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REVIEW



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Two-dimensional group-VA nanomaterials beyond black phosphorus: synthetic methods, properties, functional nanostructures and applications

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As an emerging group of two-dimensional (2D) nanomaterials, 2D group-VA layered nanomaterials have been attracting increasing attention in recent years due to their intriguing physiochemical properties and functional structures for broad and promising applications. In contrast to phosphorene and black phosphorus, 2D group-VA pnictogen elemental (As, Sb, and Bi) nanomaterials have tunable direct bandgaps, high stability, charge-carrier mobility and unique in-plane anisotropic structures, giving them great prospects for applications in significant and extensive research areas. In this review, we systematically introduced the recent advances in 2D group-VA nanomaterials beyond black phosphorus. First, the synthesis methods were summarized and grouped into top-down and bottom-up categories. Then, their fundamental properties were described, referring to their band structures and carrier transport as well as mechanical, thermal, optical, magnetic and electronic properties. Subsequently, functional nanostructures were discussed, such as heterostructures, doping, absorption, pnictogencontaining hybrids and surface functionalization. Finally, potential applications were illustrated, involving catalysis, energy storage, field-effect transistors, topological spintronic devices, electronic devices, nonlinear photonics, light-emitting devices, gas sensors, thermoelectric materials and biomedicine. Finally, the current states, challenges and perspectives for the emerging 2D group-VA nanomaterials were discussed rationally. This timely and comprehensive review is attractive for scientists from different research fields and promotes the further development of low-dimensional nanomaterials and functionalized hybrid materials.

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1. Introduction

In comparison with their bulk counterparts, two-dimensional (2D) layered nanomaterials have unique physiochemical and structural properties because of their high aspect ratios, quantum-size effects and unusual surface chemistry.1-3 Since the discovery of graphene,⁴⁻⁷ 2D layered nanomaterials have received much attention. Especially, the vast library of 2D layered nanomaterials has attracted tremendous interest. The past few decades have witnessed an explosive growth in the scientific research on various 2D layered nanomaterials, including transition-metal dichalcogenides (TMDs),⁸ graphitic carbon nitride,9-11 hexagonal boron nitride,12 layered double hydroxides,13 silicone,14 germanene,15 2D metals,16 2D metal oxides and sulphides,17,18 transition metal carbides, nitrides and carbonitrides (MXenes),19-22 2D polymers,23 2D metalorganic frameworks (MOFs),24-26 2D covalent-organic frameworks,27,28 2D perovskites,29,30 and others.31,32 A principal reason for the exploration of 2D nanomaterials is that monolayer (ML) materials have increased bandgaps and tunable electronic, optical, catalytic and electrochemical properties. 2D nanomaterials have great prospects for modern nanoscience and nanotechnology, showing wide applications in the optical, electronic, optoelectronic and biomedical fields. The majority of 2D layered nanomaterials are rediscovered and contemporary



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In recent years, scientific research interests have turned to 2D monoelemental structures, including layered black phosphorus (BP) and phosphorene and its cousins (arsenene, antimonene, and bismuthene). As a new member of the 2D layered nanomaterial family, group-VA (P, As, Sb, and Bi) nanomaterials with 2D layered monoelemental structures have emerged with increasing interest, strong momentum in their development and great potential applications.³⁷⁻⁴⁰ Unlike semimetallic group-IVA (graphene, silicene, germanene, and stanine) and metallic group-IIIA borophene materials, 2D layered group-VA monoelemental nanomaterials are semiconductors with marked and fundamental band gaps, which endow them with a great potential as promising candidates for future nanodevices. The transition from metallic conductors to semiconductors can be regulated by reducing the layer number of materials, accompanied by optical, electronic and electrocatalytic properties different from those of their bulk counterparts. This is an important aspect of the materials, which deserves further investigations. As an emerging star of post-graphene 2D layered nanomaterials, phosphorene and 2D layered BP materials have been largely studied in recent years.⁴¹⁻⁶⁴ Their tunable direct bandgap, charge-carrier mobility and unique in-plane anisotropic structures render them significant in a broad range of research fields.

Since graphene was isolated by Novoselov *et al.*,⁴ graphene studies have achieved extraordinary scientific success,⁵ opening the door to new groups of 2D materials with complementary physical properties to graphene.^{65,66} Graphene is a semimetal without a band gap, which restrains its practical use in the electronic and optoelectronic fields. In the research of novel 2D materials, generally TMDs are dominant since most of them have a band gap in the range of 1.5–2.5 eV,⁶⁷ which can be tuned by adjusting the layer number, stress level and chemical functionalization. However, this band gap range is not appropriate



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Zejun Sun was born in 1996. Since 2018, she has been a Master's candidate in the College of Chemistry and Chemical Engineering, Qingdao University. Her research interests focus on the preparation and applications of fluorescent and electronic active nanomaterials. for optoelectronic devices, where a lower range of 0.1-1 eV is usually demanded.8 In contrast, the direct band gap of ML phosphorene is \sim 1.5 eV,^{8,68} and thus it is interesting for applications in electronics and ultrafast optoelectronics. Phosphorene (2D allotrope of BP) suffers from strong reactivity under environment conditions. The exfoliated flakes of phosphorene are very oxophilic and can form a hydrophilic BP surface. This process facilitates moisture uptake from air to form phosphoric acid and related species, leading to the degradation of BP flakes.⁶⁹ Hence, the discovery and production of novel 2D materials with proper bandgaps and stability under atmospheric conditions are challenging. Recently, the field of monoelemental nanomaterials related to 2D layered As, Sb and Bi (few-layer or ML arsenene, antimonene, and bismuthene) has become one of the most developing and popular research fields.⁷⁰⁻¹¹² Building on early studies,¹¹³⁻¹¹⁷ currently, there are considerable studies on 2D layered As, Sb, and Bi nanomaterials in the literature, which explore their various synthetic methods, fundamental properties and functional nanostructures for promising applications.

The crystallization of heavy pnictogens (As, Sb, and Bi) results in a rhombohedral (β-form) layered structure,¹¹⁸ which is the most stable allotropic of pnictogen elements. Anisotropy is visible on the cleaved crystals. As and Sb have the highest anisotropies of physical properties.³⁹ Rhombohedral structures of As and other pnictogens are related to the structure of BP consisting of puckered, six-membered rings of atoms, but the individual layers are held together by stronger interactions. Different from BP, 2D (As, Sb and Bi) materials do not generate true van der Waals-bonded layered structures. The difference between BP and products with rhombohedral modifications (gray As, Sb and metallic Bi) comes from the interactions of the atomic orbitals between individual double layers. The difference between the in-plane and out-of-plane interatomic distance is substantially high, resulting in layered structures with anisotropy.³⁹ The interlayer interactions cause semimetal behavior. The (As, Sb, and Bi) elements with metallic sheen serve as superior conductors. With the most thermodynamically stable rhombohedral structures, pnictogen materials are brittle and easily pulverized. This unique property is suitable for the top-down preparation of few-layer and ML materials through mechanical exfoliation.

Before proceeding with this review, here we investigate the recent reviews relative to 2D group-VA nanomaterials. Pumera *et al.* reported a short review on the structures and properties of 2D monoelemental arsenene, antimonene and bismuthene.³⁹ Ares *et al.* reported the recent progress on antimonene as a new bidimensional material, focusing on theoretical work and experimental realizations.⁴⁰ Gablech *et al.* discussed the development of field-effect transistor-based sensors using 2D arsenene and antimonene.¹¹⁹ Wang *et al.* reported a mini-review to summarize the experimental preparation and practical applications of antimonene.¹²⁰ Zhang *et al.* explored the theoretical and experimental progress in 2D group-VA semiconductors.³⁷ Ye *et al.* reviewed bismuth-based photocatalysts for solar photocatalytic carbon dioxide conversion.¹²¹ Xu *et al.* summarized 2D bismuth-based layered materials for energy-

related applications.¹²² These reviews partially mentioned 2D group-VA materials, but they did not systematically summarize 2D layered As, Sb, and Bi (few-layer or ML arsenene, antimonene, and bismuthene) nanomaterials and pnictogenscontaining 2D materials. With respect to 2D-layer structural As, Sb and Bi materials, there are a rapidly increasing number of publications involving in the emerging and popular research field of 2D layered group-VA nanomaterials in recent years (Scheme 1), which provide relevant researchers strong motivation and a high necessity for this timely and comprehensive review.

Herein, this present review comprehensively introduces the state-of-the-art current research in 2D layered group-VA monoelemental nanomaterials beyond BP. This review covers 2D layered (As, Sb, and Bi) nanomaterials, few-layer, their ML counterparts (arsenene, antimonene, and bismuthene) and functionalized nanostructures (hybridization, doping, and functionalization). This review is divided into four sections, mainly including synthetic methods, properties, functional nanostructures and applications. We systematically summarize each section based on both theoretical predictions and experimental studies. We summarize the different synthetic methods for these 2D materials, including mechanical, sonication, electrochemical exfoliation, hydrothermal, solvothermal synthesis, and epitaxial growth. Then, we highlight their unique band structures, carrier transport, mechanical, optical, electronic, thermal and magnetic properties. Moreover, various functional nanostructures are discussed, including different heterostructures, doping, adsorption, hybrid and functionalized nanostructures based on these 2D layered materials. Finally, the broad range of promising applications of these 2D materials is elaborated, including various significant fields such as catalysis, energy storage, field-effect transistors, topological spintronic devices, electronic devices, nonlinear photonics, light-emitting devices, gas sensors, thermoelectric materials and



Scheme 1 Explosive development of 2D layered group-VA nanomaterials involving the number of publications at different publication years during the past decade.

biomedicine. The current research advances, potential challenges and future perspectives are discussed rationally (Scheme 2). This timely and overall review presents new and exciting latest advances on 2D layered group-VA monoelemental nanomaterials, which appeal to international research communities from a wide range of scientific disciplines, mainly including materials science, chemistry, physics, engineering, biology, and medicine. This review is beneficial for the further development of layered materials, mono-elemental materials, hybrid materials and functionalized low-dimensional materials.

2. Synthetic methods

2.1. Top-down methods

2.1.1. Mechanical exfoliation. The pnictogens (As, Sb, and Bi) with rhombohedral structures are very brittle, easily pulverized and exfoliated by top-down methods, such as ultrasonication and mechanical operations. Arsenene, antimonene and bismuthene were theoretically predicted,^{123,124} and examples of their synthesis have been widely reported.³⁹ The Scotchtape method is applied for β -As (rhombohedral) with high anisotropy. Grey Sb was exfoliated down to few layers through mechanical exfoliation.⁹⁵ Single- or few-layered β -arsenene (antimonene and bismuthene) was prepared through liquid-phase exfoliation (LPE) and bottom-up methods.^{39,40} However, methods for the large-scale preparation of single- and few-layered pnictogen nanosheets are limited (Table 1).

Shear exfoliation of layered materials in the liquid phase is often conducted using rotating blades mixers. Even household kitchen blenders can be used when the exfoliation process is conducted in aqueous surfactants, similar to sonication exfoliation. Gusmão *et al.* applied a shear force mixer to exfoliate nanosheets of rhombohedral layered As, Sb and Bi.⁷⁰ Bulk



Scheme 2 Schematic illustration of this review, involving synthesis methods, fundamental properties, functional nanostructures and potential applications of 2D layered group-VA nanomaterials beyond black phosphorus.

crystals of pnictogens were subjected to shear dispersion and exfoliation in the presence of aqueous surfactants (sodium cholate) using two types of kitchen blenders. The liquid-phase shear, turbulence and collisions led to gentle lateral force for self-lubricating exfoliation of the starting materials, followed by centrifugation at low rotational speeds to separate the poorly exfoliated materials in the sediment and the exfoliated nanosheets in the surfactant suspension (supernatant). After shear exfoliation, the supernatant was subjected to aqueous washing and centrifugation to achieve pnictogens. The preparation of pnictogens allows the use of kitchen blenders, rendering it a green, accessible and up-scalable method, without the need for purged media and a glove box.

Wang et al. reported a pre-grinding and sonication-assisted LPE to prepare antimonene.⁷⁸ In the presence of 2-butanol, mortar pre-grinding with a mortar provided shear force along the layer surface to produce large and thin Sb plates that were easily exfoliated into smooth and large-scale antimonene, which avoided long sonication time and antimonene destruction (Fig. 1a). Antimonene was gained after centrifugation. The low X-ray diffraction (XRD) peak at 23.7° (corresponding to the 003 facet) indicated the successful exfoliation of the bulk Sb crystals into Sb plates through pre-grinding. The diminished peaks from the 003 and 006 facets suggested that the exfoliation occurred along the *c*-axis to produce antimonene (Fig. 1b). The exfoliated antimonene had a smooth and flake-like morphology in the transmission electron microscopy (TEM) images (Fig. 1c), and its surface was principally enclosed by {001} facets, as proven by the high-resolution TEM (HRTEM) images (Fig. 1d). Its lattice fringes had an interplanar distance of ~0.36 nm.¹⁰⁴ LPE produced antimonene with a wide layer distribution. Different layered structures of antimonene were gained by centrifugation, with a remarkable Tyndall phenomenon. An increase in centrifugation speed yielded thinner antimonene with a lower yield and higher stability. This tendency was verified by Raman spectra measurements to characterize the 2D materials and provide details of their vibrational and rotational modes. The two peaks observed at 110 and 141.6 cm^{-1} are due to the E_g and A_{1g} vibration modes of the bulk Sb crystals, respectively (Fig. 1e). After pre-grinding into Sb plates, the peaks blue-shifted and shifted to larger wavenumbers with an increase in the centrifugation speed. This trend indicated that antimonene became ultra-thin. After pre-grinding and increasing the centrifugation speed, the peak intensity became weaker and close to that of micro-mechanically exfoliated Sb sheets. Weak peak intensities in Raman signals are due to a reduction in flake thickness. The Raman peaks at 180 and 250 cm^{-1} result from Sb(m) and (v) oxide, indicating the partial oxidization of the bulk Sb crystals before their preparation.98

Ares *et al.* prepared few-layered β -antimonene (FL-Sb) flakes.⁹² They started with mechanical exfoliation of freshly cleaved macroscopic Sb crystals by repetitive peeling with adhesive tape, accompanied by transfer of the Sb sheets from adhesive tape to thin layers of viscoelastic polymer. Another transfer was performed by pressing the polymer against SiO₂/Si substrates. The tape was not pressed against the substrate, and there was less adhesive. This double-step strategy allowed for

Table 1 Summary of 2D group-VA nanomaterials with the corresponding precursors, preparation methods, thickness, properties and applications

2D nanomaterials	Precursors	Preparation methods	Thickness	Properties and applications	Ref.
As nanosheets	Bulk As crystals	Aqueous shear exfoliation	Few-laver	Electrochemical application	70
Arsenene	In As substrate	Plasma-assisted process on InAs	Multilavers. ~14 nm	Multilaver arsenene nanoribbons	77
Sb nanosheets	Bulk Sb crystals	Cathodic exfoliation method	4 lavers. ~ 3.5 nm	Electrocatalysis for CO, reduction	104
Sh nanosheets	Bulk Sh crystals	Aqueous shear exfoliation	Few-laver	Electrochemical application	70
Sb nanosheets	Grav Sb powder	LPE	Multilavers. 3.0–4.3 nm	High volumetric sodium storage	71
Sh few laver film	Sh islands	Enitaxial orowth on Bi _c Te _c Se	1–5 hilavers	2D topological quantum phase evolution	164
Sh(111) thin film	Sh vanor	Enitavial prowth on Si(111)	4-30 hilavers	Evolution of tonological surface states	160
Antimonene	Bulk Sh crystals	Pre-prinding, sonication-assisted LPF	1-20 lavers, 0.5-7 nm	Hole transport laver in perovskite solar	78
				cells	
Antimonene	Layered Sb bulk	LPE	Few-layer, 4–20 nm	Nonlinear all-optical signal processing	79
Antimonene	Sb crystals	Ball-milling. LPE under sonication	Few-laver, ~4–5 nm	Energy storage, electrode for	81
				supercapacitors	
Antimonene	Bulk Sb	LPE	15–30 layers, 6–12 nm	Stable, broadband saturable absorption	84
Antimonene	Sb powder	Ultrasonic treatment, centrifugation	18 atom layers, \sim 7 nm	Large-capacity, long-life Na-ion batteries	85
Antimonene	Sb atoms	Epitaxial growth on Ag(111)	Thin layers	Highly strained, quantum spin Hall	161
				material	
Antimonene	Bulky Sb	LPE, ultra-sonication	2–5 layers, 2–5 nm	Ultra-short pulse, all-optical thresholding	87
Antimonene	Sh flakes	Micromechanical exfoliation I DF	Feur-Javer 27–15 nm	Non-covalent functionalization	88
Antimonene	Built ch	Flactrochemical explication, 11 E	Nulfilavers 21.6 nm	Roadhand nanlinear antical recoonce	00
Antimonene		Electrotititical existantial	Muuliayets, 31.0 IIII	month and a second s	60
Anumonene	SD Crystals	Solid-Source molecular beam epitaxy	10-80 layers, 4-30 nm	I OWARD SCALADIE ANUINONENE DEVICES	96 2
Antimonene	Sb atoms	Molecular beam epitaxy on Pd1e ₂	Single layer, ~ 2.8 A	Epitaxial growth, excellent air-stability	16
Antimonene	Crystal of Sb	Mechanical exfoliation	4–7 layers, 2–3 nm	Optical properties few-layer antimonene	92
Antimonene	Sb powder	van der Waals epitaxy, Sb atom vapor	${\sim}10$ atom layers, 4 nm	Polygons, transparent conductive	93
				electrode	
Antimonene	Sb crystals	LPE, assisted by sonication	Mono/bilayers, ${\sim}4~{ m nm}$	Thickness-dependent Raman behavior	94
Antimonene	Sb material	Micromechanical exfoliation, transfer	Bilayers, $\sim \!\! 1.8~{ m nm}$	Mechanical isolation, high stability	95
Antimonene	Sb vapor	Sb deposition on Bi_2Te_3 , $Sb_2Te_3(111)$	Bilayers	Change in surface-state band dispersion	162
Antimonene	InSb substrate	Plasma-assisted process on InSb	Multilayers, ${\sim}5~{ m nm}$	Nanoribbons, orange light emission	96
β-Antimonene	Sb crystals	LPE assisted with sonication	20–40 ML, 5–16.5 nm	Excellent nonlinear absorption	82
				properties	
β-Antimonene	Sb islands	Sb deposition on Bi ₂ Se ₃ surface	0.15-2 ML	β-Antimonene at Sb/Bi ₂ Se ₃ interface	163
α-Antimonene	Sb atoms	Sb deposition on Bi nanoislands	1-4 ML	Engineering multiple topological phase	86
Antimonene film	Sb droplets	Molecular beam epitaxial growth	Multilayers, ${\sim}17~{ m nm}$	Contact resistance reduction of 2D	80
			·	materials	
Antimonene ML	Sb atoms	Epitaxial growth on Ag(111)	\sim 1 ML, 2.2 Å	Flat ML film with honeycomb structure	83
Bi nanosheets	Bulk Bi crystals	Aqueous shear exfoliation	Few-layer	Electrochemical application	70
Bi nanosheets	Bi powder	Probe, ice-bath ultra-sonication	Few-layer, 6–12 nm	Tunable optoelectronic performance	137
Bi nanosheets	Bi nanoparticles	Hot-pressing method	Few-layer, 2.55 nm	Superior photoluminescence	72
Bi nanosheets	${ m Bi}({ m NO}_3)_3 \cdot 5{ m H}_2{ m O}$	Wet chemical reduction	Ultrathin layer	Electronic building blocks	175
Bismuthene	Bulk, powder Bi	Grinding, sonochemical exfoliation	Few-layer, ${\sim}4~\mathrm{nm}$	Nonlinear optics, ultrafast photonics	97
Bismuthene	Bulk, powder Bi	Grinding, sonochemical exfoliation	Few-layer, $\sim 3 \text{ nm}$	All optical switching of continuous waves	98
Bismuthene	Bi vapor	Epitaxial deposition on SiC(0001)	1 ML	High-temperature quantum spin Hall material	66
Ri film	Bi(110) clusters	Enitavial orowth on Si(111)	0 7–7 MI.	I nuv enerov electron diffraction	155
Bi film	Bi vapor	Lateral growth on Si surface	1.3-22 ML	Toward various nano-devices	156

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Table 1 (Contd.)

2D nanomaterials	Precursors	Preparation methods	Thickness	Properties and applications	Ref.
Bi film	Bi vapor	Single-crystalline growth on Si(111)	1-20 ML	Bi film growth on various substrates	157
Bi film	Bi atoms	Molecular beam epitaxial growth	4–6 ML, 6–50 nm	Dry transfer of single-crystalline thin film	75
Bi film	Bi vapor	Vapor deposition on HOPG	0.7–100 ML, 0.4–7 nm	Crystallographic orientation transition	116
Bi(111) film	Bi atoms	Growth on NbSe ₂ superconductor	5 bilayers, 2.66 nm	Topologic edge state, superconductivity	73
Bi(110) film	Bi vapor	Bi deposition on HOPG	2-4 ML	Different substrates for Bi film growth	74
Ultrathin Bi film	Bi vapor	Bi deposition on Si(111)	Few-layer	Epitaxial growth of single-crystal	158
Ultrathin Bi film	Bi vapor	Bi deposition on Si(111)-7 \times 7	Few-layer	Nanofilm allotrope and phase transformation	159
b-As $_x$ P $_{1-x}$ flakes	Bulk b-As $_x$ P $_{1-x}$	Mechanical exfoliation of b-As _x P_{1-x}	Two-atom layer, 1.3 nm	Layered anisotropic infrared semiconductor	76
Sb ₂ S ₃ nanosheets	SbCl ₃ , sulfur	Colloidal chemistry synthesis	Few-layer, 2–4 nm	Photoelectronic, phase transformation	100
$[Sb_2O_2(OH)]^+$	$Sb(OAc)_3$	Colloidal chemistry synthesis	Layered framework	Inorganic network, Lewis acid catalysis	101
Sb ₂ Te ₃ nanosheets	Sb ₂ Te ₃ materials	Micromechanical exfoliation, transfer	5 atom-layers, $\sim 1 \text{ nm}$	Reversible phase-change behavior	102
Sb-NDs \subset CNs	$ m K_3Sb_3P_2O_{14}$	Sonication LPE, hydrothermal	2D C/Sb hybrid	Advanced anodes for sodium storage	103
Sb ₂ Te ₃ nanoplates	Sb_2Te_3 bulk	Vapor-solid growth process	5 atom-layers, $\sim 1 \text{ nm}$	Scalable synthesis, single quintuple layer	169
$[\mathrm{C}_x\mathrm{N}_y\mathrm{H}_z]_n[\mathrm{Sb}_7\mathrm{S}_{11}]$	Sb ₂ S ₃ material	Hydrothermal conditions	Layered	2D Sb _x S _y structure with Sb–Sb bonding	105
Bi ₂ S ₃ nanosheets	${ m Bi}_2 { m S}_3$ powder	Probe, bath sonication, LPE	4–9 layers, 4.2–9.9 nm	High-performance photodetectors	106
Bi ₂ Te ₃ nanoplates	${ m Bi}_2{ m Te}_3$ powder	Solvothermal, vapor phase growth	Layered, 6–8 nm	Optical transmission enhancement	108
BiOI nanosheets	${ m Bi}({ m NO}_3)_3 \cdot 5{ m H}_2{ m O}$	Hydrothermal process	Layered, ${\sim}10~{ m nm}$	Visible-light driven photocatalysts	110
${ m Bi}_4{ m Ti}_3{ m O}_{12}$ sheets	Bi_2O_3 , TiO_2	Molten salt synthesis strategy	Layered	Enhanced antibiotic residue degradation	180
2D Bi nanoribbons	$NaBiO_3 \cdot 2H_2O$	Solvothermal method	Layered, ${\sim}40~{ m nm}$	Topological metallic surface states	109
2D Bi, Ag structure	Bi, Ag atoms	Bi, Ag deposition on Si(111)	Layered	Spin-spin metallic surface-state band	171
2D Bi, In structure	Bi, In atoms	Bi, In deposition on Si(111)	Layered	Large defect-free arrays of structure	172
$2D Bi_2 Se_3 crystals$	Bi, Se precursor	Assisted, seed-mediated growth	Layered, ${\sim}10~{ m nm}$	Decent charge carrier mobility, FET	177
2D BiOBr	${\rm Bi}({\rm NO}_3)_3 \cdot 5{\rm H}_2{\rm O}$	Hydrothermal process	2D MoS ₂ /BiOBr	Enhanced dye degradation,	178
				photocatalysts	
2D BiTeSe system	${ m Bi}_2{ m Se}_3,{ m Bi}_2{ m Te}_3$	Evaporative thinning technique	Layered	Changing carrier concentration and type	173
2D (Bi, In, Na) joint	Bi, In, Na atoms	Bi, In, Na deposition on Si(111)	Layered	Thermostable, ordinary codeposition	174
$2D \left[{{{\rm{B}}{\rm{i}}_2}{\rm{I}}_7}{\rm{CI}}_2 \right]_n^{3n-1}$	${ m Bi}_x { m I}_y { m Cl}_z$ dimers	Solvothermal conditions	2D honeycomb-like	Enhanced light-harvesting materials	107
2D K ₃ BiAs ₆ Se ₁₂	Bi powder	Solvothermal reaction	Layered	Be expected applying fluxes	179
$2D Bi_2Sr_2CaCu_2O_y$	Bulk Bi_2O_3	Self-flux method	Layered	High-temperature superconductivity	112
Quasi 2D Bi ₂ Te ₃	Bulk Bi_2Te_3	Mechanical exfoliation	Layered	Topological insulators, quasi-2D crystals	111



Fig. 1 (a) Illustration of the preparation of antimonene by grinding bulk Sb crystals into Sb plates and exfoliating Sb plates into antimonene. (b) XRD patterns of bulk Sb crystals, Sb plates after grinding and antimonene. (c) TEM and (d) HRTEM images of antimonene. (e) Raman spectra of bulk Sb crystals and Sb plates after grinding and antimonene obtained at different centrifugation speeds. Reproduced with permission from ref. 78, Copyright 2018 Wiley.

clean flake deposition and a high yield of larger flakes on the silicon oxide substrate.^{88,95} Martínez-Periñán prepared FL-Sb *via* the LPE process.⁸¹ Sb crystals were treated in a ball mill. Then the microcrystalline powder was suspended in an isopropanol-water (4 : 1) mixture, which was sonicated to produce a stable FL-antimonene suspension under ambient conditions. The unexfoliated material was removed through centrifugation to form a stable suspension with a high concentration of FL-bis-muthene.^{97,98} Before sonochemical exfoliation, bulk Bi was firstly grinded into Bi powder in isopropyl alcohol or ethanol. The prepared Bi solution was placed in spiral glass bottle under an ice-bath and probe sonication. The suspension was centrifuged to separate the precipitates and supernatant suspension containing FL-antimonene.

2D layered As, Sb and Bi nanomaterials with hybrid, doping and functionalized nanostructures were prepared by mechanical exfoliation. Jacobs-Gedrim *et al.* prepared 2D Sb₂Te₃ nanosheets.¹⁰² Sb₂Te₃ was sourced from 6 mm lumps. The lumps were cleaved with a razor blade to remove the outer surface that was contaminated with O₂ from the atmosphere. The Sb₂Te₃ nanosheets extracted by micro-mechanical exfoliation were transferred on a substrate with embedded interdigitated electrodes. Teweldebrhan *et al.* explored the cleavage of bulk Bi₂Te₃ into thin crystalline films.¹¹¹ After mechanical cleavage exfoliation, the thin film from the crystalline bulk Bi₂Te₃ was separated to obtain layered counterparts with few atomic planes. Layered black arsenic–phosphorus (b-AsP) materials were mechanically exfoliated into thin flakes down to atomic layers.⁷⁶ Bulk b-As_xP_{1-x} (*x*: 0–0.83) samples with nominal compositions were prepared by a vapor transport method and exfoliated into flakes using Scotch tape.

Thus far, the mechanical exfoliation methods for 2D layered pnictogen materials include shear exfoliation with kitchen blenders,⁷⁰ mortar pre-grinding with a ball mill,^{78,81,97,98} peeling with adhesive (Scotch) tapes,76,88,92,95 and cleaving with razor blades.^{102,111} Mechanical exfoliation with adhesive tape is supported on an SiO₂/Si or gold substrate surface, similar to the discovery of graphene.⁴ Shear exfoliation with a kitchen blender or razor blade is suitable for the large-scale production of defect-free 2D layered materials.125 This exfoliation is similar to sonication and also applicable to other 2D layered materials, including BP, boron nitride and MoS2.126-131 However, the preparation of high-quality layered pnictogen materials with controllable thickness and tunable bandgaps still remains a challenge. Epitaxial growth and mechanical exfoliation with viscoelastic stamps or kitchen blenders, or straightforward LPE have some drawbacks, such as low yields and time-consuming operations. The combination of mortar pre-grinding and sonication-assisted LPE promotes the achievement of smooth and large-scale 2D layered pnictogen materials. The initial pregrinding of bulk crystals provides shear force along laver surfaces to form thin plates. The LPE of plates into smooth large layered materials is conducted, which assists with sonication, and thus long sonication time and destruction of atomically thin layered materials can be avoided. Layered materials with uniform and specific numbers of layers are achieved after centrifugation treatment. Pnictogen materials with high-quality layered structures promote experimental studies on thicknessdependent bandgaps, which can pave the way for the widespread applications of 2D pnictogen materials in electronics, optoelectronics and smart nanodevices.

2.1.2. Ultrasonic exfoliation. In the case of 2D layered materials, the quality of materials prepared from mechanical or micromechanical exfoliation is quite limited, restraining their potential applications.⁹⁵ LPE is very practical due to its ability in yielding large-scale, few-layer or ML 2D materials.¹³²⁻¹³⁵ LPE has been used to generate several 2D materials on a large scale, such as few-layer BP.^{133,136} Generally, bulk crystals are immersed into mixed solvents without surfactants, followed by sonication to generate a stable suspension of micrometer-large, few-layer 2D nanomaterials under ambient conditions. Sonication-assisted LPE has been widely applied to prepare few-layer pnictogen sheets with high productivity and superior properties.

Tian *et al.* prepared 2D few-layer antimonene in a large quantity by LPE of β -Sb in the mixed (1/1, v/v) solvent of ethanol and *N*-methyl pyrrolidone (NMP) without surfactants.⁸⁵ The pregrinded β -Sb powder was treated by ultrasonic exfoliation at 200 W for 5–6 h. The mixture was centrifuged to remove the unexfoliated Sb. The dark-grey suspension containing few-layer antimonene was collected and centrifuged, followed by rinsing with ethanol and freeze-drying under vacuum. Few-layer antimonene nanoflakes were prepared by LPE.⁸⁷ Bulk Sb was exfoliated in NMP by bath-ultrasonication (40 kHz operating frequency, 100% power) for 4 h. The prepared nanoflakes were water-soluble and had lateral dimensions from ten nanometers to micrometers. Sonication (400 W, 24 kHz, 40 min) of Sb crystals in an isopropanol–water (4/1, v/v) mixture without surfactants resulted in a stable suspension of antimonene over weeks under ambient conditions.⁹⁴ The non-exfoliated materials were removed by centrifugation to form a stable dispersion containing antimonene. Antimonene on the micrometer-scale had high quality and few-layer nanosheet structures. Zhang *et al.* prepared antimonene nanosheets *via* LPE assisted with sonication, which was a fast and direct method to prepare a high-quality dispersion of few-layer antimonene.^{82,94} Due to the on-surface isolation and hypo-toxicity, no surfactant was required upon exfoliation and ultra-pure ethanol was used as the solvent. Sb crystals were ground using an agate mortar into a powder, which was then dispersed in ethanol under stirring, followed by sonication for 3 h to exfoliate the antimonene nanosheets. After the dispersion settled to precipitate large grains, the supernatant was centrifuged to collect the antimonene nanosheets.

Bi nanosheets was prepared from Bi powder (200 meshes) by sonication (Fig. 2a).137 Bi powder was added to a glass bottle with 300 mL of pure NMP, followed by ice-bath sonication (70% power, 600 W) for 6 h, probe sonication (60% power, 1800 W) for 24 h and an additional ice-bath sonication for 6 h. After centrifugation, Bi nanosheets were achieved. Bi was easily oxidized to a-Bi2O3 upon exposure to ambient conditions (oxygen and water).138 NMP was used as the solvent during the exfoliation process. NMP is a superior organic solvent for 2D material exfoliation and can prevent the oxidization of Bi atoms. The exfoliated Bi nanosheets had a uniformly distributed lateral dimension (Fig. 2b and c) and an intact lamellar structure after sonication (Fig. 2d and e). The HRTEM image indicated a lattice spacing of 0.22 nm, corresponding to the (110) plane of Bi. The energy dispersive spectroscopy (EDS) mappings from the TEM images were in accordance with the Bi morphology at exact locations (Fig. 2f). The crystal structures were characterized by XRD (Fig. 2g). Bi nanosheets are hexagonal nanocrystals without detectable impurity of other phases.139 Upon excitation with a 325 nm laser, Raman peaks were observed at 65.6 and 92 cm⁻¹ (Fig. 2h), corresponding to the E_g and A_{1g} vibration modes of Bi.75,138 A broad absorption regime was observed in the absorption spectra (Fig. 2i), which is in good agreement with the characteristics of Bi nanosheets.97 Atomic force microscopy (AFM) measurements indicated the lamellar Bi sheets had a thickness of 6-12 nm, implying few-layer Bi nanosheet structures.

2D group-VA pnictogen materials with functional nanostructures were prepared by ultrasonic exfoliation. Huang *et al.* prepared Bi₂S₃ nanosheets based on sonication-assisted LPE.¹⁰⁶ Bulk Bi₂S₃ was ground with NMP in an agate mortar. After grinding for 40 min, the Bi₂S₃/NMP suspension was treated by probe sonication (650 W, 3 h), followed by bath sonication (400 W, 48 h) at 5 °C. The final suspension was obtained by centrifugation, and the supernatant suspension containing Bi₂S₃ nanosheets was gently collected. Wang *et al.* synthesized smooth and large antimonene with uniform 2D layers using pre-grinding and sonication-assisted LPE.⁷⁸ The mortar pregrinding provided shear force along the layer surfaces to form large Sb thin plates, which were exfoliated into smooth and large antimonene, avoiding long sonication time and antimonene destruction. Similarly, FL-Sb was prepared *via* a modified LPE.⁸¹ Sb crystals were treated with a ball mill to obtain a microcrystalline powder with remarkably reduced dimensions, which was subjected to sonication-assisted LPE in an isopropanol-water mixture. Besides, few-layer bismuthene was obtained by sono-chemical exfoliation.^{97,98} Bulk Bi was ground into Bi powder with isopropanol. The Bi solution was placed in spiral glass bottle and kept under ice-bath and probe sonication. The suspension was centrifuged to collect the supernatant containing bismuthene.

The pre-grinding of bulk crystals is important for the production of nanosheets since it first produces plate structures

that are easily transformed into high-quality 2D layered materials. The thinness of the plates formed from pre-grinding improves the efficiency of exfoliation. Thus, the pre-grinding pretreatment of bulk crystals into thin plates before sonication-assisted LPE is suitable for the preparation of 2D layered materials with high-quality, few-layer and ML structures. This strategy promotes the preparation of 2D group-VA pnictogen materials and their counterparts with hybrid, doping and functional nanostructures. Furthermore, both pregrinding and sonication are accompanied with the abundant release of heat, and thus ice-bath sonication or low-temperature



Fig. 2 (a) Scheme of the proposed hydrothermal preparation of Bi nanosheets. (b) Low and (c) high-magnification scanning electron microscopy (SEM) images. (d) Low and (e) high-magnification TEM images of the few-layer Bi nanosheets. The inset is HRTEM image. (f) EDS mapping, (g) XRD pattern, (h) Raman spectra and (i) UV-vis absorption spectra of few-layer Bi nanosheets. Reproduced with permission from ref. 137, Copyright 2018 IOP Publishing.

cooling is required. Organic solvents (NMP, isopropanol, and ethanol) are used as starting materials and stabilizers for the preparation of 2D pnictogen materials.^{79,84} At a higher sonication power, bulk crystals or powder are broken into smaller (in lateral, height, and thickness) sized 2D materials. Also, an extension in sonication time benefits the achievement of few-layer or ML 2D materials.

2.1.3. Electrochemical exfoliation. Few-layer pnictogen nanosheets are prepared from bulk crystals based on cathodic exfoliation. This method is simple, economic, environmentally friendly and efficient for the mass production of classic 2D materials, including graphene and TMDs.140-144 Li et al. prepared few-layer Sb nanosheets from bulk Sb crystals through cathodic exfoliation.¹⁰⁴ In their experiments,^{89,104} a two-electrode electrochemical cell was used for exfoliation. An intact small bulk Sb with high purity and crystallinity was connected to the conducting copper wire as the cathode. Bulk Sb as the working electrode was partially placed in electrolyte to avoid electrolysis and contamination of the connected conducting wire. Pt wire (foil) with a size of 0.5 mm served as the counter electrode and the anode, and 0.2–0.5 M Na₂SO₄ aqueous solution served as the supporting electrolyte (Fig. 3a). A direct current potential with a constant voltage of -6 V or 10 V was applied between the Sb and Pt electrodes to drive electrochemical exfoliation. This process was maintained for 1 h to ensure the complete

intercalation and exfoliation of Na⁺ ions inside the cathodic Sb. After centrifugation of the electrolyte containing the exfoliated Sb nanoflakes, the sediment was washed through ultrasonication in water. The dispersion was dried at 60 °C for 24 h under vacuum and then diluted in NMP.

The anions of the supporting electrolyte had little impact on the exfoliation process. Cations with larger (Cs^{+}) or smaller (Li^{+}) sizes compared to the interplanar spacing of Sb crystals reduced the lateral sizes of the nanoflakes. In the AFM images of the electrochemically exfoliated few-layer antimonene, the nanoflake presented a height of \sim 31.6 nm (Fig. 3b), with smooth surfaces and irregular profiles. The nanoflake had a lateral size of 10.3 µm and a rigid arrangement of lattice planes (Fig. 3c and d). The inter-distance of lattice fringe was 0.228 nm, in accordance with the (100) interplanar distance of rhombohedral gray Sb.93 The Raman spectra of the multilayer rhombohedral antimonene nanoflakes (~31.6 nm) indicated that the peak positions of E_g and A_1 were blue-shifted to 113.8 and 150.9 cm⁻¹, respectively, showing a reduced intensity ratio due to the thickness reduction produced from electrochemical exfoliation (Fig. 3e). The reduced intensity ratio was due to the fast intensity attenuation in the interplanar A1 vibration modes compared to the in-plane E_g vibration modes.⁹³ The XPS spectra (Fig. 3f) had a sharp symmetric photoelectron peak at 528 eV,



Fig. 3 Characterization of multilayer antimonene. (a) Scheme of two-electrode system used for the electrochemical exfoliation of Sb, using bulk Sb, Pt wire and Na_2SO_4 aqueous solution as the working electrode, counter electrode and electrolyte, respectively. (b) AFM image of the electrochemically exfoliated multilayer antimonene nanoflake. (c and d) TEM and HRTEM images of multilayer antimonene, respectively. (e) Raman spectra of bulk Sb and 31.6 nm thick multilayer antimonene shown in (b). (f) XPS spectrum of Sb $3d_{5/2}$ peak of the exfoliated multilayer antimonene. Reproduced with permission from ref. 89, Copyright 2017 Wiley.



Fig. 4 (a) TEM images of multilayer arsenene/InN/InAs. Insets are the diffraction patterns of multilayer antimonene. (b) Theoretical atomic models of multilayer arsenene/InN/InAs layer structures. The insets are the diffraction patterns of multilayer arsenene. Reproduced with permission from ref. 77, Copyright 2016 American Chemical Society. (c) TEM images of multilayer antimonene/InN/InSb. (d) Theoretical atomic models of multilayer antimonene/InN/InSb layer structures. Reproduced with permission from ref. 96, Copyright 2016 Royal Society of Chemistry.

resulting from the Sb–Sb $3d_{5/2}$ orbital bonding. The mono-peak implied the non-oxidation feature of few-layer antimonene.

The quality of 2D layered pnictogen nanomaterials from mechanical exfoliation is limited, which restricts their largescale applications.95 Multi-layered antimonene nanoribbons were prepared from a plasma-assisted process at room temperature, which became non-continuous and showed a pile of multilayer nanoribbons.96 Few-layered antimonene monocrystalline polygons can be prepared on various substrates via van der Waals epitaxial growth.93 However, the structural variety of the cleaved surface is limited and is hard to handle.145 Epitaxial growth was used to prepare few-layered antimonene;93 however, the scalability of the method needs to be further improved. Electrochemical exfoliation is considered a facile and scalable approach to obtain large-scale nanomaterials. This approach with unique merits over conventional synthetic methods is suitable for the mass generation of 2D materials.146 In contrast to mechanical exfoliation, molecular assembly and chemical vapor deposition, the electrochemical method is inexpensive for mass production and avoids the use of harsh

chemicals through electrochemical activation, resulting in simple purification steps. However, electrochemical exfoliation needs to satisfy high requirements for the large-size production of 2D materials, which are realized in the electrochemical exfoliation production of graphene,¹⁴² MoS₂,¹⁴⁷ phosphorene,¹⁴⁸ *etc.* Besides high quality and large-scale production in a cost-effective route, the electrochemical exfoliation of 2D layered pnictogen materials is desirable for applications.^{89,104}

2.1.4. Plasma-assisted process. Tsai *et al.* explored a plasma-assisted process to obtain multilayer graphene on 4H-SiC, showing good electronic properties.¹⁴⁹ As a mature technique, the plasma-assisted process was expanded to prepare multilayer germanene on SiGe/Si and multilayer violet phosphorene on InP.^{150,151} Multilayer arsenene was prepared on InAs *via* the plasma-assisted process.⁷⁷ Multilayer arsenene is not actually continuous, similar to a pile of multilayer nanoribbons. Based on the concept of the plasma-assisted process, nitrogen ions are introduced into InAs, and then react with indium and squeeze arsenic atoms out of the surface to produce arsenene layers during thermal treatment. The synthetic process can be

optimized by tuning the experimental conditions, such as annealing time, power and plasma exposure time. The crosssectional layer nanostructure was characterized by TEM. SiO_2 was deposited on the surface using an electron beam evaporator to protect the thin film from damage from the focus ion beam during the preparation of the TEM samples. Under high magnification, a heterogeneous structure was clearly observed, which consisted of three parts, including multilayer arsenene, InN and the InAs substrate (Fig. 4a). The (110) interplanar distance (~0.43 nm) of InAs was consistent with that (~0.428 nm) of the theoretical atomic models (Fig. 4b). The InN layer resulted from the reaction between nitrogen ions and indium in InAs. Also, the InN layer was strained and served as a buffer layer to match the lattice of multilayer arsenene with that of InAs.

Diffraction patterns (inset of Fig. 4a) were measured by fast Fourier transform to derive the interplanar distances of multilayer arsenene. Two groups of reciprocal lattice points were selected for computation of the typical interplanar distances of plane groups, which were close to 0.286 and 0.181 nm, corresponding to the (110) and (01-1) interplanar distances (Fig. 4b) of rhombohedral gray As, respectively. The angle between the two lines represents the (110) and (01-1)plane groups in the diffraction patterns, which is close to that between the (110) and (01-1) plane groups in the real lattices, respectively. The top layer was identified as multilayer arsenene. A plasma-assisted process was used to prepare multilayer antimonene on InSb (Fig. 4c and d).96 The multilayer antimonene was non-continuous, similar to a pile of multilayer nanoribbons. The formation mechanism of multilayer antimonene was interpreted as follows. Intrinsic InSb (001) substrate acted as the template, and Sb element acted as the source for multilayer antimonene formation. The InSb substrates were immersed in N2 plasma produced by a radio frequency (13.56 MHz) system with 50-200 W of power for 30-60 min at $\sim 10^{-1}$ Torr. After plasma immersion, the samples were annealed at 450 °C in an N_2/H_2 (10/1, v/v) atmosphere for 30-60 min. N₂ was mixed with H₂ to prevent Sb oxidation caused by the leakage of O2. Raman analysis was used to verify the formation of antimonene layers. The surface composition was analyzed by XPS. Spherical-aberration corrected TEM with 0.1 nm resolution of the lattice image was used to observe the layer nanostructure.

Upon the use of the plasma-assisted process to prepare 2D layered materials, the E_g peak of gray As or Sb appears, which becomes more intense by extending the exposure time. Thus, the thickness of gray As or Sb prepared from the plasma-assisted process can be tuned by altering the exposure time. Also, the nitrogen content (near InAs or InSb surface) increases with an increase in plasma exposure time because of ion accumulation. The content profile is broadened by internal ion diffusion during annealing. The amount of As or Sb atoms squeezed onto the surface increases, forming a thicker gray As or Sb. In experiments, the plasma-assisted process to prepare arsenene/antimonene layers starts from nitrogen plasma immersion with high power, followed by annealing at high temperature for a short time.

2.1.5. Hot-pressing method. Hussain et al. developed a cost-effective mechanical way to produce ultrathin Bi nanosheets (BiNSs) with high crystalline metallic Bi.72 Using large thermos-compression, ultrathin BiNSs were deposited on polished Si substrates from pristine Bi nanoparticles (BiNPs) via a facile hot-pressing method (Fig. 5a). The BiNP dispersion in ethanol was dropped on an Si substrate. After drying, the BiNPs were sandwiched between two Si substrates. Then the pair was placed in the middle of steel plates from the hot-press machine. The temperature of the plates increased from room temperature to 150 °C. The pressure was increased from atmospheric pressure to 0.54 GPa. The Si substrates were pressed for 30 min at 150 °C, followed by natural cooling to room temperature at a constant pressure of 0.54 GPa. A low operation temperature was selected to avoid oxide formation. In any case, postfabrication treatment was not required.

Small agglomerates of BiNPs were compressed at optimal temperature and pressure parameters to yield BiNSs. XRD peaks were indexed with the hexagonal crystal structure of Bi (Fig. 5b). The cell parameters were in good agreement with the standard literature values from JCPDS Card no. 05-0519 (Fig. 5c). Also, there was no peak ascribed to the oxidation phase of Bi. The intensities of the (003) and (006) peaks in the BiNSs samples were enhanced compared with the XRD patterns of the raw metal BiNPs. Metals and semimetals are highly crystalline materials that endure abundant plastic deformations and induce microstructure changes. During deformation, the orientation of single crystals changes related to the direction of applied stress. The pronounced reflections of the (003) and (006) diffraction peaks are indicative to stress-induced recrystallization of BiNSs along a preferred (001) family of planes. The (012) plane is the dominant crystal phase, carrying bulk features into the nanosheets. XRD implied that the BiNSs were well textured and highly oriented mainly along the (012) phase, consistent with the HRTEM results (Fig. 5f and g) and selected area electron diffraction (SAED, Fig. 5e). The BiNSs were ultrathin and semi-transparent, with a freestanding nature and a thickness of ~2.55 nm, showing few atomic layers of Bi. EDS verified the fabrication of pure BiNSs on the Si substrate (Fig. 5h). Fig. 5d illustrates the sheet-like nanostructure of metallic phase Bi. The SAED patterns imply high crystallinity. Fig. 5i shows the HRTEM image of the overlapped D1 area of BiNSs, with the (110) crystal orientation with a fringe spacing of 0.22 nm.

The facile fabrication of 2D functional nanomaterials (semimetals, metalloids, polymers and metal oxides) is restricted because of their intrinsic non-layered lattice structures. The methods for the production of 2D structural layered materials mainly include molecular beam epitaxy (MBE) growth and wet chemical strategies. However, the productivity of MBE growth is hindered by the low accessibility, harsh conditions, special substrate requirements and alteration in intrinsic properties of materials because of interface bonding with the substrate.¹⁵² Wet chemical methods involve complex steps and produce nanosheets in small areas. The use of surfactants is often undesirable for practical applications in electronic



Fig. 5 (a) Schematic diagram of the fabrication process of BiNSs using pristine BiNPs *via* a hot-pressing method. (b) XRD patterns of rhombohedral phase pristine BiNPs and BiNSs prepared at 150 °C. (c) Schematic illustration of hexagonal crystal structure and top view, indicating a rhombohedral A7 unit cell along with the lattice spacing. (d) Low-resolution TEM image of a Bi nanosheet on Cu grid reveal a sheet-like structure. (e) SAED pattern obtained from the area highlighted by a yellow box, showing the highly crystalline nature of BiNSs. (f) HRTEM image of a Bi nanosheet at point P marked in (d) clearly showing the crystalline nature of Bi. (g) Highly magnified HRTEM image of BiNSs collected from highlighted area in (f) revealing the highly crystalline structure with crystal orientation Bi (012) and corresponding lattice spacing. (h) Energy dispersive spectrum of a Bi nanosheet collected from the highlighted area in yellow confirms the presence of metallic BiNSs lying on the Si substrate. (i) HRTEM images collected from the area highlighted as D1 in (d) showing the (110) crystal orientation. Reproduced with permission from ref. 72, Copyright 2017 Wiley.

devices, spintronic and catalysis. Thus, exploration of an alternative strategies to gain high-quality and large-area ultrathin nanostructures with clean surfaces out of layered materials is desirable and helps to further studies on fundamental properties and promising applications. Bi is one of versatile layered semimetals with odd electronic properties due to its extraordinary characteristics. Various ultrathin morphologies of Bi (nanobelts, nanoribbons, thin films and nanosheets) were prepared via the MBE growth and wet chemical methods (Table 1), which show special limitations. Thus, the development of alternative strategies to form ultrathin and large-area BiNSs from high-quality metallic Bi on arbitrary Si substrates is beneficial for understanding their fundamental properties. The hot-pressing method is a facile and cost-effective mechanical way to produce ultrathin and large-area nanosheets from highly crystalline metallic Bi. Using large thermos-compression, ultrathin BiNSs were prepared from pristine BiNPs on polished Si substrates.72

2.1.6. Other top-down methods. Metallic Sb with gray allotrope is considered barely layered based on the viewpoint of 2D layered systems. Actually, Sb is a graphite-like layered material. Sb layers consist of fused, ruffled and six-membered rings.^{153,154} The nearest and next-nearest Sb atoms can form an irregular octahedral complex, containing three atoms in each double layer slightly closer than three atoms in the next. This close packing forms a high density of 6.7 g cm⁻³ for gray Sb.¹⁵⁴ The weak bonding action between layers has the potential for the top-down production of Sb nanosheets. Similar to graphene, metallic Sb nanosheets have potential as new anode materials with high performance in sodium storage.

Gu et al. proposed a facile strategy for the preparation of freestanding metallic Sb nanosheets through LPE of bulk gray Sb powder in isopropyl alcohol and NaOH solution.⁷¹ The metallic Sb nanosheets possessed ultrathin (~4 nm), foldable features and large aspect ratios. These unique features of Sb nanosheets cause them to behave like graphene, which can be used construct uniform and compacted films with other nanosheets. The unique ultrathin and large-aspect ratios of Sb nanosheets can serve as building blocks to fabricate uniform and compacted films with graphene. In hybrid films composed of metallic Sb nanosheets and graphene with tunable densities, the notorious volume change of metallic Sb is alleviated with the aid of flexible graphene. The density of the entire electrode film is improved by harnessing the high density of Sb nanosheets. The optimized metallic Sb nanosheets-graphene films exhibit a high volumetric capacity, high-rate capability and superior cycle performance for sodium storage. Wu et al. reported the top-down preparation of inter-connected 2D carbon/ Sb hybrids.¹⁰³ The interconnected 2D carbon nanosheets with ultrasmall Sb nanodots were embedded homogenously. K₃Sb₃P₂O₁₄ with a lamellar structure was mixed with HCl solution, followed by stirring for 48 h for ion exchange. After a repeated exchange process, pure H₃Sb₃P₂O₁₄ crystals were obtained, which were dispersed in water via ultrasonication and stirring. After the addition of glucose, the mixture solution was transferred to a Teflon-lined autoclave. After reaction at 180 $^\circ\mathrm{C}$ for 10 h, solid products were obtained by filtration and freezing

dry. The products were annealed at 500 °C for 1–2 h in Ar/H₂ to achieve Sb-NDs \subset CNs. This synthetic process is facile, convenient and suitable for the preparation of other relevant materials. The combination of multi-dimensional and multi-scale nanostructures in electrode materials induces high electron/ion transport kinetics and pronounced integrity of electrode structures upon cycling, which thus provides an efficient pathway to develop advanced electrode materials.

2.2. Bottom-up methods

2.2.1. Molecular beam epitaxy. Molecular beam epitaxy (MBE) on solid substrates is used to form 2D layered pnictogen nanomaterials.75,80,90,91 Antimonene and Bi thin films can be prepared through MBE as a facile bottom-up method.¹⁵⁵⁻¹⁵⁹ Wu et al. explored monolayer (ML) antimonene growth on a 2D layered PdTe₂ substrate by MBE (Fig. 6a).⁹¹ The substrates for MBE growth of few-layer or ML 2D materials were specifically selected. PdTe₂ as the substrate for the MBE growth of ML antimonene is due to its crystal periodicity (4.10 Å surface lattice constant), which has a small mismatch (<2.3%) with freestanding antimonene (4.01 Å of the calculated lattice constant). The PdTe₂ substrate possesses a chemically stable surface. Sb atoms were fabricated on a PdTe₂ surface at 400 K. The distinct well-ordered structure was found through in situ low-energy electron diffraction (LEED). The atomic structure of ML antimonene was detected by scanning tunneling microscopy (STM) (Fig. 6b and c). First-principles calculations (FPC) based on density functional theory (DFT) were employed to elucidate the experimental results. Antimonene on PdTe₂ substrate was a continuous 2D ML, showing a buckled conformation (Fig. 6d-f). The antimonene layer weakly interacted with the PdTe₂ substrate and was quite inert in air. High-quality epitaxial antimonene with a large bandgap and high chemical stability has potential applications in nanoelectronic devices.

Si substrates were widely used in MBE growth.155-159 The high quality Bi ultrathin films were grown on Si(111) by MBE. Bi films have various microstructures, including hexagonal Bi(111) surfaces, lateral growth of semi-metal Bi films with Bi(001)/ Si(111) interface, and single-crystalline growth of Bi films on Si(111)-7 \times 7. For the preparation of antimonene, bismuthene, few-layer ultrathin Sb and Bi films, different solid substrates have been applied for epitaxy growth, such as Si(111),^{155,157-160} Ag(111),^{83,161} Ge(111),⁹⁰ SiC(0001),⁹⁹ PdTe₂,⁹¹ Bi₂Te₃,¹⁶² Sb₂Te₃(111),¹⁶² Bi₂Se₃,¹⁶³ NbSe₂,⁷³ Bi₂Te₂Se,¹⁶⁴ Bi islands,⁸⁶ oriented pyrolytic graphite (HOPG),74,116 sapphire and MoS2,80 and 2D-Sb grown under ultrahigh vacuum.90 Sb crystals with ultrahigh purity were evaporated with a Knudsen cell at 2-700 Å min⁻¹. The substrate temperature changed from room temperature to 330 °C. The Ge(111) surface was treated by cleaving with an undoped wafer, sonicating in acetone, rinsing with isopropanol and drying under an N₂ flow. The substrate was introduced in an ultrahigh vacuum system, followed by annealing at 600–700 °C for at least 1 h and flashing >800 °C for a few seconds. This process allowed for 2D-Sb epitaxy growth on Ge(111). The single-crystal antimonene films were grown on the MoS₂ surface at a low growth temperature of 200 °C by MBE.⁸⁰



Fig. 6 ML antimonene formed on PdTe₂ substrate. (a) Schematic of the fabrication. (b) STM topographic image (-2.0 V, -10 pA) of large antimonene island on PdTe₂. The inset is the LEED pattern of antimonene on PdTe₂. Six diffraction spots are due to the antimonene (1×1) structure with respect to the substrate. (c) Atomic resolution STM image (-1.5 V, -200 pA) of antimonene with enhanced visibility showing a graphene-like honeycomb. (d) Top view and side view of the buckled conformation of the antimonene honeycomb. (e) Height profile along the red line in (b), showing that the apparent height of the antimonene island is 2.8 Å. (f) Line profile corresponding to the blue line in (c), revealing the periodicity of the antimonene lattice $(4.13 \pm 0.02 \text{ Å})$. Reproduced with permission from ref. 91, Copyright 2017 Wiley.

For the blank sapphire substrates, single-crystal antimonene flakes with large wetting angles were obtained after 300 $^{\circ}$ C of post-growth annealing. The results were in well agreement with the theoretical predictions of the lower interface energies between antimonene and MoS₂. The selective growth of antimonene on the MoS₂ surface was verified on the pre-patterned MoS₂/sapphire substrate.

Bi thin films with a thickness of 6-50 nm were epitaxially grown on an Si(111) substrate in a Varian Gen II MBE growth chamber.⁷⁵ Before loading into the vacuum system, the Si(111) substrate was briefly dipped in a diluted solution of hydrofluoric acid to remove the native oxide and passivate the dangling surface bonds with hydrogen. The substrate was loaded into a high vacuum chamber within 20 min to restrict its re-oxidation because it suffered from high-temperature bakes to reduce environmental contamination and remove any remnants of native oxide. Bi growth was initiated under room temperature at 0.2 Å $\rm s^{-1}.$ The 2D growth parameters were optimized by in situ electron microscopy. Thin layers of antimonene were grown on Ag(111) by MBE.^{83,161} Ag(111) crystals were cleaned via cycles of Ar⁺ sputtering and annealed under high temperature in a preparation chamber. Sb was deposited on the Ag(111) surface from a homemade Knudson cell. The Ag(111) substrate was held at 375 K during deposition and immediately annealed at 550 K for 1 h. The sub-ML Sb deposited on Ag(111) surface formed a layer AgSb₂ surface alloy upon

annealing. The further deposition of Sb on the $AgSb_2$ surface alloy yielded an epitaxial Sb layer, which was identified as antimonene with buckled honeycomb structures. Lei *et al.* prepared bilayer Sb(111) ultrathin films on 3D topological insulator (TI) Sb₂Te₃ and Bi₂Te₃ surfaces *via* MBE.¹⁶² For the epitaxial growth of few-layer, ML ultrathin Sb and Bi(111) films, other TI substrates were employed, such as Bi₂Te₂Se,¹⁶⁴ Bi₂Se₃,¹⁶³ and NbSe₂,⁷³ and Sb(111) thin films were produced on the Si(111) surface by epitaxial growth.¹⁶⁰

Reis et al. prepared bismuthene on an SiC substrate.99 Bismuthene has a Bi honeycomb lattice on the top of the insulating silicon carbide substrate SiC(0001), which acts as a candidate for high-temperature quantum spin Hall materials. Lu et al. reported the nontrivial 2D TI phase of few-layer Bi(110) films by atomic bucking in self-assembly ultrathin Bi(110).74 A cleaved HOPG was loaded into the STM chamber and annealed overnight at 800 K. Before film deposition, the HOPG surface was checked using STM.74,116 High-purity Bi was evaporated by a Ta boat and was deposited on the HOPG substrate at 270 K. Bi nanoislands were grown on an MoS₂ substrate as the basis for antimonene growth.⁸⁶ The samples were in situ prepared under ultrahigh vacuum. Nanostructures were grown by first thermally evaporating Bi onto MoS₂ substrates, followed by evaporating Sb. Märkl et al. experimentally confirmed the realization of van der Waals heterostructures consisting of multiple bismuthene and antimonene allotropes.86 As a new allotrope, 2 ML-α-Sb is

non-trivial topologically and is energetically preferred over 2 ML- β -Sb because of its interactions with underlying Bi islands.

2.2.2. van der Waals epitaxy. Different from unstable BP, 2D group-VA materials (arsenene, antimonene, and bismuthene) were predicted to exhibit high stability and superior physical properties. The synthesis of high-quality ML or fewlayer pnictogen nanomaterials has been researched greatly, involving top-down and bottom-up methods. Currently, facile and efficient methods for the preparation of high-quality ML and few-layered 2D pnictogen nanomaterials are still required. Ji et al. designed the growth of 2D antimonene single crystals via van der Waals epitaxy.93 They reported the van der Waals epitaxy of few-layer antimonene monocrystalline polygons, their atomic microstructure and stability in ambient conditions. The highquality few-layer antimonene monocrystalline polygons were prepared on various (or flexible) substrates based on van der Waals epitaxy growth. Antimonene polygons have a buckled rhombohedral atom structure, consistent with the most stable β-phase allotrope, as predicted theoretically. First-principles and molecular dynamic simulation results prove that compared to phosphorene, antimonene is less likely to be oxidized and has higher thermodynamic stability in an O₂ atmosphere at room temperature. Antimonene polygons have high electrical conductivity and optical transparency in the visible-light range, indicating their applications in transparent conductive electrodes.

The fluorophlogopite mica substrate of $KMg_3(AlSi_3O_{10})F_2$ with an exposed (001) surface was used for van der Waals epitaxy of few-layer antimonene polygons.⁹³ A two-zone tube furnace with separate temperature controls was used. Sb

powder was placed in the source zone (T_1) and heated up to 660 °C to produce Sb vapor. The substrate was placed in the downstream area with a temperature of T_2 (380 °C), and maintained for 1 h. The furnace was cooled to room temperature (Fig. 7a). Mica substrate is suitable for van der Waals epitaxy due to the absence of dangling bonds on its ultra-smooth surface.¹⁶⁵⁻¹⁶⁸ The migration energy barrier of Sb atoms on the mica substrate was small, inducing a high migration rate along the mica substrate and fast lateral growth of 2D antimonene polygons (Fig. 7b). The absence of dangling bonds on the substrate surface is critical for the successful growth of antimonene layers. The characteristics of nonvalent Sb were verified by XPS,⁹⁶ which indicated the absence of chemical bonding between the antimonene layers and mica, consistent with the universal characteristics of van der Waals epitaxy.165 Few-laver antimonene sheets prepared on the substrate exhibited several types of polygonal shapes, such as triangles, hexagons, rhombus and trapezoids (Fig. 7c-f). The well-defined polygons presented high crystallinity. Most of the polygons showed a lateral size of 5-10 mm. The antimonene polygons had a thickness as low as 4 nm (10 atomic layers). A very tiny sheet with a lateral size of \sim 100 nm and a thickness of down to 1 nm were found (Fig. 7g and h), implying ML antimonene characteristics. The crystal growth of layered antimonene on mica was divided into nucleation and lateral growth at different durations (Fig. 7b). In the initial stage, the hot Sb vapor (carried by Ar/H_2 gas) was cooled and deposited on the mica substrate to form the nuclei. Due to the low migration barrier energy, the adatoms on the mica migrated fast to the edge of the initial nuclei, which grew along the chemically passivated surface into layers. Both



Fig. 7 Antimonene polygons prepared on mica substrates via van der Waals epitaxy. (a) Schematic illustration of the sample synthesis configurations. (b) Schematic diagram of van der Waals epitaxy. (c–f) Optical images of typical antimonene polygons with triangular, hexagonal, rhombic and trapezoidal shapes, respectively. The scale bar is 5 mm. (g) AFM image of typical triangular antimonene sheet. The thickness is 4 nm. The scale bar is 1 mm. (h) AFM image of a tiny antimonene sheet. The thickness is \sim 1 nm and the scale bar is 50 nm. Reproduced with permission from ref. 93, Copyright 2016 Nature Publishing Group.

nucleation and lateral growth were verified experimentally by AFM. During the growth period, crystal growth was finished in the first 10 min.

2.2.3. Chemical vapor deposition. Great challenges still exist in the preparation of scalable 2D structures via a controlled manner. Ultrathin nanoplates (NPs) are preferable for studying the conduction dominated by surface states due to their large surface-to-volume ratios. MBE remains the most effective method for precise layer control, but it is difficult and expensive. Yang et al. explored a vapor-solid method to prepare 2D Sb₂Te₃ NPs on the SiO₂ surface with controllable thickness.¹⁶⁹ The growth of high-density single quintuple-layer (QL) Sb₂Te₃ NPs occurred via the vapor-solid process. This process was extended to other 2D structures in the binary sesquichalcogenide family. High-purity bulk Sb₂Te₃ pieces were ground into powders and put in a quartz boat located in the center of a furnace (Fig. 8a and b). The SiO₂/Si substrate was placed ${\sim}12$ cm downstream from the furnace center. A furnace tube was sealed and pumped down to \sim 15 mTorr and flushed with ultra-pure argon several times before growth to remove oxygen. The furnace was moved to the left and was heated to over 500 $^\circ\mathrm{C}$ in 10 min, followed by another 10 min heating. Then, 50-100 sccm argon gas was introduced in the tube. The furnace was moved to the right to position the source quartz boat in the furnace center. Evaporation and growth were initiated. The growth was controlled to within 5 min due to the relative fast deposition of Sb₂Te₃ on the substrate. Then, the furnace was moved away from the source quartz boat and SiO₂/Si substrate to initiate quick cooling to room temperature in 30 min.

In the case of chemical vapor deposition (CVD), the deposition rate is inversely proportional to temperature. To optimize

the growth process, ultrathin layers of Sb₂Te₃ were obtained. Sharp edges and 120° facets were observed, indicating layerstructural rhombohedral lattice crystals of Sb2Te3.170 AFM was used to measure the ML thickness of the Sb₂Te₃ NPs. The line profiling results implied step heights of 0.921 and 1.063 nm (Fig. 8c-f). Unlike ML graphene containing one atom thickness, a single five-atom thick QL of Sb₂Te₃ was \sim 1 nm in Z-thickness. The Ultrathin Sb₂Te₃ NPs were verified to be a single QL, which meant a preferential epitaxy process for Sb₂Te₃. This vaporsolid growth for preparing 2D TI nanostructures opens new opportunities in surface-state studies and applications in lowdissipative electronic systems. 2D layered structures of Bi chalcogenide materials were explored by the CVD method.108 Bi₂Te₃ nanoplates were prepared via vapor-phase growth.¹⁰⁸ High-purity Bi_2Te_3 powder was heated to ~500 °C in a tube furnace and transformed into vapor phase. Ar gas flow was applied to the vacuum tube furnace, which carried the Bi₂Te₃ vapor to the end of the furnace, where a substrate was placed. When the temperature at the end of the furnace is lower than the center part, the molecules in the vapor start to deposit on the substrate and form ultrathin triangular or hexagonal nanoplates.

Ordered and quasi-ordered (Bi, Ag)/Si(111) metastable structures were fabricated by depositing Ag and Bi at a high annealing temperature of 470–500 °C.¹⁷¹ Several (Bi, Ag) oneatomic-layer structures on the Si(111) surface were observed by STM. A 2D spin-split metallic layer on a semiconductor surface has some prospects for spintronic applications. The codeposition of Bi and In onto the Si(111)7 × 7 surface with annealing at 250–550 °C induced the formation of ordered (Bi, In)/Si(111) stable structures.¹⁷² The Bi–In 2D compound on



Fig. 8 (a) Scheme of the furnace used for the vapor-solid synthesis of Sb_2Te_3 NPs. (b) Growth mechanism of the major process sequence for growth of Sb_2Te_3 NPs, including source flow and growth region thermal budget. (c and d) SEM images of the Sb_2Te_3 NPs. AFM images of (e) single-QL Sb_2Te_3 NP and (f) Sb_2Te_3 NP underneath a single-QL region. Reproduced with permission from ref. 169, Copyright 2015 Royal Society of Chemistry.

Si(111) structure served as a potential candidate for spintronic materials with spin-split metallic bands. 2D Bi-rich nanosheets were prepared by evaporative thinning of Se-doped Bi₂Te₃.¹⁷³ Bulk Bi₂Se₃ and Bi₂Te₃ crystals were crushed into a powder with a mortar and pestle. Then nanosheets with the Bi₂Te_{2.9}Se_{0.1} nominal stoichiometry were deposited by catalyst-free physical vapor deposition. Denisov et al. prepared a (Bi-In-Na) 2D compound on the Si(111) surface.174 Experiments were conducted using an Omicron STM and LEED operated under ultrahigh vacuum. After the samples were first outgassed at 600 °C for several hours, the atomically clean Si(111)7 \times 7 surface was *in situ* prepared by flashing to 1280 °C. Bi was deposited from a commercial cell. The deposition rate of Bi was calibrated by using the Si(111) β - $\sqrt{3} \times \sqrt{3}$ -Bi surface (1 ML Bi) as a reference for roomtemperature Bi deposition onto Si(111)7 \times 7, followed by annealing at 500 °C. In-deposition was carried out from a tantalum tube. The deposition rate was calibrated by the formation of an Si(111)4 imes 1-In surface containing 1 ML of In. Na-deposition was conducted using a commercial chromate dispenser. The deposition rate was calibrated using the Si(111) $\sqrt{3} \times \sqrt{3}$ -(Bi, Na) (1/3 ML Na) structure as the reference for the room-temperature deposition of Na onto the Si(111) β - $\sqrt{3} \times \sqrt{3}$ -Bi surface.

2.2.4. Hydrothermal synthesis. Kumar *et al.* reported a cost-effective and wet-chemical growth for the low-temperature large-scale production of Bi nanosheets.¹⁷⁵ Bi(NO₃)₃·5H₂O was taken with water, ethylene glycol and N₂H₄·H₂O in a volume ratio of 6:3:1 in a conical flask. The mixture solution was refluxed under stirring for 8 h at 80 °C. Black precipitates were collected and washed with anhydrous ethanol and water, followed by drying for 6 h under vacuum at 60 °C.¹⁷⁶ Yin *et al.* reported the hydrothermal reaction of

 $Sb(OAc)_3$, disodium 1,4-butanedisulfonate (BDS) and $HClO_4$ to afford plate-like crystals [Sb₂O₂(OH)](BDS)_{0.5}.¹⁰¹ A layered structure was created at 150-175 °C. The architecture consisted of 2D corrugated $[Sb_2O_2(OH)]^+$ layers with linear α, ω -alkane disulfonate anions residing in the inter-lamellar space. 2D antimony sulfide was prepared under hydrothermal conditions.¹⁰⁵ The $[C_8-N_4H_{26}]_{0.5}[Sb_7S_{11}]$ structure consisted of infinite chains of formula $Sb_7S_{11}^{2-}$ linked *via* Sb–Sb bonds into 2D slabs with a thickness of ~ 2.6 Å. In the presence of N,N-bis(3aminopropyl)ethylenediamine, amine and water were mixed with Sb₂S₃ under stirring to fabricate a slurry with the molar compositions of Sb_2S_3 : amine : water (1 : 1 : 30). The slurry was sealed in a Teflon-lined stainless steel autoclave and heated at 473 K for 3 days, followed by cooling slowly at 1 K min⁻¹. The solid products were collected from filtration, washing and drying treatments.

Pradhan *et al.* demonstrated a two-step method to construct large disks of 2D Bi_2Se_3 in the presence of ethylene diaminetetraacetic acid (EDTA) and Cl⁻. EDTA served as a complex agent of Bi(m).¹⁷⁷ Depending on the growth conditions, the 2D Bi_2Se_3 crystals had a flat or spiral surface. As for the seedmediated growth (Fig. 9a), nucleation seeds were prepared on the right batch. After the formation of seeds, the precursor solution in the left batch was kept at a low temperature to restrict early reaction and was slowly injected into the right batch. Consequently, the seeds on right batch grew laterally, and their lateral diameter reached 20–50 µm. The three prominent Raman peaks located at 72, 131 and 174 cm⁻¹ match with the reported A_{g}^1 , E_{g}^2 and A_{1g}^2 vibrational modes of Bi_2Se_3 , respectively (Fig. 9b). Raman spectroscopy mapping on arbitrary crystals implied that the layer number was uniform



Fig. 9 (a) Graphical illustration of the experimental setup for seed-mediated growth. (b) Raman spectrum of arbitrary 2D Bi₂Se₃ crystals. (c) Powder XRD pattern of 2D Bi₂Se₃ crystals. The asterisks denote that the marked peaks may overlap with the known diffraction patterns of 2D Bi₂Se₃. All of the assigned peaks use a three-indices system. For the (0012) states, the Miller index for the *c* axis is 12. (d) TEM image of a grown crystal. Scale bar is 2 μ m. (e) HRTEM image of the crystal and (f) its diffraction pattern. Scale bar of (e) is 5 nm and that of (f) is 5 nm⁻¹. Reproduced with permission from ref. 177, Copyright 2016 Royal Society of Chemistry.

throughout the crystals. The XRD peaks match with rhombohedral Bi₂Se₃ crystals (JCPDS no. 33-0214) (Fig. 9c). The pattern has a strong intensity of {003} family peaks, assigned to a prominent planar crystal facet of {001} planes. In the TEM images (Fig. 9d and e), the crystal structure has hexagonal lattice fringes with a correct lattice spacing of ~2.1 Å between the {110} planes. The diffraction patterns (Fig. 9f) present a clear hexagonal symmetry of spots and single crystallinity. Growth occurred along the (110) direction with the {001} facets serving as the top and bottom surfaces.

2D square-like bismuth oxyiodine (BiOI) nanosheets with a thickness of ~10 nm and exposed {001} facets were prepared *via* a hydrothermal route without surfactants and special solvents.¹¹⁰ Bi(NO₃)₃·5H₂O was dissolved in HNO₃ solution under stirring. KI solution was added dropwise, and the pH was adjusted to 5.0, generating a uniform light-yellow suspension. After agitation, the mixture was transferred to a Teflon-lined stainless steel autoclave that was heated for 6 h at 120 °C and then cooled to room temperature. A light-yellow solid powder was collected through centrifugation and washed with water to remove residual ions. The product was dried for further use. 2D bismuth oxybromide (BiOBr) was prepared and coupled with MoS₂ based on a hydrothermal process.¹⁷⁸ To fabricate MoS₂/ BiOBr, MoS₂ was added to a KBr solution under sonication. $Bi(NO_3)_3 \cdot 5H_2O$ was added to the mixture under stirring for 1 h. The mixtures were transferred to a Teflon-lined autoclave and were heated at 160 °C for 12 h. The precipitates were collected, followed by washing with water and ethanol. Hybridization of MoS₂ with 2D-BiOBr resulted in high photocatalytic activity for the photo-degradation of Reactive Black 5, despite the use of a low-powered energy saving light bulb as the light source. Hydrothermal preparation is cost-effective and can result in wet-chemical growth for the large-scale production of superior 2D layered pnictogen materials, such as 2D layered monoelemental pnictogen (Bi) nanosheets,¹⁷⁵ pnictogen-based binary (Sb₇S₁₁ or Bi₂Se₃),^{105,177} ternary (BiOI or BiOBr),^{110,178} multielemental {[Sb₂O₂(OH)] (BDS)_{0.5}},¹⁰¹ 2D layered materials and hybrids with low-dimensional materials (e.g. MoS₂ hybridized



Fig. 10 (a) XRD patterns of $a-Sb_2S_3$ NSs and $c-Sb_2S_3$ produced by annealing of amorphous NSs. (b) SEM images, (c–e) TEM images, (f) HRTEM images and the corresponding electron diffraction patterns taken on $a-Sb_2S_3$ NSs. Reproduced with permission from ref. 100, Copyright 2018 Elsevier.

with 2D-BiOBr).¹⁷⁸ Low-temperature wet-chemical growth is adopted for the large-scale production of 2D layered pnictogen nanomaterials with high productivity and superior properties.

2.2.5. Solvothermal synthesis. Wang et al. explored the synthesis of 2D amorphous Sb₂S₃ nanosheets (NSs) via a colloidal chemistry approach. Organic long-chain primary amines and oleylamine were mixed with n-dodecylamine or noctylamine, which acted as soft templates to assist the 2D formation of amorphous NSs.¹⁰⁰ Oleylamine was mixed with ndodecylamine or n-octylamine, serving as colloidal reaction solution. No sharp XRD peaks were detected due to the lack of long-range order and amorphous (non-crystalline) characteristics of Sb₂S₃ crystals (Fig. 10a). Broadened peaks indicated the formation of amorphous a-Sb₂S₃. After thermal annealing, a-Sb₂S₃ was transformed into crystalline c-Sb₂S₃. The SEM and TEM images (Fig. 10b-e) showed a-Sb₂S₃ with a 2D sheet-like morphology. EDS analysis of the a-Sb₂S₃ NSs revealed an Sb/S composition close to the theoretical stoichiometry of 2:3. The electron diffraction and HRTEM results are shown in Fig. 10f. Only a diffraction halo was observed, and no lattice fringe was detectable, verifying the non-crystalline feature of a-Sb₂S₃ NSs. In the solvothermal colloidal synthesis, organic amines acted as the soft template to define 2D growth via the coordination of metal cations with amine groups. NSs had distinct 2D features with a thickness of 2-4 nm and dimensions (length \times width) ranging from several hundreds of nanometers to several micrometers.

The solvothermal synthesis of Bi2Se3 nanoplates was explored.108 Poly(vinylpyrrolidone) with high purity was dissolved in ethylene glycol. Bi2O3 powder, selenium powder and EDTA were added to the solution under stirring to form a suspension. The suspension was sealed in a steel autoclave, and heated at 180-220 °C for 24 h. The lateral dimension of the single-crystalline products reached a few tens of micrometers, with a thickness ranging from several to a few tens of nanometers. Bi nanoribbons were prepared from solvothermal synthesis. NaBiO3 · 2H2O was dissolved in glycerol under stirring and transferred to a Teflonlined stainless steel autoclave.¹⁰⁹ After treatment with a pure N₂ gas flow, the autoclave was sealed and maintained at 200 °C for 24 h. Afterwards, the black solid product was collected by filtration, followed by washing with ethanol to remove impurities. 2D organic-inorganic bismuth halides (OIBHs) were prepared from a one-pot solvothermal reaction.¹⁰⁷ (TMP)_{1.5}[Bi₂I₇Cl₂] (TMP: N,N,N',N'-tetramethylpiperazine) had mixed halogens and a unique 2D inorganic anion structure.

2.2.6. High-temperature melting. Wu *et al.* synthesized a $K_3BiAs_6Se_{12}$ single crystal of 2D bismuth selenoarsenate containing crown-shaped anions of $[As_3Se_6]^{3-}$.¹⁷⁹ $K_3BiAs_6Se_{12}$ was prepared using the reaction mixture of K_2Se_3 , Bi, As_2Se_3 and Se powder in a 1 : 1 : 1.5 : 2 molar ratio, which were mixed in an N₂-filled glove box and loaded in a glass ampoule. After evacuation to ~10⁻³ mbar, the ampoule was flame sealed and placed in a computer-controlled furnace. The mixture was heated to 540 °C at 0.5 °C min⁻¹, and left for 5 days. The product was cooled to 100 °C at 3 °C h⁻¹. The product was washed with dry *N*,*N*-dimethyl formamide (DMF) and diethyl ether to form black platelets (40% yield based on Bi). The single crystals were stable

in DMF, pure ethanol and dry air for two months. Chung *et al.* reported 2D super-conductivity in a single crystalline nanohybrid of organic-bismuth cuprate.¹¹² Bi₂Sr₂CaCu₂O_y (Bi2212) super-conductor was obtained by self-flux treatment with Birich melts. This finely ground mixture of metal oxide and metal carbonate precursors, with the Bi/Sr/Ca/Cu nominal composition of 2.4:2:1:2 was heated to 1020 °C and slowly cooled to 800 °C. Excess Bi₂O₃ was used as a flux for crystal growth.

Liu et al. prepared Bi4Ti3O12 (BTO) nanosheets through molten salt synthesis (Fig. 11a).^{180,181} Bi₂O₃ (TiO₂) was used as a Bi (Ti) source. NaCl and KCl were used to provide a high reactive medium. The same molar ratios of Bi2O3 and TiO2 were mixed with NaCl and KCl. After grinding for 1 h in a mortar, the mixture was put into a corundum crucible with a lid, which was heated at 800 °C for 2 h in a muffle furnace at a ramp rate of 5 °C min⁻¹. The products were centrifuged and washed with water and ethyl alcohol to remove residual inorganic salts, followed by drying at 60 °C to obtain BTO nanosheets. Bismuth oxychloride (BOC) showed a layered crystal structure with [Bi2O2]2+ layers interleaved with two slabs of Cl- with BTO (Fig. 11b and c). BTO and BOC grew together to form a composite through a convenient chemical transformation process.182 An in situ chemical transformation was used to form BTO/BOC composites using BTO nanosheets as the substrate and HCl as the chlorine source. The BTO nanosheets were dissolved in HCl solution under stirring to generate a homogeneous suspension. The suspension was stirred for 12 h at room temperature. The products were collected by centrifugation, followed by washing and drying at 60 °C in an oven. HCl was used to control the weight ratios of BTO and BOC in the composites.

XPS spectra were used to describe the surface compositions and chemical states between BTO and BOC (Fig. 11d). The XPS survey spectra evidenced the presence of Bi, Ti and O elements in BOC and BTO/BOC. A new peak of Cl 2p was detected in the BTO/BOC composites. No redundant peak appeared. The Bi 4f peaks were assigned to the characteristic peaks of Bi³⁺. The binding energies of Bi, Ti and O in the BTO/BOC-3 composites had positive shifts compared to the bare BTO, which proved strong interactions at the contact interface between BTO and BOC. In the TEM images (Fig. 11e and f), the BOC NPs with a size of 5-10 nm were well-dispersed on the 2D BTO nanosheet surface without apparent agglomeration. The lattice fringe with an interplanar lattice spacing of 2.72 Å was assigned to the (200) crystal plane of BTO. The lattice fringe of 2.57 Å originated from the (111) crystal plane of BOC (Fig. 11g). EDS peaks for Bi, Ti, O and Cl elements were found in the composites, consistent with the XPS results (Fig. 11h). These results indicated that the BTO/ BOC 2D/0D composites were achieved after molten salt process and chemical transformation.

3. Properties

3.1. Band structures

Bulk arsenic (As) has three common allotropes including metallic gray, yellow and black As. Gray As is the most common



Fig. 11 (a) Schematic diagram of the synthetic process of BTO/BOC 2D/0D composites. Crystal structures of BTO (b) and BOC (c). (d) XPS spectra of BTO and BTO/BOC-3 survey scan. (e) TEM, (f) magnified TEM, (g) HRTEM and (h) EDS images of BTO/BOC-3 composites. Reproduced with permission from ref. 180, Copyright 2018 Elsevier.

and stable phase with layered rhombohedral (β -form) structures (Fig. 12a).¹¹⁸ Layered gray As crystals exist naturally. Gray As is a semimetal material with bands. When heated to 370 K,

a layered orthorhombic α -phase of As arises with a structure similar to that of BP. Orthorhombic (α -phase) As is a narrow-gap semiconductor with a band gap of 0.3 eV. Bulk antimony (Sb)



Fig. 12 (a) Top view of the relaxed group-15 (As, Sb, Bi, and P for comparison) ML allotropes with five typical honeycomb structures (α , β , γ , δ , and ε) and four non-honeycomb structures (ζ , η , θ , and ι). (b) Calculated average binding energies of all the group-15 ML allotropes, which show the energetic stability of the α and β phases of group-15 MLs. (c) Calculated phonon band dispersions of group-VA monolayers for the α and β phases. Reproduced with permission from ref. 118, Copyright 2016 Wiley.

possesses three known allotropes under normal conditions, including gray, black and explosive Sb. Bulk Sb has the same rhombohedral structure as gray As. Among the allotropes, gray Sb is the most stable. Gray Sb and As have typical semimetal characteristics in layered bulk forms. Gray Sb is a layered material. Black Sb is produced upon rapid cooling of Sb vapor, showing an identical structure to red phosphorus. Black Sb has high chemical activity in atmospheric environment. Under vacuum, black Sb can transform easily into stable crystalline gray Sb at 373 K. Explosive Sb often transforms fiercely into gray Sb under mechanical stress or heating. Explosive Sb is probably not an allotrope, but is a mixed form. Bulk bismuth (Bi) has only one stable format. Bulk Bi has a natural layered structure, which is a rhombohedral A7-type structure similar to gray As and Sb. In addition, layered Bi has a feature of metallicity.

Fig. 12 illustrates the stable phases and natural layered crystals. Two stable phases were isolated for P and As, namely the α and β phases. There is only one stable phase for Sb and Bi, namely the β phase. The natural layered crystals of As, Sb and Bi possess the β phase. Derived from bulk phosphorus, As, Sb and Bi, few-layer or ML 2D group-VA nanomaterials are termed phosphorene, arsenene, antimonene and bismuthene. In the case of layered As, Sb, and Bi crystals, arsenene has puckered and buckled ML structures, while antimonene and bismuthene are likely to exhibit buckled forms. The ML structure of 2D group-VA materials is the most stable. Zhang et al. predicted group-VA monolayers with five typical honeycombs and four non-honeycomb structures (Fig. 12a).¹¹⁸ The average binding energies for all possible group-VA ML configurations are shown in Fig. 12b. Based on the calculations, α -phosphorene with a puckered form is the most stable. In the case of arsenene, antimonene and bismuthene ML allotropes, all their β phases with buckled forms have the lowest energies. The three phases of bismuthene (α , β , and ζ) have very close average binding energies. The counterpart bulk material of α -phosphorene ML is BP, which is the most stable form for allotropic bulk crystals under standard conditions. Their counterpart bulk materials (βarsenene, β -antimonene and β -bismuthene) are β phases (rhombohedral layered As, gray Sb and Bi). Only α and β layered phases were experimentally proved in group-VA bulk crystals. The phonon spectra of free-standing group-VA monolayers with puckered and buckled forms were studied by FPC, acting as a criterion to judge structure stability (Fig. 12c). No obvious imaginary phonon mode was found, demonstrating the kinetic stability of the free-standing group-VA monolayers. Currently, α -/ β -phosphorene, β -arsenene, β -antimonene and α -/ β -bismuthene have been synthesized and characterized experimentally.

FPC was used to study the band structures and electronic properties of 2D group-VA materials.183 Especially, the electronic bandgap is an important feature of emerging 2D materials, which guides electronic and optoelectronic applications. Band gaps at different levels of group-VA monolayers for α and β phases can be calculated by theoretical predictions, such as the Perdew-Burke-Ernzerhof (PBE), Heyd-Scuseria-Ernzerhof (HSE) hybrid function, Green's function and screened Coulomb interaction (GW) methods. HSE and GW are reliable in the determination of bandgaps. PBE offers a correct physical picture, consistent with the results from the hybrid density functional theory (DFT) and GW methods. BP belongs to a typical direct-band-gap semiconductor. When BP is thinned to few-layer and ML, it retains a direct band gap.¹⁸⁴ The band gap of phosphorene sensitively depends on the layer number (Fig. 13a and b). The fundamental band gaps of semiconductors are dominated by electron-electron interactions. The optical gap of semiconductors can be predicted using the GW method with the Bethe-Salpeter equation (BSE) based on considerable excitonic effects. Group-VA elemental atoms are heavier than the carbon atom. Spin-orbital coupling (SOC) calculations of phosphorene, arsenene, antimonene and bismuthene can be used to evaluate their potential effects on electronic band structures. Zhang et al. predicted an abrupt transition from semimetallic (or metallic) As and Sb bulk crystals to wide-band-gap semiconductor arsenene and antimonene MLs.154

Arsenene and antimonene suffer from an indirect-to-direct bandgap transition under tensile strain. As predicted, the β phase with a buckled form is the most stable structure among the arsenene, antimonene and bismuthene allotropes.¹¹⁸ Based on FPC, the β phases of arsenene and antimonene monolayers possess 1.76 and 1.65 eV indirect band-gaps at the PBE level. Using the GW method, the calculated results revealed more reliable fundamental bandgaps of arsenene and antimonene, which were predicted to be 2.47 and 2.38 eV, respectively (Fig. 13c).185 The difference between their electronic and optical bandgaps (exciton binding energies) was found to be 0.9 eV for arsenene and 0.8 eV for antimonene. In addition, β-antimonene has a strong SOC effect. The band gap of β -antimonene with SOC is 1.04 eV at the PBE level (1.55 eV at HSE level) in the presence of indirect bandgaps. For the calculated imaginary part of dielectric functions of arsenene and antimonene MLs, optical absorption occurred at 1.6 eV for arsenene and at 1.5 eV for antimonene (Fig. 13d).185

Layered β -Bi crystals are characterized by small density of states around the Fermi level and had semi-metallic properties. The ML structure meant a narrow bandgap semiconductor.^{186,187} Bi is heavier than other group-VA elements. A stronger SOC

affects the band structures of bismuthene. HSE correction applied to PBE states can increase the direct bandgap to 0.80 eV. When the SOC was included, the fundamental bandgap reduced to 0.32 eV. The band structure transformed from direct bandgap into indirect bandgap.¹⁸⁶ Besides the β phase, the α phases of arsenene, antimonene and bismuthene have high thermodynamic stability, regardless of their metastable phases. After PBE (HSE) calculations, their band gaps were determined to be 0.77, 0.37 and 0.16 eV (1.66, 1.18 and 0.99 eV), respectively.¹¹⁸ Besides, α -bismuthene had a direct bandgap and transformed into an indirect bandgap semiconductor with the inclusion of SOC, similar to β -bismuthene.^{186,187} By contrast, the α phases of arsenene, antimonene or bismuthene had smaller bandgaps than the β phases with the most stable states.^{39,188–199}

3.2. Carrier transport

2D group-VA semiconductor nanomaterials have superior carrier transport properties, showing practical uses in electronic or optoelectronic devices. Carrier transport properties can be studied by mobility calculations. Theoretically, the



Fig. 13 (a) Band structures of BP ML calculated with the HSE06 functional (red solid lines) and the mBJ potential (blue dashed lines). (b) Evolution of the direct bandgap as a function of sample thickness. The functions used for structural optimization are shown in parentheses. Reproduced with permission from ref. 184, Copyright 2014 Springer Nature. (c) Band structures of MLs arsenene and antimonene calculated with PBE or GW mode. (d) Calculated imaginary part of the dielectric function ε_2 for arsenene and antimonene MLs with and without the electron–hole (e–h) interactions. Reproduced with permission from ref. 185, Copyright 2017 American Chemical Society.

carrier mobility of 2D materials relies on their intrinsic properties, including effective mass, elastic modulus and deformation potential constant.184 Based on HSE06 calculations, Qiao et al. predicted the mobility of BP, which was hole-dominated, anisotropic and rather high.184 The electron mobility was 1100–1140 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ along the armchair direction and 80 cm^2 V^{-1} s⁻¹ along the zig-zag direction. The hole mobility along the armchair direction was 640–700 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and that along the zig-zag direction reached up to 10^4 cm² V⁻¹ s⁻¹. The hole mobility of BP was higher than that of MoS_2 (200 cm² V⁻¹ s^{-1}),²⁰⁰ benefiting from the extremely small deformation potential (0.15 eV). The carrier mobility of BP has strong anisotropic characteristics due to its high anisotropic atomic structures, which result in big differences in effective mass, elastic modulus and deformation potential constant along the armchair and zig-zag directions (Fig. 14a). The high in-plane transport anisotropy of BP distinguishes it from other typical 2D materials, including graphene, silicone and hexagonal boron nitride. The carrier transport properties of arsenene, antimonene and bismuthene were evaluated by deformation potential methods.^{39,124,185,201-203} The carrier mobilities of α -/ β arsenene, β -antimonene and β -bismuthene reach several thousand cm² V⁻¹ s⁻¹. The electron and hole mobilities were calculated to be 635 and 1700 cm 2 V $^{-1}$ s $^{-1}$ for $\beta\mbox{-arsenene}$ (630 and 1737 cm² V⁻¹ s⁻¹ for β -antimonene).¹²⁴ The SOC effects hardly affected the conduction bands of As and Bi, but led to

changes in the topmost valence band, effective mass and deformation potential. Hole mobility was increased by 25% for the As MLs and 84% for the Bi MLs.

3.3. Mechanical properties

2D group-VA materials possess unique mechanical properties due to their puckered and buckled structures. BP presents special and anisotropic mechanical properties.43,204,205 Based on FPC, the maximum Young's modulus of 166 GPa is along the zig-zag direction,43 and the minimum value of 44 GPa is along the armchair direction (Fig. 14b). Along the armchair direction, BP suffers from strain up to 30%. During deformation of phosphorene in the zig-zag direction, a negative Poisson's ratio was determined in the out-of-plane direction, resulting from its puckered structures.²⁰⁴ The fantastic properties of phosphorene imply its potential as an auxetic material. As testified by theoretical studies,186,206,207 a-arsenene and a-bismuthene have directional elastic behavior. The in-plane stiffness C_x - C_y values are 20–55 N m⁻¹ for As (8.04–22.6 N m⁻¹ for Bi). Clear anisotropic Poisson's ratios for As and Bi were determined, with v_{xy} v_{yx} values of 0.33–0.91 for As (0.33–0.93 for Bi). Along the zig-zag direction, the v_{yx} values are very high for As and Bi. Significantly, the in-plane stiffness affected the robustness of the structures. The Poisson's ratio indicated a variation in electronic structures and possible metal-insulator transitions under tensile strain.



Fig. 14 (a) Effective mass of electrons and holes according to spatial directions. (b) Direction dependence of Young's modulus of phosphorene. Reproduced with permission from ref. 43, Copyright 2014 American Institute of Physics. (c) Thermoelectric figure of merit based on doping density at T = 300 K. Different long-wave relaxation times of phonons are included. The unit of doping density is m⁻². (a and c) Reproduced with permission from ref. 225, Copyright 2014 American Chemical Society. (d) Polar representation for the absorption coefficient $A(\alpha)$ of 40 nm intrinsic BP film, corresponding to normal incident light with excitation energies at a band gap of ω_0 and larger. α is the light polarization angle and $A(\alpha)$ is plotted for two values of inter-band coupling strengths. Reproduced with permission from ref. 227, Copyright 2014 American Physical Society.

The mechanical properties of 2D layered group-VA pnictogen materials were studied by theoretical calculations. The in-plane stiffness values of β -arsenene and β -bismuthene are isotropic, and their *C* values are 58 and 23.9 N m⁻¹, respectively.^{186,206,207} The isotropic Poisson's ratio for As (Bi) has a *C* value of 0.21 (0.33). The in-plane stiffness values for 2D group-VA materials are much smaller than that of other typical honeycomb materials, such as graphene and hexagonal boron nitride with *C* values of 330 and 240 N m⁻¹, respectively.

3.4. Thermal properties

The thermal properties of 2D group-VA materials were theoretically and experimentally studied.208-224 Anisotropic phonon properties in the α phases of phosphorene, arsenene, antimonene and bismuthene facilitated the achievement of asymmetrical thermal conductivity and thermoelectric efficiency.²¹⁰⁻²¹⁴ Based on FPC, Aierken et al. calculated the thermal properties of black and blue phosphorene.²¹⁰ The linear thermal expansion coefficients of BP along the zig-zag and armchair directions are anisotropic, reaching up to 20%. The blue phase is isotropic in thermal expansion. The thermal conductivity in BP was found to be anisotropic due to its orientation-dependent group velocities and phonon relaxation times.²¹⁴ In terms of theoretical calculations, the thermal conductivities at 300 K were 83.5 and 24.3 W m^{-1} K⁻¹ along the zig-zag and armchair directions, respectively. Notably, the electronic conductivity along the armchair direction is much larger than that along the zig-zag direction.²²⁵ The thermoelectric figure of merit (ZT) depends on both thermal conductivity and electronic conductivity. This feature is highly anisotropic for BP because its ZT value along the armchair direction is larger than that along the zig-zag direction (Fig. 14c). The intrinsic ZT value in phosphorene is rather low, but it increases by means of different improved methods.

Zeraati et al. evaluated the phonon dispersion and lattice thermal conductivity of *a*-arsenene through first-principles calculations for anharmonic lattice dynamics and the Boltzmann transport equation for phonons.²⁰⁸ Arsenene has a smaller and more anisotropic thermal conductivity than phosphorene. The room-temperature thermal conductivities of arsenene along zig-zag and armchair directions are 30.4 and 7.8 W m^{-1} K⁻¹, respectively. Due to the puckered structures of arsenene, its thermal conductivity is mainly provided by longitudinal acoustic phonon modes at a temperature over 100 K. Generally, the buckled structures of group-VA materials suggest the isotropic characteristics of their thermal properties. Antimonene was predicted to hold a low lattice thermal conductivity of ~ 15.1 W m⁻¹ K⁻¹ at 300 K,²¹⁵ implying a small group velocity, low Debye temperature and large buckling height. By minimizing the sample size and chemical functionalization, thermal conductivity was properly tuned to be smaller.215,216 Nevertheless, the intrinsic thermoelectric figures of merit for antimonene and bismuthene are not high enough, limiting their potential applications. Besides, their intrinsic ZT values can be effectively increased by n- or p-doping.209,217

3.5. Optical properties

2D group-VA nanomaterials have unique optical properties, which expand their potential applications. Through FPC, the optical adsorption spectra of BP were predicted.184,226 The calculated absorption spectra are anisotropic. Light is linearly polarized in the armchair and zig-zag directions. At the bandgap, the band edge of the first absorption peak was found to slightly decrease with an increase in layer thickness in the armchair direction. The optical adsorption peak was detected at 3.14 eV in the ML, which quickly decreased with an increase in thickness in the zig-zag direction. The optical detection of the crystalline orientation and optical activation of anisotropic transport properties were performed by in-plane linear dichroism. As calculated, phosphorene ML absorbed light between 1.1 and 2.8 eV along the armchair direction.²²⁶ In the same energy range along the zig-zag direction, phosphorene ML is transparent to light, covering the infrared and partial visiblelight regime. By tuning the number of stacking layers, the polarization energy window was tuned in a wide range, showing potential to fabricate smart optical devices. The optical conductivity tensor of BP was studied using the Kubo formula within a low-energy Hamiltonian.227 This method was used to express physical quantities observed in optical experiments. In terms of the calculated results, the optical conductivity of BP was similar to the optical adsorption spectrum and was sensitive to layer number (Fig. 14d).

The optical properties of arsenene, antimonene and bismuthene were studied by calculating their dielectric functions, electron energy loss spectra, absorption coefficients, refractive indices and optical reflectivity in a broad energy range.56,79,87,89,92,98,108,228-242 As confirmed, the optical properties of antimonene are suitable for its use in ultraviolet optical nanodevices, micro-electronic devices and solar cells.²²⁸ Based on the calculation results, the dielectric functions were negative, namely 5.1-9.0 eV (6.9-8.4 eV) for aantimonene (\beta-antimonene). The results illustrated its metallic characters in the UV part of electro-magnetic spectra. The electron energy loss spectra indicated the plasmon energy of ~ 9 eV, revealing its metallic behavior based on light refection. The refractive indices were close to 2.3 for α-antimonene and 1.5 for βantimonene at zero energy limit and scaled up to 3.6 in the ultraviolet region. When the magnitude and nature of bandgaps are required to be correctly reproduced, DFT band structure calculations only give superficial information on the optical properties of materials. Before the optical applications of 2D group-VA materials, theoretical predictions are required and often arise from calculations of dielectric functions based on random phase approximation. Currently, the complex dielectric functions, concomitant refractive indexes, absorption coefficients, electron loss spectra and optical reflectivity were reported in the energy range of 0-21 eV.228 The absorption process is expected to start in the infrared part of the spectrum and reach the maximum in the UV region. In the case of β -Sb, when the polarization direction of incident light is out-of-plane, the reflectivity in the visible region is high, but absorption is nearly negligible. Based on calculations, β-Sb is a polarization transparent material.²³⁰ Antimonene exhibits promising uses in opto-electronic devices, such as smart solar

3.6. Magnetic properties

The magnetic properties of layered nanomaterials depend on the volume, surface and step atoms of 2D nanostructures.²⁴³ Anisotropic magnetic properties are attractive for memory device applications, where nanomaterials are used as ferromagnets. Isotropic nanostructures of magnetic metals (Fe, Co and Ni) are generally superparamagnetic at room temperature due to nanosized confinement effects. An effective strategy to improve magnetic anisotropy is to form magnetic nanocrystals with structural anisotropy. For 2D layered group-VA nanomaterials, the doping of transition metal atoms (Ti, V, Cr, Mn, Fe, and Co) can generate magnetism in α-phosphorene.²⁴⁴⁻²⁴⁸ Other atoms (H, B, C, O, Si, S, Ge, and Sn) and gas molecules (NO and NO₂) can produce magnetic states in arsenene.²⁴⁹⁻²⁵⁷ Through FPC, the adsorption of NO and NO₂ on phosphorene had higher adsorption energies compared with other gas molecules (CO, CO₂, NH₃, and N₂).²⁵⁸ NO and NO₂ adsorption led to a magnetic moment of 1 $\mu_{\rm B}$. Among the adsorption of different gases on buckled arsenene ML, NO_x adsorbents had the largest charge transfer, showing a greater change in conductivity.257 Only the adsorption of NOx produced a magnetic moment of 1 $\mu_{\rm B}$. Theoretical calculations indicated that defects affect the electronic properties of 2D layered group-VA materials and produce magnetism in nonmagnetic pristine phosphorene, arsenene and antimonene.²⁵⁹⁻²⁶⁴ Typical point defects in arsenene and antimonene were studied.263 Most of the defective configurations retained indirect bandgaps with reduced bandgap values, and most of the single vacancy defects possessed magnetic moments due to their dangling bonds.

Abid et al. reported the magnetic properties of zig-zag arsenene nanoribbons (ZAsNRs).265 The edge magnetism for different magnetic configurations of ZAsNRs was investigated to remove instabilities. A transition was observed from the nonmagnetic to magnetic edge states. An intra-edge antiferromagnetic semiconducting ground state was found. To tune the edge states, strain engineering was applied on the magnetic ground states. At a critical value of compressive strain (-6%), a transition from magnetic edge states to nonmagnetic ones occurred (Fig. 15a). The geometrical structures and chemical termination of arsenene nanoribbons had obvious effects on their magnetic properties.²⁶⁶ Using the DFT method, the normal or one-atom terminated zig-zag nanoribbon was a weak antiferromagnetic semiconductor due to the magnetic interactions between the edge states. In the case of bare ZAsNRs, tensile strain stabilized the antiferromagnetic states with enhanced magnetic moments. Liu et al. evaluated the magnetic properties of arsenene that was functionalized by 3d transition-metal (TM) atoms.²⁶⁷ The pristine arsenene is a nonmagnetic material, but its dilute magnetism can be produced upon chemisorption of TM atoms. Magnetism is mainly due to TM adatoms and magnetic properties can be tuned through moderate external strain. TM-adsorbed arsenene is a superior candidate for



Fig. 15 (a) Evolution of the band structures of ZAsNRs for different compressive strains. Red lines represent edge states. Dashed lines represent the Fermi level. Reproduced with permission from ref. 265, Copyright 2017 Elsevier. (b) Bandgap of 2D phosphorene as a function of strain ε_x applied in the zig-zag direction. Five strain zones were identified for ε_x based on distinct band structures. Zones I, II, III, IV and V correspond to direct (d), indirect (in), direct, indirect and direct gaps, respectively. Critical strains for the gap transition are -10.2%, -2%, +8% and +11.3%. The gap closes at $\varepsilon_x = -13\%$. Reproduced with permission from ref. 272, Copyright 2014 American Physical Society. (c) Changes in valence-band top and conduction-band bottom with increase in biaxial tensile strains. Reproduced with permission from ref. 154, Copyright 2015 Wiley. (d) Electron mobility of ML phosphorene for biaxial strain at room temperature. Reproduced with permission from ref. 273, Copyright 2014 American Chemical Society. (e) Schematic band structure, spin and charge current in phosphorene channel of $F_{\rm c}$ $< F < F_{M}$. Letter "I" stands for insulating. Reproduced with permission from ref. 275, Copyright 2015 American Chemical Society.

promising applications in nanoelectronic and spintronic devices.

Min *et al.* evaluated the magnetic properties of adsorbed arsenene ML with nonmagnetic metal atoms based on FPC.²⁶⁸ Magnetism was found for Al and Ga adatoms. By studying the magnetic interactions between moments induced by Al and Ga adatoms, p–d exchange-like p–p hybridization in the ferromagnetic states was found. When the distance of Ga–Ga or Al–Al increased, the ferromagnetic interactions were extremely depressed. This phenomenon was explained using the

Heisenberg model. Al- or Ga-adsorbed arsenene is a superior candidate for application in spintronic devices. Xu et al. explored the influence of vacancies and nonmetallic atoms on the magnetic properties of buckled arsenene.269 Because of the formation of one nonbonding p-electron (from dopant C, Si) or a neighboring As atom (around O, Si and vacancies), a doping (C, Si, O, and S) atom and a vacancy induced a magnetic moment of 1.0 $\mu_{\rm B}$ in buckled arsenene. The magnetic coupling between moments caused by two (C, Si, O, and S) atoms is longrange anti-ferromagnetic. Based on the calculated density of states and spin density distribution, p-p hybridization interactions involve polarized electrons and are responsible for magnetic coupling. Magnetism in buckled arsenene can be engineered via vacancies and substitutional doping of nonmetallic atoms. Kadioglu et al. revealed that point defects modified the magnetic structure of 2D ML structural Bi.270 The interactions between foreign adatoms and bismuthene structures comprised magnetic structures. Localized states in diverse locations of bandgaps and resonant states in the band continua of bismuthene were induced upon the adsorption of different adatoms, which modified its magnetic properties. Dai et al. investigated the magnetic properties of Fe-doped and defecttuned antimonene systems.²⁷¹ A large magnetic moment was obtained in defect systems. Stable ferromagnetism was obtained in the Fe-doped system. Due to the presence of intrinsic vacancies, Fe-doped antimonene with anti-ferromagnetism order is not suitable for practical applications in spintronics nanodevices.

3.7. Electronic properties

2D layered group-VA materials have functional nanostructures and tunable electronic properties under different conditions of strains, electric fields and defects. When an externally compressive strain was applied along the zig-zag direction of phosphorene, its band gap increased and then decreased with an increase in strain (Fig. 15b), suggesting that the bandgap of phosphorene is sensitive to strain.²⁷² The bandgap reached the maximum with a critical tensile strain of 4% in the zig-zag direction. A similar bandgap change was determined under an external strain applied along the armchair direction. Under external strain, the effective mass of phosphorene causes dramatic transformation. The favorable direction of electron transport was switched with applied biaxial strain.273 Electron mobility along the zig-zag direction is much larger than that along the armchair direction, but hole mobility is not sensitive to the applied strain. An applied electric field tuned the electronic properties of phosphorene. Under an external electric field, the bandgap of few-layer phosphorene decreased (0.22 eV) with an increase in the electric field.²⁷⁴ ML phosphorene had a slight decrease (0.08 eV). By applying an external electric field, a specific band inversion was induced to acquire topological states.²⁷⁵⁻²⁷⁹ Arsenene and antimonene had an indirect-to-direct bandgap transition under small biaxial strain.¹⁵⁴ Under 0-3% biaxial strain, the minimal conduction band of buckled arsenene was retained in the Brillouin zone halfway between the G and M high-symmetry points. Upon tensile strain up to 4%, the

indirect-bandgap buckled arsenene was changed into a directbandgap semiconductor. Under tensile strain of 4–12%, arsenene maintained a direct-bandgap characteristic of semiconductors (Fig. 15c).

The electronic properties of few-layer or ML allotropes of arsenene, antimonene and bismuthene were studied under different conditions of strain, electric field and defects by means of theoretical calculations.186,206,230,263,266,280-290 Antimonene has electronic band characteristics similar to that of arsenene under biaxial tensile strain.281 Both arsenene and antimonene have a changing trend from an indirect to a direct bandgap semiconductor. Both of them are strained and present direct band structures. Electronic excitation becomes feasible and has lower phonon energies. The merits of arsenene and antimonene endow them promising applications in optical devices. The electronic band structures of arsenene and antimonene were modulated by strain and strain, resulting in a topological insulator transition.194,291 Theoretical studies suggested that strain drives normal insulators of arsenene and antimonene to novel topological nontrivial 2D materials (Fig. 15e).²⁷⁵ According to theoretical calculations, defects impact the electronic properties of 2D layered group-VA materials to yield magnetism in nonmagnetic pristine phosphorene, arsenene and antimonene.259-264 Scientists have studied the electronic band structures and bias-dependent transport properties of defective phosphorene systems. The bandgap is closed in single-vacancy phosphorene, but it reappears in the divacancy system. Vacancy defects greatly increase the current of phosphorene-based devices. Most defective configurations retain indirect bandgaps with reduced bandgap values. The defects in antimonene cause a transition from an indirect bandgap to a direct bandgap. Most single vacancy defects carry magnetic moments because of their dangling bonds. A single vacancy in antimonene endows it with metallic character. Four divacancies retained the semiconducting characters of antimonene with reduced bandgaps.263,283,292

4. Functional nanostructures

4.1. Heterostructures

2D group-VA nanomaterials can be modified to construct functional nanostructures. These functional nanostructures involve heterostructures, doping, adsorption and surface functionalization of 2D group-VA materials and pnictogencontaining 2D hybrids (Table 2). van der Waals heterostructures consist of different MLs free of dangling bonds. Previous studies reported van der Waals hybrid heterostructures based on 2D group-VA materials, such as arsenene/ graphene,293,294 antimonene/graphene,295-297 antimonene/ arsenene/WSe₂,²⁹⁹ GaAs,²³⁷ arsenene/GaS,²⁹⁸ arsenene/ MoS_2 ,^{236,300} β -As/MX₂ (TMDs),³⁰¹ arsenene/silicone,²³⁵ antimonene/germanene,238 arsenene/C3N,234 arsenene/Cd(OH)2,302 arsenene/Ca(OH)₂,³⁰³ O-arsenene/Cs₂CO₃-antimonene,³⁰⁴ and arsenene/FeCl₂.³⁰⁵ After theoretical and experimental studies, van der Waals heterostructures show superior electronic and optical properties compared to individual components. The formation of van der Waals heterostructures integrates the Table 2 Summary of 2D group-VA nanomaterials with functional nanostructures

Nanostructures	Properties	Potential applications	Ref.
Arsenene/graphene heterostructure	Interlayer coupling, tuning Schottky barrier	Ultrathin, nano-, optoelectronics	293 and 294
Antimonene/graphene	Strain, tunable electronic, Schottky	Nano-, optoelectronic devices	295–297
Arsenene/antimonene EFTs	Electron, hole mobility electronic	Ultra-scaled device in sub-10 nm	124
Hexagonal arsenene/antimonene	Many-body effect, carrier mobility	Nano-, optoelectronics, electronics	185
Arsenene-based heterostructure	Excellent power conversion	Photocatalysis, photovoltaics	309
Antimonene-based heterostructure	Biaxial strain, tunable electronic structure	Infrared detector, optoelectronics	310
Bismuthene/metal contacts	Interfacial property of ML contact system	Metal electrode in ML devices	311
Antimonene/GaAs heterostructure	Interface effect, electronic, optical property	Optoelectronics, solar cells	237
Arsenene/GaS vdW heterostructure	Tunable structural and electronic property	Photocatalysts, in valleytronics	298
Arsenene/WSe ₂ vdW	Electric-field tunable electronic	Nano-, optoelectronics	299
heterostructure	structure	, 1	
Arsenene/MoS ₂ vdW	Type-II, electronic structure	Ultrathin, nano-, optoelectronics	300
heterostructure	transition	, , , <u>,</u>	
Arsenene/MoS ₂ heterostructure	Novel electronic and optical conductivity	Improve MoS ₂ in optoelectronics	236
β -As/MX ₂ heterostructures	Tunable, diverse electronic property	Photoelectric devices	301
Arsenene/silicene heterostructure	Novel electronic and optical property	Nanoelectronics, optoelectronics	235
Antimonene/germanene composites	Structural, electronic and optical property	Optoelectronic applications	238
Black As/phosphorus ML	Direct bandgap, high carrier mobility	Promising 2D solar cell donors	312
Arsenene/BP type-II LHS	Superior electronic property	Photoelectronics, photocatalysis	313
Arsenene/C ₃ N vdW heterostructure	Tuning electronic and optical property	Nanoelectronics, photovoltaics	234
Arsenene/Cd(OH) ₂ heterostructure	Strain tunable electronic, photocatalytic	Photocatalysts for water splitting	302
Arsenene/Ca(OH) ₂ heterolayer	Electric field modulation, band alignment	Multi-functional photoelectronics	303
O-arsenene/Cs ₂ CO ₃ -antimonene	Type-II energy band alignment, p-n	Optoelectronic nanodevices	304
heterostructure	junction, 2D p–n/p–n heterostructure		
Arsenene/FeCl ₂ vdW	Electric field effect on spin splitting	Spintronic devices	305
heterostructure	1 1 0	1	
Fe-doped antimonene	Tunable electronic, magnetic property	Fe doping and defect complex	271
Fe, V, Ti-doped arsenene	Mechanical property, pristine, doped ones	Applied strain, plastic property	207
Co-doped arsenene/antimonene	Tunable magnetism, half-metallic behavior	Co-doping, strain, electronic devices	317
Li, Na-adsorbed ML antimonene	Anode material, high capacity and diffusion	Li/Na–air battery, supercapacitor	328
Li-intercalated, hole-doped arsenene	Realize 2D superconductivity	Nanoscale superconductor	321
Co/antimonene interfaces	Schottky potential barrier, spin polarization	Spin diodes, spin FETs	327
X-adsorbed arsenene (X: Al, Ga)	Ferromagnetic state, magnetic coupling	Spintronic devices	268
Metal adatoms on arsenene	Half-metal, narrow gap spin- semiconductor	Spintronics, magnetic materials	318
Half/non-metal doped arsenene	Unexpected band structure	Engineering, nanoelectronics	324
3D TM atom-adsorbed arsenene	Tuned magnetic, enriched electronic property	Electronic, spintronic materials	267
3D TM atom-doped arsenene	Structural, electronic, magnetic property	Spintronics, magnetic storage devices	256

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Table 2 (Contd.)

Nanostructures	Properties	Potential applications	Ref.
3D TM atom-doped arsenene	Magnetic property, electronic structure	Doped arsenene nanosheets	255
3D TM-doped antimonene	Spin-dependent electronic structure	Dopant character, in spintronics	319
TM-doped arsenene nanosheets	Tunable electronic structure, magnetism	New-type 2D nanosheets materials	252
n-, p-type doping of antimonene	Reduce band gap, shallow donor state	Electronics, optoelectronics	323
O/S-doped arsenene or antimonene	Efficient p-type doping, tunable band gap	Electronic, optoelectronics	304
Light atom-adsorbed arsenene	Electronic structure and magnetism	Functionalize electronic structure	254
Atom-doped ML arsenene	Diverse electronic, magnetic	Electronics, optoelectronics,	253
Atom-doped buckled arsenene	property Stability, electronic structure,	spintronics Vacancy, nonmetallic atom-doping	269
II	magnetism	De ble dit de contello construire	225
H-arsenene-F nanosneets	Ashieven to the dening stable hand	Double-side decorated nanosneets	325
CS ₂ CO ₃ -doped arsenene or	Achieve n-type doping, stable band	Electronic, optoelectronics	304
Itale deped area arconone	gap Largo magneto entical offect	Magnete entirel device enplications	240
Hole-doped buckled arsenene	Hole-doping and strain on	Magnetic device applications	322
Adatom/molecule-adsorbed	Atomic structure, physical,	Nonmagnetic semiconductors	250
Atom/molecule-adsorbed	Adatoms, molecule for physical	Magnetic, half-metallic characters	329
Atoms-doped 2D arsenene	Electronic structure, magnetic	Group IV/VI atoms-doped	320
Alloyed, doped arsenene sheets	property Unexpected electronic structure	nanosheets Mechanical sensor, spintronic	249
Arsenene with impurity doping	Tunable electronic structure,	devices Electronics, spintronics,	251
NH ₂ /NO ₂ -adsorbed arsenene	magnetism High affinity, electronic charge	optoelectronics Modified conductivity, hinding	331
	transfer	Mounea conductivity, binanig	001
CO-doped antimonene	Electric field improved sensitivity of CO	Collect and storage of CO gas	332
SO ₂ /NO ₂ -adsorbed on arsenene	Adsorption energy, distance, charge	Excellent SO ₂ and NO ₂ gas sensors	333
Molecule-adsorbed on antimonene	Effects on oxidation tendency and stability	Growth, storage and applications	334
Molecule-adsorbed on antimonene	Susceptibility of electronic property	Sensing material for gas detection	335
Molecule-doping ML arsenene	Modulating electronic, optical property	n-, p-type semiconductors, photodiodes	239
Arsenene with molecular adsorption	Control carrier, structural stability	Create arsenene p–n junctions	330
2D binary XBi (X: B, Al, Ga, In)	Topological insulating phases	Fundamental studies, applications	187
As_mSb_n seamless LHSs	Bandgap engineering, high carrier mobility	Appealing materials for devices	314
TM@AsH (TM: Cr, Mo, Cu)	Unique QAH effect, tunable quantum state	Nanoelectronics, spintronics	347
AsX (X: F, OH, CH_3) ML	Large bulk bandgap, light absorption	Transport devices, photovoltaics	348
2D arsenene oxide	Large-gap quantum spin Hall insulator	Designing topological quantum devices	354
Partial oxidized arsenene	Tunable direct bandgap semiconductor	Infra light emitter, photovoltaics	353
Functionalized Bi/Sb bilayer film	Robust 2D TI, methyl- functionalization	Topological phenomena,	349
Surface of Bi tellurohalides	Giant Rashba-type spin splitting	Ideal 2D electron systems	359
2D S/O type antimonene	Tunable electronic, mechanical,	Structure complexity, wide	326
LHS based on antimonene	Better contact, high on/off ratio	ML-trilayer LHS FETs, power	337
Copper-bismuth nanosheets	Electronic and electrochemical	devices Current electrodes in lithium-ion	351
Bismuth telluride 2D crystal	property Localized shallow band, become	batteries Semiconductor, high electric	352
·····	metallic	conductivity	

characteristics of individual components with enhanced and novel properties to explore electronic and optoelectronic devices. The phosphorene/TMD hetero-bilayer has a semiconductor characteristic, and its bandgap was reduced under vertical electric field.³⁰⁶ In the case of the phosphorene/MoS₂ heterobilayer, its power conversion efficiency reached up to 17.5%. Wang et al. performed theoretical studies on graphene/ phosphorene/graphene van der Waals heterostructures.³⁰⁷ The thermionic transport barriers were tuned by adjusting the layer number. There is weak thermal conductance across noncovalent structures. Layered van der Waals structures are potential candidate for applications in solid-state energyconversion devices. The GeSe/phosphorene van der Waals p-n heterostructure has type-II band alignment and an indirect bandgap.³⁰⁸ Under external strain, there are indirect or direct insulator-metal transitions and spontaneous electron-hole charge separation. GeSe/phosphorene heterostructures have great prospect in optoelectronic devices.

Except for phosphorene,^{37,38} 2D group-VA materials (arsenene/antimonene/bismuthene) act as building blocks for

van der Waals heterostructures.^{293-305,309-313} The structural and electronic properties of arsenene-based hetero-structures were studied. A linear Dirac-like dispersion relation exists in arsenene/graphene heterostructures. By tuning their interlayer distance, there is a transition from a p-type Schottky barrier to an n-type Schottky barrier, which facilitates the integration of arsenene and graphene with tunable functions.^{293,294} In arsenene/silience heterostructures, the p-type Schottky barriers were retained with small bandgaps, which were opened with a linear changing trend by tuning the interlayer distance.235 After the interfacial coupling of arsenene with FeCl₂, spin splitting appeared at the minimum conduction band of arsenene, with a maximum splitting energy of 123 meV in the arsenene/FeCl2 van der Waals heterostructure configuration.305 Various types of van der Waals heterostructures, such as antimonene/graphene,^{295–297} arsenene/antimonene,124,185 antimonene/germanene,²³⁸ arsenene/BP,³¹³ and antimonene/ hexagonal boron nitride,310 were theoretically predicted (Fig. 16a). Antimonene/silience had a p-type Schottky barrier with sizeable bandgaps opened at the Dirac points.



Fig. 16 (a) Diagrams of van der Waals (vdW) heterostructures on antimonene ML. (Left) Antimonene ML. (Middle) Graphene, h-BN and arsenene ML. (Right) Relative vdW heterostructures assembling with monolayers. Reproduced with permission from ref. 310, Copyright 2016 Royal Society of Chemistry. (b) Top view of the optimized atomic structures of GaAs(111) surfaces and Sb/GaAs heterostructures. Perfect, reconstructed and hydrogenated surfaces of (a–c) GaAs(111)A and (d–f) GaAs(111)B. Sb ML on perfect, reconstructed and hydrogenated surfaces of (g–i) GaAs(111)A and (d–f) GaAs(111)B. Sb ML on perfect, reconstructed and hydrogenated surfaces of (g–i) GaAs(111)A and (d–f) GaAs(111)B. Sb ML on perfect, reconstructed and hydrogenated surfaces of (g–i) GaAs(111)A and (d–f) GaAs(111)B. Sb ML on perfect, reconstructed and hydrogenated surfaces of (g–i) GaAs(111)A and (d–f) GaAs(111)B. Sb ML on perfect, reconstructed and hydrogenated surfaces of (g–i) GaAs(111)A and (d–f) GaAs(111)B. Sb ML on perfect, reconstructed and hydrogenated surfaces of (g–i) GaAs(111)A and (j–l) GaAs(111)B. Reproduced with permission from ref. 237, Copyright 2017 Royal Society of Chemistry. (c) α -AsP/GaN type-II semiconductor heterojunction. The schematic drawing for the type-II donor–acceptor band alignments between α -AsP and GaN is based on the HSE06 level. The contour plot shows power conversion efficiency vs. donor bandgap or conduction band offset. Reproduced with permission from ref. 312, Copyright 2016 Elsevier. (d) Color online top (up panel) and side (down panel) views of the different possible stacking configurations for arsenene/Ca(OH)₂ heterostructures: (a) α -stacking, (b) β -stacking and (c) γ -stacking. Optimal interlayer distances are indicated. Reproduced with permission from ref. 302, Copyright 2017 Royal Society of Chemistry.

Antimonene/graphene had a Schottky-to-Ohmic contact transition induced by compressive strain. Different from the indirect bandgap of antimonene and gapless characteristic of germanene, antimonene/germanene van der Waals heterostructures had a remarkable bandgap opened with a feature of direct bandgaps. The fabrication of stacking van der Waals heterostructures can act as a promising strategy to tune the electronic properties of 2D layered group-VA nanomaterials.

Different from the vertically stacked van der Waals heterostructures, the lateral heterostructures of 2D group-VA nanomaterials are connected in-plane by covalent bonds with atomically clean and sharp interfaces. The lateral heterostructures have potential to regulate the ultimate thickness of heterostructures for electronic and optical device applications. Arsenene and antimonene can be used as building blocks to assemble lateral heterostructures. Compared with pristine As and Sb monolayers, freestanding As/Sb lateral heterostructures with zig-zag interlines and the stitching of As/Sb monolayers inplane have high stability and intrinsic direct energy gaps without modulations.³¹⁴ Lateral heterostructures (arsenene/BP) were linked by covalent bonds to fabricate a type-II band alignment, which enhanced charge carrier separation spatially.³¹³ High charge carrier mobility often depends on the width of the building blocks (arsenene and antimonene). 2D group-VA nanomaterials with lateral heterostructures have high electronic and optoelectronic properties, superior to other types of heterostructures. 2D group-VA pnictogen materials can form various hybrid heterostructures by combination with metals,³¹¹ semiconductors, 237,298 TMDs, 236,299-301 2D inorganic nanomaterials,302-305 etc. ML bismuthene underwent metallization upon contact with metal electrodes due to strong interactions.³¹¹ ML bismuthene formed an n-type (p-type) Schottky contact with Ir/Ag/Ti (Pt/Al/Au) electrodes. The tunable interfacial properties of ML bismuthene-metal contacts render them promising application as metal electrodes in ML bismuthene devices.

Arsenene (β -As) can form heterostructures with TMDs (WSe₂, WS₂, MoS₂, and MoSe₂), showing tunable electronic properties through FPC. $^{\tt 236, 299-301}$ Arsenene/MoS $_2$ and arsenene/WSe $_2$ van der Waals heterostructures underwent a transition from type-II to type-I (then from type-I to type-II) under an external electric field. Engineered arsenene/MoS2 heterostructures consisting of two MLs MoS₂ and arsenene had novel electronic and optical conductivity. Arsenene-based heterostructures paired with MoS₂ and tetracyano/tetracyano naphtho quinodimethane formed type-II band alignments, which were used as catalysts for photocatalytic water splitting and photovoltaics with high power conversion efficiency ($\sim 20\%$).³⁰⁹ Wang et al. studied the Sb/GaAs 2D/3D van der Waals heterostructure.237 This unique heterostructure without constraint of lattice matching is suitable for achieving improved electronic and optoelectronic properties. van der Waals interactions are crucial for the stability of Sb/GaAs heterointerfaces. The interfacial coupling strength and band structural characteristics of the heterostructures were affected by interface structures (Fig. 16b). The stable Sb/GaAs heterostructures had a type-II band alignment with small bandgaps of 0.71-1.39 eV compared with the

independent Sb ML and GaAs substrates. Similar to arsenene/ GaS van der Waals heterostructures,²⁹⁸ the Sb/GaAs van der Waals heterostructures had carrier separation and high optical absorption coefficient in the visible-light range. Thus, the Sb/ GaAs heterostructure may be a superior candidate for application in optoelectronic devices, especially solar cells and photocatalysts for water splitting.

The suitable electronic structures of α-AsP enabled the generation of perfect type-II semiconductor hetero-junctions with GaN (Fig. 16c), which boosted the separation and transport of photo-generated carriers with the assistance of built-in field and high mobility.³¹² α-phase few-layer As-phosphorus alloys were prepared, paving the way to realize black As-phosphorus ML donors. Arsenene/Ca(OH)2 van der Waals heterostructures showed strain-tunable electronic and photocatalytic properties (Fig. 16d).³⁰² Electric field modulations of band alignments in arsenene/Ca(OH)₂ heterobilayers were used for multifunctional device applications.³⁰³ The electronic and optical properties of arsenene/C₃N van der Waals heterostructures were regulated by an applied vertical strain and external electric field, showing superior light-harvesting performance.234 By surface charge transfer doping of arsenene/antimonene heterostructures, atomically thin p-n/p-n nanodevices were explored.304 A type-II energy band alignment was produced in O-arsenene/Cs2CO3antimonene heterostructures, which extended light absorption into the near-infrared region and promoted the spatial separation of photo-generated electron-hole pairs.

4.2. Doping

Besides heterostructures, doping with specific species is another way to develop functional nanostructures of 2D group-VA nanomaterials. The electronic structures and properties of 2D group-VA nanomaterials can be altered by doping metallic or nonmetallic agents. Compared to traditional substitutional and interstitial doping in a lattice, the deposition of a specific atomic or molecular layer on the surface of 2D group-VA nanomaterials is an efficient strategy, which tunes or optimizes the electronic and magnetic properties for specific applications (Table 2). The physicochemical properties of the doped counterparts depend on the dopant compositions and concentrations. Alkali metals exhibit small electron affinities and transfer electrons to BP as dopants. K was deposited on fewlayer BP via an in situ surface doping technique.315 Based on FPC, the bandgap of phosphorene was tuned by this type of electron doping. With an increase in K doping, the valence band was shifted down and the phosphorene bandgap decreased. Few-layer BP was transformed from a semiconductor to a bandinverted semimetal by K doping. To tune the type of dominant charge carriers in BP, Cu was deposited on the surface of BP or intercalated between BP layers.316 The Cu adatoms deposited on BP by sputtering and integrated in field effect transistors (FETs) induced a shift in threshold voltage. After Cu deposition, the BP channel was shifted from p-type to n-type at room temperature.

According to FPC, Fe-doped antimonene had tunable electronic and magnetic properties.²⁷¹ In the Fe-doped system, a large magnetic moment and stable room-temperature

ferromagnetism were detected. The simultaneous strong orbital hybridization (p–d) and spin–orbit interaction induced significant spin splitting around the Fermi level. There was a transformation from narrow band-gap semiconductor to semimetallic material. When two intrinsic vacancies are introduced into Fe-doped antimonene, anti-ferromagnetism order appears, which limits its use in spintronic devices. DFT was used to study the mechanical properties of pristine, Fe-, Ti- and V-doped arsenene.²⁰⁷ By applying uniaxial and biaxial strains on

the pristine and doped arsenene, the Young's and bulk moduli were studied. The elastic modulus of the doped arsenene was smaller than that of the pristine arsenene, but the inharmonic region of the pristine arsenene was larger than the doped arsenene. The plastic properties of pristine and doped arsenene were studied. Upon an increase in applied strain, the second critical strain as the beginning of plastic behavior decreased due to doping. The coexistence of Co-doping and strain could control the spin states of arsenene and antimonene structures



Fig. 17 (a) Band structures of B-, C-, N-, O- and F-doped arsenene. For distinction, the bands due to dopants are indicated by red dotted lines. B-, C-, N-, O- and F-doped systems, where the isosurface corresponds to 0.003 e $Å^{-3}$. Yellow (blue) indicates charge accumulation (depletion). Reproduced with permission from ref. 324, Copyright 2015 IOP Publishing. (b) Spin density distribution of two (a) Ti-, (b) V-, (c) Cr-, (d) Mn- and (e) Fe-doped arsenene nanosheets with the most stable doping configuration. Purple and yellow isosurfaces correspond to the majority and minority spin densities, respectively. Green and gray balls represent As and the doping TM atoms, respectively. Reproduced with permission from ref. 317, Copyright 2018 Royal Society of Chemistry.

(Fig. 17).³¹⁷ The unstrained Co-doped arsenene or antimonene structure was nonmagnetic. Under strain, the magnetic moment abruptly increased to about 2 $\mu_{\rm B}$. The emergence of magnetism was reflected by the reduction in the interactions between Co and neighboring atoms by strain, causing the spin-splitting of the Co-3d states. Upon magnetism transition, modification of the electronic properties of arsenene and antimonene occurred under strain, showing novel half-metallic behaviors. Considering the remarkable charge transfer from adatoms to arsenene, metallic states were found in Li-, Na-, Al-, Co-doped systems, where the Co-doped arsenene had a half-metal property.³¹⁸

Substitutional doping of 3d transition metal (TM) atoms on arsenene or antimonene produced tunable structural, electronic and magnetic properties.256 According to the calculated binding energies, TM-substituted arsenene was robust. Magnetic states were found because of the doping of Ti, V, Cr, Mn, Fe and Ni. The Sc-/Co-doped arsenene nanosheets had nonmagnetic semiconducting properties. The substitution of As with Ti, Cr and Cu atoms led to a dilute magnetic semiconductor phase (Fig. 17).252 The magnetism of Fe-/Ni-doped arsenene was tuned by adjusting the doping concentration.255 Half-metallic states were found in Ti-, V-, Mn-, Fe- and Ni-doped arsenene and antimonene.319 Spin-polarized semiconducting states occurred with V, Cr, and Fe doping. Ti-, V-, Mn- and Fedoped arsenene nanosheets exhibited ferromagnetic coupling. Cr substitutional doping induced antiferromagnetic coupling under the most stable configuration. TM-substituted arsenene shows potential applications for spintronics and magnetic storage devices. Other types of metallic doping of arsenene involved Sn, Ga, Ge, Li and metal compounds (Cs₂CO₃),³⁰⁴ presenting tunable structural, electronic and magnetic properties.251,253,320 The high-temperature superconducting, magnetism and magneto-optical effects of hole-doped gray, ML or buckled arsenene were proven under strain conditions.^{240,321,322} In the case of n- or p-type doping of antimonene, tetrathiafulvalene and tetracyano-quinodimethane served as electron and hole dopants to obtain n- and p-type antimonene semiconductors, respectively, which widen the applications of 2D semiconductors in electronics and optoelectronics.^{239,323}

The nonmetallic doping of 2D group-VA nanomaterials was explored. Through FPC investigations on arsenene doped with non-magnetic elements, dopants from groups III, V and VII with odd numbers of valence electrons maintained the semiconducting character of the pristine system, while that (groups IV and VI) with an odd number of valence electrons caused a change in metallic character (Fig. 17).^{320,324} C-/O-doped systems were spin-polarized and modulated into half-metals by external electric fields. Buckled arsenene with doping of vacancies and nonmetal atoms was thermodynamically stable at room temperature. The substitutional doping of H, F, B, N and P did not produce magnetism in buckled arsenene. Saturation or pairing of valence electrons from the dopants and neighboring As atoms occurred.269 Vacancy and doping of C, Si, O and S induced a magnetic moment of 1.0 $\mu_{\rm B}$ in buckled arsenene, resulting from one nonbonding valence electron of C and Si or neighboring As atom around O, S and vacancy. The magnetic coupling between magnetic moments induced by two



Fig. 18 (a) Preferable adsorption sites (H, T, V and B) on an arsenene lattice. The side and top views of adsorption geometries for Li, Al, Ti, V, Cr, Fe, Co, Ni and Pd adsorptions on V site. Na, Cu, Ag, Pt and Au adsorptions on H site. Ca adsorption on T site. Reproduced with permission from ref. 318, Copyright 2016 Elsevier. (b) Spin density images for C-substituted and As-adsorbed hexagonal As. Substitutional C, adsorbed As and the nearest-neighbor As atoms are labeled. Other balls without special labels indicate As atoms. Reproduced with permission from ref. 251, Copyright 2016 Royal Society of Chemistry. (c) Top and side views of H₂, O₂ and H₂O molecules adsorbed on each 5×5 supercell of the buckled Sb. Reproduced with permission from ref. 329, Copyright 2016 American Physical Society.

elements of C, Si, O and S was long-range anti-ferromagnetic due to the p-p hybridization interactions involving polarized electrons. Arsenene and antimonene had tunable electronic structures and magnetic properties through impurity doping of H, B, C, N, O, S, Si, P, F, Cl, Br, I, Sb and Se.^{251,253,325,326} Engineered nanostructures of arsenene and antimonene with metallic or nonmetallic doping have a broad range of applications in electronic, optoelectronic and magnetic devices.

4.3. Absorption

Through interstitial deposition and stacking interactions, atoms or molecules can be absorbed onto 2D group-VA

nanomaterials to fabricate functional nanostructures. Based on FPC, Chen et al. found that Li-intercalated bilayer arsenene with AB stacking is dynamically stable and is different from the pristine bilayer with AA stacking. Electron-phonon coupling of stable Li-intercalated bilayer arsenene was dominated by low frequency vibrational modes and produced a superconductivity of T_c (8.68 K) with isotropic Eliashberg functions.³²¹ Metal adatoms on arsenene have binding energies larger than the cohesive energies of bulk metals, implying the formation of stable adsorbates. Due to the localized states from adatoms, adsorption systems have various electronic properties, such as metal, half-metal, semiconducting and spin-semiconducting behaviors. The adsorption of Cu, Ag and Au turned semiconducting arsenene into a narrow gap spin-semiconductor (Fig. 18a).³¹⁸ Arsenene functionalized with metal adatoms acted as spintronics and dilute magnetic semiconductor materials. Yang et al. studied the interface between Co(0001) and ML or bi/tri-layer antimonene with different stacking models.327 After contact, a high Schottky barrier was formed. The barrier height was tuned by different Co/antimonene stacking patterns. The Co d and Sb sp orbitals had strong hybridization near $E_{\rm F}$. Strong chemical bonds formed between Co and antimonene at the interface. The results implied applications in spin diodes and spin FETs based on antimonene. Nonmagnetic metal atoms (Li, Na, Al, Ga, Mg, Ga, Ge, and In) and TM atoms (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu) were absorbed onto ML, fewlayer arsenene, antimonene, free-standing As and Sb nanosheets.^{250,267,268,328} Magnetism was observed for nonmagnetic Al and Ga adatoms adsorbed onto arsenene ML. TM-adsorbed arsenene or antimonene systems are promising candidates for electronic and spintronic devices.

Adsorption of nonmetal atoms onto 2D group-VA nanomaterial involved adatoms of H, B, C, N, O, F, Si, P, Cl, As, Se and Sb.250,329 Adatoms produce chemisorption bonds and modify atomic structures and physical properties locally. Some adatoms cause obvious local reconstruction of atomic structures. A majority of adsorbed atoms cause localized states in fundamental bandgaps. Light atom (B, C, N, O, and F) absorbed arsenene nanosheets were studied by FPC.254 Most adatoms prefer to occupy bridge sites on arsenene nanosheets except for C adatom (valley sites). Defect states were detected in the middle gap of the F-adsorbed system. N adatoms caused n-type doping. O adatoms had negligible effects on its electronic structures. B, C, N and F adatoms induced magnetism in arsenene nanosheets. For As-adsorbed ML hexagonal arsenene (hAs) (Fig. 18b),²⁵¹ its Fermi level crossed the spin-up states, yielding metallic behaviour. Organic molecules can be adsorbed on 2D group-VA materials. Using FPC, Gao et al. proved selective organic molecular adsorption control of carrier types in arsenene.330 Tetracyano-quinodimethane (TCNQ) and tetrathiafulvalene (TTF) with electron-withdrawing and donating abilities, respectively, were selected as organic molecules. The donors were adsorbed on the surface of arsenene via a physisorption process. There was a considerable electron transfer from arsenene to TCNQ, yielding p-doped arsenene. However, the electrons transferred from TTF to arsenene are not enough to make effective n-doped arsenene. An additional tensile strain

assisted this process. Due to the precise control of carrier types and combination of the p-/n-doped components, p-n junctions can be formed in arsenene-based nanodevices and exhibit applications in transistors and photodetectors.^{239,323}

The adsorption of gas molecules onto 2D group-VA nanomaterials refers to various small molecules, including H₂, N₂, CO2, CO, O2, H2O, NH3, SO2, NO and NO2.250,329,331-335 By firstprinciples spin-polarized density functional calculations, the chemisorption of selected adatoms and physisorption of molecules on two antimonene (or ML arsenene) phases with buckled honeycomb (b-Sb, b-As) and symmetric washboard (w-Sb, w-As) structures were studied.^{250,329} Molecules such as H₂, O₂ and H₂O neither formed strong chemical bonds nor dissociated. They were physisorbed with weak binding energies without affecting the properties of antimonene (Fig. 18c). The interactions of molecules with nanomaterials are crucial for hydrogen storage, evaluation reaction and oxidation-deoxidation. Molecules weakly interact with antimonene. The binding energies are weak, showing a predominant van der Waals character. Selected metal and nonmetal adatoms formed strong bonds with antimonene by exchanging electronic charges, causing local reconstructions and defects. Electronic states from adatoms led to a diversity of electronic states, together with high carrier mobility, magnetism (spin-polarized) and halfmetal characters. Some molecules were dissociated at the edges of arsenene flake structures. Constituents were adsorbed to the edge atoms to cause local reconstructions.250

CO adsorption on pristine antimonene is physical adsorption that is then converted to chemical adsorption after doping.332 An external electric field improved the CO gas sensitivity on antimonene to realize CO sensing at room temperature. Adsorption and desorption of CO can be controlled by applying an external electric field, which is helpful to collect and store CO gas. Gas adsorption of pristine antimonene was studied by FPC, which promoted the exploration of its high-performance gas sensing.335 Atmospheric gas molecules (N₂, CO₂, O₂, and H₂O) were weakly adsorbed on antimonene. However, pollutant gas adsorbates (NH₃, SO₂, NO, and NO₂) were physically adsorbed on antimonene, showing stronger adsorption energies and elevated charge transfer due to the contributions of the frontier orbitals of the molecules being closer to the Fermi level and more apparent orbital hybridizations. Due to the moderate physical and chemical adsorption of their atom-doped analogues, appreciable charge transfer and susceptibility of electronic properties, ML antimonene and arsenene may be potential sensing materials for the sensitive detection of pollutant gases.^{257,331,333,335,336}

4.4. Pnictogen-containing hybrids

2D layered group-VA materials, such as ML or few-layer BP, As, Sb and Bi (phosphorene, arsenene, antimonene, bismuthene), can be modified by forming heterostructures, doping and absorption of atoms or molecules to develop functional nanostructures. In addition, pnictogen-containing 2D hybrids have been developed for particular applications. Sun *et al.* designed seamless lateral heterostructures (As_mSb_n LHS) that had



Fig. 19 (a) Top and side views of atomic structures of pristine arsenene ML. The shaded area represents the unit cell. Violet, light cyan, gray, red, and white balls indicate As, F, C, O, and H atoms, respectively. *b*, θ , and *h* denote the As–As bond, vertex angle and buckling distance, respectively. (b and c) Calculated phonon dispersion and electronic band structures, respectively. (d) Atomic structures of three types of chemically functionalized ML AsX (X = F, OH, and CH₃). (e) Phonon dispersion curve for AsF ML. Reproduced with permission from ref. 348, Copyright 2016 Royal Society of Chemistry. (b) Structural representation of the top and side views for (a) D-AsO and (b) C-AsO. (c) Total energies with respect to lattice constants of D-AsO and C-AsO. (d and e) Corresponding phonon spectra along the high-symmetric points in BZ. Reproduced with permission from ref. 354, Copyright 2017 American Physical Society.

excellent stabilities within pristine arsenene and antimonene.³¹⁴ Based on theoretical predictions, As_mSb_n LHS had direct and reduced energy gaps without modulations. A coveted type-II alignment and high carrier mobility were identified and had enhanced quantum efficiency. The tensile strain led to efficient bandgap engineering. Antimonene FETs based on MLtrilayer LHS can act as candidates for low-power device applications.^{336–338} Besides traditional α/β allotropes, other 2D allotropes of arsenene, antimonene and bismuthene were studied, such as square–octagon (S/O) and tricycle types, nanoribbons, nanotubes, van der Waals bilayer heterostructures, functional ultrathin films, halogenated and decorated 2D films.^{123,228,291,326,339–346} Pnictogen-containing 2D hybrids with functional nanostructures have unique, tunable and enhanced properties for particular applications.

Hydrogenated arsenene (AsH) decorated with TM atoms (Cr, Mo, and Cu) was studied by DFT.³⁴⁷ A unique quantum anomalous Hall (QAH) effect in TM@AsH was predicted. The quantum states of Mo@AsH were tuned by external strain. Under 5.0% tensile strain, its topological gap was \sim 35 meV, which is large enough to realize the QAH effect at room temperature. There is a quantum valley Hall effect in Cu@AsH

due to the inequality of its AB sublattices. The QAH effect is superior to the quantum spin Hall (QSH) effect because it can avoid inelastic scattering of two edge electrons located on one side of topological nontrivial materials. This superiority is desirable for electronics and spintronics. Candidates of 2D topological insulators (TIs) with large bandgaps were predicted, such as arsenene functionalized with F, OH and CH₃ groups (Fig. 19a).³⁴⁸ Ab initio molecular dynamic simulations implied the thermal stabilities of AsX monolayers at 500 K. The nontrivial topological phase was proven by the topological invariant Z₂ and edge states. The topological electronic bandgaps of the AsF ML were modulated by biaxial tensile strain and vertical external electric field. Pronounced light absorption in the near-infrared and visible range of the solar spectrum was expected for AsH or AsF monolayers, which are attractive for light harvesting. Nontrivial QSH insulators AsX are promising candidates for applications in dissipationless transport devices and photovoltaics. Robust 2D TIs in methyl-functionalized Bi and Sb bilayer films were predicted by FPC. Me-Bi and Me-Sb had protected Dirac-type topological helical edge states, which are suitable for QSH systems.³⁴⁹ 2D TIs with large topological energy gaps are superior platforms for topological phenomena and applications at high temperature.

Eremeev et al. reported a giant Rashba-type spin splitting in 2D electron systems that resided at the Te-terminated surface of Bi tellurohalides.³⁵⁰ BiTeCl semiconductor had an isotropic metallic surface-state band lying in deep inside bulk bandgaps. The giant spin splitting of this band ensured substantial spin asymmetry of inelastic mean free path of quasiparticles with different spin orientations. Amsler et al. developed quasi-2D CuBi nanosheets from ab initio calculations.351 Through predictions, single layers of CuBi were isolated from highpressure bulk CuBi materials. The nanosheets exhibited superior electronic and electrochemical properties. When used as a superconductor, there was a moderate electron-phonon coupling ($\lambda = 0.5$ and $T_c \approx 1$ K). The CuBi nanosheets were readily intercalated with lithium with high diffusibility and applied potential to boost the rate capacity of current electrodes in lithium-ion batteries. Li et al. studied the electronic structures of atomically thin layers of Bi2Ti3 quasi-2D crystals.352 Quintuple layers of Bi2Te3 indicated semiconductors with localized shallow bands. Weak covalent Bi-Te2 interactions in the quintuple layers allowed them to be exfoliated to bi/tri-layer nanosheets. The bi/tri-layer nanosheets of Bi2Te3 are metallic because valence electrons cannot fully occupy valence bands. Arsenene oxide transited its bandgap from an indirect band to a direct one.353 The transition is due to a new (conduction) bottom band, consisting of 4s-orbitals of partial oxidized arsenic (layered As_xO_y), p-orbitals of oxygen and unoxidized arsenic. The direct bandgap width was narrowed from the nearinfra to infra region in proportion to the oxygen content. Arsenene oxide (AsO) is a good candidate 2D material with QSH effects. Through ab initio calculations, AsO had high stability, flexibility and tunable SOC gaps (Fig. 19b).354 The maximum nontrivial bandgap of AsO reached 89 meV, which was enhanced to 130 meV under biaxial strain. AsO with oxidized

surfaces was stable against surface oxidization and degradation, which is suitable for designing topological quantum devices.

2D β-phase group-VA binary monolayers (PAs, PSb, PBi, AsSb, AsBi, and SbBi) were explored by means of DFT calculations.355 They were verified to be stable free-standing materials with versatile electronic structures, and had direct or indirect band gaps of 0.90-2.39 eV, as predicted at the HSE06 level with spin-orbital coupling corrections. A linear correlation was explored between the cohesive energy and band gaps of different composites with average ionization energies (AIEs), showing the potential to engineer desirable properties of these 2D materials from the AIEs of component atoms. These 2D binary compounds had extremely small effective masses of carriers and high electron mobility. They exhibited considerable absorption of solar energy and suitable band alignments for photocatalytic water splitting. The in-plane heterostructure could be gained by combining the elemental 2D group-VA monolayers (Sb/Bi, As/P, and As/Sb) or other 2D materials (graphene, WSe₂, MoS₂, and silicene).³⁵⁵ Binary 2D compounds with various compositions and structures are expected to hold exciting properties, such as semiconductor-topological insulator transition, magnetism and extraordinary sunlight absorbance. After experimental fabrication, novel 2D materials based on group-VA binary compounds enable applications in nanoelectronics and photocatalysts.

4.5. Surface functionalization

Surface functionalization is an efficient strategy to improve the performance of 2D group-VA materials. However, despite the tremendous progress on studies of BP-based nanostructures, a key barrier for BP applications is its degradation upon longterm exposure under ambient conditions. The origin of BP degradation is due to PO_x species generated by reaction between oxygen and lone-pair electrons perpendicular to the BP surface. 2D group-VA pnictogen materials beyond BP such as ML and few-layer As, Sb, and Bi (arsenene, antimonene and bismuthene, respectively) are promising candidates of BP or phosphorene, and have superior physical and chemical properties. Their high charge-carrier mobility, tunable direct bandgap and unique in-plane anisotropic structure give them remarkable applications in a broad range of fields. Before practical applications, various functional methods are used to modify 2D group-VA nanomaterials, including covalent, van der Waals and electrostatic functionalization. Covalent functionalization is mediated by bonding. Lone-pairs of nanomaterial surfaces interact with Lewis acids, such as TM ions, organic molecules and alkali ions. van der Waals functionalization depends on the interactions between nanomaterials and capping layers, such as graphene, hexagonal boron nitride or organic molecules. In electrostatic functionalization, the positively charged adsorbates spontaneously interact with nanomaterials modified with the negatively charged species. Surface functionalization enhances the stability of nanomaterials, and retains and promotes their specificity for long-term use. For 2D group-VA pnictogen nanomaterials, surface functionalization mainly involves physical and chemical steps. Physical steps are ball-

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mill mixing, thermal vaporization, stacking, impregnation, vacuum deposition, solvent evaporation, spin coating, *etc.* Chemical steps refer to self-assembly, chemical reaction, photoreduction, focused laser-induced oxidation, phase transformation, *etc.* These steps are widely used to develop a variety of electronic, optical, thermal, optoelectronic and magnetic devices, such as Li/Na-ion batteries, electrocatalysis for oxygen evolution reaction, visible-light photocatalysis, p–n diodes, junction FETs, photodetectors, memory devices, *etc.*

5. Applications

5.1. Catalysis

Due to their unique structural and electronic properties, 2D layered group-VA nanomaterials have attracted much attention in photo-/electrocatalysis.⁴⁸ The high surface-to-volume ratios in 2D nanostructures endow them with abundant catalytically active sites exposed on their surface. The engineering of 3D bulk materials into a 2D format enhances the exposure of active edge sites, which is the origin of high catalytic activity. 2D few-layer Sb nanosheets (SbNSs) prepared from cathodic exfoliation acted as active 2D electrocatalysts for the reduction of CO₂ to formate with high efficiency.¹⁰⁴ High activity is due to the exposure of numerous catalytically active edge sites. The cathodic exfoliation was coupled with anodic exfoliation of graphite in a single-compartment cell for the *in situ* production of few-layer SbNSs and graphene composites. The increased activity of SbNS-graphene arose from the strong electronic

coupling between graphene and SbNSs. As proven by Raman spectroscopy, a red shift in the E_g and A_{1g} peaks, especially the A_{1g} peak (7.8 cm⁻¹) was observed in SbNS-graphene. This red shift in the Raman spectrum was observed in other 2D composites,³⁵⁶⁻³⁵⁹ which is attributed to n-type doping from graphene to other materials. In SbNS-graphene, the electrons from a lower work function of graphene (4.43 eV) tend to migrate across the Sb-graphene boundary to a higher work function of SbNS (4.55-4.70 eV),^{104,360} which increases the electron density at the surface of SbNS. SbNS-graphene had a higher selectivity to formate at a lower overpotential compared with bulk Sb and SbNSs (Fig. 20a). At a potential of -0.96 V (over-potential of 0.87 V), SbNS-graphene delivered the maximal efficiency for its formation (88.5%). SbNS had the maximal efficiency of 84% at -1.06 V. The partial current density for formate from SbNS-graphene was larger than of bulk Sb and SbNSs (Fig. 20b). The current density of SbNSgraphene at -1.07 V was 1.5 (or 16) times higher than that of SbNSs (or bulk Sb). After 2D engineering of nanostructures and compositing with graphene, SbNSs were transferred from catalytically inactive materials into an active form. 2D mosaic Bi nanosheets were utilized for selective ambient electrocatalytic N₂ reduction.³⁶¹ The high electrocatalytic activity of Bi nanosheets is due to sufficient exposure of its edge sites coupled with effective p-orbital electron delocalization in mosaic Bi nanosheets. Their semiconducting feature limits surface electron accessibility and effectively enhances the faradaic efficiency.



Fig. 20 (a) Efficiency and (b) partial current density for formate at different applied potentials on bulk Sb, SbNSs and SbNS–graphene. (c) Raman spectra of SbNSs, SbNS–graphene composite and SbNSs mixed with the exfoliated graphene. (a–c) Reproduced with permission from ref. 104, Copyright 2017 Wiley. (d) 'OH trapping PL spectra of MoBi-2 over time. (e) Mott–Schottky conduction band curves of BiOBr and MoS₂. (f) Scheme of the photocatalytic reaction mechanism of MoBi-2 for RB5 degradation under a low-power energy saving light bulb. (d–f) Reproduced with permission from ref. 178, Copyright 2017 Elsevier.

Photocatalysis of 2D group-VA nanomaterials was reported. 2D square-like BiOI nanosheets with a thickness of \sim 10 nm and exposed {001} facets were prepared by a hydrothermal route without surfactants and special solvents.¹¹⁰ By evaluating the photodegradation of rhodamine B, methyl orange and phenol under visible-light irradiation, the BiOI nanosheets had high photocatalytic performance, photostability and recyclability. Thin 2D square-shape nanosheets with exposed {001} facets were responsible for their visible-light driven photocatalytic activity. The unique nanostructure offered a suitable diffusion length and self-induced internal static electric field direction of BiOI, improving the separation efficiency of photoinduced electron-hole pairs in the BiOI nanosheets. Thin 2D nanosheets have a greater percentage of {001} facet exposure. A stronger internal static electric field is induced, with improved photocatalytic activity.^{362,363} 2D BiOBr was coupled with co-catalyst MoS₂ via a hydrothermal process.¹⁷⁸ The photoactivity of the hybrid photocatalyst MoS₂/BiOBr was studied under irradiation of a 15 W energy-saving light bulb under ambient conditions using Reactive Black 5 (RB5) as the model dye solution (Fig. 20d-f). After 3 h of irradiation, the photodegradation of RB5 by BiOBr loaded with 0.2 wt% MoS₂ (MoBi-2) was 1.4- and 5.0-fold higher than that of the pristine BiOBr and TiO₂. This high photocatalytic performance resulted from the effective migration of the excited electrons from BiOBr to MoS₂, which could prolong the recombination rate of electron-hole pairs.

A layered architecture consisting of 2D corrugated $[Sb_2O_2(OH)]^+$ layers with linear α, ω -alkanedisulfonate anions residing in the interlamellar space was used as a Lewis acid catalysst.101 The cationic material had chemical robustness under high acidic aqueous conditions (pH = 1). Upon combination of the robust nature and high density of Sb^{III} sites on the exposed crystal facets, this cationic layered-material was shown to be an efficient and recyclable catalyst for the cyanosilylation of benzaldehyde derivatives with trimethylsilyl cyanide. The Lewis acidity of the Sb^{III} sites catalyzed the ketalization of carbonyl groups under green solvent-free conditions. Based on the superior electronic properties of 2D group-VA nanomaterials, they are predicted to have high photocatalytic capability. Organic-inorganic bismuth halides have tunable electronic structures with potential as the enhanced 2D lightharvesting materials.¹⁰⁷ By pairing with MoS₂ or a quinodimethane complex, arsenene-based heterostructures formed type-II band alignments, satisfying the requirements of photocatalysts for photocatalytic water splitting.³⁰⁹ Photocatalysis of BP/arsenene LHSs with superior electronic properties was predicted.313 By comparing band-edge positions with redox potentials, β-stacking $arsenene/Ca(OH)_2$ van der Waals heterostructure with strain-tunable electronic and photocatalytic properties is an excellent photocatalyst for water splitting.³⁰² Also, by comparing band-edge positions with the redox potentials of water, the arsenene/GaS van der Waals heterostructure with tunable electronic properties is a good photocatalyst for water splitting.²⁹⁸ Bi₄Ti₃O₁₂/BiOCl 2D/0D composites exhibited improved photocatalytic capacity for the degradation of the antibiotic tetracycline hydrochloride.180 Their high photocatalytic capacity is due to the matched crystal structures, suitable energy band structures, and intimate contact interfaces among $Bi_4Ti_3O_{12}$ nanosheets, ultrafine BiOCl NPs and 2D/0D composite nanostructures. Z-scheme photocatalytic water splitting was conducted based on the 2D heterostructure of BP/bismuth vanadate (BiVO₄) using visible light.³⁶⁴ Their respective band structures with staggered alignment were used for effective charge separation, allowing the reduction and oxidation of water on BP and BiVO₄. Heterojunctions of 0D Bi nanodots/2D Bi₃NbO₇ nanosheets were used for the efficient visible light photocatalytic degradation of antibiotics.³⁶⁵ Semimetal Bi increased the visible light absorption of photocatalysts and promoted the molecular oxygen activation of Bi₃NbO₇, improving its photocatalytic performance for the degradation of ciprofloxacin.

5.2. Energy storage

2D group-VA nanocrystals have higher theoretical capacities than graphite, implying their potential as electrode candidates for Li- and Na-ion batteries.366 Compared to 3D crystals, 2D group-VA materials possess superior structural characteristics, high surface area and specific capacity. According to theoretical calculations, BP has ultrafast Li-ion diffusion and large capacity for applications in Li-ion batteries.³⁶⁷⁻³⁷⁰ Li atoms formed strong bonding with P atoms, staying in the cationic state.³⁶⁷ At a high concentration of Li atoms, the phosphorene-Li complex becomes metallic and exhibits high electrical conductivity. The diffusion of Li atoms on phosphorene with a puckered honeycomb nanosheet is extremely anisotropic. Li-diffusion along the armchair direction is almost prohibited, but its diffusion along the zig-zag direction is energetically favorable. The diffusion barrier of Li atoms along the zig-zag direction was ~ 0.08 eV lower in energy than other Li-battery anode materials, such as graphene (0.3 eV) and MoS₂ (0.28 eV).³⁷¹⁻³⁷⁴ This low energy barrier led to diffusivity of 10^4 (10^2) times faster than that in graphene (MoS₂). The average voltage of adsorbed Li-atoms is \sim 2.9 V, which is suitable for phosphorene-based Li-ion batteries. Na-diffusion was anisotropic. The diffusion barrier along the zig-zag direction was predicted to be ~ 0.04 eV.^{375,376} Phosphorene was studied as an anode material for Li-/Na-ion batteries.377-384 The few-layer phosphorene sandwiched between graphene layers was used as a high-capacity anode for Na-ion batteries.378 Hybrid phosphorene-graphene materials had a specific capacity of 2440 mA h g^{-1} at a current density of 0.05 A g^{-1} . There was 83% capacity retention after 100 cycles at an operating potential of 0-1.5 V. The large capacity of this anode material is due to the intercalation of Na ions along the zig-zag direction of phosphorene and the formation of Na₃P alloys. Owing to their sandwiched structures, phosphorenegraphene hybrids with superior electronic properties are good anode materials for Na-ion batteries. BP-based hybrids were widely applied for energy storage, including Li-/Na-ion batteries, perovskite solar cells and supercapacitors.48,49,51,55,57,59

A metallic buckled SbNS–graphene film exhibited a high rate capability, high volumetric capacity and good cycle performance for Na storage.⁷¹ At a current density of 0.1 mA cm⁻², the reversible volumetric capacity in the initial cycle reached a high

value of 1226 mA h cm⁻³ for the film with a mass loading of 1.6 mg cm⁻², but it was almost stable at 650 mA h cm⁻³ after 50 cycles. The high flexibility of graphene relieved the stress of the notorious volume changes of metallic Sb. Metallic Sb nanosheets are applied in Na-ion batteries. Due to their puckered and buckled structural properties, 2D group-VA materials with low atomic packing factors are favorable for the accommodation of Li and Na atoms. The rich alloy phases of Li₃X and Na₃X (X: P, As, Sb, and Bi) give high capacities for Li-/Na-ion batteries. The high surface areas of 2D group-VA nanosheets endow a higher capacity and faster ion diffusion as anodes in Li-/Naion batteries. Wu et al. explored interconnected 2D carbon/Sb hybrids as advanced anodes for Na storage.¹⁰³ Multidimensional and multi-scale hybrid nanostructures promoted the electron-ion transport kinetics for electrode materials, and ensured the integrity of electrode structures upon cycling. The Sb-NDs \subset CNs electrode had high electronic performance for Na storage through reversibility, rate capability and cycle life

studies. The reversible capacity of Sb-NDs \subset CNs did not perceptibly decay after 100 cycles at 0.1 A g⁻¹, and had a capacity retention of 94 wt% compared with the second cycle after 100 cycles.

Antimonene is an excellent anode material in Na-ion batteries due to its high theoretical capacity of 660 mA h g⁻¹ and enlarged surface active sites. The Na storage and sodiation/ desodiation mechanisms of 2D few-layer antimonene (FLA) were explored.⁸⁵ FLA had anisotropic volume expansion along the *a/b* planes and reversible crystalline phase evolution (Sb = NaSb = Na₃Sb) during cycling (Fig. 21). Based on FPC, FLA had a small Na-ion diffusion barrier of 0.14 eV. FLA delivered a large capacity of 642 mA h g⁻¹ at 0.1C (1C = 660 mA g⁻¹) and a high rate capability of 429 mA h g⁻¹ at 5C. It retained a stable capacity of 620 mA g⁻¹ at 0.5C with 99.7% capacity retention from 10 to 150 cycles. Based on the theoretical capacity of 660 mA h g⁻¹ for Sb, the electronic use of Sb atoms for FLA reached up to 93.9% at a rate of 0.5C for over 150 cycles. The



Fig. 21 (a) Comparison of the energy levels of each functional layer. The Fermi level of antimonene is represented by a dashed line. (b) Configuration of antimonene-based device. (c) Cross-sectional SEM image of the device. (d) Current-density-voltage (J-V) curves of the devices with different architectures. (e) External quantum efficiency (EQE) spectra with EQE-data-based integrated short-circuit current densities (J_{sc}) for devices 1 and 2. (a–e) Reproduced with permission from ref. 78, Copyright 2018 Wiley. (f) Scheme for Na-ion half-cell composed of FLA. Atomic structure illustration, AFM image and profile terraces of FLA. (g) Long-term cycling performance and Coulombic efficiency of FLA and bulk Sb powder at a rate of 0.5C. (h) Rate capability of FLA. (i) CV profiles of FLA in 0.01–1.5 V at 0.1 mV s⁻¹. (f–i) Reproduced with permission from ref. 85, Copyright 2018 American Chemical Society.

investigation of the Na storage mechanism boosted the applications of 2D FLA as an advanced large-capacity and long-life Na-ion battery material. Smooth and large 2D antimonene was produced with uniform and specific number of layers.78 In experiments, the bandgap depending on antimonene thickness was finely tuned to 0.8-1.44 eV. Antimonene acted as a hole transport layer in perovskite solar cells (Fig. 21a-e), which resulted in a significant improvement in hole extraction and current (\sim 30%). This work paved the way for the widespread applications of the emerging 2D group-VA nanomaterials with superior electronic properties in optoelectronics. In addition to Na-ion batteries and perovskite solar cells, antimonene was also explored as a new 2D nanomaterial for supercapacitors.⁸¹ Antimonene served as an electrode material of supercapacitors. Antimonene improved the energy storage capabilities of carbon electrodes in cyclic voltammetry and galvanostatic charging. Antimonene presented a capacitance of 1578 F g^{-1} and a high charging current density of 14 A g⁻¹. Antimonene is an excellent material for energy storage, and due to its competitive energy and power densities of 20 mW h kg⁻¹ and 4.8 kW kg⁻¹, antimonene-based systems have excellent charge storing and cycling capabilities.

According to theoretical predictions, 2D layered group-VA pnictogen materials and pnictogen-containing 2D hybrids have applications in photovoltaics. Arsenene-based heterostructures paired with MoS₂ or quinodimethane complex can form type-II band alignments and have a high power conversion efficiency of 20% for photovoltaic solar cells.309 Sb/GaAs van der Waals heterostructures led to the separation of carriers and a high optical absorption coefficient in the visible-light range, implying these heterostructures are candidates for application in optoelectronic devices (solar cells).237 Black arsenic-phosphorus (α-AsP) ML has a direct bandgap (1.54 eV) and a mobility of over 1.4 \times 10⁴ cm² V⁻¹ s⁻¹, indicating that ML α -AsP is a superior donor for application in 2D solar cells. ML α -AsP may be the next material with broad applications in photovoltaic devices.³¹² An arsenene/C3N van der Waals heterostructure, with a broad absorption range, remarkable visible light absorption and high light harvesting, was expected and functionalized as a photovoltaic component in solar cells.234 2D Sb as a superior candidate as an anode material in Na-ion batteries has a specific capacity of 320 mA h g^{-1} , an open circuit voltage of 1.22 V and a small diffusion barrier of 0.114 eV. Its high capacity and superior Na diffusion properties demonstrate its promise for application in Na-air batteries and supercapacitors.328 Functionalized arsenene (AsH and AsF) MLs had obvious light absorption in the nearinfrared and visible range of the solar spectrum, showing adsorption peaks in the range of 0.45-1.6 eV. This feature is attractive for light harvesting. Nontrivial QSH insulators (AsF, AsOH, and AsCH₃) are promising candidates for photovoltaics.³⁴⁸ Partially oxidized arsenene with a tunable direct bandgap has potential in photovoltaic devices.353 Quasi-2D CuBi nanosheet superconductors have tunable electronic properties and moderate electron-phonon coupling ($\lambda = 0.5$ and $T_c \approx 1$ K). CuBi nanosheet intercalated with Li shows high ion diffusivity, which can act as a candidate material to boost the rate capacity of current electrodes in Li-ion batteries.351

5.3. Field-effect transistors

2D group-VA semiconductor materials are used as the body terminals of field-effect transistors (FETs). FETs are indispensable building blocks of modern integrated circuits. Compared with graphene or MoS₂ as channel materials of FETs, BP has two main merits, high on/off ratio for effective switching and charge carrier mobility for fast operation. Phosphorene FETs were fabricated based on few-layer phosphorene.44,385 Drain current modulation of FETs is in the order of 10^5 at room temperature and is four orders of magnitude larger than that in graphene. Their charge carrier mobility reached 1000 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, which is superior to that of silicon-based devices. Low on-state current and high sub-threshold swing were enhanced by optimizing gate dielectrics.385 Through the encapsulation of few-layer phosphorene between hexagonal boron nitride layers, a sandwiched heterostructure was prepared and used in FETs with ultra-clean interfaces.³⁸⁶ The device exhibited a mobility of 1350 cm² V⁻¹ s⁻¹ at room temperature and an on-off ratio exceeding 10⁵. The carrier mobility of BP is highly dependent on direction due to its structural anisotropy. A lower effective mass along the armchair direction induces a higher drive current at the same bias. A higher degree of anisotropy enhances the performance of p-type devices. The transport feature of devices depends on transport direction. The transport anisotropy is conducive to the on-state current improvement. There are some limitations in phosphorene FETs, which are attributed to their strong asymmetric ambipolar characteristics, high Schottky barrier and severe surface degradation.

To simplify circuit design and save layout area, ambipolar channel materials with both n- and p-type transports are used in complementary metal oxide semiconductor transistor logic circuits. Phosphorene FETs have ambipolar character, but ambipolar behavior is strongly asymmetric and is unfavorable for complementary logic devices. To balance ambipolar behavior, slow hole transport is improved through optimizing device structures, fabrication conditions and flake thickness. By in situ surface functionalization with Cs₂CO₃, a phosphorene FET was designed to achieve effective modulation of ambipolar behaviour.³⁸⁷ After coverage of 0.5 nm Cs₂CO₃, the on-current in electron regime was close to that in the hole regime, revealing a very symmetric and balanced ambipolar characteristic. With a thickness of Cs₂CO₃ larger than 10 nm, the electron mobility was distinctly improved, reaching 27 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, indicating improved electron transport behavior. Differently from BP or phosphorene, other 2D group-VA materials such as buckled arsenene or antimonene are highly stable when exposed to ambient conditions. ML arsenene or antimonene with a wide range of bandgaps has potential for FET applications. The performance of sub-10 nm ML arsenene/antimonene metal oxide semiconductor FETs (MOSFETs) was predicted.^{124,185} The electron mobility and hole mobility were 635 and 1700 $m cm^2 \, V^{-1}$ s^{-1} for As (630 and 1737 cm² V⁻¹ s⁻¹ for Sb), respectively.¹²⁴ Excellent performance is applicable for ultra-scaled devices in the sub-10 nm scale.

Chen *et al.* reported an ML-trilayer lateral heterostructurebased FET (Fig. 22a-d).³³⁷ A low tunneling barrier and



Fig. 22 (a) Schematic structure of double-gated ML-antimonene FET with trilayer antimonene electrodes. Interface is passivated by hydrogen atoms. Transport is along the armchair direction. Sb and H atoms are highlighted in purple and light green. (b–d) Side view of the relaxed geometric structure of electrode (slab model), electron density ($\langle \rho_l \rangle$) and average effective potential ($\langle V \rangle$) along the *y* direction for (b) trilayer contact, (c) Al contact and (d) graphene contact. (a–d) Reproduced with permission from ref. 337, Copyright 2018 Wiley. The crystal structures of QW consisting of AsO ML sandwiched h-BN sheet on top view for (e), band structure with SOC under 6% tensile strain for (f). Green circles and blue areas stand for the size and extent of substrate effects. (g) The schematic model of BN/AsO/BN heterostructure for quantum state measurements. Vertical arrows show spin orientation of electrons in the edge states and horizontal arrows show transport directions. (e–g) Reproduced with permission from ref. 354, Copyright 2017 American Physical Society.

Schottky barrier were obtained with trilayer antimonene electrodes compared with the promising 2D contact materials, graphene and metal aluminum. According to theoretical calculations to evaluate the device performance, the on/off ratio is 4.87×10^8 (1.06×10^6) with a gate length of 10 (5) nm. The lowest power supply voltage ($V_{dd} = 0.76$ V) at $V_{ds} = 0.6$ V to switch "on" and "off" is close to the requirement of 0.72 V. The on-current is enhanced and the on/off ratio is simultaneously increased *via* hydrogen passivation, offering a way to optimize device behaviors. High air stability, low off-current and high on/ off current ratio make antimonene FETs (based on ML-trilayer lateral heterostructure) a superior candidate for low-power

device applications. Co d and Sb sp orbitals have strong hybridization, resulting in chemical bonding between Co and antimonene at the interface.³²⁷ A high Schottky barrier was formed after contacting. Barrier height can be tuned by different Co/antimonene stacking patterns. Barrier height decreases with an increase in the layer number of antimonene. The results imply potential applications in spin diodes and FETs based on antimonene. 2D Bi₂Se₃ crystals with a high aspect ratio of 3500 were prepared *via* EDTA and Cl⁻ dual-assisted and seed-mediated growth at low temperature under reflux conditions.¹⁷⁷ The 2D Bi₂Se₃ crystals had a thickness of ~10 nm and an edge length of ~50 mm. Due to the large aspect

ratio of the crystals and their decent room-temperature charge carrier mobility, an FET device was easily fabricated based on 2D Bi₂Se₃ crystals. Arsenene and antimonene MOSFETs based on *ab initio* quantum transport exhibited excellent device performance.¹⁸⁵ The low power and high performance of ML arsenene MOSFETs surpassed the Schottky barrier of ML MoS₂ FETs on the sub-10 nm scale, satisfying the requirements for high-quality FETs.³⁸⁸

5.4. Topological spintronic devices

Topological insulators (TIs), as new quantum states of matters, attract much interest due to bulk insulating gaps and topologically protected boundary states. 2D TIs are promising materials compared to 3D TIs for spin transport applications because the edge states of 2D TIs are more robust against back scattering than the surface states of 3D TIs. Due to weak SOC, graphene as the first predicted 2D TI with QSH effects suffers from deficiencies of small bulk gap and low-temperature operation. 2D group-VA monoelemental MLs (phosphorene, arsenene, antimonene and bismuthene) have strong SOC effects over graphene and hold TIs phases under suitable conditions. For few-layer BP, a normal-to-topological phase transition was detected under an applied electric field along the stacking direction.275 Four-layer phosphorene transformed from a normal insulator into a topological insulator at an electric field of 0.3 V Å⁻¹. Tunable topological behavior under an electric field induces QSH effects. By using an in-plane time-periodic laser field, phosphorene ML may possess Lifshitz transitions compared to topological insulating phases.389 Through FPC, arsenene and antimonene MLs become TIs under appropriate biaxial tensile strain larger than 11.7% (14.5%).194,291 The buckled configuration of arsenene (antimonene) had the capability of enduring large tensile strain of up to 18.4% (18%). The maximum bulk gaps were gained at maximum strain. Arsenene and antimonene are promising candidate materials of 2D TIs to achieve OSH effects.

Flat honeycomb Sb or Bi ML grown on a ferromagnetic MnO₂ layer was predicted, combining large intrinsic QSH and anomalous Hall conductivity.³⁹⁰ Due to proximity effects, h-Sb and h-Bi sheets were magnetized. The Dirac points were split into different spin channels. There were intrinsic QSH states with large bandgaps of 228 meV for h-Sb and 941 meV for h-Bi. There were nearly quantized anomalous Hall states with a bandgap of 10 meV for h-Sb or h-Bi. This alternative practical method is efficient to obtain quantized intrinsic spin Hall states and anomalous Hall conductance states in a single material. TIs are obtained by chemical functionalization of arsenene, antimonene and bismuthene. 2D TIs BiX/SbX (X = H, F, Cl, and Br) MLs were predicted.³⁹¹ Their large bulk bandgaps (0.32-1.08 eV) are due to the strong spin-orbit interactions of Bi/Sb atoms. BiX MLs with honeycomb structures are stable at high temperature. Thus, 2D TIs BiX/SbX MLs with intriguing features are candidates to develop new quantum devices operating at room temperature. 2D TIs Bi/Sb/Pb bilayers with methyl-functionalization were predicted.349 Owing to the protected Dirac-type topological helical edge states, 2D TIs have suitable quantum spin Hall properties and a large nontrivial bulk gap of 0.9 eV for room-temperature applications. Antimonene oxide was used as a 2D TI with

a bandgap of 117 meV.¹⁹² Upon decoration with H and doping of magnetic atoms, Sb(111) MLs had topological properties of quantum spin-quantum anomalous Hall insulators with a bandgap of 53 meV.³⁹² According to tight-binding models, hydrogenated Sb₂H ML coated on an LaFeO₃ substrate was used to study the topological properties of Sb₂H/LaFeO₃,³⁹³ and exotic quantum spin-quantum anomalous Hall states were observed. The bandgap opened up to 35 meV, which was enlarged by strain and electric fields. The freedom degree of carriers in heterostructures-based 2D TIs is tunable. Thus, 2D TIs have promising applications in electronics and spintronics.

Bismuthene with a bandgap of 0.8 eV is a good candidate as a high-temperature quantum spin Hall materials.99 Bismuthene grown on an SiC (0001) substrate was used as the stabilizer of quasi-2D TIs to form large gaps. Due to the strong on-site SOC, the on-current and intrinsic switching speed were improved in bismuthene/SiC 2D TIs. Ultrathin Sb islands grown on Bi₂Te₂Se were fabricated to develop Sb few-layer films as 2D TI materials.¹⁶⁴ As predicted for 3-4 bilayer films, topological edge states emerged by 2D topological phase transition. Non-trivial phase transition and edge states were proven in epitaxial films based on FPC. The evolution of the topological surface states in Sb(111) ultra-thin films with 4-30 bilayers was studied.¹⁶⁰ With a decrease in thickness, inter-surface coupling degraded the spin polarization of TSS and opened new wavevector-dependent scattering channels to cause spin degenerate states. Märkl et al. reported the successful realization of α -antimonene and predicted engineering multiple topological phases in van der Waals nano-heterostructures.86 Both the hexagonal β -form and rectangular α -form of antimonene were used to build islands on top of TI α-bismuthene. 2D TIs are topologically non-trivial materials in the quantum spin Hall class. Ning et al. provided unambiguous transport evidence for the topological 2D metallic surface states in thinner Bi nanoribbons.109 The free-standing quasi-2D layers of Te₂Bi₃ crystals were researched as new TIs in spintronic applications.¹¹¹ Based on ab initio calculations, Wang et al. studied arsenene oxide (AsO) with high stability, flexibility and tunable SOC gaps (Fig. 22e-g).354 Compared with pristine and functionalized arsenene, the maximum nontrivial bandgap of AsO was 89 meV, which became 130 meV under biaxial strain. A quantum well was designed by sandwiching 2D AsO between BN sheets. The band topology of AsO was retained with a sizeable bandgap. AsO possesses fully oxidized surfaces that are stable against surface oxidization and degradation. Group-VA 2D sheets are superior 2D TIs with large bulk gaps and have potential applications in 2D quantum spin Hall devices.

5.5. Electronic devices

Unlike unstable BP, other 2D layered group-VA (As, Sb, and Bi) nanomaterials were predicted to show high stability and excellent physical properties. These unique merits were experimentally proven and have great prospects for use in advanced electronic devices. Ji *et al.* reported the van der Waals epitaxy of few-layer antimonene monocrystalline polygons prepared on various substrates.⁹³ The antimonene polygons had high electrical

conductivity of up to 10^4 S m⁻¹ and superior optical transparency in the visible-light range, which are suitable for transparent conductive electrode applications. Ultrathin and flat Bi nanosheets are beneficial for electronics and act as building blocks in catalysts, solar cells, batteries and electronic devices.¹⁷⁵ Superconductivity of ultrathin free-standing Bi films was detected on different layers of Bi film (Fig. 23a-d).73 In the case of Bi(111) ultrathin films grown on the superconducting substrate NbSe₂, the pairing potential had an exponential decay with layer thickness. Topological edge states may coexist with superconductivity, making the Bi(111)/NbSe₂ heterostructure a superior platform for exploring the Majorana fermions. 2D group-VA nanosheets can serve as semiconductor materials due to their high charge-carrier mobility, tunable direct bandgaps and in-plane anisotropic structures. Liu et al. explored a new family of layered semiconducting materials, namely black As-phosphorus (b-AsP).76 Electron transport measurements implied the semiconductor nature of b-AsP. Through infrared absorption studies and tuning chemical compositions (x) during synthesis, $b-As_xP_{1-x}$, as a layered anisotropic infrared semiconductor, exhibited tunable electronic and optical properties.

Chung *et al.* reported direct evidence of 2D high-temperature superconductivity in a single crystalline nanohybrid of organic-Bi cuprate.¹¹² The coordination compound of $HgI_2(pyridine)_2$ was intercalated into a single crystalline Bi_2 -Sr₂CaCu₂O_v high-

T_c super-conductor via an interlayer complexation reaction between pyridine molecules and Bi cuprate pre-intercalated with mercuric iodide. The superconductivity in organic intercalates of the Bi (2201) phase implied the 2D superconductivity of layered copper oxides. A distinct decrease in shielding fraction and broadening of the superconducting transition were observed after intercalation of HgI₂(pyridine)₂, which can be understood based on the enhanced fluctuation of 2D superconductors. Through FPC, the superconductivity in Liintercalated bilayer arsenene and hole-doped ML arsenene was studied, which exhibited a T_c of 8.68 K with an isotropic Eliashberg function.³²¹ A small biaxial tensile strain (2%) improved the T_c to 11.22 K due to the increase in the DOS and phonon softening. The almost flat top valence band of arsenene is suitable for 2D high-temperature superconductivity. The strain is crucial to enhance the transition temperature (T_c) . Buckled honeycomb and symmetric washboard structures of ML arsenene are stable in the freestanding form.²⁵⁰ ML arsenene as a nonmagnetic semiconductor in energy is suitable for electronic applications. Based on calculations, ML arsenene has two phases and semiconducting behavior. When ML arsenene is functionalized with two types of organic molecules (electrophilic acceptors and nucleophilic donors), the interfacial charge transfer between ML arsenene and the acceptor-donor molecules reduces the bandgap of arsenene and leads to p- and n-



Fig. 23 (a) d//dV spectra on different thickness of Bi(111) ultrathin films with and without magnetic field. d//dV spectra of Bi(111) 1–7 BLs. The superconducting gaps with strong coherence peaks are shown for all layers. (b) Fitted gap sizes of the spectra from 7 layers. The decay of gap sizes with NbSe₂ gap size of 1.1 meV was fitted exponentially against sample thickness (dashed curve). Inset is fitting for 7 bilayers (BLs) spectrum. (c and d) Magnetic field dependence of superconducting spectra on 1 BL and 4 BLs Bi(111). Spectra in (a, c, and d) are shifted vertically for a clearer view. Spectra were taken at the tunneling current of 0.2 nA. (a–d) Reproduced with permission from ref. 73, Copyright 2017 American Chemical Society. (e and f) Schematic diagram for bismuthene deposition and mode-locked fiber laser with microfiber-based bismuthene SA. Reproduced with permission from ref. 97, Copyright 2017 Wiley. (g) Diagram of the passively Q-switched laser experiments. Reproduced with permission from ref. 84, Copyright 2018 OSA Publishing.

type semiconducting behaviors.²³⁹ These n- and p-type arsenene semiconductors show promising applications in electronic and optoelectronic devices, such as photodiodes.

Quintuple layers of Bi2Te3 are semiconductors with the localized shallow bands. Bilayer and trilayer nanosheets are metallic, because valence electrons cannot fully occupy valence bands.352 A mixture of different nanosheets is responsible for the high electric conductivity of atomic thin films. Besides semiconductor and superconductivity materials, 2D group-VA materials can be used as other advanced electronic materials, such as infrared detectors,³¹⁰ metal electrodes,³¹¹ magnetic storage devices,256 and dissipationless transport devices.348 Lu et al. found the biaxial strain-tunable electronic properties of 2D As/Sb and h-BN/Sb van der Waals heterostructures with an indirect-to-direct gap transition.³¹⁰ The tunable bandgaps from 1 to 0 eV correspond to a spectrum range from near-infrared to mid-infrared wavelengths, implying the potential applications of antimonene-based heterostructures in infrared detectors and photoelectric devices. The sensitivity of the bandgaps of van der Waals heterojunctions to external strain shows applications in microelectronics, piezoelectric and biomaterials, such as flexible, wearable monitors of human body health.³⁹⁴ Theoretical studies revealed the superior interfacial properties of ML bismuthene-metal (Al, Ag, Au, Ir, Ti, and Pt) contacts, which provide guidance for the selection of metal electrodes in ML bismuthene devices.³¹¹ Through FPC, magnetic states were achieved for Ti, V, Cr, Mn and Fe doped-ML arsenene, showing uses in spintronics and magnetic storage devices.²⁵⁶ Nontrivial QSH insulators AsX (X = F, OH, and CH₃) MLs with obvious light absorption are candidates for room-temperature applications in dissipationless transport devices and photovoltaics.348 Similar to BP, other 2D layered group-VA (As, Sb, and Bi) nanomaterials will receive much attention in forthcoming studies and show significant uses in transparent electrodes, advanced electronic and optoelectronic devices.50,52,62,63,108

5.6. Nonlinear photonics

2D group-VA monoelemental nanomaterials present tunable broadband nonlinear optical properties under laser pulses and show applications in nonlinear photonic devices.³⁹⁵ Few-layer antimonene (FLA) was prepared by LPE and decorated on a microfiber to design optical devices.79,94 Considering the strong Kerr nonlinearity of FLA at 1550 nm, a nonlinear photonic device was fabricated via an evanescent field interaction scheme. The FLA-coated microfiber device operated as an all-optical Kerr switcher with an extinction ratio up to 12 dB. This device operated as a four-wave mixing-based wavelength converter with a conversion efficiency of 63 dB. The modulated high-speed signal at a radio frequency of 18 GHz could be converted with the wavelength conversion device. FLA had a high nonlinear refractive index of up to 10^{-5} cm² W⁻¹.⁸⁹ Because of their long-term stability in ambient conditions and high durability, 2D FLA-based nonlinear photonic devices (optical switchers, Kerr shutters, and beam shapers) can be used in next-generation, high-speed optical communication. Antimonene, as a new 2D group-VA material beyond

phosphorene, was predicted to exhibit significant electronics and optical properties with improved stability. FLA has broadband nonlinear optical responses and potential as superior optical Kerr media with high stability.^{89,92} The performance of FLA-based devices is superior to its unstable counterpart phosphorene. FLA serves as a nonlinear optical medium for high-speed optical switching and wavelength conversion in optical communication.^{396,397}

To employ the saturable absorber (SA) properties of FLA, an FLA-decorated microfiber was designed as an optical SA, allowing passive mode-locking and Q-switching operations at the telecommunication band.87 The microfiber had ultra-short pulse generation and all-optical thresholding with long-term stability. According to open-aperture Z-scan laser measurements, FLA is stable and has broadband nonlinear optical responses. In the mode-locking regime, pulses centered at 1.55 μ m were detected with a pulse width of ~550 fs. The intracavity pulse energy was 60 picojoules. In the Q-switching regime, a tunable pulse repetition rate of 20-50 kHz was obtained. Thus, this microfiber can serve as an effective optical thresholder to suppress the noise of pulses in transmission systems. The signal-to-noise ratio of the transmitted signals was improved up to ~ 10 dB. These results provide guidance for the applications of 2D group-V monoelemental materials in ultra-short pulse generation and all-optical thresholding with long-term stability. Zhang et al. verified the superior nonlinear absorption properties of β-antimonene sheets, which were studied based on Zscan methods.82 Both saturated absorption and optical limiting were observed. Antimonene had intense saturated absorption and two-photon absorption properties.398 The nonlinear absorption at 1064 nm excitation is slightly better than that at 532 nm excitation. Antimonene is a promising candidate as an SA and optical limiting material, such as invisible infrared laser. Based on the saturable absorption feature of 2D nanomaterials, a passive Q-switched Nd³⁺ solid-state laser with antimonene as the SA was realized (Fig. 23g).84 Upon 946 and 1064 nm laser emissions of Nd:YAG crystals, the Q-switched pulse widths were 209 and 129 ns and the peak powers were 1.48 and 1.77 W, respectively. Upon the 1342 nm laser emission of Nd:YVO4 crystals, the Q-switched pulse width was 48 ns and the peak power was 28.17 W. Antimonene can be employed as a stable broadband optical modulating device for solid-state lasers and exhibits effective long-wavelength operations.396,397

Few-layer bismuthene was prepared *via* sonochemical exfoliation, and its nonlinear optical response in the visible region was studied.⁹⁷ The nonlinear refractive index of bismuthene was $\sim 10^{-6}$ cm² W⁻¹, which was measured based on spatial self-phase modulation. Bismuthene has a direct energy bandgap at 1550 nm. Its saturable absorption properties were studied at the telecommunication band, showing an optical modulation depth of 2.03% and a saturable intensity of 30 MW cm⁻². Under the optimal laser parameters, a 652 nm femtosecond (fs) optical pulse centered at 1559 nm was generated. The results implied that bismuthene-based SA is an excellent material for application in ultrafast SA devices (Fig. 23e and f). Owing to the great potential of bismuthene in ultrafast photonics, future studies should focus on the exploration of efficient bismuthene-based

photonic devices, such as optical modulators, optical switchers and detectors. Few-layer bismuthene with a thickness of 3 nm and a lateral size of 0.2 μ m had a thickness-dependent energy gap from almost zero to 0.55 eV.⁹⁸ Considering its strong nonlinear refraction effects, all-optical switching of two laser beams was realized in the few-layer bismuthene based on spatial cross-phase modulation. The high all-optical switching implied that bismuthene-based 2D materials are candidates as all-optical switchers.^{399,400} The semi-metallic and long-term stable properties of bismuthene make it a new nonlinear optical material for applications in infrared and mid-infrared optoelectronics, such as broadband detectors, nonlinear optical switchers and modulators.

5.7. Light-emitting devices

2D group-IVA materials (graphene, silicene, germanene, and stanene) are semimetallic owing to their lack of suitable bandgaps, restraining their use in light-emitting devices. 2D group-VA materials (phosphorene, arsenene, antimonene, and bismuthene) are semiconductors and have fundamental bandgaps, making them candidates as new materials in lightemitting devices. Phosphorene acts as an atomically thin 2D optical nanomaterial and has direct exciton emission. The emission wavelength of ML or few-layer phosphorene is tunable by controlling the number of stacking layers. Few-layer

phosphorene exfoliated on a silicon substrate had intense layerdependent photoluminescence (PL).401 By measuring PL spectra, the strong PL emission peaks of phosphorene with 2-5 layers were located at 961, 1268, 1413 and 1558 nm, corresponding to the energy peaks of 1.29, 0.98, 0.88 and 0.80 eV, respectively. The PL emission peaks of few-layer phosphorene mainly originated from excitons, implying the lower bounds on its fundamental bandgaps. The key information provided in PL spectra promotes studies on the exciton features and electronic structures in phosphorene. The PL spectra of ML and bi- and trilayer phosphorene were measured at 77 K under the unpolarized photoexcitation of 2.33 eV.402 The PL peak energy matched well with the absorption spectra, verifying the direct bandgap of phosphorene. Defect state-derived near-infrared PL emission was detected in phosphorene.403 With a linear increase in excitation intensity, sublinear increase in PL intensity at 1240 nm was obtained, which verified the defect-based emission of phosphorene. The defect emission was much brighter than the exciton emission at low temperature, and the brightness of the defect emission was retained at room temperature. Bright room-temperature PL emission can serve as a light source for near-infrared optoelectronics.

The PL emission of 2D group-VA materials beyond phosphorene was demonstrated. Multilayer arsenene nanoribbons were prepared and had a PL emission peak of 540 nm at room temperature.⁷⁷ According to the green PL emission, the bandgap



Fig. 24 (a) PL emission spectra of bare Si substrate and BiNSs on Si excited at 325 nm. (b) PL emission spectra of bare Si substrate and BiNSs on Si excited at 325 nm. (c) PL spectra of the free-standing pristine BiNPs and BiNSs on Si substrate excited at 325 nm. (d) Deconvoluted photoemission spectra of BiNSs, representing energy wise distribution of PL peaks in the visible region of spectra. (a–d) Reproduced with permission from ref. 72, Copyright 2017 Wiley. (e) Raman spectra of intrinsic InSb and InSb after N₂ plasma immersion with 100 W power for 30 min, followed by annealing at 450 °C for 30 min. (f) PL emission spectra of multilayer antimonene/InN/InSb at different temperatures. Inset is the image of samples in a spectrometer chamber at room temperature. (e and f) Reproduced with permission from ref. 96, Copyright 2016 Royal Society of Chemistry.

of the multilayer arsenene nanoribbons was calculated to be \sim 2.3 eV. There are two main factors that cause bandgap opening. One is the quantum confinement effect caused by dimensionality reduction, and the other is turbostratic stacking. Multilayer antimonene nanoribbons uniformly distributed on InSb were prepared via a plasma-assisted process and had room-temperature orange PL (Fig. 24).96 Notably, the bandgap opening was induced by the quantum confinement effect of the nanoribbon structures and turbostratic stacking of the antimonene layers, including various types of stacking, such as AA stacking.⁷⁷ Based on the orange PL emission at ~610 nm, the bandgap of the multilayer antimonene nanoribbons was \sim 2.03 eV. PL measurements suggested that 2D multilayer arsenene and antimonene nanoribbons with proper band structures have potential use in transistors and light-emitting diodes. Hussain et al. prepared free-standing ultrathin Bi nanosheets (BiNSs) with superior PL (Fig. 24a-d).72 The PL spectra of the BiNSs were measured at room temperature upon excitation of 325 nm and exhibited a sharp peak at \sim 661 nm. This peak vanished upon 532 nm excitation since it came from the second harmonic generation of the 325 nm laser. The PL responses of large-area and high crystalline BiNSs may be due to the carrier confinement effect. The process-dependent crystal defect and dislocation caused the trapping of electrons and excitons in ultrathin BiNSs. Further theoretical and experimental studies are needed to study the PL emission of 2D group-VA elemental materials for their significant applications, especially in optical sensors, bioimaging, transistors, light-emitting diodes and optoelectronic devices.50,62,89,395,404-408

5.8. Gas sensors

2D materials often have large specific surface areas, high surface activities and electrical conductivity because of quantum size effects. The absence of bandgaps for typical 2D materials, such as 2D group-IVA materials, restrains their use in semiconductor devices (gas sensors). 2D group-VA materials with moderate bandgaps of 0.36-2.62 eV have emerging and fascinating physical properties, rendering them superior candidates for gas detection.^{47,409-411} The adsorption of CO, CO₂, NH₃, NO and NO₂ gas molecules on ML phosphorene was studied by FPC coupled with non-equilibrium Green's functions.²⁵⁸ Compared with graphene and MoS₂, phosphorene exhibits stronger adsorption of gas molecules with higher sensitivity and selectivity, implying its potential as an efficient gas sensor. Phosphorene is sensitive to N-containing gas molecules (NO and NO₂). There is a dramatic I-V relation change before and after gas adsorption on phosphorene. The adsorption of gas molecules on phosphorene has significant transport features and current/resistance changes. By theoretical calculations, the sensing of NO2 gas occurred on few-layer phosphorene-based FETs.⁴⁰⁹ Through Raman spectroscopy measurements, there was no obvious change in the characteristic peaks before and after target gas adsorption, implying stable NO2 adsorption on multilayer phosphorene. The limit of detection of the phosphorene-based gas sensor was estimated to be \sim 5 ppb of NO₂, showing high sensitivity for gas detection. The conductance measurements revealed that the sensor had reversible adsorption and desorption of NO_2 gas and high recovery after flushing the sensor device with Ar.

Cho et al. studied the gas-sensing performance of phosphorene, graphene and MoS2.410 Through electrical sensing measurements, the sensitivity of phosphorene was determined to be ~ 20 times higher than that of graphene and MoS₂. The excellent performance in response/recovery time, selectivity, molar response factor and adsorption verified that phosphorene is a superior gas sensing material. Besides NO₂, phosphorene was sensitive to methanol vapor.411 In the presence of other vapors, the phosphorene-based sensing device was selective for methanol and had long-term stability. Other 2D group-VA nanomaterials were predicted to be gas sensing materials, such as the typical buckled arsenene and antimonene.329,333 Arsenene had high sensitivity to gas molecules.^{257,331} Liu et al. studied the adsorption of CO, CO₂, N₂, NH₃, NO and NO₂ on ML arsenene.²⁵⁷ NO_x adsorbents had the largest charge transfer and greater changes in conductivity. The adsorption of NO_x led to a magnetic moment of 1 $\mu_{\rm B}$. Thus, arsenene is a candidate for NO and NO₂ gas sensing. Through FPC, some gases (N2, CO2, O2, H2O, and CO) were weakly adsorbed on antimonene. Other toxic air-pollution gases (NH₃, SO₂, and NO) can be strongly adsorbed on antimonene, with considerable adsorption energies and elevated charge transfers.335 This is ascribed to the contribution of the frontier orbitals of molecules closer to the Fermi level and apparent orbital hybridization. The moderate adsorption energies, appreciable charge transfer and physical adsorption features of antimonene make a potential pollutant gas sensor to detect NH₃, SO₂ and NO gases. Antimonene enabled the adsorption and desorption of these gases easily. Antimonene with NO2 activated and chemisorbed can serve as a disposable gas sensor or metal-free catalyst to detect and catalyze NO₂ gas.

The sensitivity of CO to antimonene was evaluated by FPC.332 CO adsorption on pristine antimonene is physical adsorption and it is converted to chemical adsorption after its doping with atoms. An external electric field varying from -0.5 to 0.21 eV Å⁻¹ improves the sensitivity of CO on doped antimonene, which is helpful to realize CO gas sensing at room temperature. The adsorption and desorption of CO molecules on doped antimonene can be controlled via an external electric field, which is more suitable for gas collection, storage and sensing compared to pristine antimonene. Different types of doped antimonene (Si-Sb, Al-Sb and Co-Sb nanosheets) were explored as potential sensing materials for CO detection. NO2 or SO2 gas had chemisorption on B-doped arsenene and had physisorption on pristine or N-doped arsenene with moderate adsorption energies (Fig. 25a-e).333 When two gas molecules were adsorbed on pristine or doped arsenene, a positive change in electronic properties was detected through the density of states (DOS) analysis. According to the I-V characteristic curves, the conductivity of pristine (N-doped) arsenene was enhanced obviously after NO2 (SO2) adsorption due to the increase in holecarriers. N-doped arsenene was applied as a new material for SO₂ gas sensing. Pristine arsenene has potential application in NO2 gas sensing, showing high sensitivity.

Kistanov et al. studied the interactions of antimonene with small molecules (CO, NO, NO₂, H₂O, O₂, NH₃, and H₂).³³⁴ NO, NO₂, H₂O, O₂ and NH₃ served as charge acceptors, and CO had negligible charge transfer. H₂ acted as the charge donor to antimonene, with 10 times higher charge transfer than H₂ on phosphorene. The interaction of O₂ with antimonene was much stronger than that with phosphorene. Pristine antimonene may suffer from oxidation in ambient conditions especially at elevated temperature. The kinetic barrier for the splitting of O2 molecules on antimonene is low (\sim 0.4 eV). Different from the donor role of H₂O in phosphorene, the acceptor role of H₂O on antimonene suppresses the structure degradation of oxidized antimonene by preventing proton transfer between the H₂O molecule and O₂ species to yield acids. To achieve high environmental stability, the acceptor role of H₂O can avoid the structural decomposition of 2D layered materials. The surface

oxidation layer of antimonene acts as an efficient passivation layer from the degradation of underlying layers, similar to other 2D layered materials, such as BP and graphene.^{41–63,412–414} Antimonene layers are separated and protected by noncovalent modification with O_2 and environmental molecules. Surface functionalized antimonene with high stability and antioxidant ability demonstrates promising applications in catalysis, storage and gas sensors.

5.9. Thermoelectric materials

As functional materials, thermoelectric materials convert waste heat directly into electrical energy. The performances of these materials are quantified by a dimensionless figure of merit, ZT= $S^2 \sigma T/k$, where *S* is the Seebeck coefficient, σ is electrical conductivity, *T* is temperature and $k = k_e + k_p$ is total thermal conductance, which can be split into electron (k_e) and phonon



Fig. 25 DOS of (a) NO₂/pristine-arsenene, (b) SO₂/N-arsenene and (c) SO₂/B-arsenene. The Fermi level was set as zero. (d) I-V characteristic curves of the pristine arsenene and NO₂/pristine arsenene. (e) I-V characteristic curves of N-arsenene and SO₂/N-arsenene. Reproduced with permission from ref. 333, Copyright 2017 IEEE.

 (k_p) contributions.⁴¹⁵ Materials with a ZT larger than 3 are suitable for thermoelectric generation.416 In contrast to bulk crystals, low-dimensional materials possess potential to gain a higher ZT via different engineering approaches.417,418 Based on theoretical studies, 2D group-VA materials present great potential in thermoelectric applications.^{216,218,299,419-421} Owing to their anisotropic puckered structures, group-VA crystals have strong anisotropy in electrical and thermal conductivities. The ZT value along the armchair direction is much larger than that along the zig-zag direction.^{420,422-424} By p-/n-doping and orthogonal electric fields, the thermoelectric performance of phosphorene was predicted and improved. The figure of merit ZT reached up to 1.5 along the armchair direction at room temperature.²²⁵ The influence of applied strain on the thermoelectric effect of BP was studied.419,421,425 Upon 5% applied strain along the zig-zag direction of phosphorene, the Seebeck coefficient and electrical conductivity were improved dramatically. Upon 8% applied strain along the armchair direction of phosphorene, the ZT was 2.12 at room temperature.421 High thermoelectric properties of phosphorene were achieved by cutting phosphorene along the armchair and zig-zag directions to form engineered nanostructures.426 The ZT of phosphorene nanoribbons with armchair edges was optimized to be 6.4 at room temperature, indicating their excellent thermoelectric use.

Sandonas et al. reported the thermoelectric properties of puckered phosphorene and arsenene.420 Puckered arsenene had stronger anisotropic thermoelectric responses than phosphorene. Arsenene had moderate n-type doping at 300 K. The ZT of arsenene reached up to 1.0 along the armchair direction. Buckled antimonene had a relatively low thermal conductivity, which was further lowed by chemical functionalization.216 Antimonene may be a potential and excellent thermoelectric material. Cheng et al. investigated the figure of merit, ZT, of buckled and puckered bismuthene at different temperatures.^{209,217} Based on FPC combined with the Boltzmann transport equation, buckled bismuthene had much larger ZT than its bulk structure.²⁰⁹ Large power factors $(S^2\sigma)$ and low thermal conductivity are responsible for the high thermoelectric performance of buckled bismuthene. The ZT of buckled bismuthene reached 2.4 at room temperature and 4.1 at 500 K. Based on theoretical predictions, puckered bismuthene had a high ZT of 6.4 for n-type systems at room temperature.²¹⁷ ZT distinctly exceeded that of buckled bismuthene with a ZT of 2.4.²⁰⁹ The ZT of the buckled bismuthene was higher than 2.0 in a broad region of temperature and carrier concentration. Puckered bismuthene with low deformation potential constants and excellent thermoelectric features is inherently relative to weak electron-phonon coupling strength.

Sun *et al.* investigated the thermoelectric transport properties of arsenene featuring puckered and buckled structures.²²¹ The two types of arsenene as indirect bandgap semiconductors had high charge carrier mobilities in the range of 40–800 cm² V⁻¹ s⁻¹. The puckered arsenene had low and anisotropic lattice thermal conductivities of 9.6 W m⁻¹ K⁻¹ in the armchair direction and $30.7 \text{ W m}^{-1} \text{ K}^{-1}$ in the zig-zag direction. The preferential thermal transport direction is orthogonal to electrical transport direction, which enhances the thermoelectric figure of merit in the armchair direction to 0.7 for p-doping and 1.6 for n-doping at room temperature. According to FPC, puckered arsenene is a good thermoelectric material. Sharma et al. studied the thermoelectric properties of arsenene and antimonene (Fig. 26a and b).²²⁰ Both materials had large bandgaps and low lattice thermal conductivities, resulting in large Seebeck coefficients. Compared with arsenene, antimonene has smaller phonon frequencies and group velocities at room temperature, causing sensitive thermoelectric responses. A ZT of up to 0.58 was achieved through moderate n-type doping of ~ 1013 cm⁻². The room-temperature ZT of ML bismuth was calculated to be ~ 2.1 for n-type doping and ~ 2.4 for p-type doping (Fig. 26c).²⁰⁹ The maximal ZT of 4.1 was achieved at 500 K. For the distorted bismuth (110) layer, the maximum ZT of 6.4 was achieved for n-type systems, stemming from the weak scattering of electrons.²¹⁷ The distorted Bi layer maintained a high ZT in a wide temperature and carrier concentration range. Deformation potential constant with electron-phonon scattering strength is the paradigm in the search for high-performance thermoelectric materials. The buckled antimonene had a ZT of 2.15 at room temperature.²²³ After simple biaxial strain engineering, the ZT increased to 2.9 under 3% tensile strain (Fig. 26d), which is attributed to its tunable electronic structures and reduced thermal conductance. Recently, fabricated buckled antimonene was stable in ambient conditions, making it a new candidate for application in thermoelectric devices. After engineering modification, 2D group-VA materials exhibit great potential for promising thermoelectric applications.59,219

5.10. Biomedical applications

2D layered group-VA nanomaterials have great prospects in biomedical applications, such as biosensing,42,427,428 bioimaging,429 drug delivery and release,430,431 photodynamic theranostics,432 and photothermal therapy.433 The non-toxic BP is electrocatalytic for some reactions and can act as an ideal material for biosensing.42 An electrochemical myoglobin biosensor was designed via the functionalization of BP nanosheets with poly-L-lysine and a myoglobin-specific aptamer.434 The BP-based complex was immobilized on a screen-printed electrode and the detection of myoglobin was performed via Fe²⁺/Fe³⁺ chemistry reaction. A field-effect transistor was fabricated using few-sheet BP,435 which could detect IgG via anti-IgG linked to Au NPs placed on the top of BP nanosheets. BP has a wide electrochemical cathodic window because it is not highly electrocatalytic for hydrogen evolution. Nevertheless, its anodic window is somewhat limited due to the electrochemical oxidation of BP itself, ~0.6 V (vs. Ag/AgCl) at neutral pH.436 BP shows significant anisotropic electrochemical properties, with much faster heterogeneous electron transfer at its edge sites compared with its basal plane, similar to that of graphite and MoS₂.⁴² This feature is conducive to the sensing of electroactive biomolecules at the edge plane sites of BP monocrystal electrodes.

Due to the intrinsic unique properties of BP, including negligible elemental cytotoxicity, high drug-loading potential, long blood circulation time and specific clearance pathways, in



Fig. 26 (a) Figure of merit as a function of temperature for pristine materials and (b) as a function of carrier concentration. Reproduced with permission from ref. 220, Copyright 2017 American Physical Society. (c) Calculated *ZT* value of ML Bi as a function of temperature. Black and red lines correspond to n- and p-type doping. Reproduced with permission from ref. 209, Copyright 2014 American Chemical Society. (d) Thermoelectric figure of merit of the buckled antimonene with biaxial strain deformation. Bandgap and photonic thermal conductance of buckled antimonene with biaxial strain deformation. Reproduced with permission from ref. 223, Copyright 2017 American Chemical Society.

recent years BP has been considered as a promising nanoplatform for various biomedical applications, such as bioimaging, phototherapy, drug delivery, combination therapy and theranostics.437 Zhao et al. explored Nile blue dye-modified BP nanosheets for near-infrared imaging-guided photothermal therapy.433 Because the lack of air and water stability may hinder the biomedical applications of BP, the covalent functionalization strategy was expected to enhance its stability and biocompatibility, also resulting in near-infrared fluorescence. Under the irradiation of an 808 nm laser, the dye-modified BP showed strong photothermal therapy and near-infrared imaging in MCF7 breast tumor-bearing nude mice. Besides, the photodynamic theranostics and drug release of BP have been developed towards cancer therapy in vivo, 429,430,432,435 similar to other 2D nanomaterials such as 2D boron nanosheets.438 Besides BP, other 2D layered group-VA nanomaterials have been explored for biomedical applications. Recently, Xue et al. reported a surface plasmon resonance (SPR) sensor based on 2D antimonene for the specific label-free detection of clinically relevant biomarkers miRNA-21 and miRNA-155.427 The high sensitivity of this SPR sensor depends on the strong interactions between antimonene and single-stranded DNA, and the enhanced coupling between localized-SPR of gold nanorods (AuNRs) and propagating-SPR of a gold film (Fig. 27a). This biosensor is the first report that uses antimonene for clinically relevant nucleic acid detection, constituting an extraordinary opportunity to develop lab-on-chip platforms.

Tao *et al.* developed a photonic drug-delivery platform based on 2D PEGylated antimonene nanosheets that had multiple advantages,⁴³⁹ including excellent photothermal, high drugloading, spatiotemporally controllable drug release triggered by near-infrared light and moderate acidic pH, high accumulation at tumor sites, deep tumor penetration by both extrinsic NIR light and intrinsic pH stimulus, multimodal-imaging and inhibition of tumor growth without side effects and potential degradability, which addressed several key limitations of cancer nanomedicine (Fig. 27b). Deep insights on intracellular actions improve the cellular-level understanding of antimonene-based nanosheets and other emerging 2D nanomaterials. This work first reported 2D antimonene-based photonic drug delivery platforms, probably marking an exciting jumping-off point for studies into the applications of 2D antimonene nanomaterials in cancer theranostics. Currently, the biomedical applications of 2D layered group-VA pnictogen materials and pnictogencontaining 2D hybrids are still rarely reported, such as some relative studies on antimonene.^{427,439} The forthcoming biomedical studies of 2D layered group-VA pnictogen materials are rationally driven by the explosive development of their cousin BP or other 2D materials such as graphene, TMDs, MXenes, and MOFs.

In recent years, the ultralow and non-toxic properties of BP have facilitated its explosive development in biomedical

applications. Among the 2D layered group-VA (P, As, Sb, and Bi) monoelemental nanomaterials (phosphorene, arsenene, antimonene, and bismuthene) and their 2D hybrids, the non-toxic element (P, Sb, and Bi)-based phosphorene, antimonene and bismuthene demonstrate great prospects for biosensing, bioimaging, drug release, photodynamic theranostics and photothermal therapy.⁴²⁷⁻⁴³⁹ Nevertheless, the elemental toxicity of As may hinder the experimental exploration of arsenene and its consequent biomedical applications.³⁷ A plasma-assisted process can be used to prepare multilayer or few-layer arsenene on solid substrates such as InAs. The prepared arsenene can be modified with low-toxic molecules and materials to construct



Fig. 27 (a) Fabrication of a miRNA sensor integrated with antimonene nanomaterials. Schematic illustration of the strategy employed to detect antimonene–miRNA hybridization events. (I) Antimonene nanosheets was assembled on Au film surface. (II) AuNR–ssDNAs were adsorbed on antimonene nanosheets. (III) miRNA solution with different concentrations flowed through antimonene surface, and paired up to form a double-strand with the complementary AuNR–ssDNA. (IV) The interaction between miRNA with AuNR–ssDNA results in release of AuNR–ssDNA from antimonene nanosheets. The reduction in the molecular of AuNR–ssDNA on the SPR surface results in a significant decrease in the SPR angle. Reproduced with permission from ref. 427, Copyright 2019 Springer Nature. (b) Schematic illustration of: (a) preparation of 2D AM-PEG/DOX NSs and (b) systemic administration of AM-PEG/DOX NSs as photonic nanomedicines for multimodal-imaging-guided cancer theranostics. Reproduced with permission from ref. 439, Copyright 2018 Wiley.

various functionalized nanostructures, which endow arsenene with high stability, biocompatibility and multi-functions for biomedical applications. The long-term stability of 2D group-VA nanomaterials was evaluated in previous reports.430,431,433,439 BP nanosheets had almost no cytotoxicity to 4T1, HeLa, L929 and A549 cells even at a concentration of 200 μ g mL⁻¹. After *in vivo* toxicity investigation on healthy Sprague-Dawley rats, no obvious change in liver and kidney functions was detected after the injection of BP for 7 d.430 Tao et al. conducted a long-term biodistribution study via inductively coupled plasma mass spectrometric analysis of antimony in different organs.439 The antimony levels in major organs showed a distinct trend of persistent decrease. Antimonene-based nanosheets were barely detectable after intravenous injection for 30 d. These results indicated the clearance of the nanosheets from the mouse body and may represent complete metabolic degradation. This potential degradability makes them quite promising for applications in cancer theranostics.

6. Conclusion and perspective

Different from semimetallic group-IVA and metallic group-IIIA materials, 2D layered group-VA monoelemental nanomaterials are semiconductors with a broad range of fundamental bandgaps that can be tuned from 0.36 to 2.62 eV, which give them great potential as promising candidates for application in advanced nanodevices. The recent significant advances in emerging 2D group-VA materials have aroused numerous scientists to accelerate the discovery of new 2D materials that have many intriguing physiochemical properties, functional structures and important applications. Compared with phosphorene and BP, 2D group-VA pnictogen monoelemental (As, Sb and Bi) nanomaterials possess superior stability, tunable direct bandgaps, charge-carrier mobility and unique in-plane anisotropic structures, making them superior candidates for efficient applications in extensive research areas. This present review performed a timely and comprehensive overview of the principal theoretical and experimental studies on 2D group-VA nanomaterials beyond BP reported in recent years, focusing on their general synthetic methods, fundamental properties, functionalized nanostructures and potential applications.

The synthetic methods for 2D group-VA materials were divided into top-down and bottom-up methods. The top-down methods include mechanical, ultrasonic, electrochemical exfoliation, plasma-assisted process, and hot-pressing method. The bottom-up methods mainly mention molecular beam epitaxy, van der Waals epitaxy, chemical vapor deposition, solvothermal, hydrothermal synthesis, high-temperature melting, etc. Different methods have particular merits towards various research objectives. The large-scale preparation of 2D group-VA materials with high stability against oxidation and degradation is especially crucial for enhancing their physiochemical properties and versatile practical applications. The combination of different methods is considered an effective strategy to prepare high-quality 2D group-VA materials. For the top-down methods, mechanical and electrochemical exfoliations can yield multilayer nanosheets from bulk crystals or powder. Then, ultrasonic

exfoliation efficiently transfers multilayer nanosheets into fewor single-layer nanosheets. In the case of the bottom-up methods, molecular beam epitaxy, van der Waals epitaxy and chemical vapor deposition are suitable for the preparation of 2D group-VA pnictogen monoelemental materials, while pnictogen-containing hybrids are often prepared from solvothermal and hydrothermal synthesis and high-temperature melting. The combination of two bottom-up methods can promote the realization of new 2D group-VA pnictogen hybrids or new heterostructures with unique structures and enhanced properties. The assistance of organic ligands during the preparation process can improve the stability of the products. Thus, future studies should focus on the exploration and improvement of the synthetic methods, mainly considering low-cost, environmentally friendly raw materials, facile manipulation, low-energy-consuming process and high productivity.

According to theoretical predictions and experimental studies, 2D group-VA materials belong to semiconductors and have tunable direct bandgaps, unique in-plane anisotropy and superior carrier transport capability, facilitating their promising applications in advanced electronic and optoelectronic devices. Great efforts have been devoted to the investigations of the mechanical, thermal, optical, magnetic and electronic properties of 2D group-VA materials. These fundamental properties are mentioned, but some challenges still remain. Thus, forthcoming studies need to elucidate the electron structure-related mechanisms to improve the present properties of 2D group-VA materials and extend these properties to new research fields. The combination of theoretical models and practical experiments is an indispensable way to explore new 2D group-VA nanostructures, which are expected to gain novel and superior properties. In the case of 2D group-VA pnictogen materials, some significant properties are still hardly reported, such as photothermal effects and upconversion luminescence properties. Similar to phosphorene and BP, 53,54,58,440 these nanomaterials have a wide optical absorption covering the visible-light to infrared regions, implying their excellent thermoelectric properties. They are expected to exhibit photothermal properties for phototherapy. These nanomaterials possess tunable broadband nonlinear optical absorption for application in nonlinear photonic devices and down-conversion PL for light-emission devices.^{56,395,398} These results imply the potential upconversion luminescence of 2D group-VA pnictogen nanomaterials for bioimaging applications, which need to be further verified in future studies. The forthcoming studies will be rationally driven by the explosive development of other 2D materials, such as BP, graphene, TMDs, MXenes, and MOFs.

2D group-VA nanomaterials can be further modified to fabricate various functional nanostructures for a wide range of applications. Functional nanostructures mainly involve hybrid heterostructures, doping of atoms and molecules, surface functionalization of 2D group-VA nanomaterials and pnictogencontaining 2D hybrids. Notably, the synergistic interactions between nanomaterials and other 2D or low-dimensional nanomaterials can result in novel and improved physiochemical properties in the resultant hybrid materials. Functional nanostructures consisting of 2D group-VA nanomaterials

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and zero-/one-dimensional (0D/1D) materials are barely explored. Based on the synergistic enhancement effects between typical 2D graphene (or counterparts) and zerodimensional (0D) noble nanoclusters (or quantum dots), the electronic conductivity of 2D–0D hybrids can be improved efficiently, which have high capability for use in sensors and intelligent electronic devices.^{441–446} In forthcoming studies, various novel and functionalized nanostructures, such as 2D– 0D, 2D–1D heterostructures and hybrids, will be smartly designed and fabricated based on group-VA nanomaterials. These newly developed heterostructures and hybrids are expected to exhibit novel and synergistically enhanced physiochemical properties for use in advanced nanodevices and intelligent systems.

After functional modification, 2D group-VA pnictogen materials-based systems have a broad range of significant applications involving popular research fields, such as catalysis, energy storage, field-effect transistors, topological spintronic devices, electronic devices, nonlinear photonics, light emitting devices, gas sensors, thermoelectric materials and biomedicine. These applications are explored based on both theoretical calculations and experimental studies, but the practical performance stabilities and device efficiencies of these systems are still required to be further improved when compared with typical 2D nanomaterials-based systems and commercialized nanodevices. The superior properties of 2D group-VA nanomaterials can be realized by improving their synthetic methods and functional structures. Thus, future studies should focus on rational design schemes and optimized fabrication procedures for advanced functional systems with the use of 2D group-VA pnictogen nanomaterials. The improved systems and devices with high-performance stability and efficiency will receive promising applications in current fields. They will find new opportunities for applications in other extended and significant fields, including phototherapy, biomedical imaging, electrochemical sensing, flexible and wearable devices, intelligent electronics, and versatile optoelectronics.

Conflicts of interest

There are no conflicts to declare.

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