Review

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Advances in photonics of recently developed Xenes

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Abstract: Monoelemental two-dimensional materials are well known as Xenes. The representatives graphene and phosphorene have received considerable attention because of their outstanding physical properties. In recent years, the family members of Xenes have greatly increased, and the emerging ones are gaining more and more interest. In this review, we mainly focus on the

recently developed Xenes in groups IIIA, VA, and VI. Comprehensive discussions of the latest progress are given in the aspects of basic physical properties and intriguing applications in photonics, optoelectronics, energy, and biomedicines.

Keywords: monoelemental Xene; photonics; optoelectronics; biophotonics; nonlinear optical response.

1 Introduction

The first discovery of atomically thin graphene in 2004 has opened the new era of nanomaterials and won the 2010 Nobel Prize in Physics [1]. Graphene is the truly two-dimensional (2D) nanomaterial with carbon atoms configuring into a single-layer hexagonal honeycomb network. Its excellent physical properties result from its perfect symmetry and structure dimensionality, and many photonics and optoelectronics applications are endeavored soon after its discovery [2–5]. Motivated by graphene, diverse 2D nanomaterials have been discovered in exponential growth including monoelemental and multicomponent objects, such as transition metal dichalcogenides [6–8], graphene-analogous graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) and hexagonal boron nitride ($h\text{-BN}$) [9–13], phosphorene [14–17], group IVA and group VA monoelements (silicene, germanene, stanene, arsenene, antimonene, and bismuthene) [18–22], transition metal carbides/nitrides (MXenes) [23–31], phosphorene-analogous group IVA–VIA binary compounds [32, 33], perovskites [34–38], metal-organic frameworks [39–41], nonlayered materials [42], and so on [43].

The class of monoelemental 2D crystals, known as Xenes, currently undergoes a booming development in both of theoretical and experimental researches [44–46]. Up to now, about 15 monoelemental 2D materials have been theoretically predicted and experimentally synthesized including graphene, phosphorene, and group IIIA, IVA, VA, and VIA elements [2, 14, 18, 20, 47]. They have gathered explosive attention because of their intrinsic physical properties and promising applications in electronics, optoelectronics, and energy. Recently, many

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prospective reviews relative to Xenes have been reported focusing on groups IVA and VA monoelemental nanomaterials and the undeveloped ones [48, 49]. Molle et al. gave a brief discussion on the intrinsic electronic properties and related physical properties of Xenes in group IVA and highlighted the future opportunities in exploring topological phenomena and innovative device concepts to overcome the experimental odyssey and instability [18]. Balendhran et al. reviewed the fundamental physical properties and diverse synthesis methods of silicene, germanene, and stanene [19]. With respect to 2D pnictogens (arsenene, antimonene, and bismuthene), Pumera et al. reviewed the state-of-the-art theoretical and experimental researches related to structures and properties of mono- and few-layer pnictogens [21]. Furthermore, Zhang et al. provided a comprehensive review on the latest progress of 2D group VA nanosheets related to the fundamental structural, electronic, and physical properties, as well as the fabrication strategies and promising devices applications [20].

Even though these reviews have provided sophisticated comments on semimetallic group IVA and semiconducting group VA monoelements, some newly developing Xenes like borophene, gallenene, indiene, aluminene, selenene, and tellurene are not involved. Furthermore, the rapid development of 2D nanomaterials has spawned out exponential-growing original achievements of Xenes in recent years, motivating the demand of a timely and comprehensive review. Herein, in this review, we mainly focus on diverse newly developing Xenes, discussing their crystal structures, electronic and physical properties from theoretical to experimental progresses, as well as their promising photonics applications in accompany with distinct fabrication methods.

2 Group IIIA Xenes

2.1 Fundamental aspects

2.1.1 Borophene

Borophene refers to the single-layer boron nanosheet, which has aroused growing interest in materials science and semiconductor technology. Borophene is structurally similar to graphene with a hexagonal honeycomb arrangement, but chemically different from graphene that has in-plane σ bonds and out-of-plane π bonds from sp^2 -hybridization. Ascribed to the electron-deficient feature, borophene has no electrons occupying π bonds, leading

to the instability and easy acceptance of electrons from donors. Therefore, multicenter bonds can be generated to stabilize its structure.

According to calculations, stable borophene has an interlinked 2D network with centered and vacant boron hexagons (Figure 1A), where the hexagon vacancies act as stabilizer. Multiple configurations including the planar and buckled can be obtained because of the variation of vacancy arrangement. The structural parameter η can be used to define the crystal structure of a given borophene nanosheet, which is the ratio of hexagon vacancies to triangular vacancies in a unit cell, as illustrated in Figure 1A [52]. Accordingly, multiple phases with $\eta = 0 \sim 1/3$ probably exist, where $\eta = 0$ refers to the triangle close-packed phase and $\eta = 1/3$ refers to the graphene-like honeycomb phase. Among them, the χ_3 ($\eta = 1/5$), β_{12} ($\eta = 1/6$), and α ($\eta = 1/9$) phases are commonly observed (Figure 1B) [50, 53], and the topologies of these configurations have been experimentally confirmed by scanning tunneling microscopy (STM), far-field Raman, and tip-enhanced Raman spectroscopy [54]. For example, the β_{12} phase was grown in conjunction with tiny χ_3 phase at low temperatures (<600 K), but only the χ_3 phase was dominated when temperature was increased up to 650 K [55].

More interestingly, the configurations of borophene are substrate-dependent. Predicted by theoretical calculations, buckled borophene prefers to form on Au substrate with vertical atomic undulation, while the planar polymorphs are favored on more reactive substrate such as Ag, Cu, or Ni [56]. When an electron-donating metallic substrate is adopted, the arrangement of boron atoms prefers to be a honeycomb configuration [50]. This substrate effect may stem from the competition between the hybridization energy of electrons and the strain energy of structure [56]. Thriving experimental synthesis of borophene on various substrates are developed based on these instructive theoretical researches. The first achieved borophene with out-of-plane buckling was synthesized on Ag(111) substrate in 2015 by controlled molecular beam epitaxy growth under ultrahigh-vacuum conditions [57]. It is different from theoretical prediction, and different phases were observed ascribed to the different experimental parameters. Comparing with a silver substrate, the charge-transfer coupling effect is much stronger between borophene and copper substrate. Besides, the crystal structure of borophene grown on copper is different from that grown on silver originating from diverse surface vacancy distributions [57, 58]. For example, large-area borophene (up to $100 \mu\text{m}^2$) was successfully synthesized on Cu(111) surface by molecular beam epitaxy growth, which presented novel triangular networks with

Figure 1: The geometric and electronic structures of borophene.

(A) Schematic diagram of the basic structure of borophene consisting of hexagon and triangle vacancies. (B) Some typical structural configurations of free-standing borophene. The numbers at the bottom right of each panel indicate the structural parameter η . Reproduced with permission [50]. Copyright 2016, Springer Nature. (C) The comparison of the band structure and total density of states (DOS) of pristine borophene and Be-decorated borophene. Reproduced with permission [51]. Copyright 2019, The Royal Society of Chemistry.

a hexagonal vacancy concentration of $\eta=1/5$ [55]. Consequently, the crystal structure and electronic property of borophene may be possibly manipulated by altering the substrate as well as changing experimental conditions such as temperature and deposition rate.

Although the realization of borophene on Ag and Cu substrates has facilitated its practical applications in functional devices [55, 57–61], the preparation of free-standing borophene has not been achieved up to date because the partially occupied in-plane σ bands and out-of-plane π bands are highly sensitive to surroundings. Taking advantage of this feature, the surface states and physical properties of borophene can be modified and fine-tuned by reacting with diverse chemical groups [51]. The acquisition of stable free-standing graphene-like borophene (*h*-B) is remarkable for device applications, and different kinds of strategies have been explored. Surface decorations including alkali, alkaline earth, transition, and noble metals are beneficial to the stability of *h*-B [51]. Among them, the beryllium (Be) atoms are more predominant in stabilizing *h*-B, as it can push the bonding bands below the Fermi level by charge transfer to configure a graphene-like electronic structure where bonding and antibonding bands intersect at the K point to form a Dirac cone (Figure 1C).

2.1.2 Gallenene

Gallenene is the single atomic layer of metallic gallium (Ga), which has also brought in new vigor and vitality into the Xenes family. Two kinds of gallenene, the planar *a*(100) and buckled *b*(010), with distinct atomic configurations can be obtained from the molten phase of bulk α -Ga by an advanced solid-melt interface exfoliation technique (Figure 2A, B) [62]. Both *a*(100) and *b*(010) gallenene exhibit nonlinear dispersive bands and partially filled Dirac cones near the Fermi level, behaving as metallic monolayers (Figure 2C) [62]. This metallicity is robust enough against the lattice strain induced by substrates [65]. Similar to borophene, gallenene can also be stably grown on substrates, and the stability is closely related to the adopted substrate because of the strong chemical interaction between gallenene and substrates confirmed theoretically and experimentally. By the epitaxial growth technique, a gallenene buffer layer with a $4\times\sqrt{3}$ superstructure was firstly formed on Si(111) substrate, then the hexagonal honeycomb gallenene layer was grown on it as confirmed by low-temperature STM, making it possible to be applied in FET [66]. Furthermore, the stability of gallenene is layer-dependent. Revealed by the first-principles simulation, free-standing bilayer gallenene is unstable and highly requires an underlying support, consistent with experimental results.

However, as the layer numbers increased to 3, freestanding gallene can still be stable when the temperature is about 100 K higher than the melting point of bulk Ga [67].

2.1.3 Indiene

The single atomic layer of indium named as indiene has been theoretically predicted that three different monolayer

polymorphs probably exist, i.e., the puckered, planar, and buckled indiene (Figure 2D) [63]. All the three forms are energetically stable, but only the planar and buckled indiene are dynamically stable as imaginary frequencies are present in the phonon modes of the puckered one. For the planar indiene, it behaves as a metal with two Dirac cones at K points in the Brillouin zone. With respect to the buckled indiene, it has a small indirect bandgap of 0.97 eV and behaves as a semiconductor (Figure 2E) [63, 68]. With

Figure 2: The geometric and electronic structures of gallene, indiene, and aluminene polymorphs.

(A) The crystal structure of bulk α -Ga (left) and the atomic configurations of monolayer gallene cleaving along the (010) and (100) direction before (middle) and after relaxation (right). Gallene cleaved along (010) direction forms a distorted rhombic lattice, while that cleaved along the (100) direction forms a honeycomb lattice. (B) Representative brightfield TEM, SAED, and HRTEM images for the $a(100)$ and $b(010)$ gallene nanosheets. (C) Band structure and density of states for $a(100)$ and $b(010)$ gallene monolayers. Reproduced with permission [62]. Copyright 2018, American Association for the Advancement of Science. (D) The optimized geometries of puckered, planar and buckled indiene. (E) The electronic band structures of stable planar and buckled indiene. Reproduced with permission [63]. Copyright 2016, The Royal Society of Chemistry. (F) The optimized geometries (left), phonon dispersion (middle), and electronic band structure as well as DOS (right) for planar aluminene. Reproduced with permission [64]. Copyright 2015, IOP Publishing.

the layer number increased up to 3 L, the semiconducting buckled indiene transforms into metallic [69]. To date, the researches related to indiene are scarce, and the experimental realization of indiene is absent. In view of the structural similarity of indiene to graphene, antimonene, and so on, the research activities related to experimental fabrication, property exploration, and promising application of indiene are highly expected and will flourish the field of 2D materials.

2.1.4 Aluminene

Bulk aluminum (Al) is not a layered material, but thin films can be easily shaped. Thus, monolayer aluminene with different structures (e.g. planar, buckled, puckered, and triangular) might be probably derived from the bulk counterpart [64, 70]. Based on theoretical calculations, Kamal et al. first predicted that free-standing aluminene with the planar honeycomb form (space group $P6/mmm$) is geometrically stable (Figure 2F) [64]. The band structure (Figure 2F) demonstrate that planar aluminene behaves metallically with partially occupied σ and π bands and van Hove singularity closed to the Fermi level, which can be considered as a highly hole-doped graphene and might contribute to chiral superconductivity. Later, Yuan et al. and Yeoh et al. predicted that free-standing buckled aluminene could also be thermodynamically and dynamically stable by calculating the cohesive energy and phonon dispersion [71, 72]. Its stability can be maintained under tensile strains up to 7%, but it is not stable under compressive strains. Owing to the strain effect, planar and buckled aluminene was recently reported to be stable on Cu(111) and graphene substrates based on theoretical investigations [70]. Aluminene allotropes can be preferentially grown on metallic substrates with low diffusion barrier, enabling the possibility of depositing atomically thin monolayer aluminene on appropriate surface for practical optoelectronic applications. At present the theoretical investigations on physical properties of aluminene is far from sufficient, the experimental realization of free-standing aluminene is still absent, and many efforts are still needed to promote the research on it.

2.2 Physics

2.2.1 Electronic and optical properties

The calculated band structure of free-standing triangle close-packed borophene with crystallographic symmetry of $Pmmn$ is shown in Figure 3A [57]. A bandgap is opened along Γ -Y and S-X directions (along the b direction), while

the energy band intersects with the Fermi level along Γ -X and Y-S directions (parallel to the a direction), making it an anisotropic 2D metal [57, 75]. Therefore, it presents a remarkable electrical conductivity and optical transparency along the a direction but a considerably low optical conductivity within the infrared (IR)-visible light region [73, 75]. The anisotropic optical conductivity of borophene is shown in Figure 3B. Almost negligible value is presented along different directions at the radiation energy below 3 eV because of the absence of interband transitions. However, it will increase significantly in the UV region at energy above 6.5 eV and shows a high value with series peaks [73]. Similar to borophene, indiene also possesses pronounced optical properties such as high refractive index and reflectance in the IR and visible light region [69]. Its optical properties such as absorption, refractivity, reflectivity, and optical conductivity are anisotropic depending on the light polarization [68, 69].

Structural strain is an effective strategy for tuning the electronic and optical properties of borophene [73, 74, 76, 77]. The band transition energy of borophene is red-shifted (blue-shifted) in accompany with structural variation of buckling height when applying a tensile (compressive) strain [74]. The metallicity of borophene is extremely robust against the strains. For the buckled indiene, its bandgap can be reduced even to zero under compressive strain and becomes enlarged under tensile strains without changing the dispersion of the band structure [63]. The strain effect on the optical response is anisotropic closely related to the structural anisotropy of borophene. This effect is more pronounced along the uncorrugated a direction compared with the corrugated b direction [74].

Surface functionalization is also a fascinating way to adjust the optical properties of 2D nanomaterials via modifying the basic structural and electronic properties. For examples, prominent optical conductivity peaks can be obviously detected in oxygen-decorated borophene from low-energy IR spectral region to the visible light region as shown in Figure 3C [73]. By fluorine functionalization with a concentration of 50%, the metallic borophene would be transformed into a semiconductor with dominated optical absorption in the near-infrared (NIR) and visible light region (Figure 3D, E) [74].

2.2.2 Superconducting

Borophene with small atomic mass is expected to have superconducting behavior ascribed to the strong electron-phonon coupling, which was calculated based on density functional theory (DFT) to evaluate the superconductivity

Figure 3: The comparison of geometric and electronic structure for pristine and functionalized borophene.

(A) Top: Top and side view of the borophene structure (*Pmmn*) grown on the silver surface. Bottom: The band structure of free-standing borophene. Reproduced with permission [57]. Copyright 2015, American Association for the Advancement of Science. (B) The optical conductivity of pristine borophene along $x[100]$, $y[010]$, and $xy[110]$ directions. (C) Left: Side views and top view of the oxidized borophene configuration. Green and blue spheres indicate boron atoms located at different planes. The red sphere stands for the oxygen adatom. Right: The comparison of optical conductivity of pristine and oxidized borophene. Reproduced with permission [73]. Copyright 2016, IOP Publishing. (D) The atomic configuration and band structure of the fluorinated borophene (BF_2). (E) The optical conductivity of the fluorinated borophene (BF_2). Reproduced with permission [74]. Copyright 2018, Royal Society of Chemistry.

[78]. Calculations revealed that all the borophene polymorphs are intrinsic superconductors with the critical temperature of $T_c = 10 \sim 20$ K, which increases with the concentration of boron vacancy. Experimentally, the electron-phonon coupling strength of borophene is estimated to be 0.53–0.59 according to the linewidth of Raman peaks, and the T_c for β_{12} and χ_3 phase is approximately 7.1 and 9.8 K, respectively [54]. The superconductivity was also found in pristine buckled aluminene, and tensile strain can enhance the critical temperature T_c from 6.5 to 11.9 K [72].

2.2.3 Magnetism

In Rashba or topological insulator systems, the orbital textures associated with spin arising from strong spin-orbit coupling (SOC) are found to be significant in switching the

magnetic moment of ferromagnets. Intriguingly, orbital texture without SOC is recently observed in the borophene χ - h_0 lattice with two mirror-symmetric chirality (C1 and C2; Figure 4A) [79]. It is mainly attributed to the presence of linear dispersive Dirac cone that gives rise to an orbital pseudospin with momentum locking and opposed textures at K and K' valleys (Figure 4A). Combining chirality with orbital pseudospin, the orbital texture of a bilayer borophene (C1-C1 or C1-C2 stacking) could be feasibly modified by external electric field. As shown in Figure 4B, the orbital texture of C1-C1 stacked borophene maintains the same texture before and after applying electric field, whereas the Dirac cone of C1-C2 stacked borophene presents an on/off switching behavior triggered by the electric field. The borophene with symmetry of $P6/mmm$ is predicted to possess a stable striped antiferromagnetic structure based on theoretical calculations. A negative

Figure 4: The orbital texture for borophene.

(A) The atomic structure and the orbital texture for the Dirac cone of the borophene (χ - h_p) with two chiralities C1 and C2. (B) Left: Orbital texture model of bilayer borophene with same chirality stacking (C1-C1) and opposite chirality stacking (C1-C2) before and after applied electric field. Right: 3D band structure for the same chirality stacking (C1-C1) and opposite chirality stacking (C1-C2) under electric field. Reproduced with permission [79]. Copyright 2019, American Chemical Society.

Figure 5: The plasmon dispersion of borophene polymorphs.

Anisotropic plasmon dispersion (q) of buckled triangular (B_Δ), β_{12} ($B_\square$), and χ_3 ($B_\diamond$) borophene along Γ -X and Γ -Y directions. Reproduced with permission [82]. Copyright 2017, American Chemical Society.

Poisson's ratio (out-of-plane) is appended benefiting from the coupling of atomic layers, and it can be converted from a semiconductor (0.41 eV indirect bandgap) into a half-metal by electron doping, making it a promising candidate for spintronics and nanoelectromechanical devices [80]. In addition, versatile magnetic properties can be obtained by doping transition metals (TMs) in electron-deficient hexagonal boron vacancies, where the induced ferromagnetism, paramagnetism, or antiferromagnetism depends on the type of TMs [81]. Particularly, Cr/Mn-embedded χ_3 phase exhibits high Curie temperature and ferromagnetic order with large perpendicular magnetic anisotropy, guaranteeing intriguing applications in spintronic devices.

2.3 Applications

Borophene is a metallic conductor in contrast to its semiconducting bulk counterpart. The advantages of structural flexibility, high strength, and light weight make borophene

a promising candidate for the next-generation electronic and optoelectronic devices, such as photodetectors, flexible wearables, and sensors. The conductivity and rigidity of buckled borophene ($Pmmn$) along the ridges are more significant than across the surface, making borophene a fascinating anisotropic metal and promising application in polarized devices [57]. Gallenene possesses a much lower thermal conductivity ($<1 \text{ W mK}^{-1}$) compared with graphene, silicene, and stanine [62]. Together with the high electrical conductivity, gallenene is a promising thermal barrier or electrical connector in devices. The experimental realization of atomically thin gallenene will open up brand new opportunities for the development of novel devices.

Plasmons, as one important optical property, are collective oscillations of charge carriers in solids induced by Coulomb interactions. When restricted to 2D regime, plasmons can enhance light-matter interactions under the ultra-subwavelength confinement with its frequency varying as the function of free carrier concentration ($\sqrt{n}$). With regard to borophene, high carrier concentration and

plasmonic response in the visible and NIR regions are presented, as high density of electronic states are occupied near the Fermi level [82]. Furthermore, plasmon dispersion in borophene is highly anisotropic and structural-dependent as the result of effective mass difference of charge carriers along different high-symmetry directions (Figure 5) [82].

Up to now, the investigation on group IIIA Xenes is not adequate as well as the understanding to their intrinsic and induced physical properties. Although most group IIIA Xenes are metallic, their semiconducting character is expected to be aroused by structural modifications. Exploring modulation strategies for tailoring structure and performance of group IIIA Xenes may fulfill their semiconductor technology applications. Therefore, they are potential candidates for photonics and optoelectronics devices with coexisting challenges and opportunities. Many efforts are still needed to promote their experimental fabrication, property exploration, and promising application.

3 Group VA Xenes

3.1 Fundamental aspects

Monoelemental 2D materials in group VA is another kind of hot research subject. Stimulated by phosphorene, group VA Xenes such as arsenene, antimonene, and bismuthene have provoked much attention in the past few years [20, 21, 83]. Abundant theoretical and experimental studies related to group VA Xenes would not only expand the fundamental knowledge of this material family but also flourish their applications in semiconductor technologies.

3.1.1 Arsenene

Bulk arsenic has two stable allotropes, i.e., the layered rhombohedral grey arsenic with the space group of $R\bar{3}m$ and the layered orthorhombic α arsenic (high-temperature phase) analogous to black phosphorus. The former is a semimetal whereas the latter is a semiconductor with a narrow indirect bandgap. With decreased dimension, atomic thin arsenene can be obtained from bulk arsenic crystal. Different allotropes were theoretically predicted, which include honeycomb (α , β , γ , δ , and ϵ) and non-honeycomb (ζ , η , θ , and ι) phases [84]. The most stable monolayer β -arsenene has a large indirect bandgap of 2.49 eV (Figure 6A), which would undergo an

indirect-direct bandgap transition under tensile strains, promising for UV or blue light optoelectronic devices applications [85].

3.1.2 Antimonene

The most stable allotrope of bulk antimony under ambient condition is the gray antimony with a rhombohedral structure of $R\bar{3}m$. Its atomically thin monolayer counterpart, antimonene (β phase), was firstly predicted by Zhang et al. in 2015 [85]. Buckled monolayer antimonene possesses an indirect bandgap of 2.28 eV, but it would transfer to a semimetal with the increasing layer number approaching to the bulk feature (Figure 6B) [85]. Furthermore, antimonene can be transfer to a direct semiconductor under tensile strains, and a bandgap can be opened in few-layer semimetal antimonene after surface functionalized, making it a semiconductor with possible applications in optoelectronic devices [89]. Following theoretical prediction, the experimental synthesis of antimonene by means of mechanical exfoliation [90, 91], liquid-phase exfoliation [86, 92, 93], van der Waals epitaxy [94, 95], molecular beam epitaxy [96, 97], and solution synthesis [98] was booming developed for their practical applications in optoelectronics [93, 99], photonics [100, 101, 125], energy devices [102, 103], and biomedicine [104–106].

3.1.3 Bismuthene

Stable bulk bismuth with a rhombohedral layered structure ($R\bar{3}m$) shows typical metallicity whereas the atomic thin buckled β -bismuthene is considered to be a narrow bandgap semiconductor (0.99 eV) with superior high-temperature stability based on finite temperature ab initio molecular dynamic calculations (Figure 6C) [84, 87]. The SOC effect has a significant effect on the electronic and physical properties of bismuth as it is a heavy element, and the topological insulator behavior of bismuthene grown on selected substrates have been explored experimentally [107, 108]. In addition, the bandgap of β -bismuthene would be reduced to ~ 0.3 eV by taking SOC into account (Figure 6C) [87]. Its optical absorption and emission could be changed, specifically a 0.6 eV red shift in absorption edge and luminescence energy (Figure 6D) [88]. Although free-standing single-layer bismuthene is still absent, now available theoretical reports indicate that dominant optical absorption and reflection in IR region are expected in β -bismuthene [109, 110] as well as large carrier mobility in the order of $10^2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ comparable with phosphorene

Figure 6: The atomic configuration and electronic structure of arsenene, antimonene, and bismuthene.

(A) The atomic configuration and electronic band structure of monolayer arsenene. Reproduced with permission [85]. Copyright 2015, John Wiley and Sons. (B) The atomic configuration and layer-dependent band structure of antimonene. Reproduced with permission [85]. Copyright 2015, John Wiley and Sons. Reproduced with permission [86]. Copyright 2018, John Wiley and Sons. (C) The optimized atomic structure and electronic band structure of free-standing buckled honeycomb bismuthene calculated by HSE (hybrid functional) and HSE + SOC. Reproduced with permission [87]. Copyright 2016, American Physical Society. (D) The imaginary dielectric function of bismuthene calculated by HSE + RPA (random-phase approximation) and HSE + SOC + RPA. Reproduced with permission [88]. Copyright 2019, The Royal Society of Chemistry.

[84], making it a promising material applied in high performance biophotonics and photoelectronics devices.

3.2 Nonlinear optical property

Antimonene holds remarkable nonlinear optical property. Its nonlinear saturable absorption can be evaluated by open-aperture Z-scan or P-scan method [111, 112]. The open-aperture Z-scan measurement is illustrated in Figure 7A. Normalized transmittance signals through antimonene increase gradually with the approaching focus point ($Z=0$), showing a typical single photon absorption. Few-layer antimonene was reported to hold the saturable intensity of 7.81 and 24.1 GW cm^{-2} as well as a modulation depth of 19.03% and 12.8% at the incident light of 800 and 1500 nm, respectively [112]. Its nonlinear refractive index was $2.55 \times 10^{-14} \text{ cm}^2 \text{ W}^{-1}$ at 800 nm and $7.88 \times 10^{-15} \text{ cm}^2 \text{ W}^{-1}$ at 1500 nm by applying the closed-aperture Z-scan method [112]. The saturable

absorption of antimonene was also confirmed by power-scan measurement, where the transmittance nonlinearly increases and then saturates as a function of incident laser intensity (Figure 7C) [112]. Besides saturable absorption, the optical limiting also appears with forming pit on the saturable absorption peak when excitation intensity is further increased (Figure 7B) [111]. Therefore, by controlling laser intensity, antimonene can be used either as saturable absorber in Q-switched and mode-locked laser devices for generating ultrafast laser pulse or as optical limiting material to avoid laser-induced damages.

The spatial self-phase modulation (SSPM) technique is effective in measuring the Kerr nonlinear refractive index of 2D antimonene (Figure 7D) [100, 113]. After transmitting through the suspension, diffraction rings generated by incident laser with continuous wavelength were distorted, obviously owing to the SSPM effect (Figure 7E). The number of diffraction rings (N) approximately increases with laser power (I) while it decreases

Figure 7: The measurements for nonlinear optical behavior of antimonene.

(A) The schematic diagram of experimental setup of open-aperture Z-scan measurement for nonlinear saturable absorption behavior.

Reproduced with permission [112]. Copyright 2019, Elsevier. (B) Open-aperture Z-scan measurement results of antimonene upon excitation at 1064 with different excitation intensities. Reproduced with permission [111]. Copyright 2018, The Royal Society of Chemistry.

(C) The intensity-dependent normalized transmittance of antimonene at 800 nm with a saturable intensity of 187.5 GW cm⁻². Reproduced with permission [112].

Copyright 2019, Elsevier. (D) The schematic diagram of the nonlinear optical experimental setup adopting the SSPM technique. (E) The SSPM diffraction rings of antimonene upon excitation by a laser with a continuous wavelength of 532 nm and a power of 130 mW. ①–③ Photographs taken with a camera. ④–⑥ Photographs recorded by a laser beam digital camera. ⑦–⑨ The intensity distribution of the diffraction rings. (F) The number of SSPM diffraction rings of few-layer antimonene and antimonene quantum dots as a function of laser intensity with a wavelength of 532 nm. Corresponding SSPM rings are presented in insets. Reproduced with permission [100]. Copyright 2017, John Wiley and Sons.

with laser wavelength (λ ; Figure 7F). Thus, the nonlinear refractive indexes of antimonene were determined as $2.88 \times 10^{-5} \text{ cm}^2 \text{ W}^{-1}$ at 532 nm and $0.98 \times 10^{-5} \text{ cm}^2 \text{ W}^{-1}$ at 633 nm from the ratio of N/I . The SSPM diffraction rings can be also observed in the NIR spectral region, implying the broadband nonlinear optical response of antimonene from visible to NIR [113]. Furthermore, the nonlinearity of antimonene was observed to be dependent on laser intensities. By linearly fitting the number of rings versus laser intensity, the third-order nonlinear susceptibility χ can be derived from the slope as an order of magnitude of 10^{-8} – 10^{-9} [100, 113]. Because of the giant Kerr nonlinear refractive index and small nonlinear susceptibility,

antimonene may be a promising candidate to be applied in novel nonlinear photonics devices, such as all-optical switching and wavelength conversion devices.

3.3 Photonic applications

3.3.1 Signal processing devices

Long-term stable signal processors with the advantages of high speed and large capacity are crucial for optical communication systems. The exploring of appropriate optical materials for fabricating linear and nonlinear optical

Figure 8: The performance of antimonene- and bismuthene-based microfiber, converter, modulator, and solar cell.

(A) Schematic illustration of the Kerr switcher based on antimonene-decorated microfiber. (B) Schematic illustration of a four-wave mixing wavelength converter based on the antimonene-decorated microfiber. Reproduced with permission [118]. Copyright 2018, John Wiley and Sons. (C) Module diagram of the all-optical modulator based on few-layer bismuthene. Reproduced with permission [110]. Copyright 2019, The Royal Society of Chemistry. (D) Experimental setup of the antimonene-based all-optical modulator (AOM). (E) Infrared thermograms of microfibers with (top) and without (bottom) antimonene-decorated. (F) Interferometric spectrum of the antimonene-based AOM. Reproduced with permission [125]. Copyright 2019, John Wiley and Sons. (G) The configuration of the perovskite solar cell device used antimonene as the hole transport layer (HTL). (H) The comparison of current density-voltage (J_{sc} -V) curves for perovskite solar cells with (Device 2) and without (Device 1) antimonene-based HTL. (I) EQE and integrated short-circuit current densities (J_{sc}) as a function of incident light wavelengths for device 1 and device 2. Reproduced with permission [86]. Copyright 2018, John Wiley and Sons.

devices in all-optical signal processing is compelling and urgent in the field of optical communication. Taking advantages of the optical nonlinearity of 2D materials, optical devices such as all-optical switcher [36, 114–117], wavelength converter [114, 116, 118–120], signal regenerator [121], and all-fiber phase filter [122–124] are spurted out.

Antimonene is promising for fabricating nonlinear photonics devices because of the excellent nonlinear optical response properties. Its applicability is recently assessed by depositing the liquid-phase exfoliated few-layer antimonene onto a microfiber, where an all-optical Kerr switcher with extinction ratio of 13 dB and a four-wave mixing wavelength converter with conversion efficiency of 63 dB are designed (Figure 8A, B) [118]. High stability and durability can be maintained in these antimonene-based

photonics devices during all-optical signal processing in broadband, making them promising for optical communication systems.

Bismuthene is also a potential candidate for laser engineering, information processing, and all-optical communication networks with photonic response in a wide spectral range. A bismuthene-based saturable absorber (SA) exhibits a saturable intensity of 30 mW cm^{-2} and optical modulation depth of 2.03%. Owing to the strong nonlinear refraction effect, bismuthene is served as an excellent switcher that can trigger all-optical switching of two distinct laser beams based on spatial cross-phase modulation [126]. Utilizing bismuthene-based SA to fabricate a fiber laser, an ultrafast pulse (652 fs) can be generated at the near-infrared band of 1559.18 nm [127]. By using the nonlinear Kerr

effect, a bismuthene-based all-optical signal processing fiber system was fabricated, which is competent for optical Kerr switching and four-wave mixing-based wavelength conversion processing [128]. Based on the prominent photothermal effect, a bismuthene-based all-optical phase modulator was successfully designed with multifunctionalities such as phase shifting, intensity and wavelength modulating, and information loading. The phase shifting of signal light can be tuned up to $\sim 22\pi$ at a pump power of 42 mW, and the intensity modulation frequency can be lifted up to 2.5 kHz. It also presents the capability of transferring optical information from pump light to signal light under positive/negative logic regime (Figure 8C) [110].

3.3.2 Ultrafast laser pulse

Utilizing materials with nonlinear saturable absorption properties to fabricate Q-switched and mode-locked lasers is one key aspect of generating ultrafast pulse with short duration, high repetition rate, and broad bandwidth [129–132]. The Q-switched lasers are fundamental components for nonlinear frequency conversion, industrial material processing, and optical information transmission. Specially, all-optical active Q-switchers are highly required for laser pulse generation because of their broad operation bandwidth and large modulation depth.

A photothermal-based all-optical modulator has been successfully fabricated by dropping antimonene from liquid-phase exfoliation onto a microfiber with the diameter of 10 μm , which is able to generate Q-switched laser pulses as shown in Figure 8D [125]. By modulating the control light into antimonene-decorated microfiber, heat can be produced because of the photothermal effect with a temperature rise of 6.4°C at pump power of 350 mW, giving rise to the phase shift of signal light (Figure 8E). Together with the large modulation depth up to 25 dB (Figure 8F), the as-fabricated fiber laser can achieve a tunable repetition rate varying from 0.96 to 6.64 kHz, promising for pulse laser and all-optical information processing. Furthermore, antimonene is also potential for dual-wavelength laser device, which can be applied in radar, imaging, communication, biomedical, and environmental monitoring by producing terahertz laser. Recently, an antimonene-based dual-wavelength passively mode-locked erbium-doped fiber laser is fabricated as a powerful source for the generation of terahertz waveband, where two dominant peaks present in the frequency spectrum at 1561.3 and 1562.7 nm with the difference of 0.17×10^{12} Hz [133].

Bismuthene is a potential SA candidate for ultrafast photonics devices [134–136]. Based on bismuthene

SA, stable soliton pulses at 1561 nm can be obtained in a mode-locked erbium-doped fiber laser with pulse duration of 193 fs and repetition rate of 8.85 MHz [22]. Further employing the bismuthene-based SA in a Tm-doped mode-lock fiber laser, a pulse generation with 2 μm NIR-wavelength output was also presented [136]. When taking bismuthene-decorated fiber as SA, a high-splitting-threshold ultrafast fiber laser (pulse duration 1.3 ps) at 1531 nm can be realized for optical communications [137], and a dissipative soliton Y-doped mode-locked fiber laser at 1 μm regime was also fabricated [134], which presents a saturation intensity of 13 mW cm^{-2} , a modulation depth of 2.2%, a dissipative soliton pulse with a width of 30.25 ps, and a repetition rate of 21.74 MHz at 1034.4 nm.

3.3.3 Optoelectronics

Group VA Xenex present a great potential in high-performance optoelectronic devices because they possess not only attractive wide bandgaps to the benefit of broadband photoresponse ranging from UV to NIR but also higher carrier mobility in the order of $10^2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [84]. For example, the intrinsic electron/hole mobilities in monolayer β -arsenene and β -antimonene are calculated to be 21/66 and 150/550 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively [138]. Theoretical investigation has always been crucial in exploring the basic properties and the applications of materials. Double-gated metal oxide semiconductor field effect transistors (<10 nm) based on arsenene and antimonene are theoretically simulated and show satisfying high performance with low power consumption [138]. Furthermore, a thermophotovoltaic cell based on AC-stacked bilayer antimonene is proposed with a high energy conversion efficiency up to 31% based on DFT calculations, which is superior to traditional thermophotovoltaic materials such as Ge, GaSb, and InGaAs [139]. Inspired by theoretical predictions, the exploration and realization of practical application in optoelectronic devices have ignited numerous studies in recent years. Fabricating a few-layer bismuthene as a photoanode in a photoelectrochemical photodetector, preferable photoresponse activity and environmental robustness are presented in alkaline (KOH) and neutral (Na_2SO_4) electrolytes [140]. By using antimonene as a hole transport layer, hole extraction can be promoted, and radiative recombination of charge carriers can be prevented in the perovskite solar cells ascribed to the photoinduced charge separation effect (Figure 8G). Thus, a 30% improvement of short-circuit current densities (J_{sc}) in perovskite solar cells is achieved in the presence of antimonene as well as a high external

quantum efficiency (EQE) up to 55–60% in the visible region (Figure 8H, I) [86].

3.3.4 Biomedical photonics

Numerous 2D materials such as graphene [141, 142], transition metal dichalcogenides [143], phosphorene [144], and MXenes [145] have been effectively adopted to fabricate biomedicine platforms. Phosphorene also shows its successful biomedical applications [146–150]. Stimulated by it, the exploration of other group-VA Xenes is highly required. The successful fabrication of antimonene-based platforms will spur extensive researches of pnictogen nanomaterials and their derivatives in biomedical applications.

A PEGylated drug-delivery platform based on antimonene is fabricated for cancer theranostics (Figure 9A) [151]. This platform holds multiple advantages such as moderate acidic pH, excellent multimodal-imaging property, high drug-loading capacity (e.g. doxorubicin (DOX) loading capacity of 150%), spatiotemporally controlled drug release, deep tumor penetration, effective tumor accumulation, and

significant tumor growth inhibition without side effects and degradation. In acidic condition (24% at pH=5.0), more DOX can be released from antimonene than in alkaline condition (7.4% at pH=7.4) as shown in Figure 9B, because the protonation of amino groups in DOX is easier in acidic condition and it leads to the increased hydrophilicity of DOX and subsequent easy release. Photons play a crucial role in enhancing the penetrating quality of PEG-antimonene/DOX nanosheets into the target because of the outstanding photothermal effects with the conversion efficiency of 41.8%. Stimulated by an 808 nm NIR laser, the total amounts of released DOX can be significantly enhanced in either acidic or alkaline conditions ascribed to the NIR-induced local hyperthermia. Strong fluorescence signal is exhibited in the PEG-antimonene/DOX incubated MCF-7 tumor spheroid from periphery to center (Figure 9C). In addition, laser irradiation can also enhance the cell uptake of PEG-antimonene/DOX nanosheets attributed to the increased cell membrane permeability from photothermal effect. Therefore, a dramatic therapeutic effect is presented that nearly all the MCF-7 cells (91.5%) are killed with the assistance of NIR laser irradiation.

Figure 9: The performance of antimonene- and bismuthene-based microfiber, converter, modulator, and solar cell.

(A) The systemic illustration of the PEG-antimonene/DOX drug-delivery platform as photonic nanomedicines for multimodal-imaging-guided cancer theranostics. (B) Release profiles of DOX at different pH conditions with or without NIR laser irradiation (808 nm, 0.8 W cm⁻²). (C) The comparison of fluorescence intensity and images of tumor spheroids with and without laser irradiation. Reproduced with permission [151]. Copyright 2018, John Wiley and Sons. (D) The fabrication and detection mechanism of an antimonene-based SPR sensor for miRNA sensing. (E) The SPR spectra of antimonene sensor for detecting miRNA-21 with concentrations varying from 10⁻¹⁷ to 10⁻¹¹ M. The shift of SPR angle is indicated by the red arrow. (F) The comparison of the low LOD of the antimonene-based miRNA SPR sensor with other state-of-the-art sensors. Reproduced with permission [104]. Copyright 2019, Springer Nature.

Surface plasmon resonance (SPR) is an advanced technique for detecting the interaction between biomolecules in terms of high reproducibility, nondestructiveness, and label-free detection, which is widely applied in the fields of biosensing, drug screening, environmental monitoring, and so on [152]. Based on first-principles calculation, antimonene is expected to be an outstanding SPR biosensor that holds strong chemical interaction with single-stranded DNA (ssDNA) in terms of higher adsorption energies and larger work function increment compared with graphene. An antimonene-based SPR biosensor is devised to detect miRNA molecules by monitoring the change of refractive index as the sensitivities of ssDNA and double-stranded DNA (dsDNA) are different [104]. The detection mechanism is illustrated in Figure 9D. The AuNR-ssDNA complex can be tightly absorbed on the surface of the SPR chip because of the strong interaction between antimonene and ssDNA. Coupling with target miRNA, the hybridized products dissociate from the SPR chip because of the low affinity of dsDNA toward antimonene, and the amount of miRNA can be evaluated from the shift of SPR signals. The resonance angle in the SPR spectra of the AuNR-ssDNA absorbed chip predominantly shifts to lower angle with the increasing miRNA concentration as shown in Figure 9E. Comparing with other 2D materials-based biosensors, this antimonene-based one holds unprecedented high sensitivity in terms of extremely low limit of detection (LOD) as 10^{-17} M (~ 30 molecules per 5 μ l sample; Figure 9F), showing great potential in sensitive detection of biological imaging, clinical therapy, and environmental monitoring [104].

Furthermore, antimonene is also a preeminent enzymatic biosensing platform used to detect phenol because of its high analytical behavior in terms of sensitivity, selectivity, specificity, and reproducibility [153]. The LOD of antimonene-based enzymatic biosensor for the detection of phenol is 850 nM, superior to other group VA monoelemental Xenes, such as phosphorene, arsenene, and bismuthine, because of its highest exfoliation degree and lowest oxidation-to-bulk ratio.

4 Group VIA Xenes

Tellurium and selenium are both chalcogens (VIA) which possess interesting chain structure in bulk crystals as shown in Figure 10A. Each Te or Se atom is covalently bonded to two nearest neighbors to form a helical chain along [0001] direction, and the helical chains are parallelly stacked into hexagonal structure by van der Waals interactions [155].

4.1 Fundamental aspects

4.1.1 Tellurene

Two-dimensional Te crystal, named as tellurene, is theoretically predicted to possess five different phases, namely α , β , γ , δ , and ε phases. This nomenclature of tellurene phases follows references [156] and [154]. To avoid confusion, it should be noted that the β , γ , and ε phases were first theoretically predicted by Jia and co-workers, which were named as β -, α -, and γ -Te, respectively, in the original text [157]. The geometrical configurations and formation energies of these phases are shown in Figure 10B and C, respectively.

The α -tellurene (α -Te) possesses a rectangular lattice, which is composed of parallel-arranged helical Te chains. It can be considered as the dimension reduced phase from bulk Te by cleaving along the (10 $\bar{1}$ 0) crystal plane, causing the space group of $P2_1$ for even Layers and $P2$ for odd Layers [156]. For few-layer α -Te, significant structure relaxation can be found at outmost layers, which gradually decays toward inner parts, implying that a thick α -Te would exhibit a bulk property while particular properties could only be observed in the surface [156].

The β -tellurene (β -Te) also possesses a rectangular lattice. It can be considered as the consequence of slight reconstruction of in-plane neighboring helical chains in α -Te, making it transformed from chain structure to buckled plane [156, 157]. Even-layers β -Te possesses the space group of $P2_1/m$ while odd-layers has $P2/m$ [156]. Monolayer α -Te is not stable, and it would transform into monolayer β -Te, whereas multiple-layer α -Te is always more stable than multiple-layer β -Te [156, 158]. An in-plane compressive strain may promote the $\alpha \rightarrow \beta$ phase transition.

The γ -tellurene (γ -Te) has a 1T-MoS₂-like rhombus structure. Mono- or few-layer γ -Te is expected to be obtained from a reconstruction of $3N$ atomic layers ($N=1, 2, 3, 4, 5$) stacking along the [0001] direction [156–158]. The free-standing monolayer γ -Te is predicted to be more stable than the monolayer β -Te [154, 156–158]. A possible $\alpha \rightarrow \gamma$ phase transition may take place when the tensile strain along the chain direction is beyond the critical value (12%) [156]. γ -Te may be experimentally achieved by thickness control when depositing Te atoms on a substrate with the helical chains perpendicular to the interface [157].

The δ -tellurene (δ -Te) can be formed by cutting along the parallel (11 $\bar{2}$ 0) planes from the bulk counterpart with reserved helical chain structure similar to α -Te. The space group is $P2$ for both the odd and even layers of δ -Te [156]. Monolayer δ -Te is not stable because the helical chains are not close-packed and high surface energy is presented,

Figure 10: The geometric structure and formation energy of tellurene polymorphs.

(A) Crystal structure of bulk Te or Se with helical chains stacking into hexagonal structure (Left: side view with labeled crystal orientations and planes; Right: overview with electron isosurfaces of 0.9e Bhor⁻³); (B) Side view and top view of α -, β -, γ -, δ -, and ϵ -tellurene (z is the direction of vacuum layer, y is the direction along atomic chain); (C) Layer-dependent formation energy of α -, β -, γ -, δ -, and ϵ -tellurene. Reproduced with permission [154]. Copyright 2018, The Royal Society of Chemistry.

whereas for few-layer δ -Te, closed-packed inner parts would compensate the higher surface energy and lead to a comparable formation energy with α -, β -, and γ -Te [156].

The formation of ϵ -tellurene (ϵ -Te) is similar to γ -Te. The 2H-MoS₂-like γ -Te has a rhombus lattice, and it can be considered as a result of shearing-type phase transition from γ -Te [154, 157]. It is predicted that ϵ -Te is metallic and unstable above ~ 200 K [157].

Up to date, experimentally acquired and observed tellurene is often in the form of α -Te or β -Te, while other phases are rarely reported. The formation of α or β phase may depend on the strain state of tellurene during fabrication processes [156]. In most cases, the acquired

nanosheets or nanoflakes are in the α form as it is more stable when the layers are larger than two. For examples, mono- and few-layer α -tellurene are obtained by molecular beam epitaxy growth on graphene/6H-SiC(0001) substrate [159], which shows an in-plane rectangular lattice of 4.42×5.93 Å². The β -tellurene is successfully grown on highly oriented pyrolytic graphite through molecular beam epitaxy [157], where a smaller rectangular lattice of 4.3×5.4 Å² is observed, matching well with the calculated 4.17×5.49 Å². Although the grown β -Te is metastable, it would not transform to the more stable α phase because of the large energy barrier. It is worth pointing out that a possible thickness-dependent phase transition is observed,

where the thicker tellurene (thickness >80 Å) is identified as α -Te from the observed lattice constants of 4.33×5.91 Å², whereas the thinner tellurene (thickness ~ 20 Å) is identified as β phase from the smaller lattice constants of 4.26×5.42 Å² [160].

4.1.2 Selenene

Unlike tellurene that has multiple allotropes, some phases of 2D Se (selenene) may not exist as revealed by theoretical prediction, e.g. the δ and ε phases [157]. Here, the nomenclature of allotropes is the same with tellurene from the aspect of structural feature, which should be noticed when reading references such as references [157, 161, 162]. Similar to α -Te, the α -selenene (α -Se) is composed of parallel-aligned independent one-dimensional helical chains, which has been synthesized experimentally [163, 164]. In terms of β phase, there is a disagreement on the existence of monolayer β -selenene in references [157, 161, 162] from theoretical prediction. It is reported in reference [162] that the β -Se is thermodynamically metastable and dynamically

stable with the lattice constants of $a=4.20$ Å and $b=4.99$ Å, but its existence is negative in the other two references. However, for the γ phase, the existence of monolayer γ -selenene (γ -Se) from calculations are well agreed in references [157, 161, 162], which is predicted to possess a rhombic cell with the lattice constants of $a=b=3.75$ Å. But disagreement is still found on the thermodynamic stability. In references [157, 162], γ -Se is considered to be the most stabilized, whereas in reference [161], it is metastable compared with α -Se. In addition, a new metastable allotrope named S-Se with a square structure ($a=b=3.65$ Å) is reported as shown in Figure 11A, which shows a buckled configuration with a height difference of 0.78 Å [161]. The summary geometric and electronic features of allotropes of tellurene and selenene are listed in Table 1 for comparison.

4.2 Electronic and optical property

Revealed by DFT calculations, monolayers β -Te and γ -Te are predicted to be indirect bandgap semiconductors with bandgaps of 1.17 and 0.76 eV, respectively

Figure 11: The band structure and optical performance of tellurene and selenene.

(A) Top and side views of S-Se and its band structure with (red) and without (black) SOC effect. Inset is the zoom-in of the selected region. Reproduced with permission [161]. Copyright 2014, IOP Publishing. (B) Layer-dependent bandgap of α -Te. Inset is the differential STM image of α -Te grown on graphene/SiC substrate. Reproduced with permission [159]. Copyright 2017, American Chemical Society. (C) Calculated absorption spectra of few-layer α -Te (absorbance per layer with the polarization direction of incident light perpendicular to atomic chain direction). Reproduced with permission [158]. Copyright 2018, Elsevier. (D) Photoluminescence of α -Te nanoplate excited by 325 nm laser with components from Gaussian deconvolution. Reproduced with permission [165]. Copyright 2014, American Chemical Society.

Table 1: Comparison of crystal structure of allotropes in tellurene and selenene.

	Tellurene		Selenene	
	Lattice (Å)	Bandgap (eV)	Lattice (Å)	Bandgap (eV)
α phase	$a=4.33\sim4.36$ [156,158] $b=5.78\sim5.81$ [156,158]	1.17 [158] (2L, HSE+SOC)	$a=4.13$ [161] $b=4.99$ [161]	2.57 [161] (1L, HSE+SOC)
β phase	$a=4.17\sim4.26$ [156,157] $b=5.49\sim5.77$ [156,157]	1.47 [157] (1L, HSE+SOC)	$a=4.20$ [162] $b=4.99$ [162]	2.53 [162] (1L, HSE+SOC)
γ phase	$a=b=4.15$ [157]	0.75 [157] (1L, HSE+SOC)	$a=b=3.74\sim3.75$ [161,162]	1.04~1.06 [161,162] (1L, HSE+SOC)
δ phase	$a=7.75$ [156] $b=5.73$ [156]	Not reported	Unknown	Unknown
ε phase	$a=b=3.92$ [157]	0 [157] (1L, HSE+SOC)	Unknown	Unknown
S phase	/	/	$a=b=3.65$ [161]	0.12 [161] (1L, HSE+SOC)

[157], as well as bilayer α -Te with bandgap of 1.17 eV [158]. However, for monolayer ε -Te, it is predicted to be metallic [157]. Tellurene is expected to possess excellent carrier mobility. Extraordinarily large hole mobility in the order of $10^4\sim10^6$ cm² V⁻¹ s⁻¹ is theoretically expected in 5L and 6L α -Te, whereas electron mobility ($10^3\sim10^4$ cm² V⁻¹ s⁻¹) is predicted to be 1~2 orders smaller than the hole for 4~6L α -Te [158]. For monolayer β - and γ -Te, the room-temperature carrier mobilities are expected to be several hundreds to thousands of cm² V⁻¹ s⁻¹ [157]. With the increasing layer numbers, α -Te gradually transforms into direct bandgap semiconductor with decreased gap value as 0.95 eV for 3L, 0.83 eV for 4L, 0.72 eV for 5L, and 0.66 eV for 6L [158]. This layer-dependent bandgap is also experimentally demonstrated by scanning tunneling spectroscopy (STS), where the bandgap decreases from 0.92 eV for 1L to 0.49 eV for 13L as shown in Figure 11B [159]. Similar decreasing bandgap with increased thickness is also observed in β -tellurene, where the bandgap is revealed as ~0.65 eV for 5L, ~0.58 eV for 6L, and 0.53 eV for 7L [160].

Owing to the helical chain structure, tellurene is found to have a broad photoelectric response in the range from visible to near-infrared region. It shows an ultra-strong anisotropic photoresponsivity and an extremely high extinction ratio of ~2812 at the photon energy of 3.4 eV, which is superior to the bilayer antimonene (~145) and phosphorene/blue phosphorene (~240) [166]. The layer-dependent light absorption is also predicted in few-layer α -Te, where substantially increased absorption efficiency goes with decreased thickness. As shown in Figure 11C, the per layer absorbance of the green light (2.42 eV) increases from 4.4% for bulk to 7.3% for 2L, and absorbance of violet light (3.24 eV) increases from 4.3% for bulk

to 8.4% for 2L with the polarization direction perpendicular to the chain direction [158]. The photoluminescence behavior of Te nanoplate (thickness ~30 nm) is presented when excited by a 325 nm laser as shown in Figure 11D [165]. The primary luminescence peak covers the range of 400~550 nm (2.2~3.1 eV), and three component peaks appear (413, 434, and 463 nm) after Gaussian deconvolution. The photoluminescence peak at 413 nm is considered as the electron radiation transition from the p -antibonding triplet of the conduction band to the p -bonding triplet of the valence band, and the peak at 434 and 463 nm might be the electron radiation transition from the p -antibonding triplet of the conduction band to the p -lone-pair triplet of the valence band.

Monolayer γ -Se is predicted to be a semiconductor with an indirect bandgap of 1.05 eV [161, 162], which possesses a rather high electron mobility of 6.97×10^3 cm² V⁻¹ s⁻¹ and a hole mobility of 9.48×10^3 cm² V⁻¹ s⁻¹, exhibiting excellent bipolar conductivity [162]. Monolayer β -Se is predicted to be an indirect bandgap semiconductor (2.53 eV), which presents a considerable in-plane spontaneous ferroelectric polarization and a potential room temperature ferroelectricity application [161, 162]. More interestingly, a Dirac cone is predicted in the band structure of monolayer S-Se, where a gap of 0.11 eV can be opened by taking into account the SOC as shown in Figure 11A. Anisotropic band dispersion is presented around the Dirac point with different Fermi velocities of 1.26×10^6 and 0.24×10^6 m s⁻¹ [161]. Experimentally, ultrathin selenene nanosheets with lateral of 40~120 nm and thickness of 3~6 nm are acquired from liquid-phase exfoliation, which exhibit robust chemical stability and strong photoluminescence effect, ensuring their potential optical applications [163].

4.3 Devices applications

The semiconductive group VIA Xenes, tellurene and selenene, possess narrow bandgaps and excellent carrier mobilities similar to group VA Xenes such as antimonene and bismuthene. Together with their excellent air stability, superb optical absorption, and tunable bandgap from mid- to near-infrared, tellurene and selenene are promising materials that can be applied in UV-vis optoelectronic devices, signal processing devices, laser devices, biomedical platforms, and other relevant photoelectric fields.

4.3.1 Photodetectors

As far as we know, the first reported 2D Te-based photodetector is fabricated by van der Waals epitaxy growing Te nanosheets on mica substrate [165]. The obtained single crystal nanosheets exhibit hexagonal morphology with a thickness of 30–80 nm and size of 6–10 μm , having the (001) crystal plane parallel to the (001) surface of the mica substrate. Then the Te-based photodetector is in situ fabricated on flexible mica sheets (Figure 12A). Pronounced photoresponse is observed under the irradiation of 473 nm laser, showing stable and repeatable on-off switching behavior with the photoresponsivity of 162.4 A W^{-1} and 4.4 s response time and 2.8 s recovery time. Stable photoresponse behavior can be reserved after 100 times bending of the substrate, indicating its promising application in flexible and wearable devices. Recently, the solution-synthesized quasi-2D tellurene nanosheets are successfully applied to solar-blind deep ultraviolet (DUV) photodetector [170]. It exhibits a high photoresponsivity of $6.5 \times 10^4 \text{ A W}^{-1}$ and an EQE as high as $2.26 \times 10^6\%$ under the illumination of 261 nm UV light with a power of 0.08 nW, which surpasses most of 2D materials-based DUV photodetectors. More importantly, this tellurene-based DUV photodetector presents excellent air stability for 90 days without any protection.

A thickness-dependent photoresponse behavior from negative to positive is shown in Figure 12B [167]. Large and clean ultrathin α -Te nanosheets are first obtained by excessive lithiation and hydrolysis processes in layered MTe_2 ($\text{M} = \text{Ti}, \text{Mo}, \text{W}$) matrix. Then tellurene-based devices are fabricated by standard lithography with deposited gold as electrode, where the thickness of tellurene plays an important role in adjusting the optoelectronic performances. Negative photoresponse behavior is exhibited for the nanosheets with thickness less than 5 nm, where the maximum photoresponse ratio (5.88) is achieved at 3.02 nm. With further increased thickness ($>5 \text{ nm}$), the photoresponse ratio becomes positive and goes rising-falling with the maximum ratio of 11.5 at 9.12 nm. A

two-competitive-mechanism is proposed to explain this anomalous behavior. Oxygen-assisted surface electron trapping leads to the negative response, while photo-generated electron-hole separation gives rise to the positive response. The switchable response is ascribed to the competition between oxygen-assisted surface electron trapping and photo-generated holes. When thickness is small enough, the conductive contribution from photo-generated holes could be suppressed by the negative photoresponse.

Tellurene is also demonstrated to be an excellent candidate for applying in high-performance infrared photodetectors. Air-stable quasi-2D tellurium nano-flakes with thickness of 10–20 nm and indirect bandgap of $\sim 0.31 \text{ eV}$ are obtained through solution-synthesis, which present high hole mobility of $450 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 300 K and $1430 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 77 K [168]. By employing $\text{Au}/\text{Al}_2\text{O}_3$ optical cavity substrates, the Te nano-flakes are employed to assemble short-wave infrared photodetectors (Figure 12C). The peak responsivity can be adjusted from 1.4 (responsivity 13 A W^{-1}) to $2.4 \mu\text{m}$ (responsivity 8 A W^{-1}) by changing the thickness of Al_2O_3 cavity, and the peak specific detectivities (D^*) of $2.9 \times 10^9 \text{ cm Hz}^{1/2} \text{ W}^{-1}$ at 297 K (responsivity 16 A W^{-1}) and $2.6 \times 10^{11} \text{ cm Hz}^{1/2} \text{ W}^{-1}$ at 78 K (responsivity 27 A W^{-1}) are acquired at wavelength of $1.7 \mu\text{m}$. In addition, a waveguide-integrated tellurene photodetector is designed in a complex $\text{graphene}/\text{Ge}_{23}\text{Sb}_7\text{S}_{70}/\text{tellurene}$ structure as shown in Figure 12D [169]. The optimized noise equivalent power at room temperature is $0.03 \text{ fW Hz}^{-1/2}$ at the wavelength of $3 \mu\text{m}$ by taking experimental data of carrier density (10^{11} cm^{-2}), carrier mobility ($240 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), and photocarrier lifetime (280 ns). The obtained noise equivalent power value indicates that the optimized device length is a coordinated result between optical absorption and detector length.

Liquid-phase exfoliation is a facile method to prepare ultrathin Te and Se nanosheets [171, 172]. The as-prepared 2D Te nanosheets [171] (lateral dimensions 41.5–177.5 nm, thicknesses 5.1–6.4 nm) exhibit excellent light absorption from the ultraviolet to visible light region. The photoresponse behavior is evaluated by applying them in the photoelectrochemical-type (PEC-type) photodetector. Photoresponse with good cycle stability are presented during on/off switching, and higher photocurrent intensity can be obtained by increasing voltage, light power intensity, or concentration of KOH electrolyte. The photocurrent of $\sim 0.36 \mu\text{A cm}^{-2}$ and photoresponsivity of $\sim 3.0 \mu\text{A W}^{-1}$ is exhibited in 1.0 M KOH electrolyte at 0.6 V with light power density of 118 mW cm^{-2} . The photoresponse performance of Se nanoflakes (thickness 5–10 nm) based photodetector are evaluated by photoelectrochemical measurements, where a

Figure 12: The performance of tellurene-based photodetectors.

(A) Te-based photodetector fabricated on flexible mica sheet showing on/off switching behavior. Reproduced with permission [165].

Copyright 2014, American Chemical Society. (B) Thickness-dependent photoresponse performance of Te-based photodetector (voltage 3 V, incident light power 19.9 mW cm^{-2}). Reproduced with permission [167]. Copyright 2018, John Wiley and Sons. (C) Schematic of Te-based optical-cavity-enhanced short-wave infrared photoconductor and its tunable responsivity. Reproduced with permission [168]. Copyright 2018, American Chemical Society. (D) Schematic of waveguide integrated tellurene photodetector and simulated optical intensity distribution. Reproduced with permission [169]. Copyright 2019, American Chemical Society.

significant self-powered behavior (without bias voltage) is demonstrated as well as the voltage and light dependent photoelectric responses [172]. Furthermore, long-term cycle stability, high photocurrent density of $1.28 \mu\text{A cm}^{-2}$, and photoresponsivity of $10.45 \mu\text{A W}^{-1}$ are also exhibited in these photodetectors at the bias voltage of -0.6 V and light power density of 121 mW cm^{-2} .

4.3.2 Transistors

By adopting ab initio calculations and quantum transport simulations, the interfacial characteristics of monolayer β -tellurene (ML β -Te) based field-effect transistors are systematically studied with graphene and bulk metal as electrodes (Sc, Ag, Cu, Au, Ni, Pt, and Pd; Figure 13A)

eV), and Cu, Ni, Ag, Pt, and Pd in both directions (hole SBH, 0.45, 0.37, 0.37, 0.28, and 0.20 eV in the a direction; 0.32, 0.42, 0.30, 0.27, and 0.28 eV in the b direction). A highly satisfying lateral p -type Ohmic contact could be formed when ML β -Te is on the surface of graphene, where a very small hole SBH is predicted because of the matched work function and weak FLP at the interface, indicating graphene is a suitable electrode material served in β -Te-based transistor.

The first tellurene based field-effect transistor is fabricated by taking Ni and Pd/Au as electrodes [174]. The thickness-dependent device performances including on/off ratio, field-effect mobility, and air stability are revealed by using flakes with thickness from ~ 0.5 (monolayer) to >35 nm (Figure 13B). The on/off ratio steeply decreases from $\sim 1 \times 10^6$ to less than 10 when thickness approaches the maximum depletion width of the films. The peak mobility of ~ 700 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ is achieved at a thickness of ~ 16 nm and decreases gradually with a further increased thickness at room temperature. Excellent room temperature air stability is demonstrated in a 15-nm-thick transistor during a 2 month period without significant degradation, and this stability is valid for almost nanosheets down to 3.4 nm. However, flakes thinner (e.g. 1–1.7 nm) would be invalid after exposed in air for 2 to 3 days. Furthermore, a prominent on-state current (1 A mm^{-1}) is presented by combining down-scaled channel length and high- k dielectrics, which is higher than any reported 2D material transistor.

The unipolar p -type electrolyte-gated transistors are fabricated by taking solution-grown tellurene flakes with lateral size of 10–100 μm and thickness of 4–30 nm [175]. Besides the good on/off current ratios (10^5 – 10^6) with small operating voltages (less than 2 V), an insulator-metal transition is observed by tuning the gate voltage as well as the charge densities of $\sim 1.6 \times 10^{13} \text{ cm}^{-2}$ and mobility up to $\sim 500 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (Figure 13C). A systematic data-driven investigation is carried out on the relationships between processing, structure, and properties of solution-grown tellurene [176]. Polyvinylpyrrolidone (PVP), serving as crystal-face-blocking ligand, plays an important role in modulating the yield and dimension of as-prepared tellurene as well as the physical properties, leading to the fabrication of tellurene-based field-effect transistors with satisfying performance (Figure 13D). By using medium weight PVPs (e.g. PVP-58K), the maximized mobility ($\sim 500 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) and minimized variability of the on/off ratio in tellurene devices can be achieved.

Through physical vapor deposition, large-size and high-quality Se nanosheets are synthesized with lateral size up to 30 μm and thickness down to 5 nm [164]. The growth orientation along $\bar{1}210$ and strong in-plane

anisotropic are demonstrated by scanning transmission electron microscopy and angle-resolved Raman spectroscopy. When applying these nanosheets to back-gating field-effect transistors, the p -type transport characters are presented with on-state current density of $\sim 20 \text{ mA mm}^{-1}$ ($V_{\text{ds}} = 3 \text{ V}$), and the intrinsic hole mobility is determined to be $0.26 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 300 K. In addition, excellent photoresponsivity (263 A W^{-1}) with short response time (rise/fall time 0.1/0.12 s) is exhibited in these phototransistors.

4.3.3 Nonlinear optics

Similar to the above discussed antimonene, tellurene also exhibits nonlinear optical properties. Revealed by SSPM, the strong nonlinear optical response behavior of liquid-phase-exfoliated Te nanosheets (lateral size 130–210 nm, thickness 11.9–16.8 nm) is characterized by the parameter of dN/dI , where the N is the number of diffraction rings and I is the intensity of incident laser beam [177]. At laser wavelengths of 457, 532, and 671 nm, the dN/dI is obtained as 0.458, 0.331, and $0.260 \text{ cm}^2 \text{W}^{-1}$, and the nonlinear refractive index is acquired as 7.37×10^{-5} , 6.202×10^{-5} , and $6.148 \times 10^{-5} \text{ cm}^2 \text{W}^{-1}$, respectively. A nonlinear photonic diode Te/SnS_2 is prepared to implement the nonreciprocal light propagation through the combination of strong nonlinear Kerr effect in Te and reverse saturable absorption in SnS_2 nanosheets. Then a tellurene-based light-modulate-light system is designed for all-optical switching/modulation by means of spatial cross-phase modulation method. The “ON” and “OFF” modes can be realized by modulating pump light to probe light with Te nanosheets acting as information converter (Figure 14A). In addition, the broadband nonlinear absorption from the near-infrared to the visible region is also exhibited. Low saturable intensity and large modulation depth are presented under low energy photon excitation, whereas two-photon absorption in the visible region is exhibited under high energy excitation [177]. Excellent saturated absorption property of tellurene indicated that it can be utilized in all-solid-state or fiber laser devices to produce ultra-short laser pulse with ultra-high peak power, and the two-photon absorption behavior of tellurene makes it a promising optical limiting material to guarantee the validity of sensitive optical devices and the safety of human eyes.

Similar to the above discussed bismuthene, tellurene and selenene are also excellent candidates to be used as saturable absorber. For tellurene, it is capable of pulse operations. Large-energy dissipative soliton operation is able to get a pulse with maximum width of 5.87 ps, maximum average output power of 23.61 mW, and the

Figure 14: The performance of tellurene- and selenene-based photonic devices.

(A) The achieved ON/OFF modes in the all-optical light-modulate-light system based on 2D Te Ns dispersions and spatial cross-phase modulation. Reproduced with permission [177]. Copyright 2019, John Wiley and Sons. (B) Schematic setup of the mode-locked fiber laser with Se-SA and typical laser output pulse optical spectrum. Reproduced with permission [163]. Copyright 2017, John Wiley and Sons.

largest energy of 1.94 nJ. However, by taking noise-like pulses operation, a pulse with average output power of 106.6 mW and an energy of 8.76 nJ can be obtained [178]. By adopting selenene decorated microfiber as saturable absorber, an optical modulation device is fabricated as shown in Figure 14B, where stable soliton mode-locking performance can be achieved with excellent ultrashort pulse generated in optical communication band [163].

4.3.4 Photoacoustic imaging and spectrometry

Free-standing Te nanosheets from liquid-phase exfoliation are also capable of biomedical application. Te nanosheets with the diameters of ~300 nm and thicknesses of ~10 nm are designed into a biomedicine platform for simultaneous photodynamic therapy and photoacoustic imaging, whose stability and biocompatibility can be further improved by glutathione (GSH) functionalization [179]. With the irradiation of laser with wavelength of 670 nm, potent intracellular reactive oxygen species can be generated at the tumor site to kill cancer cells, and the strong light absorption in the near-infrared region ensures the high imaging performance of multispectral optoacoustic tomography as shown in Figure 15A.

The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry is able to detect and characterize biomacromolecules in a facile, sensitive, and high-throughput way. Making use of Te nanosheets (lateral size >1 μm, thickness ~40 nm), the desorption/ionization of small

molecules such as nucleobases, fatty acids, and amino acids is investigated (Figure 15B) [180]. Two mechanisms are considered to play critical roles in the desorption/ionization process, one is electronic transitions mechanism and another one is laser-induced thermal mechanism. High desorption/ionization efficiency in negative ion mode and low matrix ion interference in low-molecule-mass region are demonstrated because of the excellent light absorption of Te nanosheets in the UV region. The application of Te nanosheets may promote and expand the analysis region of the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry technique.

5 Conclusion and outlook

So far, over 15 diverse monoelemental Xenes in the main group have been theoretically and experimentally explored for their advanced applications in engineering and functional devices. Current frontier researches of monoelemental Xenes are concerned in this review covering application fields of optoelectronics, energy, photonics, and biophotonics. At the present stage, the researches on group III Xenes such as gallene, indiene, and aluminene are still in the initial theoretical prediction stage with rarely reported practical application in functional devices, whereas group VA and VIA Xenes including arsenene, antimonene, bismuthene, tellurene,

Figure 15: The biomedical applications of tellurene. (A) Schematic procedure of Te nanosheets@GSH and their potential applications in multispectral optoacoustic tomography and photodynamic therapy. The growth rate of tumor was significantly suppressed. Reproduced with permission [179]. Copyright 2018, The Royal Society of Chemistry. (B) Schematic detection process of bisphenol A and the mass spectra of bisphenol A obtained by utilizing Te nanosheet. Reproduced with permission [180]. Copyright 2018, Springer Nature.

Table 2: The comparison of photodetectors based on the state-of-the-art 2D materials.

Material	Type	λ (nm)	R (A W ⁻¹)	EQE (%)	D^* (Jonse)	Ref.
Te	FET	261	6.5×10^4	2.26×10^6	3.73×10^8	[170]
Te	FET	473	162.4	—	—	[165]
Te	FET	1700	16	—	2.9×10^9	[168]
Te	PEC	380–800	1.16×10^{-6}	—	2.3×10^6	[171]
Se	PEC	380–800	1.05×10^{-5}	—	—	[172]
Graphene	FET	1550	6.1×10^{-3}	—	—	[181]
BP	FET	900	4.3×10^6	10^9	—	[182]
BP	FET	3390	82	—	—	[183]
BP	PEC	380–800	5.4×10^{-6}	—	—	[184]
MoS ₂	FET	445–2717	50.7×10^{-3}	—	1.55×10^9	[185]
MoS ₂ /P(VDF-TrFE)	FET	635	2570	—	2.2×10^{12}	[186]
MoS ₂ /GaN	FET	265	187	—	2.34×10^{13}	[187]
InSe	FET	254	5.68×10^4	—	10^{13}	[188]
		490	3.574×10^4	—	10^{13}	
		850	2.975×10^3	—	10^{12}	
GaS	FET	633	64.43	12,621	—	[189]
GaSe	FET	254	2.8	1367	—	[190]
β -Ga ₂ O ₃	FET	254	3.3	1600	4.0×10^{12}	[191]
h-BN	FET	212	1×10^{-4}	—	2.4×10^8	[192]

Table 3: The comparison of saturable absorber based on the state-of-the-art 2D materials.

Material	Saturable intensity (MW cm ⁻²)	Optical modulation depth (%)	λ (nm)	Pulse width (fs)	Ref.
Sb	10.8	6.4	1557.5	552	[101]
Bi	48.2	5.6	1561	193	[22]
Bi	113	2.5	1531	1300	[137]
Bi	0.3	2.4	1557.5	621.5	[135]
Bi	13	2.2	1034.4	30,250	[134]
Te	34.3	5.06	1573.97	5870	[178]
Te/PVP	78,140	27	1556.57	829	[193]
Se		2.13	1555.67	3100	[163]
Graphene	53.25	2.93	1558.88	432.47	[194]
BP	12	21	1559.5	670	[131]
BP	12.5	3.31	1558.14	2180	[195]
BP	14.98	10.03	1555	102	[196]
BP	0.25	7	1560.7	570	[197]
MoS ₂	1850	15.9	1054.3	800,000	[198]
MoS ₂	0.34	35.4	1568.9	1280	[199]
MoS ₂ /PVA	34	4.3	1569.5	710	[200]
WS ₂	157.6	15.1	1568.3	1490	[201]

and selenene have garnered tremendous achievements in optoelectronics, photonics, and biomedicines.

The comparison between Xenes-based devices (photodetectors and saturable absorber) and that based on state-of-the-art 2D materials is listed in Tables 2 and 3. It is clear from Table 2 that 2D Te holds broadband spectral response from deep-ultraviolet to short-wave infrared region and presents high photoresponsivity in DUV photodetection. Its performance is inferior to 2D InSe photodetectors but superior to many other reported 2D DUV photodetectors, such as 2D GaSe [190], β -Ga₂O₃ [191], and *h*-BN [192]. Even in the visible light region, it also shows higher photoreponsivity than the promising MoS₂ [185]. From the performance comparison of diverse 2D materials, it can be speculated that group VIA Xenes are more promising in photodetectors owing to their one-dimensional van der Waals chain structure. This interesting feature would trigger in-depth explorations of their physics and applications in optoelectronic devices. Similar to most of 2D saturable absorbers, Xenes-based SAs are also promising for the generation of ultrafast laser pulses either in picosecond or femtosecond levels (Table 3). For example, the bismuthene SA-based laser can generate an ultrafast pulse as short as 193 fs compared with BP [22, 196], and Xenes SA-based mode-locked lasers usually have low pulse energies (<1 nJ) [178]. Thus, it can be expected that Xenes-based SAs would open a brand-new way in high-energy pulse operations for the generation of high-power, large-energy, and ultrafast fiber lasers with ongoing explorations. Further

improvement of nonlinear optical measuring methods for 2D materials including Xenes is highly required to obtain accurate nonlinear absorption parameters, and the stability researches of Xenes SA-based ultrafast lasers are important for practical applications.

With the increasing development of technological revolution, in-depth innovations and significant improvements of monoelemental Xenes are highly required in the coming years. Several aspects are worthy to be noticed. First, the exploration of facile and massive preparation strategy is crucial for obtaining even-sized free-standing nanosheets applied in functional devices, especially the group IIIA members that are currently realized on selected substrates. Second, theoretical researches are fundamental in discovering novel physical properties of Xenes. The physical natures of Xenes are far from known, and extensive explorations are still needed. Third, structural modulation and surface modification are significant for discovering novel properties of Xenes. Most group IIIA Xenes are metallic and few-layer group VA Xenes are semimetallic, whose comprehensive applications in semiconductor devices seem to be hampered. Therefore, exploring effective strategies such as defect engineering, strain engineering, and surface functionalization to modulate the electronic structures and open bandgaps may fulfill their semiconductor technology applications. In this case, they are potential candidates for photonics and optoelectronics devices. Compelling potentials and opportunities are hold for researchers to construct increasingly sophisticated knowledge framework along with challenges.

Although the investigation and understanding on Xenes are not sufficient at present, it could be greatly promoted by the ongoing frontier researches on geometries, microstructures, and physical properties. We can also expect that the practical applications of Xenes and other 2D materials in electronics, optoelectronics, energy, and biomedicines will be effectively broadened along with a possible technological evolution in the near future.

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