduced with permission [28]. Copyright 2017, Wiley-VCH.

and modulation of terahertz waves [33]. Notably, the strong and broadband light-matter interaction in graphene can be controlled effectively through tuning the Fermi energy with external stimulus such as electric gating, making it favorable for various optical modulations [29, 34]. In addition to linear optical response, graphene exhibits strong nonlinearity within the visible and near-infrared spectral range, including saturable absorption [35], Kerr effect [36], optical bistability [37], and soliton propagation [38, 39]. These distinguished optical properties mentioned above make graphene a favorable material for optical modulation; more about the modulation mechanism and graphene-based devices will be discussed later.

2.2 Transition metal dichalcogenides

2D TMDs refer to a group of atomically thin materials with the formula of MX_2, where M is a transition metal element (e.g. Mo and W) and X is a chalcogen (S, Se, or Te). They show properties that are complementary to yet distinct from those in graphene. Inspired by graphene, 2D TMDs were first experimentally isolated in 2010 [10, 40], leading to the extensive study of 2D semiconductors. Graphene by nature is semimetallic without a bandgap, while 2D TMDs own bandgaps ranging from 1 to 2.5 eV, covering the spectra from visible to the infrared (Figure 1). Notably, these 2D materials transit from indirect bandgap to direct bandgap when the thickness decreases from multiple layers to monolayer, due to the strong quantum confinement effects [41]. This induces orders of magnitude enhancement of the photoluminescence for the monolayer, compared to multiple layers [10]. When interacting with photons, 2D TMDs show strong excitonic effects. They exhibit multiple absorption peaks from ultraviolet to near infrared spectra due to excitonic and interband transitions [10], and the absorption of excitonic peaks can be up to 30%, showing strong interaction with light. Moreover, due to the symmetry-breaking structure, monolayer TMDs (generally odd layers) show strong second-order nonlinearity, offering the potential for nonlinear optical applications such as wavelength convertors [42, 43]. In addition, the strong spin-orbit coupling in 2D TMDs induces valley selective optical properties, which brings greater flexibility for optical modulation [13, 44, 45].

2.3 Black phosphorus

Black phosphorus, similarly to graphene, is a single-element layered semiconductor material with a honeycomb structure, whose bandgap spans from 0.3 eV to 1.5 eV [46], bridging the gap between the zero-gap graphene and the relatively wide bandgap of TMDs, as shown in Figure 1. One of the intriguing optical properties of black phosphorus is that it shows layer-dependent direct bandgap. For example, monolayer black phosphorus, also known as phosphorene, owns a bandgap around 1.5 eV, while the bandgap decreases to around 0.8 eV when the layer number increases to three [47]. The carrier mobility in phosphorene is as high as 1000 $cm^2\ V^{-1}S^{-1}$, which is much higher than those in TMDs [48], offering potential for ultrafast modulation. Unlike the centrosymmetric structures of graphene and TMDs, the puckered structure of black phosphorus shows anisotropic in-plane electric and photonic properties [49], leading to anisotropic optical absorption and photoluminescence. In addition, optical properties of black phosphorus can be tuned through doping and polarization [50], offering new perspectives for optical modulation.

In addition to these 2D materials discussed above, a lot of more novel 2D materials have been explored recently, including topological insulators [51–53], MXenes [54, 55], and perovskites [56–60]. These materials also show extraordinary optoelectronic properties, and some of them have been implemented for optical modulation too. As predicted, there are more than 1000 2D materials [61]; it is believed that there is plenty of room to explore in the 2D plateau.

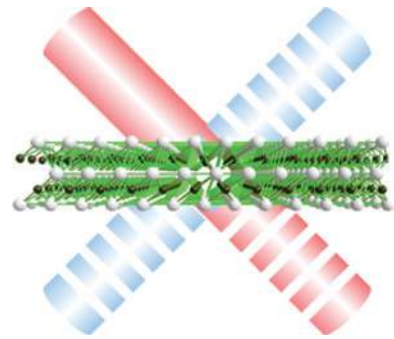

Figure 2: Schematic diagram of all-optical modulation. Signal light is controlled and modulated by another switching light beam. The light-light interaction is realized through nonlinear medium, and the core of the all-optical modulation is to either control or modulate the real or imaginary parts of the refractive index of the medium.

3 Principles of all-optical modulation

Generally, the optical response of materials can be described by the complex refractive index or dielectric constant $\tilde{n} = \mathrm{n} + i\beta$, in which the real part represents the refractive index and the imaginary part reflects the absorption property. The refractive index can be modified by external stimulus (e.g. electric fields, optical fields, magnetic fields, temperature and pressure), which lays the foundation for optical modulation. Optical modulation can be categorized in different ways. Depending on the ways it operates (signal light is modulated by itself or another light beam), it can be classified into passive and active modulation. According to the attribute of light, it can be classified as amplitude modulation, phase modulation, polarization modulation, and so on. Depending on the principles of operation, it can be classified into all-optic, electro-optic, thermo-optic, magneto-optic, and so on. According to how the property of the materials change during light modulation, it can be classified into absorptive modulation and refractive modulation, corresponding to primarily the change in the imaginary and real part of the refractive index, respectively.

All-optical modulation is a light-control-light scheme where a switching light beam (e.g. ultrafast laser pulse) is used to control the propagation of signal light beam, in which the light-light interaction is achieved through the optical nonlinear effects of nonlinear media, as illustrated in Figure 2. When excited by laser pulse, the carrier densities and distribution in 2D materials might change dramatically, which in turn induces the change in both the real and the imaginary parts of their complex refractive index; thus, 2D materials can be used for both phase and amplitude modulation. So far, most of all-optical modulation with 2D materials are based on third-order nonlinear response of a material and thermo-optic effect. The former includes saturable absorption and Kerr effect, while the latter relies on the temperature-dependent refractive index change of a material. The operation principles for different types of all-optical modulation are presented below.

3.1 Saturable absorption

Saturable absorption is a third-order nonparametric nonlinear effect, describing that the absorbance of a material depends on the intensity of the incident light. For a two-level saturable absorber, the total absorption coefficient $\alpha(I)$ can be described as [62]

$$\alpha(I) = \frac{\alpha_0}{1 + I / I_s} + \alpha_{NS}, \tag{1}$$

where α_0 is the linear absorption coefficient, I_s is the saturation intensity, and α_{NS} is the nonsaturable losses, which is a constant linear loss.

As can be seen from Eq. (1), the absorption for a saturable absorber decreases with increasing incident light intensity, leading to higher transmission at strong incident light, which can be used for optical modulation effectively. The saturable absorption effects originate from the Pauli blocking or band filling effects [63]. According to the Pauli exclusion principle, two identical fermions such as electrons cannot occupy the same quantum state simultaneously; thus, there are only limited positions for electrons in the conduction band of a semiconductor. When irradiated by intense light, electrons in a valence band of a saturable absorber are excited to fill the conduction band. The material could not absorb more photons when the excited states are filled, leading to an increase in transmission (saturable absorption).

Many 2D materials exhibit excellent saturable absorption properties such as large modulation depth, low saturation intensity, and short relaxation time. Graphene, the best known 2D material with zero bandgap, will generate nonequilibrium carrier population in the valence and conduction bands relaxed through thermalization when excited optically, thus leading to strong saturable absorption with ultrafast response [64]. Semiconductor 2D materials such as TMDs [65, 66] and black phosphorus [67, 68] with finite bandgaps exhibit novel saturable absorption properties due to the excitation of abundant valence electrons under strong optical incidence. Saturable absorber is a key component for generating ultrashort laser pulse, and many works have demonstrated pulsed lasers using 2D materials as saturable absorber, which will be presented later.

3.2 Kerr effect

The optical Kerr effect is a third-order nonlinear phenomenon stating the light-induced instant refractive index change of a nonlinear medium, which is proportional to the intensity of the incident light. It can be described as below:

$$\mathrm{n} = n_0 + n_2 I \quad (2)$$

where n_0 is the linear refractive index, n_2 is the nonlinear refractive index, and I is the intensity of the incident light.

The optical Kerr effect is responsible for lots of nonlinear phenomena, including self-focusing, self-phase modulation, cross-phase modulation, four-wave mixing, and modulation instability. The change of refractive index will induce optical phase shift, leading to various types of modulation. 2D materials possess extraordinary Kerr nonlinearity and show great potential for optical modulation. For example, graphene owns a nonlinear refractive index of 10^{-11}–10^{-15} m^2/W in the telecommunication band, as reported by a number of groups [36, 69, 70], which is orders of magnitude larger than that of typical bulk materials (10^{-18} m^2/W for silicon [71] and 10^{-19} m^2/W for silicon nitride [72]). TMDs [73–75] and black phosphorus [76] also show high third-order nonlinearity and have been widely used for optical modulation.

In addition to the saturable absorption and Kerr effects discussed above, optical parametric processes, including harmonic generation [42, 43, 77, 78] and four-wave mixing [79–81], have also been demonstrated in various 2D materials, which can be applied to wavelength conversion. Moreover, spatial self-phase modulation shows great potential for optical modulation as well [76].

3.3 Thermo-optic effect

Thermo-optic effects refer to the temperature-dependent refractive index of a material, which have been widely used in silicon photonic circuits [82, 83]; it can be described as

$$\Delta n = \frac{dn}{dT} \times T \quad (3)$$

where Δn is the change in refractive index and T and $\frac{dn}{dT}$ are temperature and thermo-optic coefficient of materials, respectively.

As discussed, the change in refractive index will lead to phase shift of the propagation light, which have been widely used for optical modulation. Among these applications, phase modulation via interferometric or resonant structures is commonly used. A heater integrated with a waveguide is used to increase the local temperature and subsequently change the refractive index, leading to variation of the optical path of the light propagated through.

2D materials can be used as efficient and compact heater when integrated with waveguide, owing to the broadband absorption and high thermal conductivity. When excited by external stimulus such as optical pulses [84], the excited carriers will transfer their energy to phonons during the relaxing process, thus increasing the temperature of the material. As 2D materials possess high thermal conductivity (e.g. 10^3 W/m/K for graphene, much higher than copper) at ambient temperature [85], the heat will readily spread to surrounding media [86], acting as an efficient heat generator and conductor [87]. Various types of optical modulation using 2D materials as heater for all-optical modulation have been demonstrated and will be discussed more in details later.

Here, we only discuss the three main principles that have been used for all-optical modulation. Indeed, some other effects such as photodoping [88] and coherent absorption [89] have been implemented for all-optical modulation as well.

4 All-optical modulation with 2D materials

All-optical modulation with 2D layered materials has been extensively investigated over the past a few years, leading to various prototypes of optical modulators. In this section, we review the state-of-art all-optical modulation based on 2D layers materials categorized by their modulation type and spatial configurations. Fiber-based all-optical modulation is introduced first, including the passive and active modulation types, then all-optical modulation with 2D layered materials in free space are reviewed.

4.1 Fiber-based all-optical modulation

Optical fibers with engineerable end faces and sidewalls offer a compact and flexible platform to study light-matter interaction phenomena, showing great potential for investigating photonic properties of 2D materials. Besides, fibers have been widely used in applications such as telecommunications and lasers, integrating novel materials with fiber to enable new applications is an important and intriguing research directions, and 2D materials have brought tremendous new opportunities. In this section, we review all-optical modulation utilizing 2D materials based on fibers.

4.1.1 All-optical passive modulation with fiber

To generate ultrashort pulses in laser cavity, a critical component is the amplitude-modulation element, which can strengthen the modulation instability of the optical fibers [90]. 2D materials recently have become the most studied amplitude modulation element in pulsed lasers. Driven by the increasing need for ultrafast lasers, fiber lasers with 2D materials as saturable absorbers are among the earliest and most successfully photonic applications of 2D materials [5, 63, 91]. 2D materials with excellent saturable absorption properties have been widely explored to generate ultrashort pulses in fiber laser systems, owing to their broadband optical response and ultrafast carrier dynamics.

The first 2D materials-based fiber laser was reported in 2009 using graphene as saturable absorber [64]. Bao et al. demonstrated a mode-locked fiber laser operating at telecommunication band (~1567 nm), by depositing atomic layer graphene onto the end face of a fiber, with a pulse duration of 756 fs and a repetition rate of 1.79 MHz. Schematic diagrams of the fiber laser system and output spectrum are shown in Figure 3A and B, respectively. The average output power was up to 2 mW. Since then, graphene-based fiber lasers with different configuration have been demonstrated, trying to optimize the laser output parameters including pulse duration, repetition rate, and wavelength [94–101]. Here, we just name a few. Sotor et al. demonstrated a graphene-based fiber laser with pulse duration down to ~88 fs with a stretched-pulse design [95]. To obtain a higher repetition rate, Martineza and Yamashita reported a fiber laser with a fundamental repetition rate up to 9.67 GHz, by utilizing a short cavity length (around 10 mm long fiber Fabry-Perot cavity) and graphene saturable absorber [96]. Sun et al. demonstrated a graphene-based fiber laser with wavelength tunability covering the range 1525–1559 nm by incorporating filters into the fiber cavity [102].

As discussed, graphene's unique band structure ensures a broadband optical response from the visible to the far-infrared, with carriers relaxing on the ultrafast scale, and graphene-based fiber lasers covering from visible to infrared have been demonstrated extensively. However, in practice, a relatively large saturation fluence at wavelengths shorter than the near-infrared has hindered graphene's applications at the spectral end side [103]. In contrast to graphene, TMDs and black phosphorus show finite bandgaps and resonant light absorptions in the visible and mid-infrared range, which offers an alternative to graphene saturable absorber in these wavelengths. For example, Luo et al. demonstrated a fiber laser operating in the visible range with layered TMDs as saturable absorber; schematic diagrams of the laser system and output spectrum are shown in Figure 3C and D, respectively. The pulse duration was around 200 ns with 28.7 nJ pulse energy, and the repetition rate was from 232 to 512 kHz. Qin et al. reported a fiber laser with black phosphorus as saturable absorber operating in the mid-infrared range (~2.8 μm); the laser configuration and output laser spectrum are shown in Figure 3E and F, respectively [93]. The pulse duration was 1.18 μs with pulse energy of 7.7 μJ, and the repetition rate was 63 kHz. In addition, fiber lasers based on black phosphorus operating in the near-infrared range have been demonstrated extensively as well [104–108]. What's more, TMD-based saturable absorber can also work below the bandgap, possibly due to the subbandgap absorption from crystallographic defect [109] and edge sates [110], which extends their working wavelength to the infrared range [67, 111–118]. In addition, fiber lasers based on emerging layered materials, including bismuthine [119–121], Bi_2Se_3 [122–124], Sb_2Te_3 [125], and MXene [126, 127], have also been demonstrated, operating mainly in the near-infrared range. Indeed, there are numerous studies on fiber laser using 2D materials as saturable

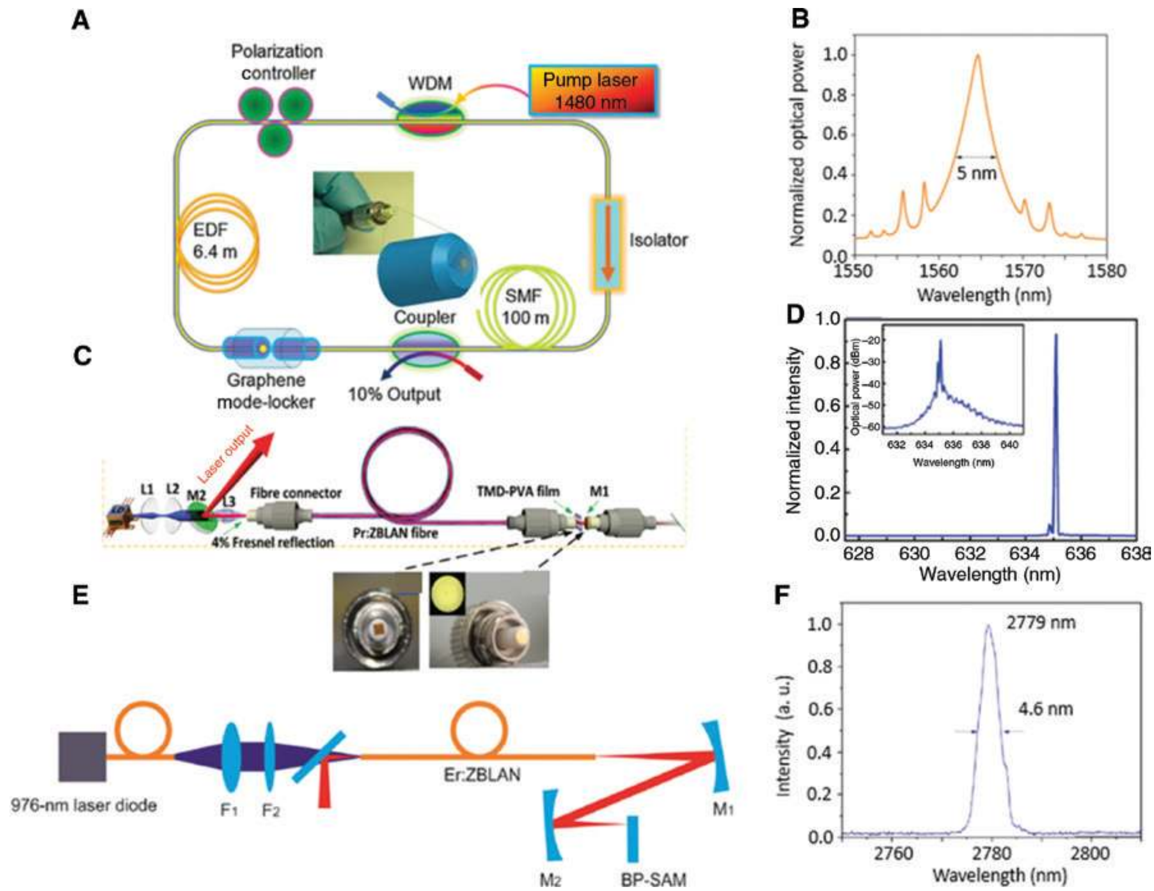

Figure 3: Typical ultrafast fiber laser system using 2D materials as saturable absorbers.
(A and B) Schematic diagram of typical fiber laser with atomic layer graphene as saturable absorber and its output spectrum operating at the telecommunication band [64]. (C and D) Typical fiber laser system utilizing TMDs as saturable absorber operating at visible range and its output spectrum [92]. (E and F) Q-switched fiber laser system operating at far mid-infrared spectral range utilizing black phosphorus as saturable absorber and its output spectrum [93]. (A and B) Reproduced with permission [64]. Copyright 2009, WILEY-VCH. (C and D) Reproduced with permission [92]. Copyright 2016, The Royal Society of Chemistry. (E and F) Reproduced with permission [93]. Copyright 2015, Optical Society of America.

absorber, and only a few of them are mentioned here. For a more complete review, we refer the readers to specific review papers [63, 128]. The intriguing saturable absorption properties, ultrafast carrier dynamics, and broadband optical response of 2D materials have attracted extensive research into 2D materials-based ultrafast lasers, which are also among the earliest active devices based on 2D materials and are close to real applications [5]. It can be predicted that fiber laser based on 2D materials with high pulse energy, high repetition rate, short pulse duration, low threshold, and chip integrated configuration will be developed in the near future [28].

4.1.2 All-optical active modulation with fiber

In addition to fiber laser utilizing 2D materials as passive amplitude modulator, another important application of optical modulation is active optical modulator. In this configuration, one light beam is controlled by another beam of light effectively, which are essential parts of optical communications and interconnections. Fiber-based active optical modulator or switcher utilizing 2D materials have attracted lots of attention too, owing to their extraordinary optoelectronic properties [129–131]. Here, we review the state-of-art active all-optical modulators based on 2D materials categorized by their working mechanism, including saturable absorption, thermo-optic effects, and Kerr effects.

4.1.2.1 Absorptive modulation

Thanks to the ultrafast optical response and feasibilities to integrate onto functional photonic structures, Li et al. reported a graphene-clad microfiber all-optical modulator in 2014 [132]. The basic structure of the modulator is shown in Figure 4A; a tapered single-mode optical fiber with a waist diameter of about 1 μm was cladded by a mechanically exfoliated double-layer graphene film. A 1500 nm

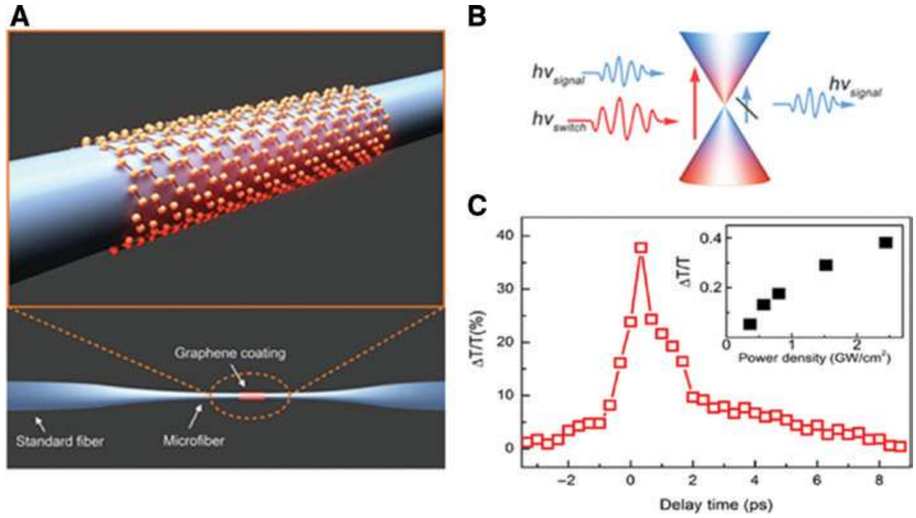

Figure 4: 2D materials-based absorptive modulation with fiber.
(A) Schematic illustration of an all-optical modulation scheme based on graphene-clad microfiber. (B) Schematic diagram of the working mechanism of the all-optical modulation based on saturable absorption. (C) The response time measured by pump-probe technique for the modulator, the inset shows the dependence of the modulation depth on pump intensity [132]. (A–C) Reproduced with permission [132]. Copyright 2014, American Chemical Society.

laser light was coupled into the fiber as signal light, which experienced substantial absorption loss by graphene as it propagates along. Due to the saturable absorption effects, the absorption loss reduced when a 1064 nm pulse laser was introduced, thus enabling effective modulation of the signal light. The schematic diagram of the working mechanism is shown in Figure 4B. The measured response time of the modulator is ~2 ps (Figure 4C), showing the potential for optical signal processing of bandwidth up to several hundred GHz. The modulation depth and peak power of the switching laser are 38% and around 40 W, which can be improved by optimizing the geometries of fiber or the graphene coating [133]. To reduce the threshold of the saturable absorption, Meng et al. demonstrated a graphene-doped polymer nanofiber with a pulse peak power threshold down to ~3 W [134]. To further improve the modulation depth, Chen et al. demonstrated a stereo graphene-microfiber structure, showing a modulation depth of 7.5 dB, which is attributed to the much longer light-matter interaction length [135]. However, the insertion loss was increased at the same time due to the increased linear absorption length of the graphene. By further optimizing the geometries or composition of the fiber and graphene layers, this type of absorptive all-optical modulators with a good balance between modulation depth and insertion loss can be expected.

4.1.2.2 Thermo-optic modulation

In contrast to absorptive modulation that relies on amplitude modulation based on absorption loss, thermo-optic modulation is a type of phase modulation that changes the phase of the propagation light. In 2015, Gan et al. demonstrated a graphene-assisted all-optical switch based on photothermal effect by integrating graphene onto one arm of a fiber-based Mach-Zehnder interferometer [136]. The schematic experimental setup is shown in Figure 5A. By sending a pump laser beam of 980 nm, the signal light was effectively modulated, and the interreference spectra of the modulator is shown in Figure 5B. A phase shift exceeding 21π with a nearly linear slope of 0.091π/mW was obtained, which enables all-optical switching with an extinction ratio of 20 dB. A microfiber-based ring resonator assisted by graphene's photothermal effect has also been reported, showing low threshold optical bistability and switching [138]. In addition to graphene, all-optical modulators based on the thermo-optic effects of other 2D materials have been investigated extensively too [138–141]. For example, Wang et al. demonstrated an all-optical modulator based on a Mach-Zehnder interferometer comprising of few-layer fluorinated phosphorene-deposited microfiber, showing a maximal phase shift of 8π and conversion efficiency of 0.029 π/mW [136]. The experimental setup and measured output spectra are shown in Figure 5C and D, respectively. Although all-optical thermo-optic modulation shows good modulation depth, the modulation speed is on the order of microseconds, limiting its applications where high speed is required.

4.1.2.3 Kerr modulation

As discussed above, the response time of thermo-optic phase modulation is limited by the thermo inertia. Another

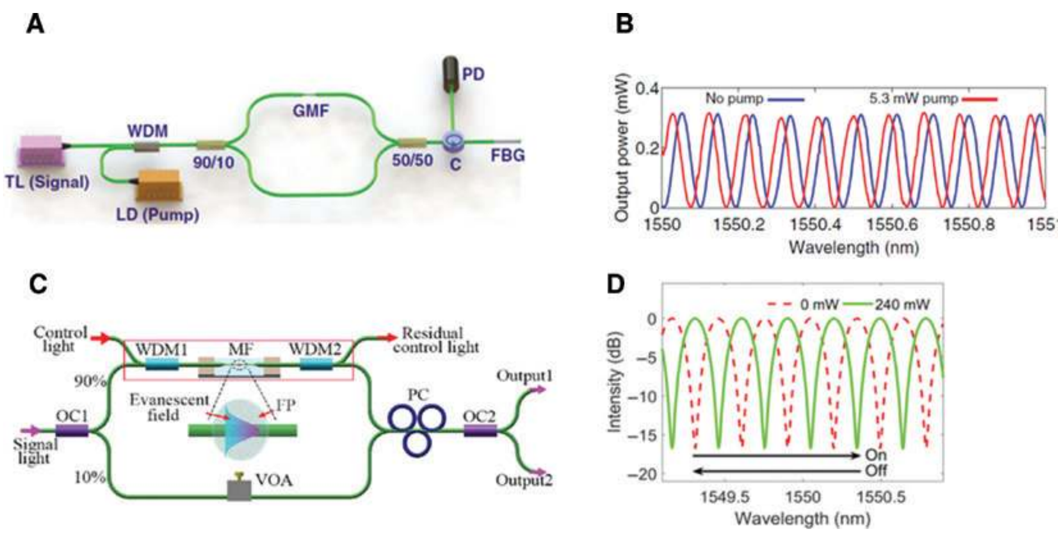

Figure 5: 2D materials-based thermo-optic modulation with fiber.
(A) Schematic experimental setup of an all-optical modulator by cladding graphene layer onto one arm of a Mach-Zehnder interferometer; the phase shift was induced by thermo-optic effect. (B) Measured interference fringes of the modulator shown in part (A) with (red) and without (blue) pump [137]. (C) Schematic experimental setup of a phosphorene-based all-optical modulator; FP represents fluorinated phosphorene. (D) Measured interference spectra of the modulator shown in part (C) with (green solid line) and without (red dashed line) pump [136]. (A and B) Reproduced with permission [137]. Copyright 2015, American Chemical Society. (C and D) Reproduced with permission [136]. Copyright 2018 WILEY-VCH.

type of phase modulation based on optical Kerr effects might offer a possible solution to this issue. In 2016, Yu et al. demonstrated an all-optical modulator based on the Kerr effect of graphene, utilizing a Mach-Zehnder interferometer structure with a much smaller fiber diameter compared with the thermo-optic ones (Figure 6A) [142]. When excited by laser pulse, ultrafast phase modulation was achieved due to Kerr effects, while the ultrafast loss modulation occurred at the same time as a result of saturable absorption. The temporal response of this modulator compared with loss modulation and switch pulse is shown in Figure 6B. Experimental results showed much higher modulation depth (~4.6 times) compared with the absorption-based ones. In addition to graphene, some novel types of all-optical modulators have also been demonstrated. Based on the large Kerr coefficient and broadband optical response of topological insulators, Chen et al. reported an all-optical modulator based on layered Bi_2Te_3-coated microfiber, and the schematic model of the modulator is shown in Figure 6C. Both the pump and signal light are coupled into the fiber at the same time, and the linear polarized signal light encounters cross-phase modulation as propagating through the Bi_2Te_3-coated microfiber due to the strong Kerr effect, leading to effective modulation of the signal light coming out from a liner polarizer. The output signal of this modulator with and without the pump is shown in Figure 6D. This modulator offers a new perspective of using topological insulators for all-optical modulation, which can be potentially used in all-optical signal processing. What's more, it also inspires us to explore other novel 2D materials for all-optical modulation.

4.2 Free space all-optical modulation

In addition to fiber-based configurations, all-optical modulation in free space based on 2D materials has been well studied too, owing to the flexibilities and ease of reach of this configuration. Compared to the fiber-based optical modulation, free-space ones can handle much higher optical power and cover an ultra-broadband spectral range from ultraviolet to terahertz, not limited by the availability of the low-loss waveguiding media.

In 2012, Weis et al. demonstrated an all-optical terahertz modulator over a frequency range from 0.2 to 2 THz based on photodoping effects. They showed that a single layer of graphene on top of silicon can significantly enhance the attenuation and modulation depth [144]. Wen et al. further demonstrated an all-optical terahertz modulator based on single-layer graphene on germanium and studied the temporal response systematically, which is driven by a 1550 nm continuous-wave laser. The schematic diagram of the modulator is shown in Figure 7A [88]. The temporal responses of the modulator with and without photodoping for germanium and

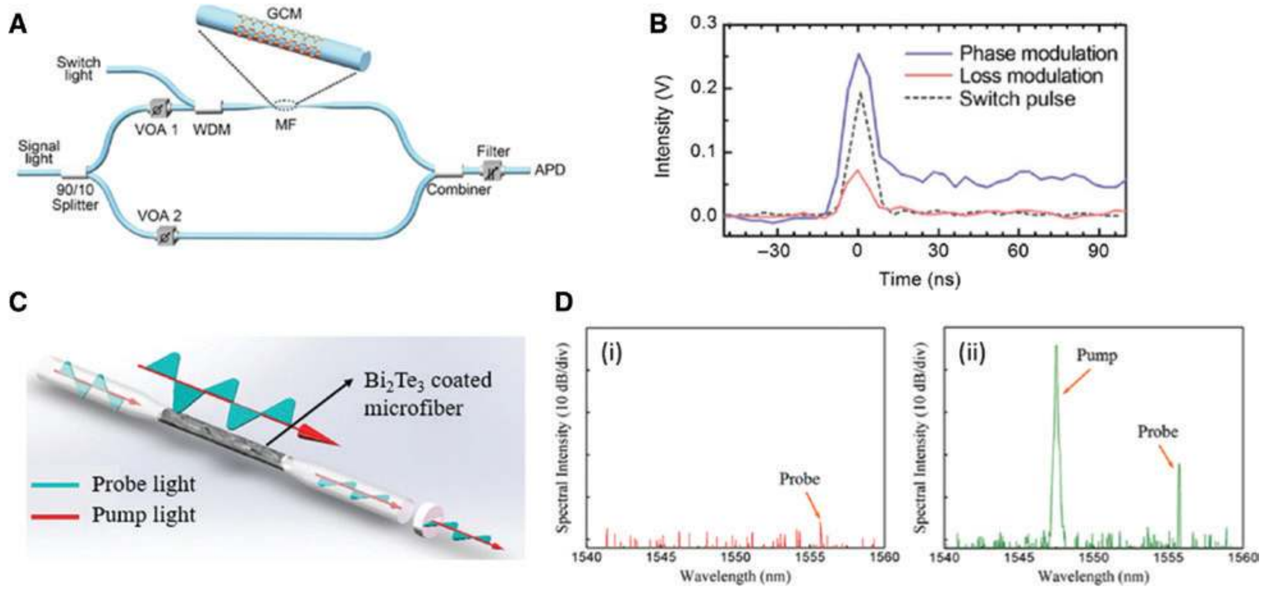

Figure 6: 2D materials-based Kerr modulation with fiber.
(A) Schematic experimental setup of an all-optical Kerr modulator by graphene-clad microfiber with a diameter of 1.1 μm. (B) Temporal profiles of pulse-modulated signals from the modulator (blue line) compared with the loss-based modulation (red line) and the switching pulse (black dashed line) in nanosecond time scale [142]. (C) Schematic model of topological insulators Bi_2Te_3-based all-optical modulator. (D) Output spectra of the modulator shown in part (c) without (i) and with (ii) the pump [143]. (A and B) Reproduced with permission [142]. Copyright 2016, Optical Society of America. (C and D) Reproduced with permission [143]. Copyright 2015, WILEY-VCH.

graphene-on-germanium samples are shown in Figure 7B; the inset shows the pumping power-dependent modulation depth [88]. The modulation speed of this type of modulator is limited below 1 MHz due to the size-induced parasitic capacity of the graphene compared to the beam size of the terahertz wave.

Recently, some novel 2D materials and new mechanism have been proposed to realize all-optical modulation. For example, Zhang et al. demonstrated a prototype of novel all-optical modulator based on in-plane anisotropic saturable absorption properties of layered SnSe [145], as schematically shown in Figure 7C. By altering the polarization states of the switching laser, the signal light can switch between the “on” and “off” states (Figure 7D), realizing effectively all-optical modulation. Although the comprehensive performance of this type of modulator, such as modulation speed, needs to be characterized thoroughly, this work generally offers a novel perspective to realize all-optical modulation with anisotropic 2D materials. What’s more, Wu et al. reported an all-optical modulator based on spatial cross-phase modulation enabled by perovskites working under ambient environment [146]; a schematic configuration of the modulator is shown in Figure 7E. Due to the excellent nonlinear optical effects of perovskites, the spatial profiles of signal light can be effectively modulated based on the spatial cross-phase interaction; the typical modulation results are shown in Figure 7F, which shows that perovskites can be good candidates to be used for all-optical modulation.

Although 2D materials show extraordinary optical response, the atomic thickness limits their interactions with light [12, 32, 147]. To further increase the light-matter interaction strength, 2D materials have been integrated onto various photonic cavities forming hybrid structures [42, 53, 148–151]. Shi et al. demonstrated a prototype of all-optical modulator based on a graphene-cladded photonic crystal [152]. They demonstrated a 3.5 nm resonance wavelength shift and a 20% quality factor change by introducing a 1064 nm continuous-wave control laser; the shift was nearly 2 times compared with the one with electrical modulation. In addition, they showed that the saturation threshold of the hybrid structure is around 2 orders of magnitude lower compared with graphene on silica, which are originated from optically induced transparency and hot carrier effects. As photonic cavities are a powerful tool to enhance light-matter interactions, it is expected that more cavity-assisted all-optical modulators will be devised and demonstrated in the future [151, 153].

5 Discussion and perspective

As introduced in section 4, 2D materials-based all-optical modulation has attracted tremendous attention and

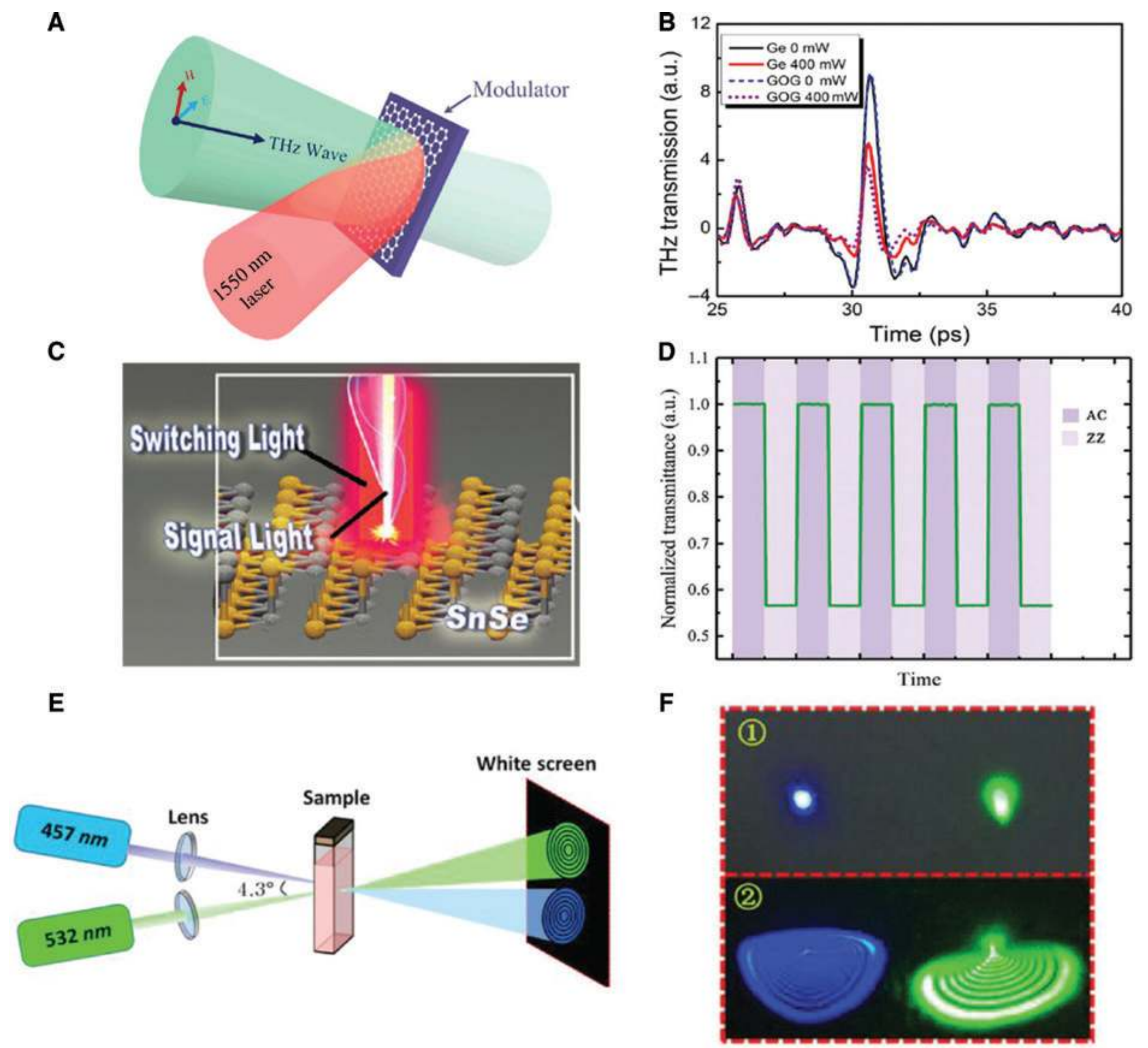

Figure 7: 2D materials-based all-optical modulation in free space.
(A) Schematic configuration of all-optical terahertz modulators. (B) Temporal profiles of the transmittance of graphene-on-germanium (GOG) compared with the pure Ge substrate with and without photodoping [88]. (C) Schematic diagram of a novel all-optical modulator based on anisotropic layered materials SnSe. (D) Transmittance of the signal light with switching light of two orthogonal polarizations [145]. (E) Schematic of a novel spatial all-optical modulator based on the spatial cross-phase modulation. (F) Typical experimental results of the all-optical modulators; spatial profiles of the signal (blue) and switching laser (green) beam before (upper figure) and after (lower figure) the cross-phase interaction [146]. (A and B) Reproduced with permission [88]. Copyright 2014, Nature Publication Group. (C and D) Reproduced with permission [145]. Copyright 2019, WILEY-VCH. (E and F) Reproduced with permission [146]. Copyright 2018, WILEY-VCH.

made rapid progress since the first demonstration of the graphene-based saturable absorber [64]. However, there are still challenges to be resolved for the practical applications of such all-optical modulators. For example, methods to fabricate large-scale and high-quality 2D materials are still not mature. Here, we discuss the challenges facing 2D materials-based all-optical modulators and point out some of the further directions based on our understanding.

5.1 2D materials as passive saturable absorber

2D materials-based saturable absorbers, especially for graphene, have been widely investigated, which are close to practical applications. Compared to commercially available semiconductor saturable absorber mirrors (SESAMs), graphene saturable absorber possesses broader spectral response, a shorter recovery time, and weaker wavelength-dependent saturation fluence [28, 154], whereas graphene-based saturable absorbers suffer from laser-induced damage due to the atomic thickness and heating accompanied with the nonlinear process, limiting the maximum output power [108, 155] and duty cycle of the ultrafast laser [142]. Moreover, graphene-based saturable absorbers show much higher saturation fluence compared with SESAMs, especially near the bandgap of the SESAM materials [154]. Thus, graphene-based saturable absorbers only have advantages for lasers with temporarily ultrashort pulses (pulse duration near or even less than 100 fs) and widely tunable wavelengths [156], and more efforts are required to improve the general performance. For other 2D semiconductor-based saturable absorbers such as TMDs and black phosphorus, they show strong wavelength-dependent saturation fluence similar with SESAMs, but they also share the advantages of graphene as being flexible and disadvantages as being volatile to thermal damage [157–159].

5.2 2D materials as active all-optical modulators

Optical modulators or switches are characterized by many interplayed parameters, including modulation speed, modulation depth, insertion loss, and energy consumption. 2D materials-based all-optical modulators possess both advantages and disadvantages, depending on the operation mechanism and structures. For thermo-optic all-optical modulation, the speed is usually below 1 MHz, due to the slow thermal diffusion. However, the modulation speed can be improved by optimizing the configuration and size of the components. For example, the modulation speed of a graphene-coated microfiber increased dramatically (around two orders) when decreasing the fiber diameter from 10 μm [137] to 1 μm [142]. In contrast, the modulation speed of all-optical modulators based on nonlinear effects usually depends mainly on the intrinsic response of the materials, operating potentially up to hundreds of GHz [132] or even higher [160, 161]. In terms of modulation depth, it depends on the configuration a lot. For direct absorptive modulation, the modulation depth of all-optical scheme is not as high as the electrical gating ones under the same initial absorption condition theoretically [28], but more analysis is required for specific case. For modulator of resonant or interferometric structure, the modulation depth equals to the extinction ratio, once the phase shift of one π can be achieved, which can be further improved by optimizing the structure design [137, 162]. With regard to insertion loss and energy consumption, all-optical modulators generally induce more insertion loss and require more energy per bit compared to electric gating ones, due to the relatively high threshold of third-order nonlinear effects. Thus, all-optical modulators own superior advantages when ultrafast modulation (generally beyond 100 GHz) is required, but more efforts are needed to decrease the insertion loss and energy consumption of current all-optical modulators for more general utilization.

5.3 Prospects

As discussed above, 2D materials-based all-optical modulation has attracted lots of interests and is growing rapidly, owing to the requirement of more efficient and ultrafast optical interconnects. While they are still at early stage, some challenges remain as discussed in subsections 5.1 and 5.2, which may in turn offer driving force for further research. Some of the possible important directions are summarized below.

5.3.1 All-optical modulators based on emerging novel materials and their heterostructures

As reported, there are over 1000 2D materials to be explored showing fascinating properties [61]. In addition, heterostructures (Figure 8A) consisting of stacking up different 2D materials or the same material with twist angles show intriguing optoelectronic properties [163, 164]. Considering the rich compositions of 2D materials and their versatile combination, it is expected that some of them will be suitable for high-performance all-optical modulation.

5.3.2 All-optical modulation based on plasmonic structures

2D materials-based plasmonic structures have attracted great attention, as they can offer tight optical confinement and strong field enhancement. For example, a 2D semiconductor nonlinear modulator with ultrafast response time has been demonstrated [165], as illustrated in Figure 8B. These plasmonic structures enhance the light-matter interaction dramatically and bring new opportunities for all-optical modulation, with low power consumption and insertion loss [167, 169]. In addition, the relaxation time of surface plasmons is usually on

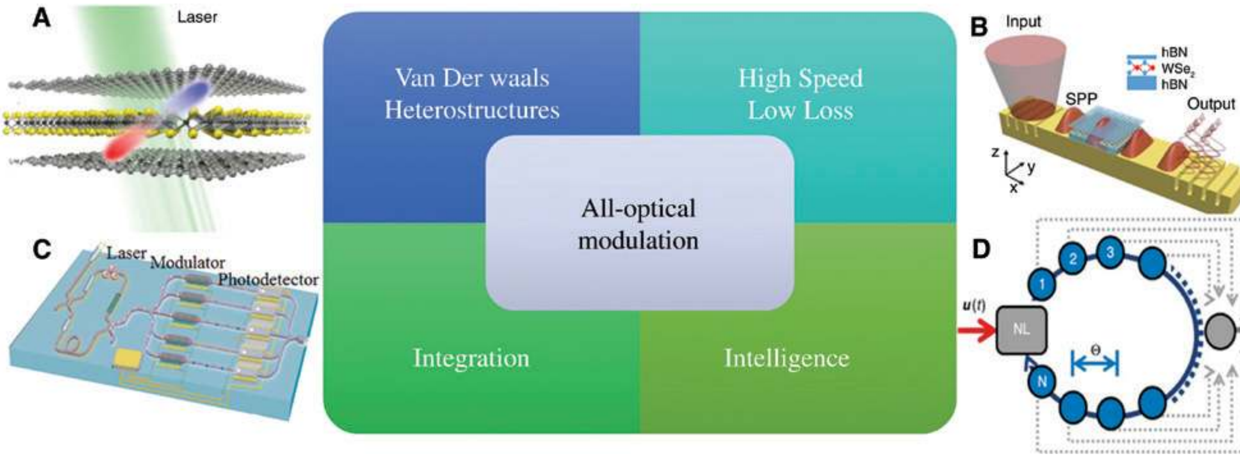

Figure 8: Promising development directions of all-optical modulation with 2D layered materials.
(A) Schematic of heterostructures consisting of different kinds of 2D layered materials [166]. (B) Diagram of ultrafast modulators enabled by interaction between surface plasmon polaritons and excitons in 2D materials [167]. (C) Schematic illustration of integrated 2D material-silicon hybrid photonic circuit [165]. (D) Schematic illustration of computation using nonlinear transient states generated by a single nonlinear element subject to delayed feedback [168]. (A) Reproduced with permission [166]. Copyright 2016, Nature Publication Group. (B) Reproduced with permission [167]. Copyright 2019, Nature Publication Group. (C) Reproduced with permission [165]. Copyright 2012, American Chemical Society. (D) Reproduced with permission [168]. Copyright 2013, Nature Publishing Group.

the order of 10 fs, which offers opportunities of ultrafast modulation with 2D materials.

5.3.3 On-chip all-optical modulation

With the growing demand of data storage and high-performance computing, there has been a major trend to integrate optical components on silicon chip for real applications (Figure 8C). 2D materials are compatible with the silicon platform and are expected to play a more important role in silicon photonics [20], and integrating 2D materials-based all-optical modulators onto silicon platform will be an important direction to explore, which is essential for all-optical on-chip networks. In addition, artificial intelligence also drives the development of all-optical technology. For example, a photonic architecture to process information at unprecedented data rates has been demonstrated (Figure 8D), showing great potential for all-optical information processing [168].

5.3.4 New mechanism and configuration for 2D materials-based all-optical modulation

In section 4, we presented two novel prototypes of all-optical modulation based on the anisotropic structure and spatial cross-phase modulation effect, which are distinctively different from the conventional ones. It is expected that new mechanisms or structures such as magneto-optic effects will be explored for all-optical modulation.

6 Conclusion

In conclusion, we have discussed the basic properties of typical 2D materials and the principle of all-optical modulation based on them, followed by a review of the state-of-art all-optical modulators based on 2D materials, and then we discussed the challenges and opportunities facing this kind of modulators. Overall, 2D materials-based all-optical modulation has attracted great attention and made tremendous progress in different aspects, including theoretical design, material characterization, integration methods, and structural configuration. These results suggest that there are great opportunities for 2D materials-based all-optical modulation, while challenges remain for practical applications. It is expected that research into 2D materials-based all-optical modulation will keep a fast pace, considering the rapid development of 2D materials and all-optical networks.

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