ChemComm

FEATURE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2025, **61**, 14312

Engineering noncentrosymmetry in 2D atomic crystals *via* chemical vapor deposition

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In contrast to extensively studied centrosymmetric 2D materials, noncentrosymmetric 2D atomic crystals (2DACs) exhibit unique properties—such as nonlinear optical responses, ferroelectricity, and piezoelectricity—making them promising for next-generation optoelectronics and quantum devices. Despite their potential, the controlled synthesis and scalable fabrication of these materials remain challenging, limiting further exploration of their physics and applications. This Feature Article highlights our group's recent advances in engineering noncentrosymmetry in 2DACs *via* chemical vapor deposition (CVD). We discuss three key strategies: (1) thinning of intrinsically noncentrosymmetric bulk crystals (*e.g.*, nonlayered materials), (2) precise manipulation of van der Waals (vdW) stacking sequences to break inversion symmetry in 2DACs, and (3) alternative routes including self-intercalation, heterostructure assembly, and etching. By correlating synthesis protocols with emergent properties, we demonstrate how CVD enables tailored asymmetry at the atomic scale. Finally, we provide a forward-looking perspective on unresolved challenges, such as achieving phase purity and large-area homogeneity, and propose future research directions for integrating noncentrosymmetric 2DACs into functional devices. This review aims to serve as a roadmap for the controlled synthesis and property exploration of noncentrosymmetric 2DACs.

Received 24th June 2025,
Accepted 18th August 2025

DOI: 10.1039/d5cc03564c

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Introduction

Two-dimensional atomic crystals (2DACs), including graphene, transition metal dichalcogenides (TMDs), hexagonal boron nitride (h-BN), black phosphorus, and bismuth oxide, exhibit exceptional optical, magnetic, electrical, and spin properties owing to quantum confinement effects at the atomic scale.[1] The electronic behaviour of 2DACs spans semimetallic, semiconducting, and insulating regimes, and their ultrathin profiles—for example, monolayer graphene with a thickness of merely ~0.3 nm—surpass the physical scaling limits of conventional silicon-based materials, offering promising pathways toward sub-1 nm transistor technologies.[2,3] Furthermore, the stacking of different 2DACs facilitates heterostructure engineering,[4] enabling the integration of multiple functionalities within a single device and unlocking unprecedented opportunities for the miniaturization and integration of optoelectronic semiconductor systems.

Beyond dimensionality control, the intrinsic crystal structure and symmetry—particularly the presence or absence of inversion symmetry—also play a decisive role in dictating the fundamental physical properties of 2DACs.[5] Based on inversion symmetry, 2DACs can be classified into centrosymmetric and noncentrosymmetric crystals (Fig. 1a and b).[6] These two types exhibit pronounced differences in their band structures, optical responses, and charge transport behaviours. Centrosymmetric 2DACs, such as monolayer graphene (Fig. 1a) and h-BN, remain invariant under spatial inversion ($r \rightarrow -r$). Their high structural symmetry endows them with broadband optical absorption and high carrier mobility, making them suitable for applications in broadband photodetectors and ultrafast optoelectronic devices. In contrast, noncentrosymmetric 2DACs—such as monolayer MoS_2 (Fig. 1b) and WSe_2—lack spatial inversion symmetry, giving rise to distinct properties such as strong second-order nonlinear optical responses (*e.g.*, second harmonic generation, SHG), valleytronic phenomena, and anisotropic photoresponse.[7,8] These characteristics make noncentrosymmetric 2DACs uniquely advantageous for applications in polarization control, nonlinear optics, and ferroelectric, and quantum devices.[9] By effectively engineering symmetry breaking, noncentrosymmetric 2DACs are poised to drive the development of next-generation semiconductor technologies toward greater efficiency and intelligence.

Despite their attractive physical properties and theoretical prevalence, noncentrosymmetric 2DACs have remained considerably less explored than centrosymmetric 2DACs.[10] This research gap is particularly striking given that, from a crystallographic standpoint, noncentrosymmetric crystals are theoretically more abundant. According to crystallographic theory, only 11 of the 32 crystal point groups possess a centre of inversion, categorizing them as centrosymmetric; the remaining 21 are noncentrosymmetric, as summarized in Table 1. Thus, from a symmetry classification perspective, noncentrosymmetric crystals are theoretically more abundant. However, achieving controllable synthesis of noncentrosymmetric 2DACs at the atomic scale remains highly challenging within current mainstream chemical vapor deposition (CVD) methods. Tailoring atomic configurations and achieving large-area, high-quality growth of noncentrosymmetric 2DACs are still significant hurdles. This difficulty primarily stems from the fact that commonly used growth substrates are typically centrosymmetric.[11] During the

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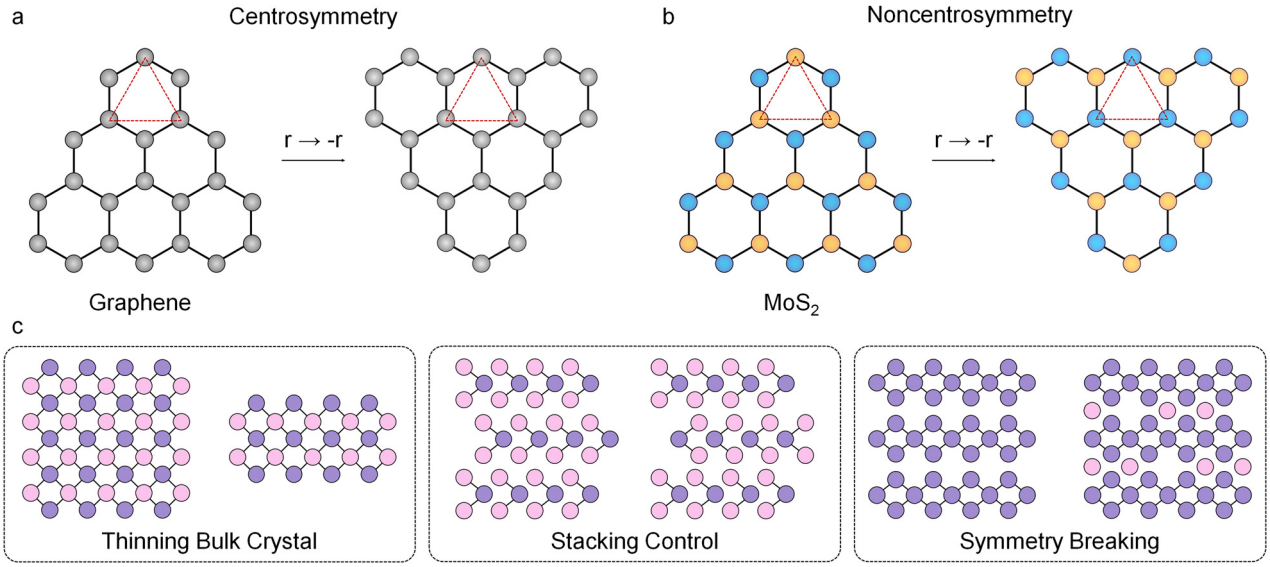

Fig. 1 Schematic illustration of the (a) centrosymmetric atomic configuration of graphene, (b) noncentrosymmetric atomic configuration of monolayer MoS_2. (c) Three distinct synthesis strategies for achieving noncentrosymmetric 2DACs.

Table 1 Classification of the 32 crystallographic point groups into centrosymmetric (with inversion centre) and noncentrosymmetric (without inversion centre) categories

Crystal system	Centrosymmetric point groups	Noncentrosymmetric point groups
Triclinic	$\bar{1}$	1
Monoclinic	$2/m$	2, m
Orthorhombic	mmm	222, $mm2$
Tetragonal	$4/m$, $4/mmm$	4, $\bar{4}$, 422, $4mm$, $\bar{4}2m$
Hexagonal	$6/m$, $6/mmm$	6, $\bar{6}$, 622, $6mm$, $\bar{6}m$
Trigonal	$\bar{3}$, $\bar{3}m$	3, 32, $3m$
Cubic	$m\bar{3}$, $m\bar{3}m$	23, 432, $\bar{4}3m$

growth of noncentrosymmetric 2DACs, antiparallel domains inevitably form because their formation energies are equivalent on centrosymmetric substrates. Consequently, in contrast to the relatively facile synthesis of centrosymmetric 2DACs like graphene, growing noncentrosymmetric 2DACs continues to be a formidable challenge. Overcoming these obstacles requires a comprehensive understanding of the growth mechanisms, precise control over experimental parameters, and the development of novel synthetic strategies. Our research group is actively exploring innovative approaches, aiming to balance thermodynamic and kinetic factors to realize the controlled CVD growth of noncentrosymmetric 2DACs.

In this Feature Article, we summarize our recent advances in the controlled synthesis of noncentrosymmetric 2DACs *via* CVD, with particular emphasis on symmetry engineering. Specifically, we highlight three key approaches: (1) direct thinning of noncentrosymmetric bulk crystals into 2D layers; (2) symmetry manipulation through controlled stacking of vdW 2DACs; and (3) alternative pathways including self-intercalation, heterostructure formation, and selective etching. These approaches offer versatile pathways for tailoring inversion asymmetry and unlocking emerging functionalities. Fig. 1c provides an integrated summary of our methodology. Taken together, our efforts not only deepen the mechanistic understanding of symmetry control in 2DAC growth, but also pave the way for the integration of noncentrosymmetric 2DACs into next-generation optoelectronic and semiconductor devices. Looking ahead, we highlight critical challenges such as the precise control of phase purity and the scalable synthesis of uniform large-area noncentrosymmetric 2DACs, and outline future directions for their seamless integration into functional device applications. This work aims to serve as a roadmap for the controlled synthesis and property exploration of noncentrosymmetric 2DACs.

Characterization techniques for noncentrosymmetric 2D atomic crystals

Noncentrosymmetric 2D atomic crystals exhibit unique physical properties such as piezoelectricity, ferroelectricity, second-harmonic generation (SHG), and chiral optical responses. The characterization of noncentrosymmetry is essential for understanding their symmetry-dependent functionalities in applications ranging from nonlinear optics to quantum materials. Since centrosymmetric and noncentrosymmetric phases can have similar average structures, specialized techniques are required to distinguish them. These methods can be broadly categorized into diffraction-based, microscopy-based, and optical spectroscopy based approaches. Below, we discuss key experimental techniques and their specific capabilities in probing noncentrosymmetry.

Diffraction-based techniques

X-ray diffraction (XRD). Identifies crystal structures based on scattering patterns. In centrosymmetric crystals, diffraction intensities follow Friedel's law, but this symmetry breaks in noncentrosymmetric crystals due to anomalous scattering,

requiring complementary methods like resonant XRD, SHG, or transmission electron microscopy (TEM) for confirmation.

Convergent beam electron diffraction (CBED). Sensitive to atomic displacements breaking symmetry, CBED provides atomic-scale resolution and can directly be used to visualize noncentrosymmetry at defects or domain walls. It is superior to XRD and TEM in symmetry analysis due to its combination of real-space imaging and reciprocal-space analysis.

Microscopy-based techniques

Scanning transmission electron microscopy (STEM). Allows atomic-scale imaging of symmetry-breaking displacements and provides chemical specificity through electron energy-loss spectroscopy (EELS)/energy-dispersive X-ray spectroscopy (EDS). It is ideal for nanoscale systems where bulk-averaging techniques fail, offering sub-Ångström resolution, polarity mapping, and correlative analysis of structural, chemical, and symmetry data.

Piezoresponse force microscopy (PFM). Critical for materials exhibiting piezoelectricity or ferroelectricity, PFM maps the electromechanical response with high spatial resolution, observing domain dynamics and polarization reversal. Its ability to link topographical and electromechanical properties distinguishes it from bulk techniques like XRD or SHG.

Optical spectroscopy techniques

Second harmonic generation (SHG). This probes broken inversion symmetry through nonlinear light–matter interactions. SHG microscopy offers non-invasive, label-free imaging with sub-micron resolution, making it suitable for both real-time monitoring and structural analysis.

Raman spectroscopy. Sensitive to symmetry-forbidden vibrational modes in noncentrosymmetric materials, Raman spectroscopy provides structural and chemical insights with non-destructive, sub-micron spatial resolution.

Circular dichroism (CD) and optical rotation. These techniques measure differential interactions with circularly polarized light, detecting asymmetry in chiral systems.

Sum frequency generation (SFG) spectroscopy. This is surface-sensitive and ideal for probing symmetry-breaking at interfaces or monolayers in 2D materials. SFG offers high resolution, chemical identification, and operando compatibility, making it valuable for investigating edge states and interfacial polarization.

Noncentrosymmetry engineering

The deliberate design and manipulation of noncentrosymmetry in 2D atomic crystals have emerged as a powerful paradigm for unlocking unconventional electronic, optical, and quantum properties. CVD, as a scalable and tuneable synthesis method,[12] offers unique opportunities to precisely manipulate symmetry-breaking effects in 2D atomic crystals. In recent years, our group has made significant advancements in systematically engineering the symmetry of 2D atomic crystals through CVD, which can be primarily classified into three main strategies: (i) intrinsic noncentrosymmetric 2D crystals, where controlled thinning techniques enable the realization of atomically thin layers with inherent polarity or chirality; (ii) noncentrosymmetric stacking of 2D layers, achieved through thermal gradients, interlayer symmetry control, heterostructuring, or twist-angle modulation to artificially break inversion symmetry; and (iii) centrosymmetry breaking in 2D atomic crystals, induced *via* doping, intercalation, or selective etching to disrupt native symmetric configurations. Each approach offers distinct routes to tailor symmetry-dependent functionalities—such as piezoelectricity, valley polarization, or nonlinear optical responses—while addressing fundamental challenges in scalability, stability, and interfacial control. The following sections delve into our group's recent breakthroughs in CVD-based symmetry engineering, while systematically contrasting these advances with seminal works from other groups. By bridging critical knowledge gaps between synthesis control and symmetry–property relationships, it is expected to provide a fresh insight into the symmetry breaking of 2D atomic crystals.

Thinning of intrinsically noncentrosymmetric bulk crystals

The fabrication of 2D derivatives from nonlayered, intrinsically noncentrosymmetric bulk crystals poses distinct synthetic challenges that fundamentally differ from conventional vdW material exfoliation, primarily due to their three-dimensional covalent/ionic network structures characterized by omnidirectional strong bonding (*e.g.*, Si–O tetrahedra in quartz or Zn–S sp^3 bonds in ZnS). The absence of natural cleavage planes renders mechanical exfoliation ineffective, while even advanced techniques like ion intercalation frequently fail to achieve layer separation without inducing phase degradation, owing to the substantial energy barriers inherent in these materials. Furthermore, conventional CVD synthesis often results in nonuniform, island-like growth morphologies with stochastic defect formation (*e.g.*, anti-site vacancies in GaN), as the anisotropic growth kinetics of noncentrosymmetric units compete with substrate interactions, ultimately limiting the production of continuous, thickness-controlled monolayers. These combined factors underscore the significant hurdles in realizing atomically thin versions of such materials while preserving their structural integrity and noncentrosymmetric properties.

To solve the problems, our group has demonstrated various strategies during CVD, such as substrate engineering and surface passivation, to obtain large-area 2D nonlayered atomic crystals with unprecedented thickness control, ranging from a few-nanometers to sub-nanometer dimensions, while maintaining excellent crystallinity and intrinsic noncentrosymmetric properties.

Transition metal carbides (TMCs) such as molybdenum carbide (Mo_2C) and tungsten carbide (WC) are a unique class of materials that combine exceptional mechanical hardness, metallic conductivity, and catalytic activity, making them indispensable for applications ranging from electrocatalysts, mainly for hydrogen evolution (HER) and CO_2 reduction reactions, to next-generation electronics.[13] However, realizing their ultrathin 2D counterparts, which could unlock novel quantum phenomena and enhanced catalytic

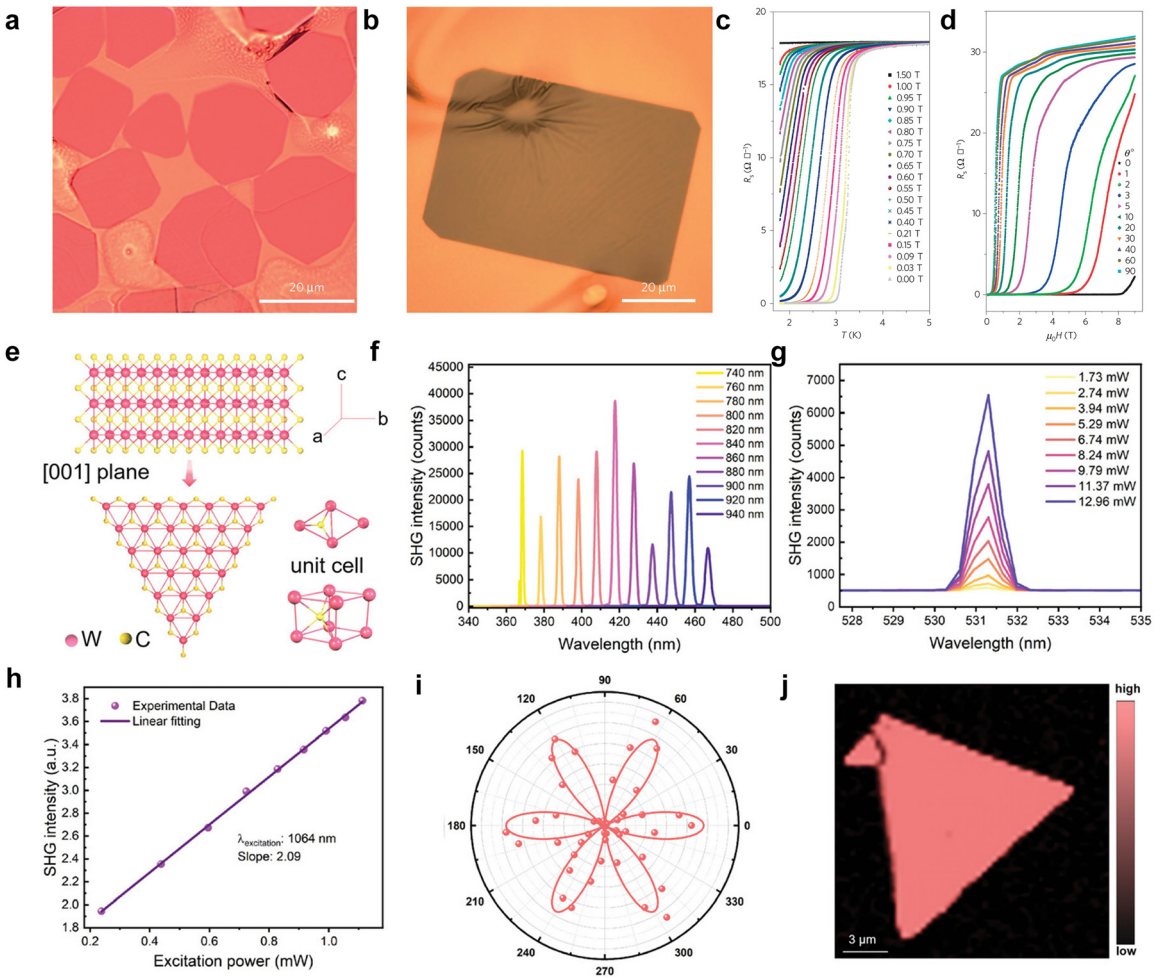

Fig. 2 Noncentrosymmetry engineering in 2DACs through thinning the nonlayered crystals. (a) and (b) The microscopic images of ultrathin Mo_2C. (c) Perpendicular magnetic field strength-dependent superconducting curves of the ultrathin Mo_2C. (d) Magnetic field-dependent superconducting curve of the ultrathin Mo_2C. Reproduced with permission.[14] Copyright 2015, Springer Nature. (e) The atomic structure of WC crystals. (f) Wavelength-dependent SHG responses of WC crystals. (g) Illumination intensity-dependent SHG responses of WC crystals. (h) SHG intensity as a function of laser power with linear fit. (i) Polarization-dependent SHG intensity reveals WC crystal anisotropy. (j) SHG mapping result of the produced ultrathin WC crystal. Reproduced with permission.[22] Copyright 2024, Wiley-VCH.

performance, faces additional obstacles including thickness nonuniformity and environmental instability, as these ultrathin carbides are highly susceptible to surface oxidation and structural degradation.

Building upon the pioneering work of Xu *et al.* who first synthesized large-area (>100 μm) 2D α-Mo_2C crystals (Fig. 2a and b) *via* liquid Mo–Cu alloy-catalyzed CVD in 2015,[14] revealing thickness-dependent superconducting transitions characteristic of 2D systems (Fig. 2c and d), our group has also developed advanced CVD strategies to overcome these fundamental limitations. We have achieved unprecedented control over crystal morphology and thickness while maintaining excellent crystallinity and intrinsic noncentrosymmetric properties. It is worth mentioning that liquid metals possess unique properties that make them particularly valuable for synthesizing 2D ultrathin atomic crystals, with their exceptional fluidity playing a pivotal role in enabling precise thickness control and large-area uniformity. For decades, liquid metal catalysis has been extensively investigated for 2D material synthesis,[15–18] and has proven equally transformative for fabricating ultrathin nonlayered materials.[19] Specifically, our liquid Cu-catalyzed CVD technique enables precise modulation of catalyst layer thickness, yielding ultrathin Mo_2C crystals with tuneable size.[20] Furthermore, we extended this methodology to create novel heterostructures, including the tailored growth of Mo_2C/graphene[21] and WC/graphene heterostructures.[22]

In terms of the preparation of WC/graphene, we selected a liquid Cu–Zn alloy as the growth substrate and realized a selective growth of WC/graphene heterostructures or ultrathin WC crystals through tuning the concentration of Zn in the alloy. To be specific, the existence of Zn would suppress the growth of graphene, thus WC/graphene heterostructures occur when the concentration of Zn in the liquid Cu–Zn alloy is relatively low (3.16–12.67%). In contrast, >25.33% Zn concentration would enable the fabrication of solely WC. Fig. 2e shows the atomic structure of 2D WC atomic crystal. Noted that SHG

microscopy directly confirmed the preserved noncentrosymmetric character in ultrathin (<3 nm) WC domains (Fig. 2f and j), posing a critical validation of their structural integrity and potential for nonlinear optical applications.

In addition to TMCs, transition metal oxides (TMOs) represent another important class of nonlayered materials with strong three-dimensional bonding networks (*e.g.*, ionic/covalent or mixed-valence interactions).[23] Their unique electronic structures and surface chemistries enable extraordinary functionalities, including catalysis, electronics, spintronics, optoelectronics, energy storage, and quantum materials. However, unlike vdW materials, these oxides—such as TiO_2, ZnO, and WO_3—typically exhibit omnidirectional chemical bonds, making their exfoliation or synthesis in ultrathin forms particularly challenging.

In order to prepare ultrathin TMOs, researchers have taken a lot of efforts on the strategies such as flux assisted growth,[24,25] surface oxide (also known as liquid metal printing),[26] additive-assisted growth,[27] and others, and have gained significant achievements on the successful growth of 2D ultrathin SiO_2,[18] MoO_2,[25] Ga_2O_3,[28] In_2O_3,[29] SnO_2,[30] Bi-doped/Cu-doped/ZnO-doped Ga_2O_3,[31,32] *etc.*

Building upon these achievements, our group reports the controlled synthesis of ultrathin 2D Ga_2O_3 single crystals *via* liquid Ga-catalyzed CVD method.[33] The dynamic liquid Ga surface enables: (i) large-area growth of hexagonal α-Ga_2O_3 through oxygen-regulated reactions, and (ii) thickness control *via* oxygen dosage modulation. Phase engineering to β-Ga_2O_3 is further achieved by temperature tuning.

In another work, our group has developed an innovative surface-assisted passivation growth strategy to overcome the long-standing challenge in synthesizing ultrathin TMOs (Fig. 3a).[34] Through precise Se-mediated surface passivation, we have successfully achieved the growth of remarkably thin β-Bi_2O_3 crystals with unprecedented thickness control down to 0.77 nm and large lateral dimensions up to 163 μm, as shown in Fig. 3b, representing a major breakthrough in 2D nonlayered material synthesis. The key to our success lies in the engineered bonding between Se atoms and unsaturated Bi atoms on the β-Bi_2O_3 surface, which not only passivates the surface but also dramatically suppresses vertical growth. More importantly, the intrinsic noncentrosymmetric nature of these ultrathin β-Bi_2O_3 crystals has been unambiguously confirmed by strong SHG response, as shown in Fig. 3c. Moreover, the noncentrosymmetric nature of thus-produced β-Bi_2O_3 crystals enables polarization-sensitive photodetection with the merits of record-high photoresponsivity of 71.91 A W^{-1}, outstanding detectivity reaching 6.09×10^{13} Jones, and high-resolution UV imaging performance at 365 nm (Fig. 3d). The schematic diagram of the polarization-sensitive photodetection based on β-Bi_2O_3 is shown in Fig. 3e and f exhibits the typical polarization-dependent photocurrent.

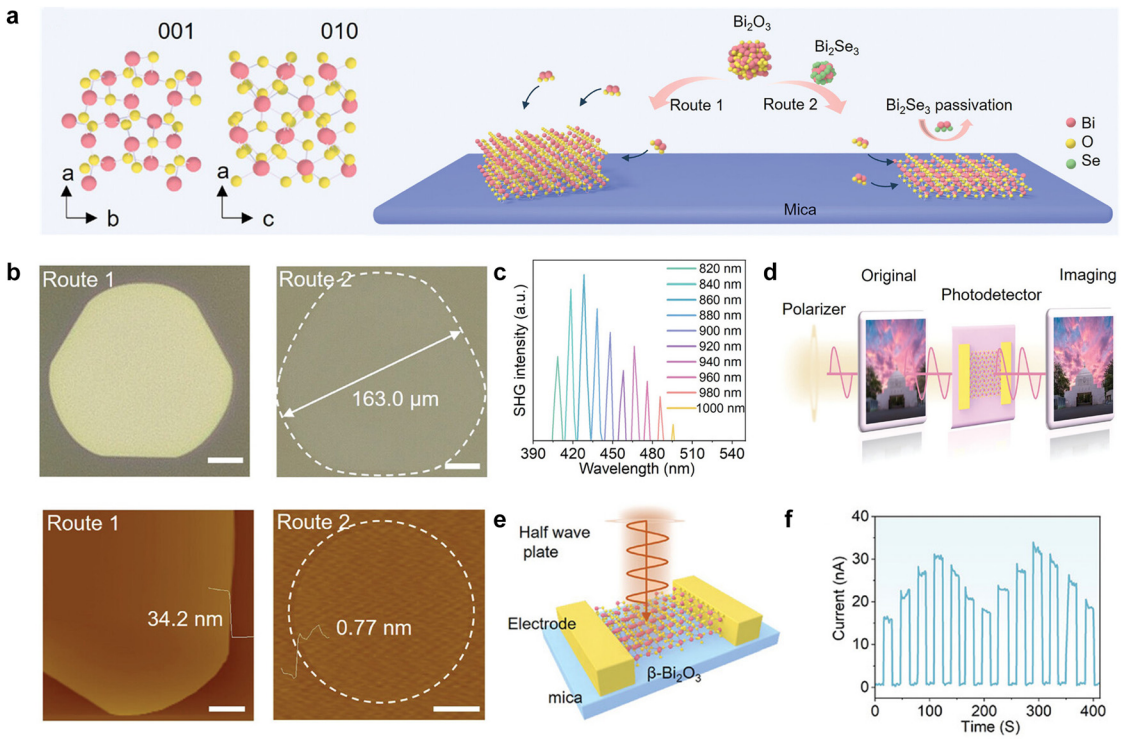

Fig. 3 Noncentrosymmetry engineering in 2DACs through thinning the nonlayered materials. (a) The atomic structure of β-Bi_2O_3 and the schematic diagram of the surface passivation strategy. (b) A comparison of the thickness of the product produced respectively from Route 1 and Route 2 (surface passivation). (c) Wavelength-dependent SHG responses of the ultrathin β-Bi_2O_3. (d) The polarization imaging ability of the ultrathin β-Bi_2O_3. (e) The device configuration of the polarization-sensitive photodetector based on the produced ultrathin β-Bi_2O_3. (f) Typical polarization-sensitive *I*–*t* curve of the device, demonstrating a high anisotropy. Reproduced with permission.[34] Copyright 2025, Wiley-VCH.

Building upon this work, researchers recently demonstrated a vapor–liquid–solid–solid (VLSS) growth strategy to achieve sub-1 nm nonlayered 2D β-Bi_2O_3 crystals *via* topological transformation of BiOCl precursors.[35] The resulting p-type transistors exhibit superior hole mobility (136.6 $cm^2 V^{-1} s^{-1}$) and on/off ratio (1.2×10^8), enabled by strong Bi $6s^2 6p^3$–O $2p^4$ hybridization at the valence band maximum – a distinct mechanism from our earlier surface-passivation approach. While both methods achieve atomic thickness control, this work shifts focus from noncentrosymmetric photodetection to high-performance p-channel electronics, collectively expanding the 2D oxide toolkit for complementary applications.

Noncentrosymmetric stacking of 2D layers

Noncentrosymmetric stacking refers to the artificial assembly or self-assembly of 2D layers in a manner that breaks inversion symmetry, creating heterostructures with novel properties such as piezoelectricity, valley polarization, or nonlinear optical responses. Unlike naturally occurring centrosymmetric stacking (*e.g.*, AB stacking in bilayer graphene), this approach requires precise control over interlayer rotation, lattice mismatch, or compositional asymmetry to stabilize noncentrosymmetric configurations.

The practical realization of such designed stacks faces fundamental challenges rooted in both thermodynamics and kinetics. From an energetic perspective, nature favours centrosymmetric configurations (*e.g.*, AB-stacked graphene or AA′-stacked MoS_2) due to their optimal interlayer registry and minimized vdW interaction energy, typically making noncentrosymmetric arrangements metastable by several meV $atom^{-1}$ – a thermodynamic hurdle that often leads to spontaneous relaxation during growth or device operation. On the synthesis front, achieving and maintaining precise noncentrosymmetric alignment demands extraordinary control at sub-Ångström precision (*e.g.*, $<0.1^\circ$ twist angle accuracy or $<5\%$ lattice mismatch tolerance), while simultaneously addressing interfacial challenges like charge transfer-induced reconstruction, thermal expansion mismatch, and chemical incompatibility between dissimilar layers. These combined factors currently limit the reproducible fabrication of high-quality, large-area noncentrosymmetric stacks.

To solve the problems, our group reports a substrate-guided CVD strategy to precisely engineer crystal symmetry in $SnSe_2$

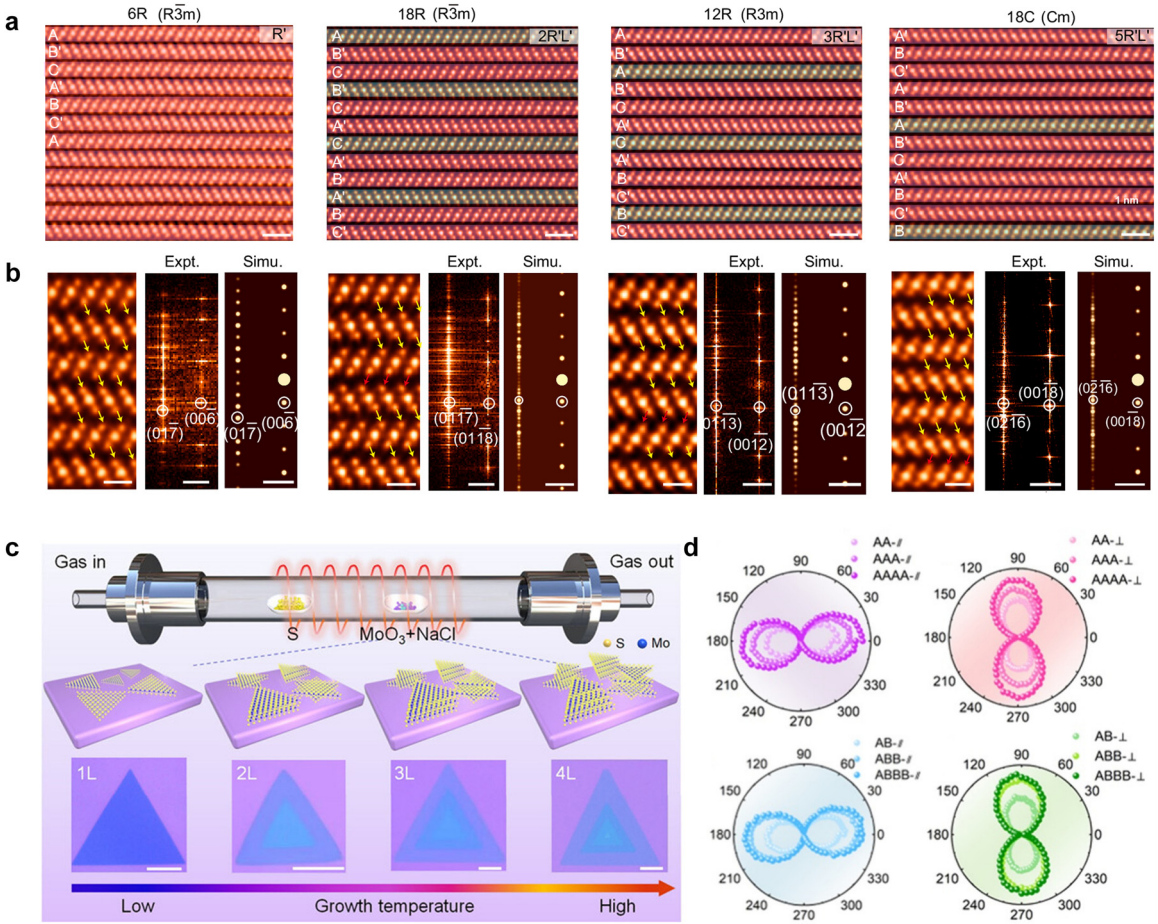

Fig. 4 Engineering noncentrosymmetry in 2DACs through noncentrosymmetric stackings. (a) Side views of the atomic configurations of 6R, 18R, 12R, and 18C phases. (b) Experimental and simulated fast Fourier transform results of different phases. Reproduced with permission.[36] Copyright 2024, Springer Nature. (c) The schematic illustration of the TGACVD method for producing multilayer MoS_2 domains. (d) Layer-number- and stacking-dependent polarized Raman spectrums. Reproduced with permission.[37] Copyright 2024, American Chemical Society.

superlattices,[36] overcoming the inherent challenge of symmetry control in 2D materials caused by interlayer gliding. By leveraging charge transfer from mica substrates, we successfully stabilized unconventional AB′-stacked $SnSe_2$ with alternating mirror and glide symmetries, as well as higher-order phases (6R, 12R, 18R, and 18C) that exhibit stacking-dependent nonlinear optical responses as predicted by first-principles calculations. Furthermore, PFM characterization results also demonstrated good ferroelectric properties of the AB′-stacked $SnSe_2$ crystals, directly pointing out its intrinsic noncentrosymmetric characteristic. The captured atomic structures of these phases and corresponding FFT are shown in Fig. 4a and b.

In another work, we have achieved a successful preparation of noncentrosymmetric-stacked MoS_2 multilayers through a customized thermal gradient assembly CVD (TGACVD) method.[37] The schematic illustration of TGACVD method is shown in Fig. 4c. The theoretical simulation results demonstrate that the formation energy differences between various stacking configurations with identical layer numbers are substantially smaller than those between structures with different layer counts. Therefore, our strategy enables a precise construction of diverse noncentrosymmetric stacking arrangements such as AA-stacked bilayers, AAB/ABB-stacked trilayers, and AAAA/AAAB/ABBA-stacked quadralayers. We observe distinct layer-number- and stacking-dependent oscillatory SHG responses in multilayer MoS_2, consistent with prior reports of interlayer-interference-mediated SHG modulation.[38–40] Besides, these stackings also show angle-dependent polarization Raman intensities in both parallel and cross modes, as shown in Fig. 4d. This work directly provides a route for tuning the degree of noncentrosymmetry by engineering stacked structures. On this basis, we have also fully investigated the sliding ferroelectric properties of AAA/ABB/AAB/ABA-stacked trilayer MoS_2, achieving both record-high endurance more than 10^{11} and an interesting ferroelectricity order as AAA > AAB > ABB, with their polarization strengths up to 0.11 μC cm^{-2}.[74]

A recent work reported by Liu *et al.* mentions a homoepitaxial growth of rhombohedral-stacked MoS_2, providing a feasible approach toward the large-scale synthesis of noncentrosymmetric materials.[41] The authors identify Mo-substituted sulfur vacancies as key defects promoting rhombohedral-stacked nucleation and achieve wafer-scale (2-inch) growth. They further fabricate ferroelectric semiconductor field-effect transistors with rhombohedral-stacked-MoS_2 channels, showcasing non-volatile memory functionality.

In addition, twist angle control has emerged as a powerful strategy for creating noncentrosymmetric stacked structures in 2D atomic crystals.[42] While early studies primarily relied on mechanical exfoliation followed by artificial stacking to achieve twisted configurations,[43] recent advances have demonstrated the direct synthesis of twist-controlled materials through CVD approaches.[44–49] These emerging CVD techniques enable more scalable and precise fabrication of twisted heterostructures with well-defined angular alignment, opening new possibilities for systematic investigation and practical applications of twist-angle-dependent phenomena in noncentrosymmetric systems. Correspondingly, our group has successfully achieved precise twist angle control in graphene/Mo_2C vertical heterostructures, enabled by the unique fluidity of liquid copper catalysts during high-temperature growth.[50]

Beyond twist engineering, the formation of commensurate heterostructures itself can break inversion symmetry, as demonstrated in a recent work on epitaxial MoS_2/WS_2 bilayers raise by Lau's group.[51] Through scalable one-step CVD, they achieved untwisted heterostructures exhibiting unexpected out-of-plane ferroelectricity and piezoelectricity (approximately sixfold stronger than monolayer In_2Se_3), enabled by interlayer charge transfer and symmetry breaking without requiring Moiré patterns.

Our group has extensively explored such symmetry-breaking heterostructures, including $MoSe_2$/MOFs heterostructure,[52] graphene/hBN lateral heterostructure,[53–55] graphene/SiO_2 heterostructure,[18] MXene/DPA heterostructure,[56] MXene/$MoSe_2$ heterostructure,[57] and others,[58–60] establishing forming heterostructures as a universal platform for designing noncentrosymmetric 2D systems through both twisted and commensurate stackings.

Centrosymmetry breaking in 2D atomic crystals

In addition to the above two strategies, the deliberate breaking of centrosymmetry in 2D atomic crystals has also emerged as a powerful strategy to unlock novel quantum phenomena and functionalities, such as piezoelectricity, nonlinear optical responses, and valley polarization. Unlike intrinsic noncentrosymmetric materials, where asymmetry is inherent to their crystal structure, centrosymmetric 2D materials require external interventions to disrupt their inversion symmetry. Traditional approaches, including strain engineering and electric field gating, often face limitations in scalability and stability.

Our group demonstrated robust centrosymmetry breaking through self-intercalation and controlled etching strategies during CVD process, which enabled precise modification of atomic arrangements while preserving material integrity. The self-intercalation approach introduces foreign atoms into the vdW gaps, locally distorting the crystal lattice and inducing long-range symmetry lowering. Meanwhile, selective etching creates patterned vacancies that break global inversion symmetry.[61] These methods offer scalable and tuneable routes to engineering symmetry-dependent properties, surpassing the constraints of conventional techniques.

For example, we have demonstrated a temperature-driven CVD approach to precisely synthesize self-intercalated $Ta_{1+x}S_2$ (x = 10–58%) with controllable H/T phases, where nonperiodic Ta intercalation at vdW gaps breaks the intrinsic centrosymmetry of $Ta_{1+x}S_2$.[62] Fig. 5a shows the growth mechanism of the self-intercalated $Ta_{1+x}S_2$. Atomic-resolution STEM confirms octahedral-site Ta occupancy, which disrupts both the crystal symmetry and Fermi surface. Crucially, this symmetry breaking activates a robust thickness-independent nonlinear optical (NLO) response in otherwise centrosymmetric T-phase $Ta_{1+x}S_2$, as verified by consistent SHG (Fig. 5b). Our work establishes self-intercalation as a general strategy to engineer noncentrosymmetry and NLO properties in 2D materials.

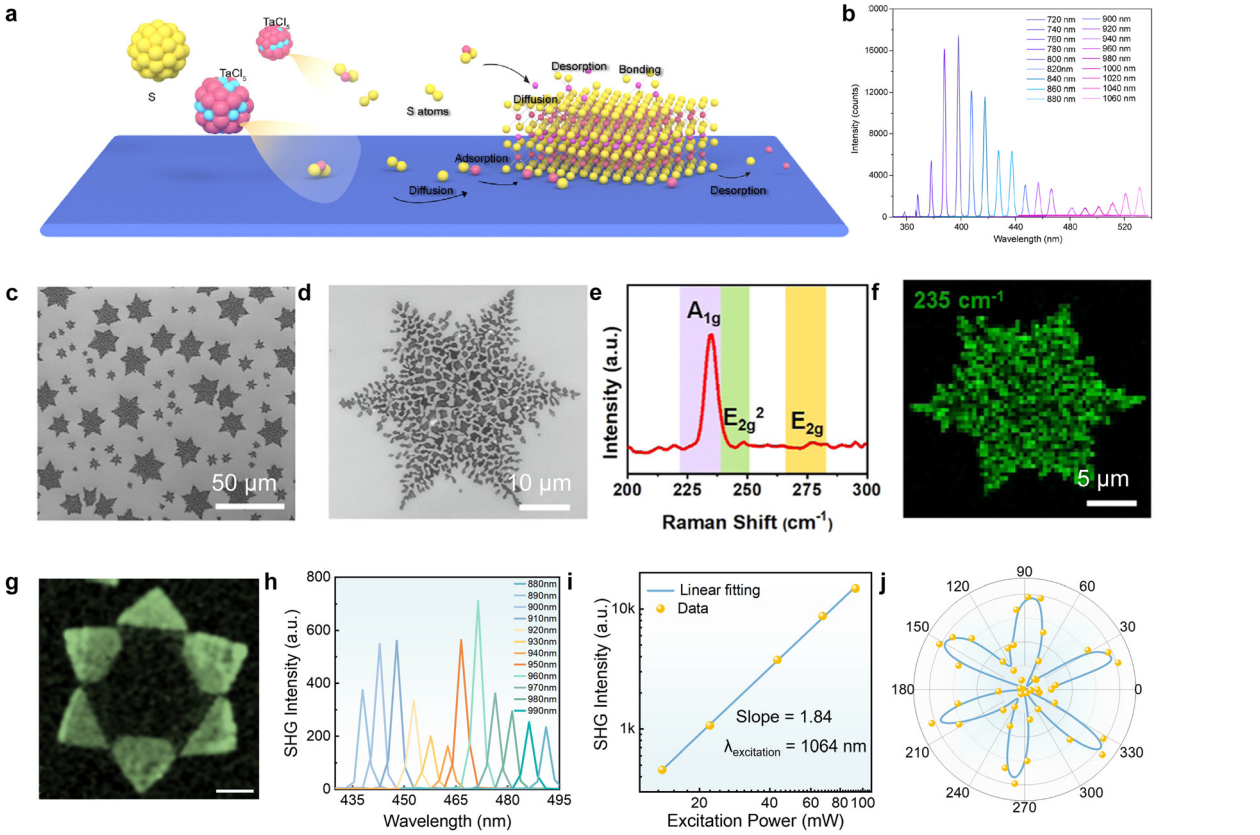

Fig. 5 Engineering noncentrosymmetry in 2DACs through breaking the centrosymmetry in 2DACs. (a) The scheme of the growth mechanism for the self-intercalation. (b) Wavelength-dependent SHG responses of the self-intercalated TaS_2. Reproduced with permission.[62] Copyright 2024, American Chemical Society. (c) Zoom-out SEM image of the etched $MoSe_2$ domains. (d) Zoom-in SEM image of an individual etched $MoSe_2$ domain. (e) The Raman spectrum of the etched domain, demonstrating the characteristic peaks of $MoSe_2$. (f) Raman mapping result of the domain. Reproduced with permission.[64] Copyright 2022, American Chemical Society. (g) SHG mapping results of the kirigami bilayer MoS_2. (h) Wavelength-dependent SHG responses of the kirigami MoS_2 domain. (i) Log–log plot showing linear fitting of SHG intensity *versus* laser power. (j) Angle-resolved SHG measurements demonstrate kirigami MoS_2's anisotropic response. Reproduced with permission.[65] Copyright 2025, Royal Society of Chemistry.

The nonperiodic Ta intercalation in our work represents a general nonstoichiometric strategy to disrupt centrosymmetry, complementing recent advances in engineering piezo/ferroelectricity through native metal intercalation in 2D chalcogenides. As demonstrated in related studies, such intrinsic nonstoichiometry (*e.g.*, intercalated $Mn_{1+x}Se_2$ or $Fe_{1+x}Te_2$) induces vdW layer sliding and metal-atom displacement, creating unconventional piezo/ferroelectricity in otherwise centrosymmetric systems.[63] These intercalation-driven effects enable functional devices like 2D nanogenerators and ferroelectric memristors, collectively establishing native metal intercalation as a universal route to break inversion symmetry and activate emergent properties in nonstoichiometric 2D materials.

In terms of controllable etching, we have developed an oxygen-assisted anisotropic CVD etching method to create patterned $MoSe_2$ structures with controlled edge geometries.[64] Fig. 5c–f show the SEM images of etched $MoSe_2$ flakes, the Raman spectrum and Raman mapping results of a $MoSe_2$ flake, demonstrating the uniform feature of the product. Atomic-scale characterization reveals preferential formation of zigzag-terminated edges, as confirmed by density functional theory calculations showing their energetic favourability. Importantly, this edge-selective etching locally breaks centrosymmetry in the otherwise symmetric $MoSe_2$ flakes, introducing noncentrosymmetric configurations at patterned interfaces. The etched structures exhibit enhanced optoelectronic performance, demonstrated by ambipolar photoresponse in $MoSe_2$/P3HT heterojunction transistors. This approach provides a top-down route to engineering local symmetry breaking in 2D materials through controlled anisotropic etching.

In another work, we developed a precision etching strategy to convert specific bilayer MoS_2 regions into monolayer structures through selective layer removal, thereby creating designed kirigami patterns with controlled Mo- and S-zigzag edge configurations.[65] This local thickness reduction from bilayer to monolayer effectively breaks the original centrosymmetry of AB-stacked bilayer MoS_2, as unambiguously confirmed by the emergence of strong SHG signals from the etched monolayer regions, as demonstrated in Fig. 5g–j. The resulting heterostructures – combining intact bilayer and etched monolayer domains – exhibit enhanced nonlinear optical responses, demonstrating how spatially controlled etching can serve as an effective approach to engineer noncentrosymmetry and activate nonlinear optical functionalities in 2D materials.

Our findings not only establish new pathways for centrosymmetry manipulation but also provide insights into the

design of functional 2D materials for optoelectronics, quantum devices, and energy harvesting applications.

Challenges and perspectives

The pursuit of noncentrosymmetric 2D atomic crystals has evolved along three primary strategies in our group: (i) thinning intrinsically noncentrosymmetric bulk crystals, (ii) precise manipulation of vdW stackings, and (iii) alternative centrosymmetry breaking routes including self-intercalation and etching. While these approaches have significantly expanded the library of symmetry-broken 2D systems, critical challenges remain in their development and implementation.

For thinning of nonlayered materials, the primary obstacle lies in overcoming the strong isotropic bonding that renders conventional exfoliation ineffective. Although our advanced techniques like liquid–metal-assisted thinning (*e.g.*, for Mo_2C) have shown promise, achieving atomic-level precision in thickness control, the scalability of these methods is challenging, as most demonstrations are limited to micrometer-scale flakes.

In the realm of vdW stacking manipulation, while twist engineering has emerged as a powerful tool (*e.g.*, graphene/Mo_2C heterostructures), several limitations persist. First, the thermodynamic instability of twisted configurations often leads to relaxation at room temperature, necessitating new stabilization strategies such as interfacial strain engineering or defect pinning. Second, the precise control of stacking angles below 1° remains technically demanding, requiring advanced *in situ* monitoring techniques. Recent advances in epitaxial confinement and laser-assisted stacking may provide solutions, but their generalizability across material systems needs further exploration. For heterostructure assembly, interface contamination and lattice mismatch can compromise the designed symmetry breaking. However, the interlayer coupling mechanisms in artificially stacked systems are not fully understood, particularly for mixed-dimensional or multi-component heterostructures.[66,67]

The third category—alternative symmetry-breaking routes—faces distinct challenges. Self-intercalation (*e.g.*, $Ta_{1+x}S_2$) often suffers from inhomogeneous distribution of intercalants, while etching approaches (*e.g.*, MoS_2 kirigami) struggle with edge-defect proliferation. Moreover, the development of universal characterization protocols is crucial to quantify the degree of symmetry breaking across different material systems and fabrication methods. Despite these challenges, recent advances, such as coherently confined single-metal-atom chains in 2D atomic crystals,[68] nano-folding edge engineering,[69] and high-entropy alloys,[70–73] bring fresh insights into the centrosymmetry breaking.

From a fundamental perspective, several open questions demand attention. The critical thickness limit for maintaining noncentrosymmetric properties in thinned crystals is poorly understood for many material systems. In stacked heterostructures, the role of Moiré potentials in modifying symmetry-governed properties (*e.g.*, nonlinear optical response) requires systematic investigation. For chemically modified systems (intercalated or etched), the trade-off between defect density and symmetry-breaking efficiency needs rigorous assessment.

Looking ahead, the field is poised to make transformative advances through convergent methodologies. The integration of machine learning with high-throughput synthesis could accelerate the discovery of optimal symmetry-breaking parameters. *In situ* microscopy techniques may unravel atomic-scale dynamics during thinning, stacking, or intercalation processes. For applications, the co-design of materials and devices will be essential—for instance, developing etching protocols tailored for photonic circuits or stacking sequences optimized for quantum emitters.

Ultimately, the goal is to establish design rules that connect specific symmetry-breaking methods (thinning, stacking, or chemical modification) with target functionalities (piezoelectricity, valleytronics, or nonlinear optics). As the field matures, the focus should shift from proof-of-concept demonstrations to reproducible fabrication and device integration, enabling practical applications in quantum information, energy conversion, and ultracompact optoelectronics. The three-pronged strategy outlined here—thinning, stacking, and alternative routes---provides a comprehensive framework to advance this exciting field toward both fundamental discoveries and technological breakthroughs.

Author contributions

Yongshuai Wang: writing – original draft; Qing Zhang: writing – review & editing, funding acquisition; Lin Li: writing – review & editing; Fan Wu: writing – review & editing; Dechao Geng: writing – review & editing, supervision, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this study's findings are available from the corresponding author upon reasonable request.

Acknowledgements

This work was supported by the National Key R&D Program (2023YFB3609001 and 2021YFA0717900), the Natural Science Foundation of China (grants 52472168), the Natural Science Foundation of Tianjin (grants 22JCJQJC00080), the Haihe Laboratory of Sustainable Chemical Transformations, the Beijing National Laboratory for Molecular Sciences (BNLMS 202309), the Hebei Natural Science Foundation (E2024208084), the Chinese Postdoctoral Science Foundation (2024M760101 and GZB20230004), and the Fundamental Research Funds for the Central Universities.

Notes and references

1 G. Kim, B. Huet, C. E. Stevens, K. Jo, J.-Y. Tsai, S. Bachu, M. Leger, S. Song, M. Rahaman, K. Y. Ma, N. R. Glavin, H. S. Shin, N. Alem, Q. Yan, J. R. Hendrickson, J. M. Redwing and D. Jariwala, Confinement of excited states in two-dimensional, in-plane, quantum heterostructures, *Nat. Commun.*, 2024, **15**(1), 6361.

2 F. Wu, H. Tian, Y. Shen, Z. Hou, J. Ren, G. Gou, Y. Sun, Y. Yang and T.-L. Ren, Vertical MoS2 transistors with sub-1-nm gate lengths, *Nature*, 2022, **603**(7900), 259–264.

3 Y. Zhao, J. Liao, S. Bu, Z. Hu, J. Hu, Q. Lu, M. Shang, B. Guo, G. Chen, Q. Zhao, K. Jia, G. Wang, E. Errington, Q. Xie, Y. Zhang, M. Guo, B. Mao, L. Lin and Z. Liu, Automated processing and transfer of two-dimensional materials with robotics, *Nat. Chem. Eng.*, 2025, **2**(5), 296–308.

4 A. Quellmalz, X. Wang, S. Sawallich, B. Uzlu, M. Otto, S. Wagner, Z. Wang, M. Prechtl, O. Hartwig, S. Luo, G. S. Duesberg, M. C. Lemme, K. B. Gylfason, N. Roxhed, G. Stemme and F. Niklaus, Large-area integration of two-dimensional materials and their heterostructures by wafer bonding, *Nat. Commun.*, 2021, **12**(1), 917.

5 L. Du, T. Hasan, A. Castellanos-Gomez, G.-B. Liu, Y. Yao, C. N. Lau and Z. Sun, Engineering symmetry breaking in 2D layered materials, *Nat. Rev. Phys.*, 2021, **3**(3), 193–206.

6 Z. Lin, C. Wang, Y. Xu and W. Duan, Hidden physical effects in noncentrosymmetric crystals, *Phys. Rev. B*, 2020, **102**(16), 165143.

7 P. Zheng, W. Wei, Z. Liang, B. Qin, J. Tian, J. Wang, R. Qiao, Y. Ren, J. Chen, C. Huang, X. Zhou, G. Zhang, Z. Tang, D. Yu, F. Ding, K. Liu and X. Xu, Universal epitaxy of non-centrosymmetric two-dimensional single-crystal metal dichalcogenides, *Nat. Commun.*, 2023, **14**(1), 592.

8 J.-P. Wang, Y.-Q. Fang, W. He, Q. Liu, J.-R. Fu, X.-Y. Li, Y. Liu, B. Gao, L. Zhen, C.-Y. Xu, F.-Q. Huang, A. J. Meixner, D. Zhang and Y. Li, Non-Centrosymmetric 2D Nb_3SeI_7 with High In-Plane Anisotropy and Optical Nonlinearity, *Adv. Opt. Mater.*, 2023, **11**(15), 2300031.

9 T. Xi, H. Jiang, J. Li, Y. He, Y. Gu, C. Fox, L. Primeau, Y. Mao, J. Rollins, T. Taniguchi, K. Watanabe, D. van der Weide, D. Rhodes, Y. Zhang, Y. Wang and J. Xiao, Terahertz sensing based on the nonlinear electrodynamics of the two-dimensional correlated topological semimetal TaIrTe4, *Nat. Electron.*, 2025, **8**, 578–586.

10 G. Cui, J. Qi, Z. Liang, F. Zeng, X. Zhang, X. Xu and K. Liu, Growth of Noncentrosymmetric Two-Dimensional Single Crystals, *Precis. Chem.*, 2024, **2**(7), 330–354.

11 Z. Gao, S. Wang, J. Berry, Q. Zhang, J. Gebhardt, W. M. Parkin, J. Avila, H. Yi, C. Chen, S. Hurtado-Parra, M. Drndić, A. M. Rappe, D. J. Srolovitz, J. M. Kikkawa, Z. Luo, M. C. Asensio, F. Wang and A. T. C. Johnson, Large-area epitaxial growth of curvature-stabilized ABC trilayer graphene, *Nat. Commun.*, 2020, **11**(1), 546.

12 Z. Han, R. Zhang, M. Li, L. Li, D. Geng and W. Hu, Recent advances in the controlled chemical vapor deposition growth of bilayer 2D single crystals, *J. Mater. Chem. C*, 2022, **10**(37), 13324–13350.

13 Y. Fan, L. Li, Y. Zhang, X. Zhang, D. Geng and W. Hu, Recent Advances in Growth of Transition Metal Carbides and Nitrides (MXenes) Crystals, *Adv. Funct. Mater.*, 2022, **32**(16), 2111357.

14 C. Xu, L. Wang, Z. Liu, L. Chen, J. Guo, N. Kang, X.-L. Ma, H.-M. Cheng and W. Ren, Large-area high-quality 2D ultrathin Mo_2C superconducting crystals, *Nat. Mater.*, 2015, **14**(11), 1135–1141.

15 Y. Fan, M. Li, X. Jia, L. Li, Q. Zhang, E. Gao, D. Geng and W. Hu, Self-Assembly Graphene Arrays on a Liquid Cu–Ag Alloy, *Chem. Mater.*, 2021, **33**(22), 8649–8655.

16 Y. Fan, L. Li, G. Yu, D. Geng, X. Zhang and W. Hu, Recent Advances in Growth of Large-Sized 2D Single Crystals on Cu Substrates, *Adv. Mater.*, 2021, **33**(1), 2003956.

17 L. Li, M. Li, R. Zhang, Q. Zhang, H. Li and D. Geng, Liquid Cu–Zn catalyzed growth of graphene single-crystals, *New J. Chem.*, 2023, **47**(45), 20703–20707.

18 L. Li, Q. Zhang, M. Li, R. Zhang and D. Geng, Cu-Vapor-Assisted Growth of 2D SiO_2 Flakes and As-Oriented Graphene Arrays, *ACS Appl. Electron. Mater.*, 2024, **6**(6), 4449–4456.

19 M. Li, Q. Zhang, Y. Fan, L. Li, D. Geng and W. Hu, Mass-Mediated Phase Modulation of Thin Molybdenum Nitride Crystals on a Liquid Cu-Mo Alloy, *Chemosensors*, 2023, 82.

20 D. Geng, X. Zhao, L. Li, P. Song, B. Tian, W. Liu, J. Chen, D. Shi, M. Lin, W. Zhou and K. P. Loh, Controlled growth of ultrathin Mo_2C superconducting crystals on liquid Cu surface, *2D Mater.*, 2017, **4**(1), 011012.

21 D. Geng, X. Zhao, Z. Chen, W. Sun, W. Fu, J. Chen, W. Liu, W. Zhou and K. P. Loh, Direct Synthesis of Large-Area 2D Mo_2C on In Situ Grown Graphene, *Adv. Mater.*, 2017, **29**(35), 1700072.

22 M. Li, Q. Zhang, L. Li, Z. Han, W. Gao, H. Ren, D. Geng and W. Hu, Substrate Engineering toward Selective Growth of Ultrathin WC Crystals and Heterostructures via Liquid Cu-Zn Catalyst, *Adv. Funct. Mater.*, 2024, **34**(32), 2316159.

23 M. Li, Y. Guo, L. Li, D. Geng and W. Hu, Recent Advances in Growth, Properties and Applications of 2D Inorganic Molecular Crystals, *Chin. J. Chem.*, 2023, **41**(15), 1849–1860.

24 P. Zhang, X. Wang, H. Jiang, Y. Zhang, Q. He, K. Si, B. Li, F. Zhao, A. Cui, Y. Wei, L. Liu, H. Que, P. Tang, Z. Hu, W. Zhou, K. Wu and Y. Gong, Flux-assisted growth of atomically thin materials, *Nat. Synth.*, 2022, **1**(11), 864–872.

25 L.-Y. Deng, Q. Zhang, W.-Y. Li, X.-Y. Ye, Y.-F. Zhao, S.-Z. Chen, Y.-L. Wang, X.-H. Wang, H.-P. Chen, Z.-Y. Yu, Q. Yan, S.-Y. Cheng, T.-L. Guo, W.-P. Hu, F. Ding and J. Sun, KCl acts as a flux to assist the growth of sub-millimeter-scale metallic 2D non-layered molybdenum dioxide, *Rare Met.*, 2025, **44**(1), 404–416.

26 L. Li, Q. Zhang, D. Geng, H. Meng and W. Hu, Atomic engineering of two-dimensional materials via liquid metals, *Chem. Soc. Rev.*, 2024, **53**(13), 7158–7201.

27 Q. Zhang, X. Xiao, L. Li, D. Geng, W. Chen and W. Hu, Additive-Assisted Growth of Scaled and Quality 2D Materials, *Small*, 2022, **18**(17), 2107241.

28 K. Huang, L. Guo, L. Liu, X. Chen, C. Su, P. Li, Z. Deng, W. Wu and L. Zhang, Liquid metal-based printing synthesis of bismuth-doped gallium oxide and its application for a photodetector, *J. Mater. Chem. C*, 2023, **11**(36), 12156–12162.

29 C. K. Nguyen, A. Mazumder, E. L. H. Mayes, V. Krishnamurthi, A. Zavabeti, B. J. Murdoch, X. Guo, P. Aukarasereenont, A. Dubey, A. Jannat, X. Wei, V. K. Truong, L. Bao, A. Roberts, C. F. McConville, S. Walia, N. Syed and T. Daeneke, 2-nm-Thick Indium Oxide Featuring High Mobility, *Adv. Mater. Interfaces*, 2023, **10**(9), 2202036.

30 C. K. Nguyen, P. D. Taylor, A. Zavabeti, H. Alluhaybi, S. Almalki, X. Guo, M. Irfan, M. A. Kobaisi, S. J. Ippolito, M. J. S. Spencer, S. Balendhran, A. Roberts, T. Daeneke, K. B. Crozier, Y. Sabri and N. Syed, Instant-in-Air Liquid Metal Printed Ultrathin Tin Oxide for High-Performance Ammonia Sensors, *Adv. Funct. Mater.*, 2024, **34**(31), 2309342.

31 Q. Li, B.-D. Du, J.-Y. Gao and J. Liu, Liquid metal gallium-based printing of Cu-doped p-type Ga_2O_3 semiconductor and Ga_2O_3 homojunction diodes, *Appl. Phys. Rev.*, 2023, **10**(1), 011402.

32 Q. Liu, J. Guo, J. Li, L. Feng, L. Chen, Z. Hua, L. Yang, X. Zhang and B. Liu, Room-Temperature Preparation of Large-Area Transparent Two-Dimensional ZnO-Doped Ga_2O_3 Nanostructure-Based Layers: Implications for Optoelectronic Nanodevices, *ACS Appl. Nano Mater.*, 2023, **6**(4), 3027–3035.

33 M. Li, L. Li, Y. Fan, L. Huang, D. Geng and W. Yang, Controlled growth of 2D ultrathin Ga_2O_3 crystals on liquid metal, *Nanoscale Adv.*, 2021, **3**(15), 4411–4415.

34 Y. Guo, Q. Zhang, Z. Ren, L. Li, W. Ma, X. Shen, J. Dong, R. Li, D. Geng and W. Hu, Surface-Assisted Passivation Growth of 2D Ultrathin β-Bi_2O_3 Crystals for High-Performance Polarization-Sensitive Photodetectors, *Adv. Mater.*, 2025, **37**(3), 2410163.

35 Y. Xiong, D. Xu, Y. Zou, L. Xu, Y. Yan, J. Wu, C. Qian, X. Song, K. Qu, T. Zhao, J. Gao, J. Yang, K. Zhang, S. Zhang, P. Wang, X. Chen and H. Zeng, Vapour–liquid–solid–solid growth of two-dimensional non-layered β-Bi_2O_3 crystals with high hole mobility, *Nat. Mater.*, 2025, **24**(5), 688–697.

36 Z. Han, S. Wu, C. Huang, F. Xuan, X. Han, Y. Long, Q. Zhang, J. Li, Y. Meng, L. Wang, J. Zhou, W. Hu, J. Qiao, D. Geng and X. Zhao, Atomically engineering interlayer symmetry operations of two-dimensional crystals, *Nat. Commun.*, 2024, **15**(1), 10835.

37 A. Fan, Q. Zhang, Z. Ren, L. Li, Z. Han, W. Ma, X. Shen, J. Dong, X. Yu, D. Geng and W. Hu, Layer Number and Stacking Engineering of MoS2 Crystals for High-Performance Polarization-Sensitive Photodetector, *ACS Appl. Mater. Interfaces*, 2024, **16**(43), 59626–59636.

38 S. Huang, X. Ling, L. Liang, J. Kong, H. Terrones, V. Meunier and M. S. Dresselhaus, Probing the Interlayer Coupling of Twisted Bilayer MoS2 Using Photoluminescence Spectroscopy, *Nano Lett.*, 2014, **14**(10), 5500–5508.

39 Z. Zeng, X. Sun, D. Zhang, W. Zheng, X. Fan, M. He, T. Xu, L. Sun, X. Wang and A. Pan, Controlled Vapor Growth and Nonlinear Optical Applications of Large-Area 3R Phase WS2 and WSe2 Atomic Layers, *Adv. Funct. Mater.*, 2019, **29**(11), 1806874.
40 X. Huang, S. Luo, G. Guo, J. Zhang, L. Ren, Q. Chen, J. Zhong and X. Qi, Angle-Dependent Oscillatory Interlayer Coupling in Twisted MoS_2/$TaSe_2$ Heterostructure. The, *J. Phys. Chem. C*, 2024, **128**(8), 3393–3399.
41 L. Liu, T. Li, X. Gong, H. Wen, L. Zhou, M. Feng, H. Zhang, N. Zou, S. Wu, Y. Li, S. Zhu, F. Zhuo, X. Zou, Z. Hu, Z. Ding, S. Fang, W. Xu, X. Hou, K. Zhang, G. Long, L. Tang, Y. Jiang, Z. Yu, L. Ma, J. Wang and X. Wang, Homoepitaxial growth of large-area rhombohedral-stacked MoS2, *Nat. Mater.*, 2025, **24**, 1195–1202.
42 R. L. Merino, D. Călugăru, H. Hu, J. Díez-Mérida, A. Díez-Carlón, T. Taniguchi, K. Watanabe, P. Seifert, B. A. Bernevig and D. K. Efetov, Interplay between light and heavy electron bands in magic-angle twisted bilayer graphene, *Nat. Phys.*, 2025, **21**, 1078–1084.
43 W. Ma, Q. Zhang, L. Li, D. Geng and W. Hu, Small twist, big miracle—recent progress in the fabrication of twisted 2D materials, *J. Mater. Chem. C*, 2023, **11**(45), 15793–15816.
44 M. Xu, H. Ji, L. Zheng, W. Li, J. Wang, H. Wang, L. Luo, Q. Lu, X. Gan, Z. Liu, X. Wang and W. Huang, Reconfiguring nucleation for CVD growth of twisted bilayer MoS2 with a wide range of twist angles, *Nat. Commun.*, 2024, **15**(1), 562.
45 M. Xu, H. Ji, M. Zhang, L. Zheng, W. Li, L. Luo, M. Chen, Z. Liu, X. Gan, X. Wang and W. Huang, CVD Synthesis of Twisted Bilayer WS2 with Tunable Second Harmonic Generation, *Adv. Mater.*, 2024, **36**(19), 2313638.
46 S. Liu, B. He, W. Yang, X. Zhou, X. Xue, M. Liu, Y. Zhao, X. Wang, J. Si, F. Wang, Z. Zhang, L. Peng and G. Yu, In Situ Growth of High-Quality Single-Crystal Twisted Bilayer Graphene on Liquid Copper, *Adv. Mater.*, 2024, **36**(11), 2312125.
47 L. Sun, Z. Wang, Y. Wang, L. Zhao, Y. Li, B. Chen, S. Huang, S. Zhang, W. Wang, D. Pei, H. Fang, S. Zhong, H. Liu, J. Zhang, L. Tong, Y. Chen, Z. Li, M. H. Rümmeli, K. S. Novoselov, H. Peng, L. Lin and Z. Liu, Hetero-site nucleation for growing twisted bilayer graphene with a wide range of twist angles, *Nat. Commun.*, 2021, **12**(1), 2391.
48 M. Liu, S. Wang, H. Huang, X. Xue, X. Zhou, Z. Chen, S. Liu, X. Liu, J. Dong, W. Niu, Y. Liu, L. Wang and G. Yu, Oxygen-Assisted CVD Growth of High-Quality Twisted Bilayer Graphene, *Adv. Mater.*, 2025, 2506242.
49 Q. Zhang, D. Geng and W. Hu, Chemical vapor deposition for few-layer two-dimensional materials, *SmartMat*, 2023, **4**(3), e1177.
50 M. Li, Q. Zhang, L. Li, W. Gao, H. Ren, D. Geng and W. Hu, Precursor Engineering for Synergetic Growth of Superposition Multiheterostructures, *Small Methods*, 2025, 2401418.
51 L. Rogée, L. Wang, Y. Zhang, S. Cai, P. Wang, M. Chhowalla, W. Ji and S. P. Lau, Ferroelectricity in untwisted heterobilayers of transition metal dichalcogenides, *Science*, 2022, **376**(6596), 973–978.
52 S. Wang, Q. Zhang, A. Fan, L. Li and D. Geng, Enhanced carrier transport of monolayer MoSe2 through interlayer coupling with in situ grown metal–organic frameworks, *Chem. Commun.*, 2024, **60**(84), 12201–12204.
53 M. Li, Y. Sun, X. Xue, X. Lu, Z. Guo, Y. Han, J. Dong, D. Geng, L. Li and W. Yang, Growth and Etching of Centimeter-Scale Self-Assembly Graphene–h-BN Super-Ordered Arrays: Implications for Integrated Electronic Devices, *ACS Appl. Nano Mater.*, 2022, **5**(1), 774–781.
54 L. Li, J. Dong, D. Geng, M. Li, W. Fu, F. Ding, W. Hu and H. Y. Yang, Multi-stage anisotropic etching of two-dimensional heterostructures, *Nano Res.*, 2022, **15**(6), 4909–4915.
55 Z. Han, M. Li, L. Li, F. Jiao, Z. Wei, D. Geng and W. Hu, When graphene meets white graphene – recent advances in the construction of graphene and h-BN heterostructures, *Nanoscale*, 2021, **13**(31), 13174–13194.
56 Q. Zhang, E. Li, Y. Wang, C. Gao, C. Wang, L. Li, D. Geng, H. Chen, W. Chen and W. Hu, Ultralow-Power Vertical Transistors for Multilevel Decoding Modes, *Adv. Mater.*, 2023, **35**(3), 2208600.
57 P. Wang, Q. Zhang, A. Fan, L. Li, D. Geng and W. Hu, Enhancing electrocatalytic hydrogen evolution performance through homogeneous deposition of 2H-Phase MoSe2 on $Ti_3C_2T_x$, *FlatChem*, 2024, **47**, 100705.
58 Q. Zhang, M. Li, L. Li, D. Geng, W. Chen and W. Hu, Recent progress in emerging two-dimensional organic–inorganic van der Waals heterojunctions, *Chem. Soc. Rev.*, 2024, **53**(6), 3096–3133.
59 Q. Zhang, X. Ye, Y. Zheng, Y. Wang, L. Li, Z. Gao, J. Wu, H. Dong, D. Geng and W. Hu, Controllable growth of centimeter-scale 2D crystalline conjugated polymers for photonic synaptic transistors, *J. Mater. Chem. C*, 2022, **10**(7), 2681–2689.
60 Q. Zhang, A. Fan, M. Li, W. Ma, Z. Han, Y. Wang, L. Li, H. Meng, D. Geng and W. Hu, Space-Confined Vertical Growth of Large-Size Organic Semiconductor Single Crystals, *ACS Appl. Mater. Interfaces*, 2024, **16**(49), 68120–68130.
61 M. Li, L. Li, Y. Fan, F. Jiao, D. Geng and W. Hu, From Top to Down—Recent Advances in Etching of 2D Materials, *Adv. Mater. Interfaces*, 2022, **9**(31), 2201334.
62 Z. Han, X. Han, S. Wu, Q. Zhang, W. Hu, Y. Meng, Y. Liang, J. Hu, L. Li, Q. Zhang, Y. Zhang, X. Zhao, D. Geng and W. Hu, Phase and Composition Engineering of Self-Intercalated 2D Metallic Tantalum Sulfide for Second-Harmonic Generation, *ACS Nano*, 2024, **18**(8), 6256–6265.
63 Y. Hu, L. Rogée, W. Wang, L. Zhuang, F. Shi, H. Dong, S. Cai, B. K. Tay and S. P. Lau, Extendable piezo/ferroelectricity in non-stoichiometric 2D transition metal dichalcogenides, *Nat. Commun.*, 2023, **14**(1), 8470.
64 Q. Zhang, W. He, L. Li, D. Geng, Z. Xu, H. Chen, W. Chen and W. Hu, Oxygen-Assisted Anisotropic Chemical Etching of MoSe2 for Enhanced Phototransistors, *Chem. Mater.*, 2022, **34**(9), 4212–4223.
65 W. Ma, Q. Zhang, J. Zhu, Y. Guo, Y. Sun, L. Li and D. Geng, Edge-induced selective etching of bilayer MoS2 kirigami structures via a space-confined method, *Nanoscale Horiz.*, 2025, **10**(5), 957–965.
66 L. Li, Q. Zhang, H. Li and D. Geng, Liquid metal catalyzed chemical vapor deposition towards morphology engineering of 2D epitaxial heterostructures, *Chem. Commun.*, 2023, **59**(99), 14636–14648.
67 R. Zhang, M. Li, L. Li, Z. Wei, F. Jiao, D. Geng and W. Hu, The More, the Better–Recent Advances in Construction of 2D Multi-Heterostructures, *Adv. Funct. Mater.*, 2021, **31**(26), 2102049.
68 W. Qin, S. Guo, Z. Liu, P. Zhang, C. Zhu, Y. Wu, R. Qiao, Z. Liu, W. Guo and Z. Zhang, Coherently confined single-metal-atom chains in 2D semiconductors, *Nat. Commun.*, 2025, **16**(1), 4924.
69 E. Chini, F. Esposito, V. Benekou, M. Muhyuddin, E. Lunedei, G. Ruani, R. Rizzoli, G. Calabrese, F. Liscio, F. Corticelli, L. Seravalli, P. D'Angelo, V. Palermo, C. Santoro, A. Candini, D. Gentili and M. Cavallini, Edge Engineering in MoS2 by Chemically Induced Nano-Folding, *Small Structures*, 2025, 2500046.
70 J. Liang, G. Cao, Y. Zhang, Z. Li, X. Wan, J. Jiao, K. Yang, L. Xiao, Y. Guo, M. Zeng and L. Fu, Synthesis of High-Entropy Alloy Polyhedra Using Liquid Metal Dewetting, *J. Am. Chem. Soc.*, 2025, **147**(20), 16742–16746.
71 T. Ying, T. Yu, Y.-S. Shiah, C. Li, J. Li, Y. Qi and H. Hosono, High-Entropy van der Waals Materials Formed from Mixed Metal Dichalcogenides, Halides, and Phosphorus Trisulfides, *J. Am. Chem. Soc.*, 2021, **143**(18), 7042–7049.
72 H. Que, B. Li, L. Sun, P. Zhang, H. Jiang, X. Wang, K. Si, B. Gao, Q. He, Y. Jia, Y. Yang, J. Wei and Y. Gong, Synthesis of two-dimensional transition metal phosphorous chalcogenides and their high-entropy alloys, *Nat. Synth.*, 2025, **4**(5), 582–591.
73 Z. Wang, X. Chen, Y. Ding, X. Zhu, Z. Sun, H. Zhou, X. Li, W. Yang, J. Liu, R. He, J. Luo, T. Yu, M. Zeng and L. Fu, Synthesis of Two-Dimensional High-Entropy Transition Metal Dichalcogenide Single Crystals, *J. Am. Chem. Soc.*, 2025, **147**(2), 1392–1398.
74 A. Fan, Q. Zhang, Z. Yang, L. Li, M. Li, K. Zhang, J. Gao, F. Wu, M. Wu, D. Geng and W. Hu, Tailored Sliding Ferroelectricity for Ultrahigh Fatigue Resistance in Stacked Trilayer MoS2 Crystals, *Sci. Adv.*, 2025, **11**, eadv8192.