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Atomic and structural modifications of two-dimensional transition metal dichalcogenides for various advanced applications

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Two-dimensional (2D) transition metal dichalcogenides (TMDs) and their heterostructures have attracted significant interest in both academia and industry because of their unusual physical and chemical properties. They offer numerous applications, such as electronic, optoelectronic, and spintronic devices, in addition to energy storage and conversion. Atomic and structural modifications of van der Waals layered materials are required to achieve unique and versatile properties for advanced applications. This review presents a discussion on the atomic-scale and structural modifications of 2D TMDs and their heterostructures *via* post-treatment. Atomic-scale modifications such as vacancy generation, substitutional doping, functionalization and repair of 2D TMDs and structural modifications including phase transitions and construction of heterostructures are discussed. Such modifications on the physical and chemical properties of 2D TMDs enable the development of various advanced applications including electronic and optoelectronic devices, sensing, catalysis, nanogenerators, and memory and neuromorphic devices. Finally, the challenges and prospects of various post-treatment techniques and related future advanced applications are addressed.

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1. Introduction

Since the discovery of monolayer graphene (Gr) in 2004,¹ two-dimensional (2D) transition metal dichalcogenides (TMDs) and their heterostructures have gained significant attention owing to their numerous unique physical and chemical properties, such as high electron mobility,² thermal conductivity,³ topological insulation,⁴ Moiré superlattices,⁵ unconventional superconductivity,^{6,7} piezoelectricity,^{8,9} giant magnetoresistance,¹⁰ non-linear optics,^{11–13} and Weyl semimetals.^{14,15} These unique properties have numerous applications in electronics, optoelectronics, spintronics, valleytronics, energy harvesting, and quantum computation. However, the physical and chemical properties of as-grown 2D TMDs often do not meet the specific requirements for advanced applications.

For example, monolayer molybdenum disulfide flakes grown by chemical vapor deposition (CVD) do not exhibit high carrier mobility in field-effect transistors (FETs) because of intrinsic sulfur vacancies (S_v) (S_v density $\approx 1.24 \times 10^{13} \text{ cm}^{-2}$), which

limits electronic device applications.¹⁶ This shortcoming can be easily solved by using post-treatment techniques such as thermal annealing under a sulfur-rich atmosphere. Therefore, post-treatment is a promising method of controlling the physicochemical properties of TMDs and, thus, enables the development of various advanced applications.

Although the post-treatment of TMDs and their heterostructures are important for numerous device applications, only specific topics related to defect engineering, phase engineering, and substitutional doping have been reviewed.^{17–19} Furthermore, applications have not been comprehensively discussed in conjunction with post-treatment methods. Therefore, post-treatment methods for TMDs and their heterostructures must be investigated by focusing on atomic-scale and structural modifications along with their device applications.

In this review, various post-treatment approaches for the atomic-scale and structural modifications of TMDs are summarized (Fig. 1). Atomic-scale modification is classified into four categories: (I) vacancy generation, (II) substitutional doping, (III) functionalization, and (IV) repair. Structural modification consists of two categories: (V) phase transition and (VI) heterostructures. These modifications modulate the material properties including optical, electronic, catalytic, magnetic properties and so on. Therefore, various advanced applications including electronic and optoelectronic devices, catalysis, energy storage, sensors, piezoelectricity, nanogenerators, and memory and neuromorphic devices according to each post-

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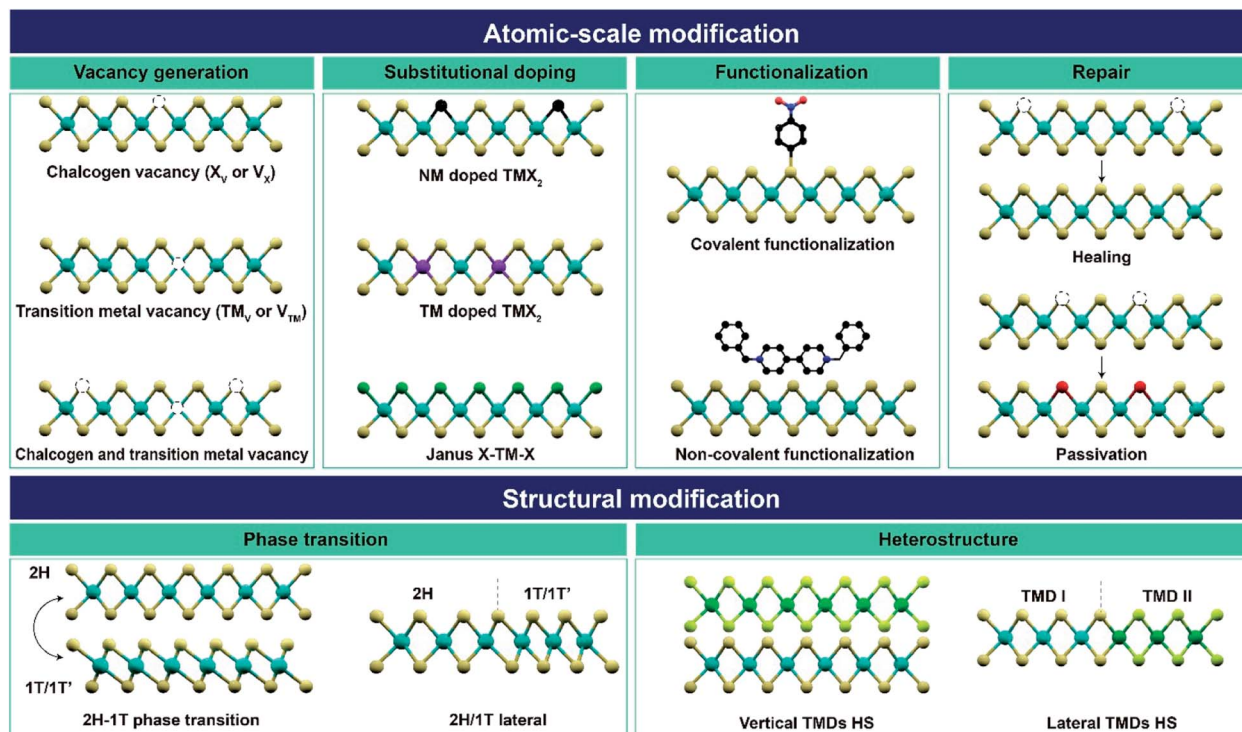


Fig. 1 Overview of atomic-scale and structural modifications of 2D TMDs and vdW heterostructures via various post-treatment techniques (X – chalcogen; TM – transition metal; V – vacancy; NM – non-metal; HS – heterostructure).

treatment are discussed. Finally, the challenges and prospects of post-treatment techniques and important issues to be resolved in near future are addressed.

2. Atomic-scale modification of TMDs

This section details various atomic-scale modifications (namely, vacancy generation, substitutional doping, functionalization, and repair) of TMDs for device applications. In the first sub-section, vacancy generation methods, including plasma treatment, electron-beam irradiation, thermal annealing, and chemical treatment, are introduced for FETs, electrocatalysts, CO_2 hydrogenation, and Li-air batteries. The second sub-section describes the substitutional doping of non-metals and metals for applications, such as FETs, biosensors, catalysis, and piezoelectricity. In the third sub-section, covalent and non-covalent functionalizations are discussed for CoVID-19 sensors, triboelectric nanogenerators (TENGs), multifunctional optoelectronic devices, and memory and neuromorphic device applications. The last sub-section describes the repair of atomic defects in TMDs for high-performance flexible piezoelectric nanogenerators (PENGs), photodiodes, superconductors, and low contact resistance in FETs.

2.1. Vacancy generation

Vacancy generation in TMDs is highly desirable for controlling the performance of catalytic, electronic, and optoelectronic

devices via modulating the carrier concentration and tuning the catalytic activity. The focus in most of the previous studies was chalcogen vacancy generation (hereafter, S and Se vacancies are denoted as S_v and Se_v , respectively). Vacancy generation can be categorized into (i) dry etching processes, including plasma treatment, electron/ion-beam irradiation, and thermal annealing, and (ii) wet chemical etching processes.

Dry etching process. The dry etching process has the advantage of precisely controlling vacancy density. Plasma consists of electrically charged particles that are produced after the ionization of gases.²⁰ Argon plasma, for example, effectively generates defects in TMDs, including MoS_2 ,^{21–23} WS_2 ,²¹ $MoSe_2$,²⁴ WSe_2 ,²⁵ and $PtSe_2$.²⁶ To prevent severe damage to TMDs, mild plasma treatment with H_2 or He is employed.²⁷ The atomic structure of WSe_2 after plasma treatment shows S_v generation (Fig. 2a). The corresponding Raman spectra of one-, two-, and five-layer WSe_2 before and after H_2 plasma treatment display no changes in the peak positions of the characteristic phonon modes (E_{2g}^1 and A_{1g}) and their intensities (Fig. 2b), indicating that the crystal lattice of WSe_2 remains even after the selective removal of Se atoms by plasma. The Se/W ratio of WSe_2 after plasma treatment is slightly decreased from 2.05 to 1.98 (less than ~5 at% of Se_v). The photoluminescence (PL) spectra of the WSe_2 monolayer after H_2 plasma treatment are broadened and quenched (Fig. 2c). Oxygen plasma treatment is used for the formation of oxygen-transition metal bonds, such as Mo–O in MoS_2 , Re–O in ReS_2 , and Te–O in WTe_2 after the removal of chalcogen atoms.^{28–31} In the case of WTe_2 , oxygen plasma can efficiently eliminate Te or W atoms, resulting in the formation



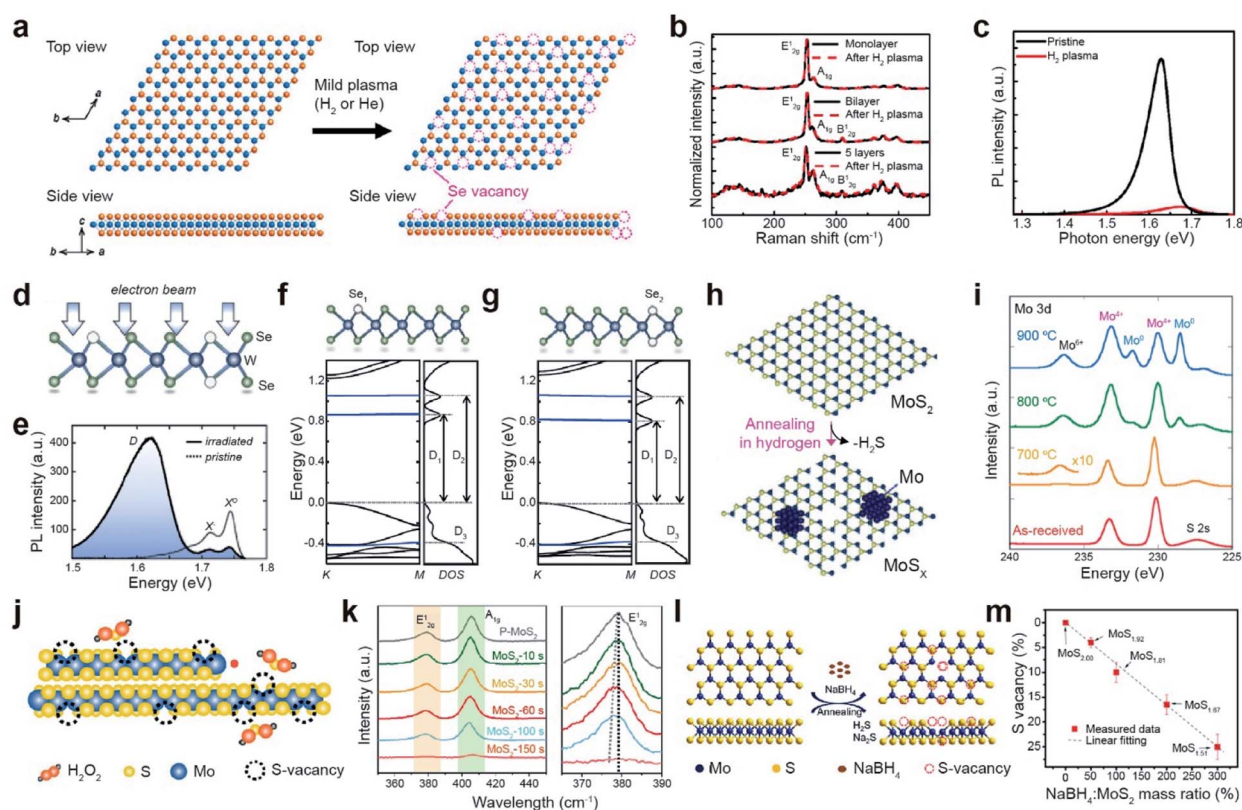


Fig. 2 Vacancy generation of 2D TMDs with dry (plasma treatment, electron beam irradiation, and thermal annealing) and wet chemical etching processes. **Plasma treatment:** (a) atomic structure of WSe₂ layers before and after the H₂ plasma treatment, illustrating the creation of Se vacancies. (b) Raman spectra of monolayer, bilayer, and five-layer WSe₂ before and after H₂ plasma treatment, respectively. (c) PL spectra of the WSe₂ monolayer before and after H₂ plasma treatment at room temperature. **Electron beam irradiation:** (d) illustration of the atomic structure of WSe₂ with a single selenium vacancy (Se₁) and double selenium vacancy (Se₂) after electron beam irradiation. (e) PL spectra of the pristine and electron beam irradiated WSe₂, taken at 5 K. (f and g) DFT band structures of Se₁ and Se₂. **Thermal annealing:** (h) schematic illustration of the thermal texturization process of MoS₂ by thermal annealing under a H₂ atmosphere. With increasing S_V density, a Mo cluster is also generated. (i) XPS spectra of the Mo 3d core level for as-received and annealed bulk MoS₂ samples. **Chemical etching:** (j) schematic of the chemical etching process with H₂O₂. (k) Raman spectra of MoS₂ with different etching times with H₂O₂. Right Raman spectra show a red-shift of the E_{2g} peak according to the etching time. (l) Schematic of the desulfurization process of MoS₂ via solid-phase reduction. (m) S_V content variation as a function of NaBH₄: MoS₂, obtained from XPS measurement.²⁷ Copyright 2016, American Chemical Society. (d–g) Adapted with permission.³⁵ Copyright 2021, American Physical Society. (h and i) Adapted with permission.⁵¹ Copyright 2016, American Chemical Society. (j and k) Adapted with permission.⁵² Copyright 2020, American Chemical Society. (l and m) Adapted with permission.⁵⁴ Copyright 2019, American Chemical Society.

of transition metal and chalcogen vacancies, in addition to W–O and Te–O bonds.³²

Electron beam irradiation can precisely control the generation of chalcogen vacancies *via* several mechanisms such as the knock-on effect, ionization, beam-induced chemical etching, and ballistic displacement.^{33,34} The atomic structure of electron-beam-irradiated WSe₂ presents both single (Se₁) and double selenium vacancies (Se₂) (Fig. 2d).³⁵ The neutral (X⁰) and negatively charged (X[−]) exciton peaks of pristine WSe₂ are observed in its PL spectra. The additional broad defect band (D) with attenuated X⁰ and X[−] intensities are observed for irradiated WSe₂ by performing scanning electron microscopy (SEM) with ~10⁷ electrons per μm² (Fig. 2e). The density functional theory (DFT) band structures of Se₁ and Se₂ represent the formation of unoccupied midgap bands (D₁ and D₂), in addition to the occupied one below the valence-band maximum (D₃) (Fig. 2f and g).³⁵ The number of chalcogen vacancies in MoS₂ and

MoSe₂ can be precisely controlled by an electron beam in *in situ* transmission electron microscopy (TEM).^{36,37} In addition to electron beams, ion beams such as argon,^{38,39} helium,^{40–42} manganese,⁴³ gallium,^{44,45} and gold,⁴⁶ can be employed to generate vacancies. For example, the S_V content in MoS₂ and WS₂ monolayers gradually increases with Ar⁺ ion beam irradiation.^{47–50}

Thermal annealing is a simple method for creating chalcogen vacancies *via* thermal desorption. A H₂ atmosphere is commonly used during thermal annealing to etch away chalcogen atoms *via* H₂S and H₂Se formation (Fig. 2h). The thermal texturization process of MoS₂ flakes is also observed.⁵¹ The XPS spectra of the Mo 3d core level for MoS₂ after annealing at elevated temperatures (700, 800, and 900 °C) shows the gradual evolution of peaks at 232 and 229 eV (assigned to the Mo⁰ doublet) and 236.5 eV (assigned to Mo⁶⁺), in addition to a doublet at 233 and 230 eV (assigned to Mo⁴⁺ 3d_{3/2} and 3d_{5/2},

respectively) for pristine MoS₂ (Fig. 2i). Such evolution of a Mo⁰ doublet and Mo⁶⁺ peaks is attributed to the formation of Mo metal clusters (by the removal of S atoms) and MoO₃ at S_V sites (due to Mo oxidation under air), respectively. In contrast, the S 2p doublet in the S 2p core-level spectra is still present, indicating that some MoS₂ can be maintained, regardless of the annealing temperature.

Wet chemical etching process. Wet chemical etching is a facile and mild strategy for creating atomic chalcogen and transition metal vacancies. Various reagents, such as H₂O₂,^{52,53} NaBH₄,^{54–56} hydrazine,⁵⁷ and HCl,⁵⁸ have been utilized. For example, MoS₂ nanosheets are immersed in a H₂O₂ solution to generate vacancies (Fig. 2j). The Raman spectra of the MoS₂ nanosheets with H₂O₂ treatment show that both the E_{2g}¹ and A_{1g} peaks gradually broaden and eventually disappear, indicating that the S and Mo atoms are progressively etched away over the treatment time (Fig. 2k).⁵² Phonon softening related to the redshift of the E_{2g}¹ peak is also observed. The significant intensity changes in the E_{2g}¹ and A_{1g} peaks are attributed to a high vacancy generation of ~15 at% after chemical etching for 150 s. NaBH₄ is used for solid-phase reduction to create S_V in the basal plane of MoS₂ (Fig. 2l).⁵⁴ NaBH₄ exclusively reduces Mo⁴⁺ to Mo^{δ+} (δ < 4), resulting in the removal of sulfur atoms by forming H₂S and Na₂S. The concentration of S_V-MoS₂ increases almost linearly with the mass ratio of NaBH₄ : MoS₂, indicating that the concentration of vacancies can be efficiently controlled by the amount of reagent (Fig. 2m). Hydrazine is used to donate electrons to WS₂, in addition to creating S_V.⁵⁷

Although various types of dry etching processes (*i.e.* plasma treatment, electron/ion beam irradiation, and thermal annealing) are employed for vacancy engineering, the detailed mechanisms of vacancy generation are still not well-understood. Plasma or ion beams are more desirable for patterned device applications, whereas thermal annealing is preferable for catalytic applications. Chemical wet etching frequently induces the formation of undesired vacancies and oxides.

Applications. The vacancies in TMDs can be utilized for various applications, including FETs, electrocatalytic microcells for hydrogen evolution, CO₂ hydrogenation catalysts, and Li-air batteries. Anion vacancies, such as S_V and Se_V, serve as n-type dopants. Thus, the electrical conductivity of TMDs increases with the vacancy concentration until a certain point and then decreases at high concentrations because of the collapse of the crystal structure.^{27,59–61} The optimized concentration of Se_V minimized contact resistance by forming edge contacts in a homojunction (Fig. 3a). Mild H₂ plasma was introduced to selectively generate Se_V in the contact region in the WSe₂ FET. As a result, the on-current was significantly increased by a factor of 20, attaining a low subthreshold swing (SS) of 66 mV dec^{−1} (Fig. 3b).²⁷ Furthermore, semiconductor-to-metallic transitions in MoS₂ and WS₂ were also observed with low-energy He plasma and He⁺ beam irradiation treatments.^{61–63} This transition was attributed to the emergence of mid-gap states near the Fermi level at an appropriate vacancy concentration.

The edge of 2H-MoS₂ acts as an active site for hydrogen evolution, whereas the basal plane is inactive.⁶⁴ In addition, low electrical conductivity limits the electrocatalytic activity of

MoS₂. Vacancy generation in MoS₂ is very useful for activating its basal plane for the hydrogen evolution reaction (HER) and increasing its electrical conductivity.^{65–67} For example, the basal plane of MoS₂ was irradiated with a He⁺ beam (Fig. 3c). Consequently, with increasing S_V concentration, the linear sweep voltammetry (LSV) curves shifted toward the Pt reference up to an optimum concentration of 5.7 cm^{−14} cm^{−2},⁶⁸ which is clear evidence of the activation of the basal plane by vacancy generation. When the S_V concentration was increased above this threshold, the LSV curves shifted backward (Fig. 3d), attributed to the collapse of the MoS₂ structure. Many approaches, including NaClO treatment,⁶⁹ ozone treatment,⁷⁰ and laser treatment,⁷¹ have been used for vacancy generation to enhance the HER activity of TMDs. In quantum information applications, single-photon emission from the defects of the WSe₂ monolayer induced by e-beam irradiation has recently been reported.⁷²

The basal plane of S_V-MoS₂ is an ideal active site for low-temperature hydrogenation of CO₂ to selectively produce methanol *via* the following reaction mechanism: (i) dissociation of CO₂ to surface-bound CO* and O* at S_V sites, (ii) hydrogenation of CO* to CH₃O*, and (iii) synthesis of CH₃OH (inset of Fig. 3e). As a result, S_V-rich MoS₂ nanosheet catalysts showed a high methanol selectivity of 94.3% and CO₂ conversion of 12.5%. Furthermore, they were stable over 3000 h at 180 °C (Fig. 3e).⁷³ S_V in MoS₂ nanoflowers prepared by thermal annealing in a hydrogen environment also improves solar-driven CO₂ photoreduction.⁷⁴ The rate of CO production was enhanced approximately 2-fold after S_V generation.

Chalcogen vacancies provide abundant active sites for the intercalation/deintercalation of guest ions (Li⁺, Na⁺, and K⁺), which leads to enhanced reaction kinetics and improved specific capacities. For example, sulfur vacancies in MoS₂ can intrinsically promote O₂ adsorption, enhancing the electrochemical performance of Li-O₂ batteries.⁷⁵ The core-shell MoS₂-_x@CNT composite synthesized by hydrothermal and thermal annealing was treated with NaBH₄ to increase S_V concentration (Fig. 3f). The initial discharge/charge profile at 200 mA g^{−1} was significantly boosted up to discharge/charge specific capacities of 19 989/17 705 mA h g^{−1} with an overpotential of 0.99/0.26 V (Fig. 3g).⁷⁶ Furthermore, S_V improves polysulfide conversion kinetics in Li-S batteries,⁷⁷ facilitates the absorption of Na⁺/Zn²⁺, and increases the conductivity of Na/Zn-ion batteries.^{78,79}

2.2. Substitutional doping

The substitutional doping of TMDs is classified into two main categories: impurity doping with partial substitution and Janus structures with full replacement of chalcogen atoms of the top layer (out of three atomic layers) in TMDs. Impurity doping is an important technique for precisely controlling the electrical and other intrinsic properties of TMDs for next-generation high-end electronics, optoelectronics, medicine, and energy harvesting applications.^{80,81} Several approaches have been developed to tune the characteristics of TMDs by substituting chalcogen atoms (X) or transition metals (M) *via* atomic doping.^{82,83}



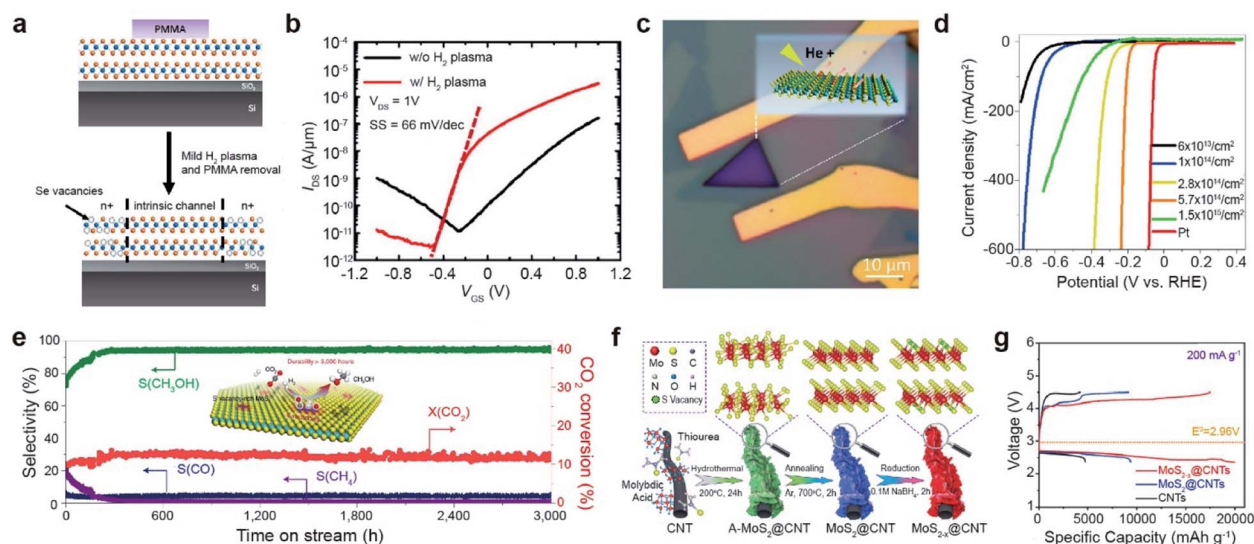


Fig. 3 Vacancy-driven applications: FET, electrocatalyst for hydrogen evolution, CO₂ hydrogenation catalyst, and Li–air battery. **FET:** (a) schematic of selective vacancy generation with H₂ plasma treatment and (b) corresponding I_{DS} – V_{GS} curves of the WSe₂ FET with/without plasma treatment, measured under 1×10^{-5} Torr. **Electrocatalyst for hydrogen evolution:** (c) optical image of He⁺ ion beam irradiated MoS₂. (d) LSV curves of MoS₂ at various S_V concentrations and Pt wire. **CO₂ hydrogenation catalyst:** (e) long term stability test of the S_V -MoS₂ nanosheet catalyst in the hydrogenation of CO₂ at 3000 mL g_{cat}^{−1} h^{−1}, measuring the selectivity (*S*) of CH₃OH, CO, and CH₄ and conversion (*X*) of CO₂ over 3000 h. **Li–air battery:** (f) synthesis process of MoS₂–*x*@CNTs. (g) Charge/discharge profiles at 200 mA g^{−1} in the voltage range from 2.35 to 4.5 V. (a and b) Adapted with permission.²⁷ Copyright 2016, American Chemical Society. (c and d) Adapted with permission.⁶⁸ Copyright 2019, American Chemical Society. (e) Adapted with permission.⁷³ Copyright 2021, Springer Nature Limited. (f and g) Adapted with permission.⁷⁶ Copyright 2022, Wiley-VCH.

Depending on the relative valency of the dopant atoms, they act as electron donors or acceptors. When a Janus group-VI chalcogenide MXY (top layer X, bottom layer Y = S, Se, and Te; X ≠ Y) is formed, the out-of-plane mirror symmetry is broken. This unique asymmetrical feature of Janus structures arises from different atomic radii and electronegativities of X and Y atoms, thus enabling novel applications such as piezoelectric devices and electrocatalysts.^{84,85}

Impurity doping. Non-metallic (NM) doping of TMDs has been performed by substituting chalcogen atoms with O, Te, Cl, N, P, and F atoms.^{86–94} For example, carbon doping was carried out *via* plasma-induced CH₄ gas exposure of WS₂ monolayers (Fig. 4a).⁹⁵ No noticeable damage was observed in the monolayers, and their PL intensity progressively decreased and shifted toward lower energy values with increasing carbon content (Fig. 4b). Theoretical simulations predicted that, unlike single C doping, CH doping provided the most stable and lowest local strain on WS₂. The calculated bandgap of pristine WS₂ was 1.791 eV, whereas that of carbon-doped WS₂ had a direct bandgap of 1.574 eV (Fig. 4c). After carbon doping, the energy gap is decreased by raising new acceptor levels above the valence band of WS₂ owing to the hybridization of W d-orbitals and C p-orbitals. The extra holes can move to new levels, implying that CH impurities act as p-type dopants.

Transition metal (TM) doping at the M site of a TMD is conducted in three steps: (i) generation of chalcogen vacancies, (ii) replacement of transition metal-adjacent chalcogen vacancy sites, and (iii) healing of chalcogen vacancies.^{96–100} For example, WS₂ monolayers were first grown with S_V sites, followed by

subsequent exposure to a Sn-rich atmosphere using SnS as a precursor at 550 °C (Fig. 4d).¹⁰¹ The characteristic PL peak of WS₂ was gradually attenuated with doping time and dopant concentration (Fig. 4e). Moreover, Sn dopants in the WS₂ lattice act as electron donors (*i.e.*, n-type dopants). Another strategy for TM doping is the direct use of a metal flux with the aid of electron beam evaporation (Fig. 4f).^{97,102} In this case, dopant beams (such as Nb and Re) with low kinetic energy are generated by thermal evaporation of high-melting-point metals on an exposed TMD. The beam flux is modulated to supply metal dopants during the entire doping process to enhance structural reconstruction and regulate the formation of metal-doped TMDs. Concurrently, a Se beam is continuously supplied to heal possible Se vacancies during the doping process. Accurate and position-selective doping can be achieved when patterned TMD materials are used.¹⁰² Molecular dynamics (MD) simulations showed a gradual structural change with Nb and Se exposure (Fig. 4g). When a Nb atom hit a W atom with substantial energy (simulation time is varied from 0 to 100 fs), the W atom was released from the original position. Simultaneously, the Nb atom replaced the vacancy created by the released W atom. Fig. 4h displays an atomic-resolution high-angle annular dark-field (HAADF)-scanning transmission electron microscopy (STEM) image of monolayer WSe₂ after exposure to a Nb beam. The cutouts from the white squares in Fig. 4h clearly show the atomic structure of Nb-doped WSe₂; bright and dark spots at W sites in the hexagonal lattice are assigned to W and Nb atoms (as shown in the structural model).



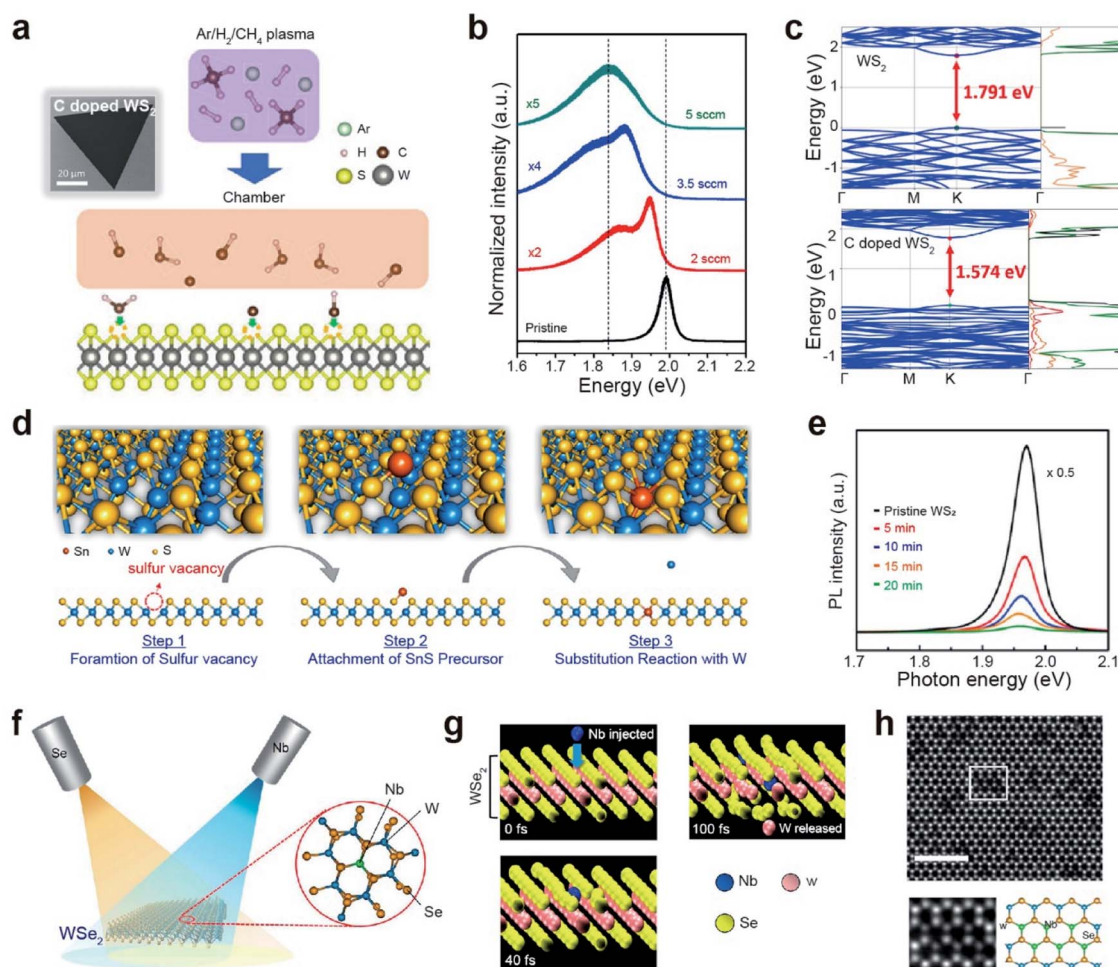


Fig. 4 Non-metallic and metallic impurity doping in TMDs: plasma-assisted, thermal annealing, and beam epitaxy. **Non-metallic doping:** (a) schematic of the plasma-assisted doping experiment (right) and SEM image (left) of the carbon-doped monolayer WS₂. (b) PL spectra of the pristine and carbon-doped monolayer WS₂ with different methane flow rates (2, 3.5, and 5 sccm, respectively). (c) Band structure and density of states (DOS) of monolayer pristine WS₂ and CH-doped WS₂. **Transition metal doping:** (d) doping mechanism of Sn substituting into the W site in the WS₂ layers. (e) PL spectrum of monolayer WS₂ before and after 5, 10, 15, and 20 min of Sn doping. (f) Schematic representation of Nb doping in WSe₂ with a dopant (Nb) and a chalcogen (Se) beam. (g) Snapshots of the Nb substitutional doping process in WSe₂ after 0, 40, and 100 fs, respectively, obtained by *ab initio* molecular dynamics simulation. (h) Representative HAADF-STEM image of monolayer WSe₂ after doping of Nb. The scale bar corresponds to 2 nm. Cut out from the white squares is matched with the structural model as shown. In the structural model, blue, green, and yellow balls represent W, Nb, and Se atoms, respectively. (a–c) Adapted with permission.⁹⁵ Copyright 2019, American Association for Advancement of Science. (d and e) Adapted with permission.¹⁰¹ Copyright 2019, American Chemical Society. (f–h) Adapted with permission.¹⁰² Copyright 2021, American Chemical Society.

A summary of impurity doping in CVD-grown monolayers and exfoliated TMDs is presented in Table 1.

Janus structures. Janus TMD structures can be obtained using two representative methods: (i) thermal annealing under a chalcogen-rich atmosphere and (ii) H₂ plasma stripping and thermal chalcogenization at low temperature (hereafter denoted as remote plasma-assisted chalcogenization).^{103–106}

In the past, Janus structures were constructed by a thermal-annealing process under a secondary chalcogen atmosphere. For example, Janus MoSSe and MoSeS structures were produced by annealing MoSe₂ and MoS₂ at temperatures of ~800 and ~450 °C under S and Se atmospheres, respectively.^{103,104} However, high temperatures are unfavorable for 2D Janus

monolayers because of a high probability of alloy or defect formation, such as chalcogen vacancies and cracks.

Remote plasma-assisted chalcogenization consists of two consecutive steps: (i) remote hydrogen plasma treatment of a CVD-grown MoS₂ monolayer to strip off sulfur atoms from the top layer and replace them with hydrogen atoms and (ii) replacement of H atoms with Se through a thermal selenization process at ~450 °C to form a structurally stable Janus MoSSe monolayer (Mo atoms are covalently bonded to the underlying S and top-layer Se atoms) (Fig. 5a).¹⁰³ Similarly, a room-temperature atomic layer substitution (RT-ALS) process was recently developed (Fig. 5b–i).¹⁰⁷ This less disruptive technique employs hydrogen radicals produced by a remote plasma to strip chalcogen atoms on the top layer of an as-grown TMD.

Table 1 Impurity doping of CVD-grown and exfoliated monolayer TMDs with transition metal (TM), non-metal (NM), chalcogen (X), and halogen (H) atoms

Category	Doping sites	Dopants	Host	Type	Doping method	Application	References
X	X site	Te	MoS ₂ , WS ₂	p	NaOH assisted Te deposition	—	87
X	X site	Te	MoS ₂	—	Te vapor deposition	—	88
H	X site	Cl	MoS ₂ , MoSe ₂	n	Cl ion implantation	Electronics	89
NM	X site	N	MoS ₂ , WS ₂	p	N ₂ plasma treatment	Electronics	91
NM	X site	P	MoS ₂ , WS ₂	p	PH ₃ plasma treatment	Electronics	93
H	X site	F	MoS ₂	p	SF ₆ plasma treatment	Electronics	94
NM	X site	C	WS ₂	p	CH ₄ plasma treatment	FET	95
TM	M site	V	MoTe ₂	p	Vapor	Ferromagnetism	96
TM	M site	Nb	WSe ₂	p	Molecular beam epitaxy	—	97
TM	M site	Nb, Co	WSe ₂	—	Physical ion implantation	Ferromagnetism	98
TM	M site	Co	WSe ₂	—	Physical ion implantation	Ferromagnetism	99
TM	M site	Mo/Ti	MoS ₂ , MoTe ₂	—	Mo/Ti diffusion	—	100
TM	M site	Sn	WS ₂	n	SnS vapor	Electronics	101

Concurrently, vaporized chalcogens (Se or S) are supplied to substitute stripped atoms, resulting in an asymmetric Janus structure at room temperature in the form of MXY (M = Mo

or W, X = S or Se, and Y = Se or S). Fig. 5b(ii) depicts the formation of a Janus structure: (I) before H and chalcogen adsorption, (II) adsorption and diffusion of two H atoms to the

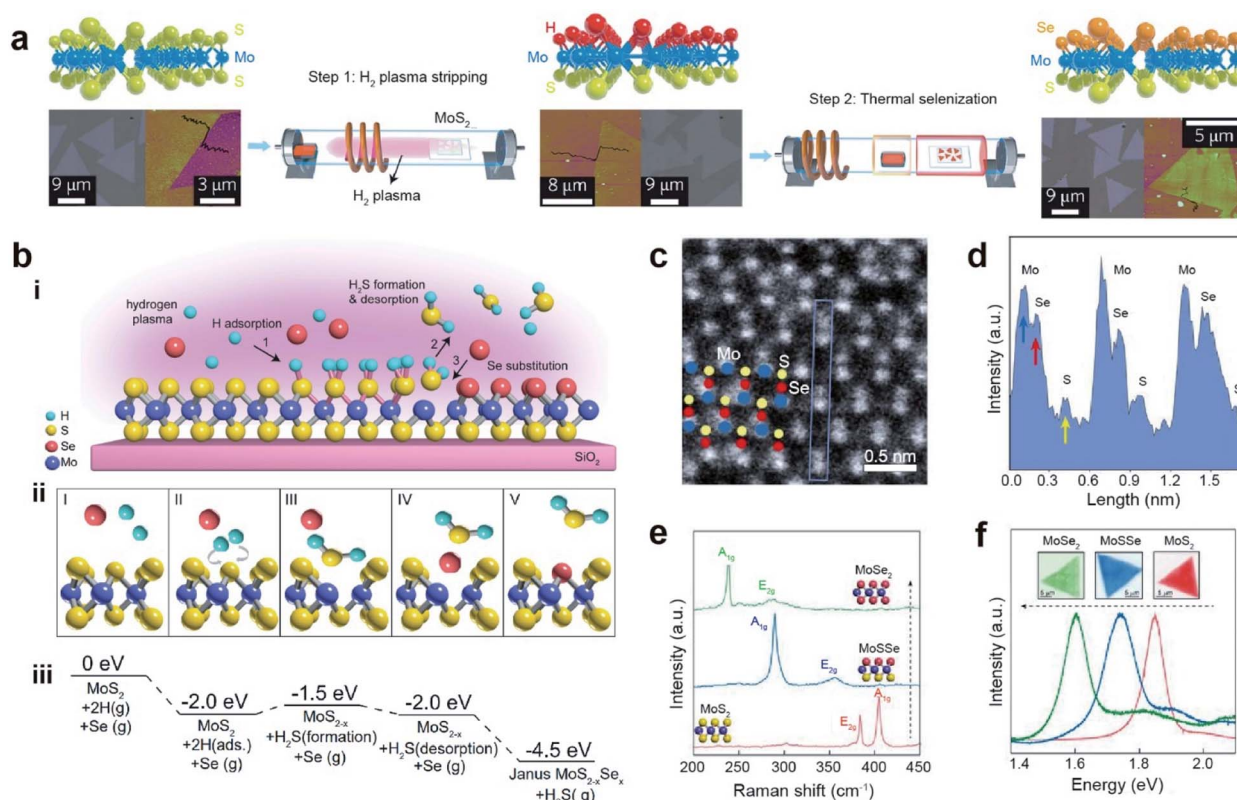


Fig. 5 Janus formation via remote plasma-assisted chalcogenization. (a) Atomic structure (top), optical (bottom left), and AFM (bottom right) images of CVD-grown MoS₂, hydrogenated MoS₂, and Janus MoSSe₂ monolayer after two steps of H₂ plasma stripping and thermal selenization. (b) (i) Schematic of the room temperature atomic layer substitution (RT-ALS) process of monolayer MoS₂. (ii) Schematic of the five key reaction steps in the RT-ALS process (cartoons from left to right): (I) before H adsorption, (II) two H atom adsorption and diffusion to the same S, (III) formation of H₂S, (IV) desorption of H₂S, and (V) Se occupation of the S vacancy. Purple, yellow, red, and green balls are Mo, S, Se, and H atoms, respectively. (iii) Free energy of each step in B, relative to that of the first step. (c) Tilted STEM image of MoSSe (seen from a vertical direction). Corresponding Mo, Se, and S atoms are shown with blue, red, and yellow circles, respectively. (d) Intensity profile for the atomic structure in the blue box in (c) shows the different intensities of individual Mo, Se, and S atoms. (e and f) Raman and PL spectra of pristine monolayer MoS₂, Janus MoSSe, and fully converted MoSe₂ respectively. (a) Adapted with permission.¹⁰³ Copyright 2017, Springer Nature Limited. (b–f) Adapted with permission.¹⁰⁷ Copyright 2021, National Academy of Sciences.



same S, (III) formation of H_2S , (IV) desorption of H_2S , and (V) Se occupation of the S vacancy. The free energy values for each step are shown in Fig. 5b(iii). The tilted ADF-STEM image reveals that Se atoms are located on one side of the monolayer MoSSe , while S atoms are on the opposite side. This is direct evidence of a Janus structure (Fig. 5c). The corresponding intensity profile in Fig. 5d clearly shows individual Mo, Se, and S atoms with peak intensities proportional to their atomic numbers. Furthermore, the MoS_2 A_{1g} (404 cm^{-1}) and E_{2g} (383 cm^{-1}) modes in the Raman spectra shifted to 288 cm^{-1} and 355 cm^{-1} , respectively, due to disrupted symmetry in the vertical direction caused by the formation of a Janus structure (Fig. 5e). After further selenization processing of Janus MoSSe was performed, a sharp peak at $\sim 239\text{ cm}^{-1}$ and a broad peak at $\sim 284\text{ cm}^{-1}$ were formed, which are the signature peaks of the A_{1g} and E_{2g} modes in monolayer MoSe_2 . In addition, the PL shifts from 1.85 eV (pristine MoS_2) to 1.72 eV (Janus MoSSe) and finally to 1.60 eV (converted MoSe_2) are clearly observed (Fig. 5f).^{103,105}

Room-temperature doping with remote plasma-assisted chalcogenization offers the possibility of producing high-quality TMDs and 2D Janus structures, which will advance the fabrication techniques for industrial applications as a desirable emerging platform.

Applications. The tunable material properties obtained by substitutional doping of TMDs have been utilized to realize novel applications, including electronics, biosensors, catalysis, optoelectronic applications, magnetization, and photocatalysis.

Impurity doping is widely used to modulate the electrical properties of TMD materials.⁹¹ For example, the I - V transfer curve of n-type-doped multilayer MoS_2 obtained by N_2 plasma exposure distinctly shows a positive threshold voltage (V_{th}) shift, which is consistent with the p-type dopant behavior of nitrogen in MoS_2 (Fig. 6a). Moreover, Mn-doped MoS_2 (Mn-MoS_2) was used to selectively detect dopamine (DA) levels in serum and artificial sweat.¹⁰⁸ Abnormal levels of dopamine in the body can be symptomatic of several disorders such as Alzheimer's disease, schizophrenia, and Parkinson's disease.¹⁰⁹ Previously, DA detection was achieved by employing highly sophisticated methods, such as mass spectrometry, liquid chromatography, and electrochemical detection measurements.¹¹⁰ Therefore, a low-cost but accurate diagnostic tool for the detection of DA levels is essential. A wearable DA sensor was fabricated on a flexible polyimide (PI) sheet with a Mn- MoS_2 working electrode (WE), a pyrolytic graphite sheet (PGS) counter electrode (CE), and an Ag paste reference electrode (RE) (Fig. 6b). DA concentrations as low as 50 nM were successfully detected in artificial sweat containing 5 mM glucose (Fig. 6c). Furthermore, Co-doped defective MoS_2 (Co- MoS_2) exhibits superior dinitrogen-to-ammonia conversion activity compared with pristine MoS_2 and CoS_2 (Fig. 6d).¹¹¹ Such a high faradaic efficiency and production rate are attributed to the effective activation of the dinitrogen molecule for the dissociation of the $\text{N}\equiv\text{N}$ triple bond in defective MoS_{2-x} .

The electrocatalytic conversion of CO_2 into sustainable fuels is considered the most efficient approach for achieving carbon neutrality.¹¹² Nb-doped MoS_2 can reduce CO_2 to produce useful hydrocarbon derivatives, such as methane and ethanol, along

with H_2 (Fig. 6e). The CO formation turnover frequency (TOF) of Nb-doped MoS_2 in an ionic liquid is one order of magnitude higher than that of Ta-doped MoS_2 or Ag NPs in the overpotential range of 50–150 mV. Furthermore, the current density of Nb-doped MoS_2 in LSV experiments was approximately 2 and 50 times higher than that of pristine MoS_2 and Ag NPs, respectively.

The Janus structure of TMDs has been reported to possess piezoelectric properties due to its non-symmetrical structure, which generates electrical polarization in response to externally applied mechanical stress.¹⁰³ The resonance-enhanced piezo-response force microscopy image of Janus MoSSe shows the presence of piezoelectric properties (Fig. 6f), which are not observed in pristine MoS_2 . In addition, Janus TMD monolayers effectively activate TMD basal planes for the HER.¹⁰⁴ Janus SMoSe (for MoSSe) and its reverse configuration of SeMoS (for MoSeS) were constructed by atomic substitution of pure MoS_2 and MoSe_2 , respectively (Fig. 6g). Both Janus SMoSe and SeMoS monolayers exhibit lower overpotentials in the LSV curves than pure MoS_2 and MoSe_2 . Moreover, the HER activity of SeMoS surpasses that of SMoSe , which is attributed to the greater thermoneutral Gibbs free energy (ΔG_{H}) for SeMoS in the presence of Se_V (-0.007 eV for SeMoS and 0.060 eV for SMoSe). The unique structure of Janus TMDs enables band edge modulation and electronic transfer when heterostructures are designed. Taking advantage of the type-II band alignment of MoSSe-MoS_2 , a back-gate transistor was fabricated to measure the four-probe output characteristics (Fig. 6h).¹⁰⁷ A plot of current density (I_{D}/W) versus bias voltage (V_{M}) at various applied back-gate voltages (V_{G}) shows weak rectification behavior at the lateral junction.

2.3. Functionalization

Functionalization leads to improvement in the optical, electronic, and sensing characteristics of TMDs for next-generation devices. Functionalization with organic molecules is categorized into (i) covalent functionalization *via* chemisorption and (ii) non-covalent functionalization *via* physisorption.^{113,114} Functional groups in an organic molecule effectively tune the Fermi level of TMDs *via* an electron-donating or electron-withdrawing mechanism. Hydroxyl ($-\text{OH}$), alkoxyl ($-\text{OR}$), and amine groups ($-\text{NH}_2$) donate electrons (*i.e.*, they are n-type dopants) to TMDs, while nitro ($-\text{NO}_2$), cyano ($-\text{CN}$), and trihalogenated methyl ($-\text{CX}_3$) groups withdraw electrons (*i.e.*, they are p-type dopants) from TMDs.^{115–118}

Covalent functionalization. Covalent functionalization involves a chemical reaction to form covalent bonds between TMDs and organic molecules. Representative approaches include direct functionalization of metallic TMDs, functionalization of aryl diazonium salts, and functionalization of thiol derivative molecules.

Semiconducting 2H-TMDs, such as MoS_2 , WS_2 , and MoSe_2 , are chemically unreactive because they are free from dangling bonds on their surfaces. However, after the phase transition from 2H to negatively charged metallic 1T-TMDs *via* lithiation, they become reactive to covalent functionalizations with alkyl



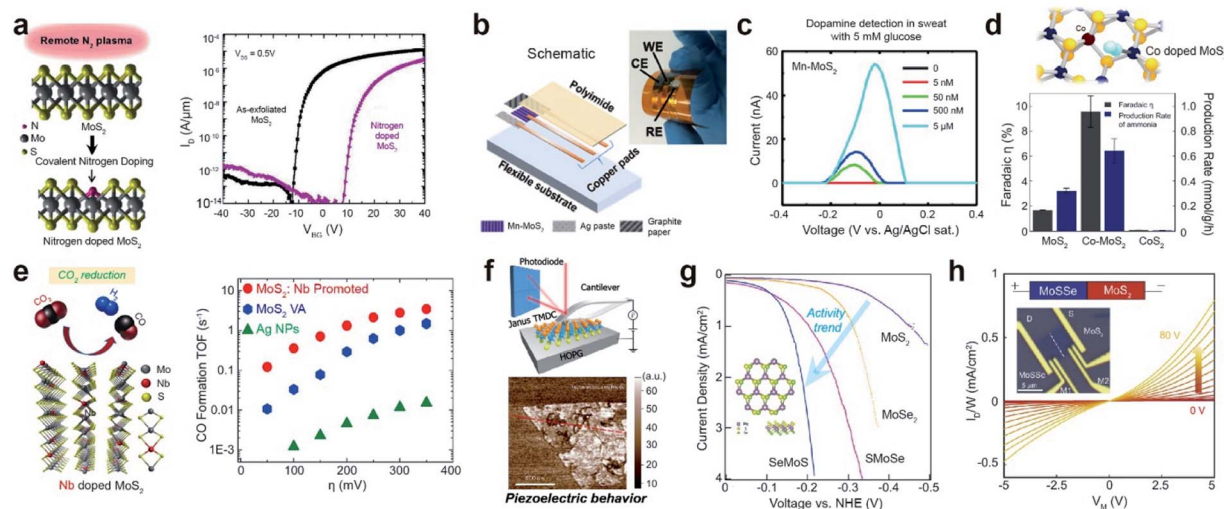


Fig. 6 Applications of substitutionally doped TMDs: electronic, biosensor, catalysis, and piezoelectricity. **Electronic:** (a) schematic of covalent nitrogen doping in MoS₂ upon N₂ plasma surface treatment (left) and $I_{DS}-V_{GS}$ characteristics of a multilayer nitrogen-doped MoS₂ FET (right). **Biosensor:** (b) assembled integrated sensor for detecting dopamine (DA) levels. (c) Differential pulse voltammetry results with DA in biologically complex samples (artificial sweat containing 5 mM glucose). **Nitrogen and CO₂ reduction catalysis:** (d) NRR performance of MoS_{2-x}, Co-doped MoS_{2-x}, and CoS₂ at 0.3 V overpotential. Co doping of MoS_{2-x} dramatically increases its faradaic efficiency. CoS₂ is inactive for the NRR. (e) Schematic representation of Nb-MoS₂ and reduction of CO₂ (left), in addition to the calculated CO formation TOF at different applied potentials for Ag NPs, VA-MoS₂, and VA-Mo_{0.95}Nb_{0.05}S₂ in a CO₂ environment (right). **Piezoelectricity:** (f) schematics and isolated Janus MoSSe monolayers measured by resonance-enhanced piezoresponse force microscopy. HER electrocatalyst: (g) HER polarization curves of monolayer MoS₂, MoSe₂, SMoSe, and SeMoS. Electronic: (h) four-probe output characteristics (current density (I_D/W) versus bias voltage (V_M)) with various back-gate voltages (V_G) for MoSSe-MoS₂. (a) Reproduced with permission.⁹¹ Copyright 2016, American Chemical Society. (b and c) Reproduced with permission.¹⁰⁸ Copyright 2020, the American Association for Advancement of Science. (d) Reproduced with permission.¹¹¹ Copyright 2019, American Chemical Society. (e) Reproduced with permission.¹¹² Copyright 2019, American Chemical Society. (f) Reproduced with permission.¹⁰³ Copyright 2017, Springer Nature Limited. (g) Reproduced with permission.¹⁰⁴ Copyright 2017, American Chemical Society. (h) Reproduced with permission.¹⁰⁷ Copyright 2021, National Academy of Sciences.

halides and diazonium salts (Fig. 7a).¹¹⁹ For example, the MoS₂ exciton peak in the PL spectra almost completely disappeared after the phase transition (Fig. 7b) and two prominent peaks evolved in functionalized 1T-MoS₂ (Fct-1T-MoS₂). The peak at ~1.6 eV may be attributed to the band structure modification by covalent functionalization, while the peak at ~1.9 eV is related to the up-shift of the MoS₂ exciton emission.¹¹⁹ The appearance of PL peaks indicates that the metallic 1T phase is converted to the semiconducting 1T one after functionalization. This was further confirmed by the characteristics of the fabricated field-effect transistor.

Aryl diazonium functionalization can occur at the nearest S_V sites of MoS₂. S_V sites, where charge is accumulated, reduce 4-nitrobenzenediazonium tetrafluoroborate (4-NBD), resulting in nitrophenyl (NP) radical grafting after N₂ release (Fig. 7c).¹²⁰ Localized charge density adjacent to the grafting sites is renormalized after functionalization, further triggering a chain-like growth propagation of subsequent NP molecules over MoS₂ sulfur sites (top panels in Fig. 7d). A higher S_V density promotes numerous initiation reaction sites for the propagation of NP molecules over the entire MoS₂ basal plane (bottom panels in Fig. 7d). The semiconducting nature of MoS₂ is still maintained after functionalization. The NP functionalization of S_V-MoS₂ obeys pseudo-second-order (adsorbate-surface and adsorbate-adsorbate interactions) reaction kinetics,¹²¹ whereas the functionalization of Gr obeys first-order (adsorbate-surface

interactions) reaction kinetics.¹²² On the other hand, S sites in MoS₂ can be directly functionalized with NP radicals *via* active chemical reduction of 4-NBD ions, using potassium iodide as an electron donor (Fig. 7e).¹²³ Similarly, alkyl halide-functionalized 1T'-MoS₂ is activated using metallocene reducing agents, which facilitate high surface coverage with alkyl halide groups.¹²⁴ In addition, n-type doping with KI (reducing agent) itself has been observed, providing advantages for low contact resistance and increased charge carrier mobility for FET devices.¹²³

One of the advantages of diazonium salts, in terms of functionalization, is the controllability of the terminated molecules, which enables the engineering of the MoS₂ electronic structure. 1T-MoS₂ readily reacts with various diazonium salts, including different functional groups (NO₂Ph, Cl₂Ph, BrPh, MeOPh, and Et₂NPh) (Fig. 7f).¹²⁵ Each functional group has a particular Hammett parameter (Fig. 7g). The measured work function of the functionalized MoS₂ increased almost linearly with the Hammett parameter, indicating that the work function of MoS₂ can be controlled by functional groups. This surface energy change strongly influences HER catalytic activity. In fact, HER performance is significantly improved by electron-donating Et₂NPh groups.¹²⁵ Furthermore, covalent functionalization of 1T'-MoS₂ with Et₂NPh improves the stability of electronic transport properties for at least two weeks under atmospheric conditions.¹²⁶



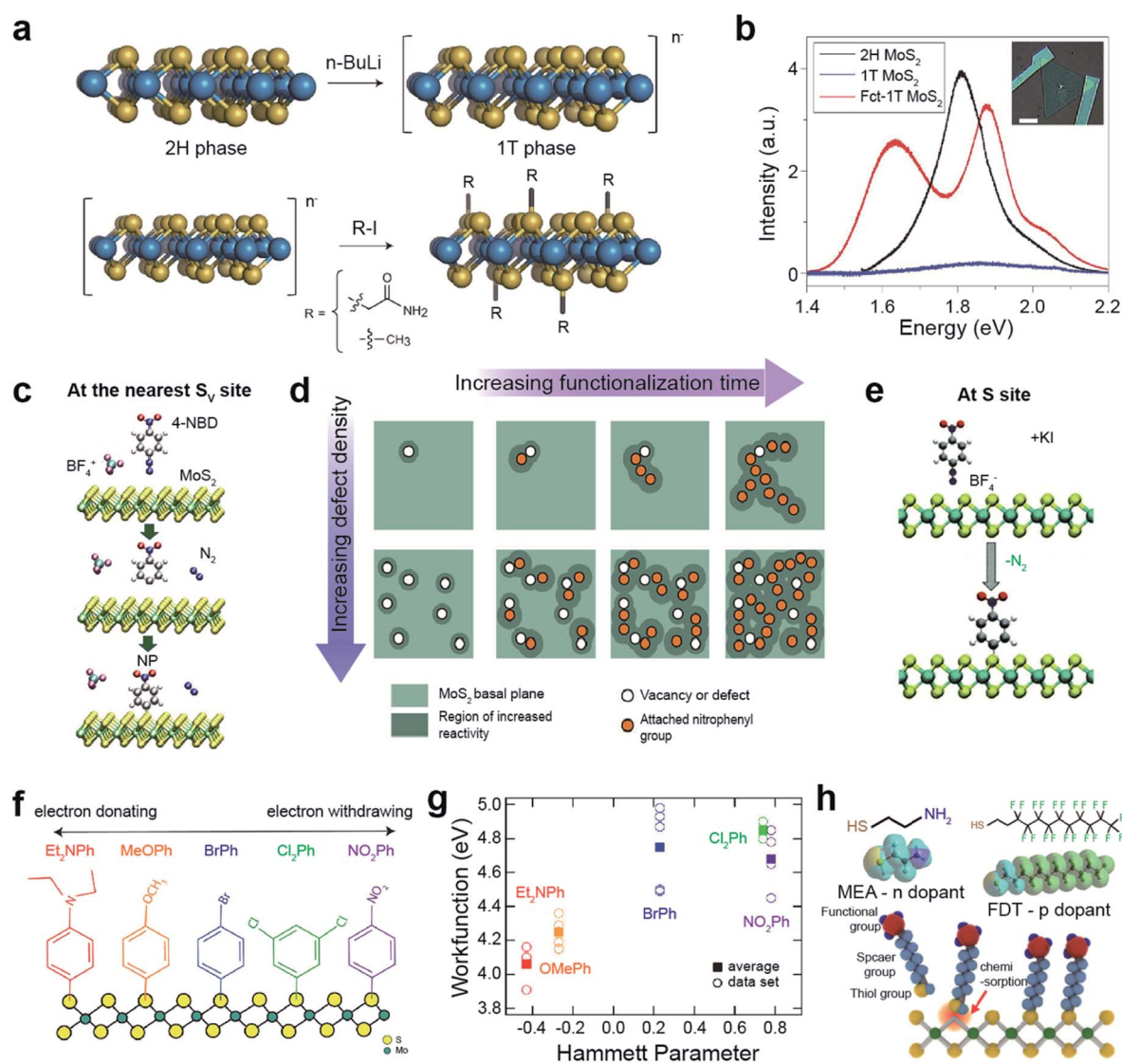


Fig. 7 Covalent functionalization of 2D TMDs: direct functionalization on metallic TMDs, aryl diazonium salt functionalization, and thiol derivative molecule functionalization. **Direct functionalization on metallic TMDs:** (a) schematic of the conversion of 2H-MoS₂ to a negatively charged 1T phase via phase transition using *n*-butyl lithium (*n*-BuLi) (top) and subsequent covalent functionalization with alkyl halides (2-iodoacetamide and iodomethane) (bottom). (b) PL spectra of 2H-MoS₂, 1T-MoS₂ and functionalized MoS₂ (Fct-1T-MoS₂). **Aryl diazonium salt functionalization:** (c) schematic representation of MoS₂ functionalized by 4-nitrobenzene diazonium (4-NBD) tetrafluoroborate (BF₄⁻) via reduction of a diazonium salt, resulting in a nitrophenyl (NP) radical grafting. (d) Schematic illustration of the reaction mechanism of MoS₂ with 4-NBD as a function of defect concentration and time. (e) Schematic representation of the direct functionalization of MoS₂ with 4-nitrobenzene diazonium (4-NBD) using KI activation. (f) Schematic representation of functionalized 1T'-MoS₂ with various diazonium salts including different functional groups (NO₂Ph, Cl₂Ph, BrPh, MeOPh, and Et₂NPh). (g) Work function of functionalized MoS₂ with various diazonium salts as a function of the functional group Hammett parameter. **Thiol derivative molecule functionalization:** (h) schematic representation of the chemisorption of thiol molecules onto S_v-MoS₂ and the molecular structures of mercaptoethylamine (MEA) and perfluorodecanethiol (FDT). (a and b) Adapted with permission.¹¹⁹ Copyright 2015, Springer Nature Limited. (c and d) Adapted with permission.¹²⁰ Copyright 2018, American Chemical Society. (e) Adapted with permission.¹²³ Copyright 2021, Royal Society of Chemistry. (f and g) Adapted with permission.¹²⁵ Copyright 2018, American Chemical Society. (h) Adapted with permission.¹³⁰ Copyright 2015, American Chemical Society.

Another approach is the selective functionalization of TMD chalcogen vacancies or edge sites with thiol derivative molecules via a conjugation reaction.^{127–129} MoS₂ can be functionalized with thiol molecules (2-mercaptoethylamine, MEA, and 1H,1H,2H,2H-perfluorodecanethiol, FDT) at S_v sites by soaking for 72 h (Fig. 7f). The charge density of functionalized MoS₂ was strongly affected by the terminated molecules. NH₂ groups in

MEA donate electrons to MoS₂ (charge density from 9.4×10^{11} to 1.4×10^{12} cm⁻²), whereas F groups in FDT withdraw electrons from MoS₂ (charge density -7.0×10^{11} to -1.8×10^{11} cm⁻²).¹³⁰ Likewise, functionalization with aromatic or alkyl thiols tunes the electronic structure of MoS₂. For example, in the case of alkyl thiols, the Fermi energy level (E_F) upshifts with

increasing chain length, such as for 1-propanethiol, 1-non-anethiol, and 1-dodecanethiol.¹³¹

Phase transition requires harsh chemical treatment of TMDs with a highly pyrophoric compound (*n*-butyllithium), which deteriorates the quality of the material.^{132,133} The diazonium salt functionalization approach is commonly used to engineer the electronic structure of TMDs. Thiol-derivative functionalization with TMDs is inherently limited by the number of vacancy sites.

Non-covalent functionalization. Non-covalent functionalization consists of the physisorption of organic molecules on the surface of TMDs/Gr without chemical bond formation.^{134–136} This enables chemical doping and formation of heterojunctions on TMDs.

Chemical doping of organic molecules on carbon nanotubes (CNTs) and Gr has been extensively studied using two main approaches: (i) modulating the reduction potential of molecules (water bucket model)¹³⁷ and (ii) controlling electron-donating (*e.g.*, amine, $-\text{NH}_2$, and hydroxyl, $-\text{OH}$) and electron-withdrawing groups (*e.g.*, nitro, $-\text{NO}_2$, and trihalogenated methyl, $-\text{CX}_3$). Analogous strategies have been widely adopted for TMDs. The water bucket model describes the charge transfer between molecules and host materials induced by the difference in reduction potentials. Species with a lower reduction potential give electrons to those with a higher one.¹³⁷ Material's reduction potential can be calculated by using the following equation: $\phi/e = V$ (V vs. SHE) + 4.44 V, where ϕ , e , V , and SHE denote the work function, electron, reduction potential, and standard hydrogen electrode, respectively.¹³⁸ For MoS_2 , the reduction potentials of 0.84 eV (vs. SHE) for 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ) and 0.46 eV (vs. SHE) for 7,7,8,8-tetracyanoquinodimethane (TCNQ) indicate that they withdraw electrons from MoS_2 (p-type doping), whereas -0.32 eV (vs. SHE) for nicotinamide adenine dinucleotide (NADH) indicates that they donate electrons (n-type doping) (Fig. 8a).^{139,140} A drastic enhancement in the PL intensity was observed for MoS_2 after functionalization with F_4TCNQ and TCNQ (Fig. 8b). In contrast, after functionalization with NADH an attenuation of the PL intensity was detected (Fig. 8c).¹⁴¹ These experimental results demonstrate the E_{F} shift of MoS_2 according to p-type and n-type dopants.

Molecules with distinct functional groups can be n- or p-type dopants of TMDs. For example, mechanically exfoliated WSe_2 flakes were exposed to vapors of trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane (PFS) with $-\text{CF}_3$ functional groups for p-type doping, and *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (AHAPS) with $-\text{NH}_2$ functional groups for n-type doping (Fig. 8d). Before this, however, WSe_2 flakes were treated with ozone (UVO_3) to improve the functionalization uniformity and ensure high surface coverage. The *I*-*V* transfer curves of the WSe_2/PFS and $\text{WSe}_2/\text{AHAPS}$ FETs, fabricated on Si/SiO₂ with Au contact electrodes, show p-type and n-type characteristics with enhanced hole and electron mobilities of $150 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $17.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively (Fig. 8e and f). Moreover, asymmetric doping obtained by sandwiching bilayer WSe_2 with AHAPS (bottom) and PFS (top) shows distinct ambipolar transport properties with electron and hole mobilities of $5.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively (Fig. 8g).¹⁴² To

achieve better ambipolar transport characteristics, monolayer WSe_2 was subjected to a hybrid functionalization (covalent and non-covalent functionalizations) using two different dopants, 4-NBD and diethylenetriamine. It drastically enhanced the hole and electron mobilities to $82 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.¹⁴³ In addition, a reduction in the energy bandgap (~ 0.24 eV) was observed for WSe_2 , with asymmetric doping with $\text{C}_{60}\text{F}_{48}$ and graphite. This behavior is a consequence of the accumulation of holes and electrons at the bottom and top Se layers.¹⁴⁴

Various heterojunctions can be easily constructed by the deposition of organic layers on TMD surfaces. Fig. 8h shows a typical prototype of a type-II organic/TMD heterojunction (pentacene/ MoS_2). When an electron in MoS_2 is excited by a photon, a hole is transferred to the p-type pentacene layer within a very short time ($\tau_2 = 6.7$ ps) (Fig. 8i). This enables the extension of the interlayer exciton lifetime to as long as ~ 5 ns at the pentacene/ MoS_2 interface (Fig. 8j).¹⁴⁵ This dynamic process originates from the quenching of the PL intensity of pentacene/ MoS_2 when compared to pristine MoS_2 . Similarly, $\text{MoS}_2/\text{PTCDA}$, WS_2/PTCDA , and $\text{MoS}_2/\text{rubrene}$ also exhibit a type-II p-n heterojunction.^{134,146,147} Such an extended charge recombination time can improve the quantum efficiency of optoelectronic devices such as diodes, bipolar transistors, photodiodes, and so on.^{148–150}

Applications. COVID-19 sensors, TENGs, multifunctional optoelectronic devices, and memory and neuromorphic devices are some of the applications discussed here. The development of rapid diagnostic tools for the detection of severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) is highly needed. Real-time reverse transcription-polymerase chain reaction (RT-PCR) is the only specific diagnostic test based on unique sequences of viral ribonucleic acid (RNA). It is, however, very time-consuming. Hence, having rapid, effective, label-free, point-of-care, and low-cost sensors for detecting viral antigens is crucial.^{151–153} WSe_2 monolayers were functionalized with 11-mercaptoundecanoic acid (MUA) and activated with *N*-hydroxysuccinimide (NHS) for the detection of SARS-CoV-2 spike proteins (Fig. 9a). Fig. 9b illustrates the response of the device during real-time detection of SARS-CoV-2 under different concentrations of the spike protein. The number of antibodies with SARS-CoV-2 spike protein increased with the concentration (red line), while antibodies without SARS-CoV-2 spike protein showed a slight decrease (blue line). Moreover, the biosensor based on WSe_2 FETs after functionalization with MUA can detect SARS-CoV-2 spike protein down to $25 \text{ fg } \mu\text{L}^{-1}$ in 0.01 M phosphate-buffered saline (PBS) solution,¹⁵⁴ which is $\sim 10^4$ orders of magnitude higher than the detectivity of Gr-based biosensors (1 fg mL^{-1}).¹⁵⁵

With the rapid development of the Internet of Things (IoT), over 50 billion IoT sensors already exist and are expected to surpass 200 billion by 2025.^{156,157} Among various energy harvesters, TENGs can convert waste mechanical energy into electrical energy under ambient conditions. WS_2 nanosheets were functionalized *via* thiol conjugation reactions at S_{V} sites with various alkanethiol molecules, such as mercaptopropionic acid (MPA), mercaptohexanoic acid (MHA), mercaptooctanoic



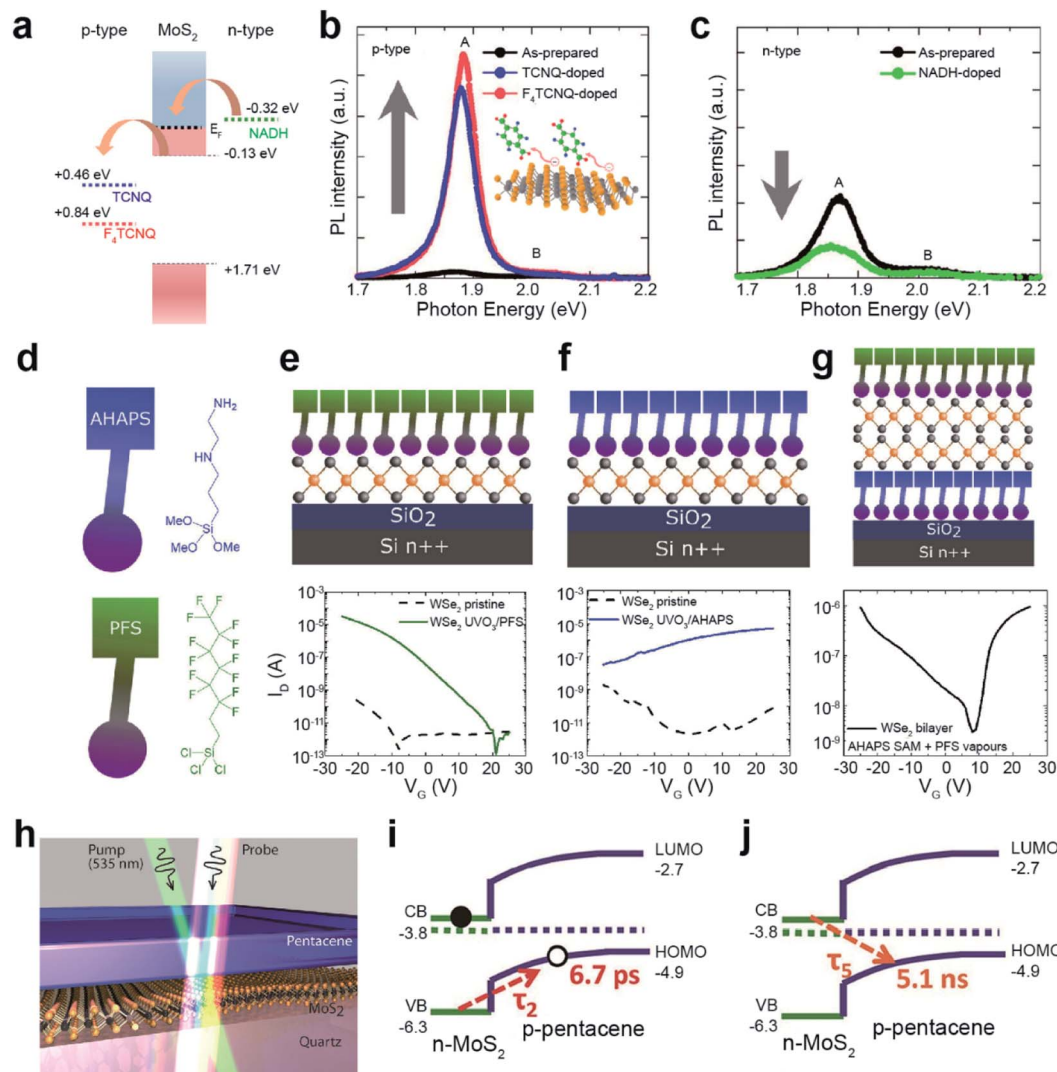


Fig. 8 Noncovalent functionalization of 2D TMDs through chemical doping and heterojunction formation. **Chemical doping:** (a) reduction potentials (vs. SHE) of F₄TCNQ and TCNQ for p-type doping and NADH for n-type doping. PL spectra of MoS₂ after (b) p-type and (c) n-type doping. (d) Schematic of PFS and AHAPS. (e–g) Schematic of PFS-doped WSe₂, AHAPS-doped WSe₂, and double-side doped bilayer WSe₂ with PFS and AHAPS (top) and their corresponding *I*–*V* transfer curves (bottom). **Heterojunction formation:** (h) illustration of the MoS₂/pentacene p–n heterojunction probed by transient absorption spectroscopy. (i and j) Exciton dynamics of a type-II heterojunction. (a–c) Adapted with permission.¹⁴¹ Copyright 2013, American Chemical Society. (d–g) Adapted with permission.¹⁴² Copyright 2019, American Chemical Society. (h–j) Adapted with permission.¹⁴⁵ Copyright 2017, American Chemical Society.

acid (MOA), and MUA. A TENG device was fabricated using functionalized WS₂ and poly(ethylene terephthalate) (PET) as the negative and positive active layers, respectively. Indium tin oxide was used as an electrode (Fig. 9c). Thiol-containing ligands with different alkane chain lengths act as triboelectrification layers in TENGs. A high-precision micro-mechanical tester was used to press and release a TENG device with a vertical force of 6 N and a frequency of 1 Hz. Pristine WS₂ and alkanethiol-functionalized WS₂ TENGs exhibited an output voltage of 1.1 V, 8.8 V (MPA), 10.6 V (MHA), 11.4 V (MOA), and 12.2 V (MUA) under open-circuit conditions (Fig. 9d). The MUA-WS₂ TENG exhibited a maximum power density of 138 mW m^{−2}. The persistent output voltage of the MUA-WS₂ TENG device was maintained after 14, 28, 56, and 98 days, confirming

high stability and durability.¹⁵⁸ This indicates that alkanethiol functionalization of defective WS₂ surfaces *via* ligand conjugation suppresses reactions with reactive oxygen and reduces the number of catalytically active sites. Moreover, a stable triboelectric output voltage was observed for the MUA-WS₂ TENG device even after 10 000 cycles. Several 2D materials, including MoS₂, WS₂, MoSe₂, Gr, and Gr oxide (GO)-based TENGs, were fabricated to utilize their triboelectric charging nature. The work functions of the materials decreased in the following order: MoS₂ (4.85 eV) > MoSe₂ (4.70 eV) > Gr (4.65 eV) > GO (4.56 eV) > WS₂ (4.54 eV). Hence, MoS₂ is likely to be triboelectrically more negative than the other materials. Furthermore, MoS₂ is functionalized with benzyl viologen (BV, n-type) and gold chloride (AuCl₃, p-type), resulting in positive and negative

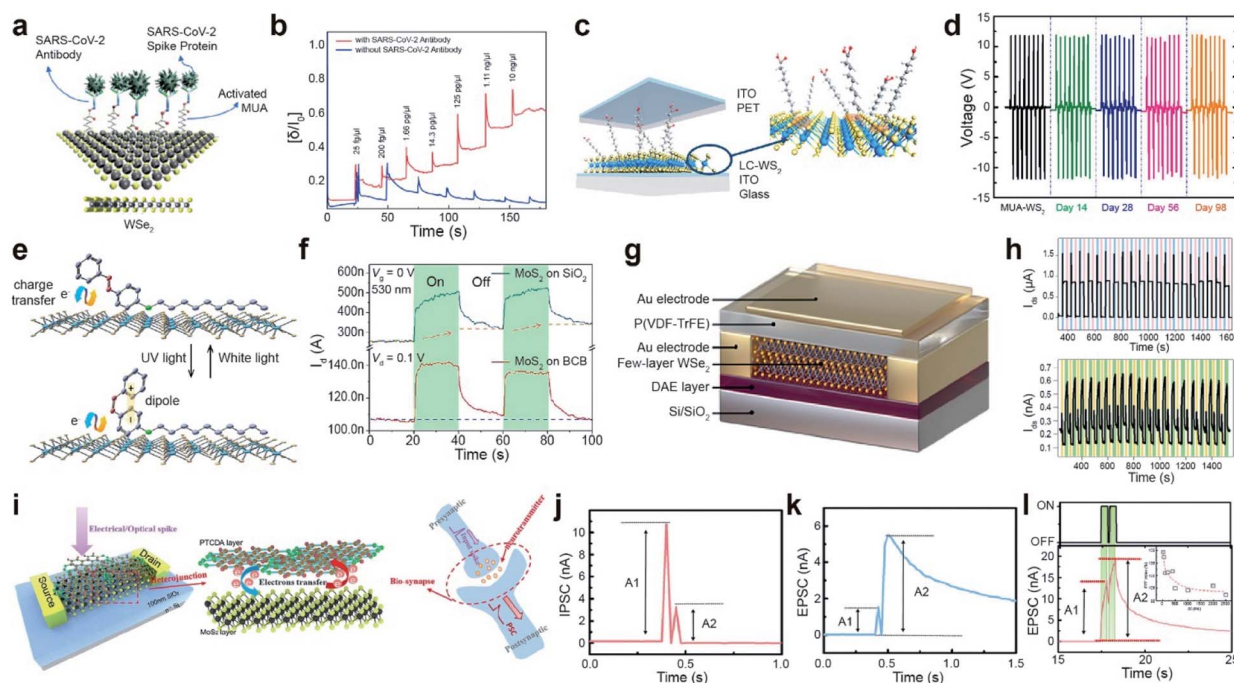


Fig. 9 Functionalization for various advanced applications: CoVID-19 sensors, TENGs, multifunctional optoelectronic device, and memory and neuromorphic devices. **CoVID-19 sensors:** (a) schematic of 11-MUA-functionalized WSe₂ for a CoVID-19 sensor. (b) Real-time detection of various SARS-CoV-2 antigen spike proteins with (red curve) and without antibodies (blue curve) using $V_{DS} = 1$ V and $V_{GS} = -0.5$ V with a functionalized WSe₂ FET. **TENGs:** (c) Schematic of a ligand-conjugated WS₂ TENG device. (d) Output voltages of pristine WS₂ and ligand-conjugated WS₂ TENG devices. **Multifunctional optoelectronic device:** (e) schematic of a photomolecular switch device with photochromic molecules (4-(decyloxy)azobenzene) on MoS₂. (f) Time-resolved photoresponse of MoS₂ FETs on BCB and SiO₂ substrates under 530 nm light illumination. **Memory device:** (g) schematic of the DAE/WSe₂/FeFET device. (h) Switching behavior for 20 cycles induced by applying a cyclic ± 60 V pulse bias (top) and UV-Vis illumination (bottom). **Neuromorphic device:** (i) schematic of a MoS₂/PTCDA heterojunction operated under both electrical/optical pulses (presynaptic input) and corresponding output current (postsynaptic output). The electron transfer process at the heterojunction interface is analogous to the release of neurotransmitters in biosynapses. (j and k) IPSC/EPSC behavior triggered by a pair of relatively negative V_{CG} (gate voltage) pulses. (l) EPSC behavior stimulated by a pair of laser pulses. The inset shows the corresponding PPF index A_2/A_1 as a function of laser pulse interval time. (a and b) Adapted with permission.¹⁵⁴ Copyright 2021, American Chemical Society. (c and d) Adapted with permission.¹⁵⁸ Copyright 2021, American Chemical Society. (e and f) Adapted with permission.¹⁶⁰ Copyright 2019, American Chemical Society. (g and h) Adapted with permission.¹⁶² Copyright 2021, Wiley-VCH. (i–l) Adapted with permission.¹⁶³ Copyright 2019, Wiley-VCH.

values over a triboelectric series (by changing the work function accordingly). These results suggest that triboelectric charging can be tuned through functionalization.¹⁵⁹

Another example of the application is a photomolecular switch device, which was fabricated using thin photochromic azobenzene (AZO) physisorbed on MoS₂ that was a trap-free benzocyclobutene (BCB)/SiO₂/Si substrate (Fig. 9e). The AZO molecules on MoS₂ undergo reversible isomerization between the *cis* and *trans* states upon exposure to white and UV light illumination, which efficiently modulates the charge transfer process between AZO and the underlying 2D MoS₂. The photoresponse of the MoS₂ FET device on BCB represents a fast saturation under 530 nm light illumination for 20 s, whereas it shows a steady increase for MoS₂ on a SiO₂/Si substrate (Fig. 9f). This high response originates from the suppression of the persistent photoconductivity (PPC) effect. Furthermore, a high thermal stability of over 15 h was demonstrated for the photomolecular switching of metastable *cis/trans* states.¹⁶⁰ In addition, a type-II heterojunction phototransistor was developed using an organic phosphonic acid monolayer (12-(benzo[*b*

benzo[4,5]thieno[2,3-*d*]thiophen-2-yl)dodecyl) (BTBT) stacked over a MoS₂ monolayer. It exhibits an unprecedented responsivity of 475 A W⁻¹ and high external quantum efficiency of $1.45 \times 10^5\%$. BTBT provides effective charge transfer *via* π - π interactions and successfully eliminates recombination and charge scattering.¹⁶¹

A ternary-responsive multilevel memory device was fabricated with few-layer WSe₂ *via* asymmetric non-covalent functionalization. A photochromic diarylethene (DAE) layer functionalized WSe₂ at the bottom, while a ferroelectric poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) layer was placed on the top of WSe₂ to form a multi-stimuli-responsive Janus WSe₂ FET device (Fig. 9g). The device successfully generated two states because of the polarization of P(VDF-TrFE) in the downward/upward direction for a cyclic ± 60 V pulse bias. One cycle consisted of +60 V for 2 s (blue region), 0 V for 30 s, -60 V for 2 s (violet region) and 0 V for 30 s (Fig. 9h (top)). Switching with a photochromic DAE was also demonstrated under UV-Vis illumination, where one cycle consisted of 5 s under UV illumination (orange region), 20 s in the dark, 20 s



under Vis light (green region), and 20 s without illumination (Fig. 9h (bottom)). Moreover, a multistimuli-responsive asymmetrically functionalized Janus WSe₂ device was successfully achieved by modulating the population ratio of polarized P(VDF-TrFE) and photoisomerization DAE. This generated nine unique ferroelectric states and 84 photogenerated states, respectively. The overall maximum of 756 current levels was stored in a single device. The cyclic endurance (10 cycles) and data retention (over 1000 h) confirm the consistency of the device and present high-density non-volatile memory devices.¹⁶²

A multifunctional neuromorphic device was fabricated *via* non-covalent functionalization of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on MoS₂, which forms a type-II heterostructure (Fig. 9i). The charge transfer phenomenon between MoS₂ and PTCDA mimics neurotransmitter release in biological synapses (right panel of Fig. 9i). The MoS₂/PTCDA hybrid synaptic transistor was operated under an electrical field by applying a pair of negative gate voltage (V_{cg}) pulses (−12 V for 25 ms and −20 V for 25 ms). It exhibited inhibitory post-synaptic current (IPSC) behavior ($A_2 < A_1$) and excitatory post-synaptic current (EPSC) behavior ($A_2 > A_1$), which correspond to synaptic paired-pulse depression (PPD) and paired-pulse facilitation (PPF) behavior, respectively (Fig. 9j and k). Similarly, a typical EPSC behavior is observed by applying a pair of 532 nm laser pulses (green irradiation with a pulse width of 400 ms, an interval of 100 ms, and a V_{DS} of 0.1 V) (Fig. 9l). Under both operating modes, the type-II MoS₂/PTCDA hybrid heterojunction synaptic device performed consistently and successfully mimicked biological synapse functions by an efficient charge transfer process at the hybrid interface.¹⁶³

2.4. Repair

Atomic chalcogen vacancies in TMDs attenuate their electrical and optical properties (as seen by low PLQY, high Schottky barriers, and limited carrier mobility), which is translated to poor electronic and optoelectronic device performances.^{164–169} Therefore, the repair of atomic defects is critical for the realization of high-performance devices. Atomic chalcogen vacancies can be repaired using the same chalcogens for healing and other elements for passivation.

Healing. Hydrosulfurization and post-sulfuration/selenization treatments effectively heal chalcogen vacancies in TMDs.¹⁷⁰ For example, atmospheric oxygen atoms can easily react with S_{V} or Se_{V} and passivate CVD-grown or exfoliated TMDs (Fig. 10a).^{171,172} Two possible reactions can occur between oxygen atoms and TMDs: (i) formation of oxygen-substituted TMDs ($\text{MoS}_{2-x}\text{O}_x$) and (ii) creation of SO_2 or SeO_2 volatile compounds. DFT calculations show that the removal of S atoms is thermodynamically favorable ($E = -0.49$ eV, negative oxidation enthalpy), whereas it is unfavorable for Se atoms ($E = +0.75$ eV, positive oxidation enthalpy). Bright triangular spots corresponding to single O atoms were observed in the scanning tunneling microscope (STM) image (Fig. 10b). Such $\text{MoS}_{2-x}\text{O}_x$ compounds are completely healed and transformed to defect-free MoS₂ by simple thermal annealing at 200 °C under a H₂S atmosphere (Fig. 10c).¹⁷³ It is noted that $\text{MoS}_{2-x}\text{O}_x$ shows better

HER performance than defect-free MoS₂ because the presence of oxygen atoms in TMDs decreases the ΔG_{H} for hydrogen adsorption, by bringing it closer to thermoneutral conditions.¹⁷³

The post-selenization process is performed on defected monolayer MoSe₂ *via* pulsed laser vaporization of selenium to repair Se_{V} (Fig. 10d). The temperature plays a crucial role in selenization, where the optimum temperature range is between 600 and 700 °C. The I - V transfer curves show major carrier type conversion from p-type characteristics for high Se vacancies ($\sim 20\%$ V_{Se}) to n-type characteristics for healed Se vacancies ($\sim 9\%$ V_{Se}). Moreover, the obtained hole and electron mobilities were ~ 0.011 and $0.021 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively (Fig. 10e).¹⁷⁴ Selective post-sulfuration on patterned MoSe₂ readily forms MoSe₂/MoS₂ heterojunctions and exhibits a type-I band alignment.¹⁷⁵

Another healing method for S_{V} in MoS₂ (S_{V} -MoS₂) involves the use of S-containing organic molecules.¹⁷⁶ For example, S_{V} -MoS₂ was coated with 3-mercaptopropyl trimethoxysilane (MPS) and subsequently annealed at 350 °C under a H₂/Ar atmosphere. The healing process involves the following reaction: $\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3 + S_{\text{V}}\text{-MoS}_2 \rightarrow \text{CH}_3(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3 + \text{MoS}_2$. The reaction kinetics of S_{V} -MoS₂ and MPS involve two representative steps of chemical adsorption between S_{V} and thiol groups in MPS and dissociation of the S–C bond with an energy barrier of 0.51 and 0.22 eV, respectively (Fig. 10f). The S_{V} density was dramatically reduced from $\sim 6.5 \times 10^{13}$ to $\sim 1.6 \times 10^{13} \text{ cm}^{-2}$, for topside MPS treatment. Electrical transport properties were measured for three FET samples on Si/SiO₂: exfoliated MoS₂ (black), top-side-treated MoS₂ (blue), and double-side-treated MoS₂ (red) (Fig. 10g). The double-sided MPS treatment further reduced short-range scattering and charge impurities and thus enhanced the carrier mobility of $81 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature.¹⁷⁷ The carrier mobility of these samples at low temperature (10 K) was further increased to $14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $106 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $320 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively (Fig. 10h). The catalytic properties of MPS-treated MoS₂ drastically decrease due to the depletion of electrochemically active sites, thereby increasing the overpotential and the Tafel slope.¹⁷⁸

As an alternative, bis(trifluoromethane) sulfonamide (TFSI) was employed to heal S_{V} in MoS₂ and WS₂.¹⁷⁹ The exfoliated MoS₂ that was treated with TFSI exhibited a 190-fold increase in the magnitude of the PL peak intensity (Fig. 10i), consisting of a brighter PL image than that of the pristine one (Fig. 10j).¹⁸⁰ An increased quantum yield QY (>95%) and longer lifetime (~ 10 ns) were also observed due to the elimination of the non-radiative recombination. TFSI-treated MoSe₂ and WSe₂ exhibited a moderately reduced QY. TEM analysis revealed that Se_{V} sites in WSe₂ were not passivated by S atoms.¹⁸¹

Passivation. Passivation has been conducted not only to improve the optical and electrical properties of TMDs but also to stabilize their structures. To enhance the PL intensity of MoSe₂, the passivation of Se with Br atoms was introduced (Fig. 10k).¹⁸² CVD-grown MoSe₂ shows a 30-fold increase in PL intensity after HBr treatment due to Se_{V} passivation and p-doping effects.¹⁸² For example, the electrical and optical properties of WSe₂ and ReSe₂ can be improved *via* HCl treatment. The halogen atoms efficiently repair the Se_{V} sites and shift the



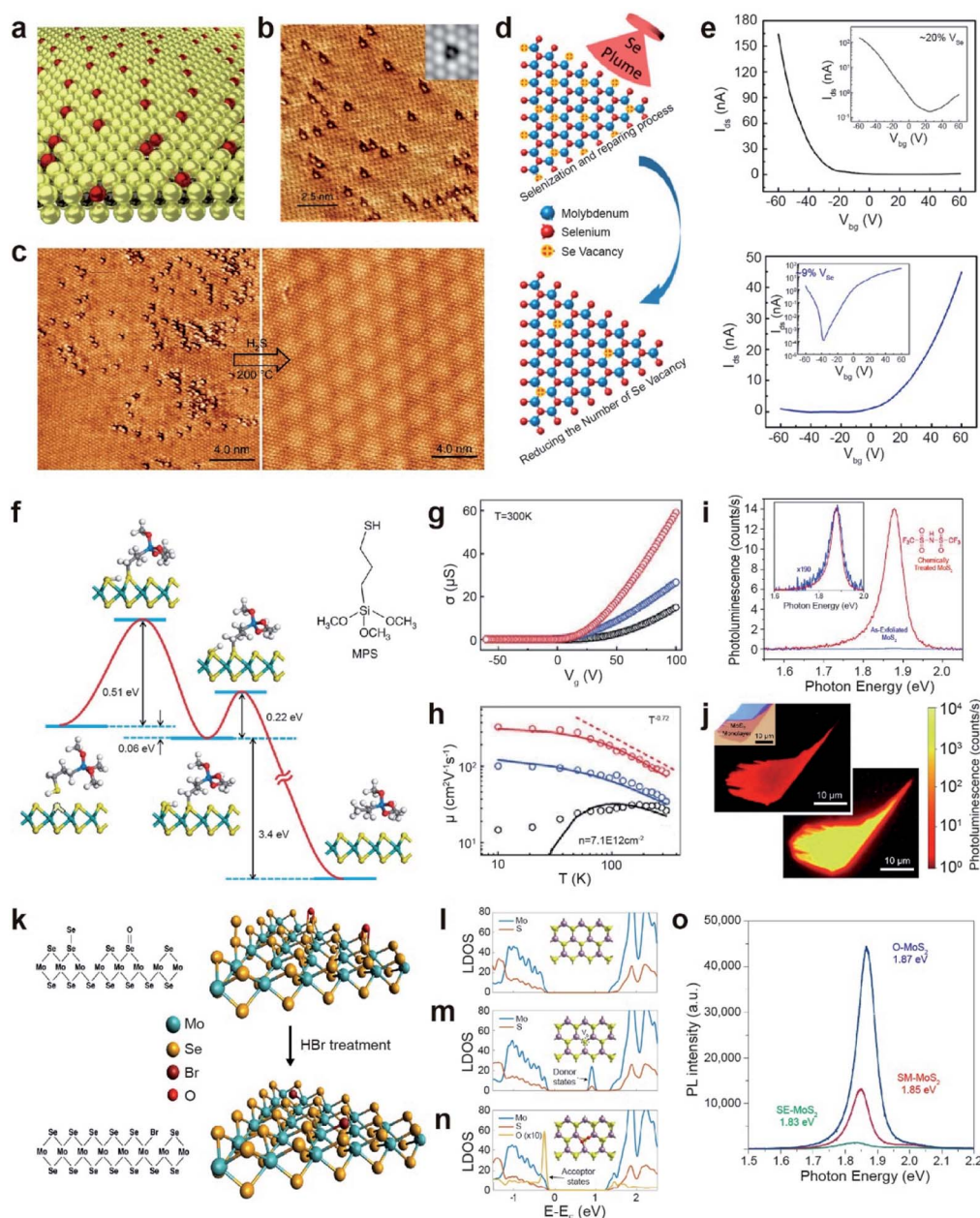


Fig. 10 Repair of 2D TMDs: healing and passivation. **Healing:** (a) schematic representation of atmospheric oxygen atoms getting adsorbed on a MoS_2 monolayer. (b) STM image of O atoms (bright spots) absorbed at S_V (dark triangles) sites. Inset: simulated STM image. (c) STM images of MoS_2 before and after H_2S healing at 200°C . (d) Schematic illustration for post-selenization repair of Se_V in MoSe_2 . (e) Transfer curves of high Se_V ($\sim 20\%$) (top) and healed Se_V ($\sim 9\%$) (bottom) samples. (f) Illustration of reaction pathways for repairing S_V - MoS_2 using 3-MPS organic molecules. (g and h) Electrical conductance (σ) as a function of gate voltage, carrier mobility and measurement temperature of exfoliated (black), single side treated (blue) and double side treated (red) samples. (i) PL spectra of exfoliated MoS_2 (blue) and TFSI-treated MoS_2 (red). The inset shows the $190\times$ magnified PL spectra of as-exfoliated MoS_2 . (j) Confocal PL mapping image of exfoliated MoS_2 (top) and TFSI-treated MoS_2 (bottom). **Passivation:** (k) schematic of Se_V passivation with Br in MoSe_2 by HBr treatment and the corresponding atomic structures. (l–n) LDOS of (l) pristine MoS_2 (top), (m) S_V - MoS_2 (middle), and (n) O- MoS_2 (bottom). (o) PL spectra of SE- MoS_2 , SM- MoS_2 , and O- MoS_2 grown under oxygen conditions (O- MoS_2), sulfur-mild conditions (SM- MoS_2) and sulfur-excess conditions (SE- MoS_2), respectively. (a–c) Adapted with permission.¹⁷³ Copyright 2018, Springer Nature Limited. (d and e) Adapted with permission.¹⁷⁴ Copyright 2016, American Chemical Society. (f–h) Adapted with permission.¹⁷⁷ Copyright 2014, Springer Nature Limited. (i and j) Adapted with permission.¹⁸⁰ Copyright 2015, American Association for the Advancement of Science. (k) Adapted with permission.¹⁸² Copyright 2016, American Chemical Society. (l–o) Adapted with permission.¹⁸⁶ Copyright 2022, Springer Nature Limited.

defective states from the donor level to the acceptor level (*i.e.* transforming from n-type to p-type).^{183–185} Single S_V or point defects can be efficiently passivated by oxygen atoms. The local

density of states (LDOS) of pristine MoS_2 , S_V - MoS_2 , and O- MoS_2 shows the annihilation of the donor state in S_V - MoS_2 and the creation of an acceptor state below the top of the valence band

in O-MoS₂ (Fig. 10l–n).¹⁸⁶ Three different conditions were adopted for the preparation of three distinct MoS₂ monolayers by growing them under oxygen (O-MoS₂), sulfur-mild (SM-MoS₂), and sulfur-excess (SE-MoS₂) conditions. The neutral A-exciton peak intensity of the O-MoS₂ is dominant in the PL spectra (Fig. 10o). This is ascribed to suppressing the non-radiative recombination and p-doping effect by new acceptor states.¹⁸⁶

The healing of atomic chalcogen vacancies using organic thiol molecules is still under debate. Three possible reaction mechanisms include repair, functionalization, and dimerization.¹⁸⁷ The energy barrier rate-determining steps for both functionalization and repair mechanisms are almost similar, indicating that these are competing reactions.¹⁸⁸ Moreover, numerous factors, such as the nature of thiol molecules, concentration of S_v, reaction temperature, and time, are critical in determining the reaction mechanism. Furthermore, thiophenol molecules (C₆H₅SH) can heal and adsorb on Se_v in WSe₂. The adsorbed thiophenol molecule displays a vertical configuration, which is consistent with experimental STM images.¹⁸⁹ The mechanisms of defect passivation and/or healing are still not clearly understood for TFSI-treated TMDs. TFSI treatment increases the PL lifetime but limits the carrier mobility by the charge scattering mechanism.^{181,190} In order to overcome this issue, exfoliated MoS₂ and WS₂ were first treated with thiol molecules (3-*n*-octylthiophene, dipropyl sulfide, or ethanethiol) to control S_v, followed by TFSI treatment. The two-step treatment effectively eliminates sub-gap states and lowers the Fermi level, which greatly improves the PL lifetime and enhances carrier mobility.¹⁹¹

Application. Successfully repaired TMDs can be utilized in various applications, including flexible PENGs, superconductors, FET contact resistance, and photodiodes. Monolayer 2D TMDs exhibit strong piezoelectric properties when an external force is applied because of their broken inversion symmetry.¹⁹² A flexible PENG was fabricated by using healed MoS₂, obtained *via* a thermal annealing treatment at 1000 °C for 30 min under H₂S gas (Fig. 11a and b). The lateral piezoelectric response was measured by applying an external electric field between two electrodes. Fig. 11c illustrates the piezoelectric responses of as-grown monolayer MoS₂, S-treated MoS₂ (healed MoS₂), and α -quartz as a function of the applied external bias. The piezoelectric output current and voltage were measured under a tensile strain of 0.48% with a strain rate of 70 mm s⁻¹. The piezoelectric response of the S-treated MoS₂ surpasses that of the pristine monolayer MoS₂ and α -quartz. The inset in Fig. 11c shows that the piezoelectric coefficients (d_{11}) are 3.73 pm V⁻¹, 3.06 pm V⁻¹, and 2.3 pm V⁻¹ for S-treated MoS₂, pristine MoS₂, and α -quartz, respectively. The output current and voltage generated by the S-treated MoS₂ PENG device (100 pA and 22 mV) are \sim 3 and 2 times higher than those of the pristine MoS₂ PENG device (30 pA and 10 mV), respectively.¹⁹³

A photodiode was fabricated using selective healing of patterned MoS₂. Self-healing is carried out by the hydrogenation of poly(3,4-ethylenedioxythiophene)-poly(4-styrenesulfonate) (PEDOT:PSS). Fig. 11d displays the optical image of the selectively healed MoS₂ FETs, where regions 1 and 2 are healed MoS₂,

regions 3 and 4 are as-grown MoS₂ FETs, and regions 2 and 3 indicate homojunctions. The transfer characteristics of the as-grown MoS₂ and self-healed MoS₂ are shown in Fig. 11e. V_T shifted toward zero after self-healing, indicating unipolar n-type electrical transport behavior. The MoS₂ homojunction photodiode exhibits a high photoresponsivity of 308 mA W⁻¹ (observed at zero source-drain bias) with excellent air stability (Fig. 11f), as a result of efficient electron-hole separation at the homojunction.¹⁹⁴

Recently, research on ultrathin superconductors has been exclusively conducted after the advancement in exfoliation (from bulk down to monolayer) and encapsulation techniques of 2D materials. However, monolayer TMDs possess a high density of defects, eventually resulting in the localization of Cooper pairs and decreasing transition temperature (T_c) for metal-to-insulator transitions.^{195–197} S_v sites in ultrathin TaS₂ are passivated by oxygen to form oxygenated TaS₂ in air (Fig. 11g). Theoretical calculations predict that oxygen passivation in monolayer TaS₂ significantly decreases the carrier density of pure TaS₂. Transport measurements were performed for three- (3L) and five-layered (5L) TaS₂ devices, either in a fresh (denoted by new) or oxygenated (denoted by aged) form (Fig. 11h). The T_c values of both 3L and 5L TaS₂ increase with oxygen, owing to the increase in electron-phonon coupling.¹⁹⁸

FETs were fabricated using three different types of monolayer MoS₂: those grown under oxygen conditions (O-MoS₂), mild sulfur conditions (SM-MoS₂), and excess sulfur conditions (SE-MoS₂) (Fig. 11i). The I - V transfer curves of O-MoS₂ display a positive V_{th} ($+21.0 \pm 4.6$ V), whereas a negative V_{th} was observed for SE-MoS₂ (-17.0 ± 9.7 V) and SM-MoS₂ (2.8 ± 4.9 V). The contact resistance (R_C) of the three devices was determined using the Schottky barrier height (SBH) at the interface (Fig. 11j).¹⁸⁶ The O-MoS₂ FET exhibits a low R_C value of \sim 1 k Ω μ m, whereas high R_C values of 3.9 and 7.8 k Ω μ m are observed for SM-MoS₂ and SE-MoS₂ FETs, respectively (at the same carrier density (n_{2D}) of 4×10^{12} cm⁻²). This is ascribed to the reduced SBH in O-MoS₂ owing to the absence of donor states and the Fermi level closer to the CBM of MoS₂.

3. Structural modification

This section presents a discussion on two structural modifications of TMDs for various device applications: (i) phase transition and (ii) heterostructure formation. In the first sub-section, the structural phase transition from trigonal prismatic 2H to octahedral 1T or distorted 1T' is addressed, with potential applications in wireless energy harvesting, solar cells, electrocatalysts, Li-ion batteries, and memory and neuromorphic devices. In the second sub-section, the construction of vertical van der Waals and lateral heterostructures is described, with several applications, such as photocatalysts, photodetectors, solar cells, magnetic applications, and sensors.

3.1. Phase transition

TMDs exist in a wide range of crystalline phases, from trigonal prismatic 2H to octahedral 1T or distorted 1T'.¹⁹⁹ The stability



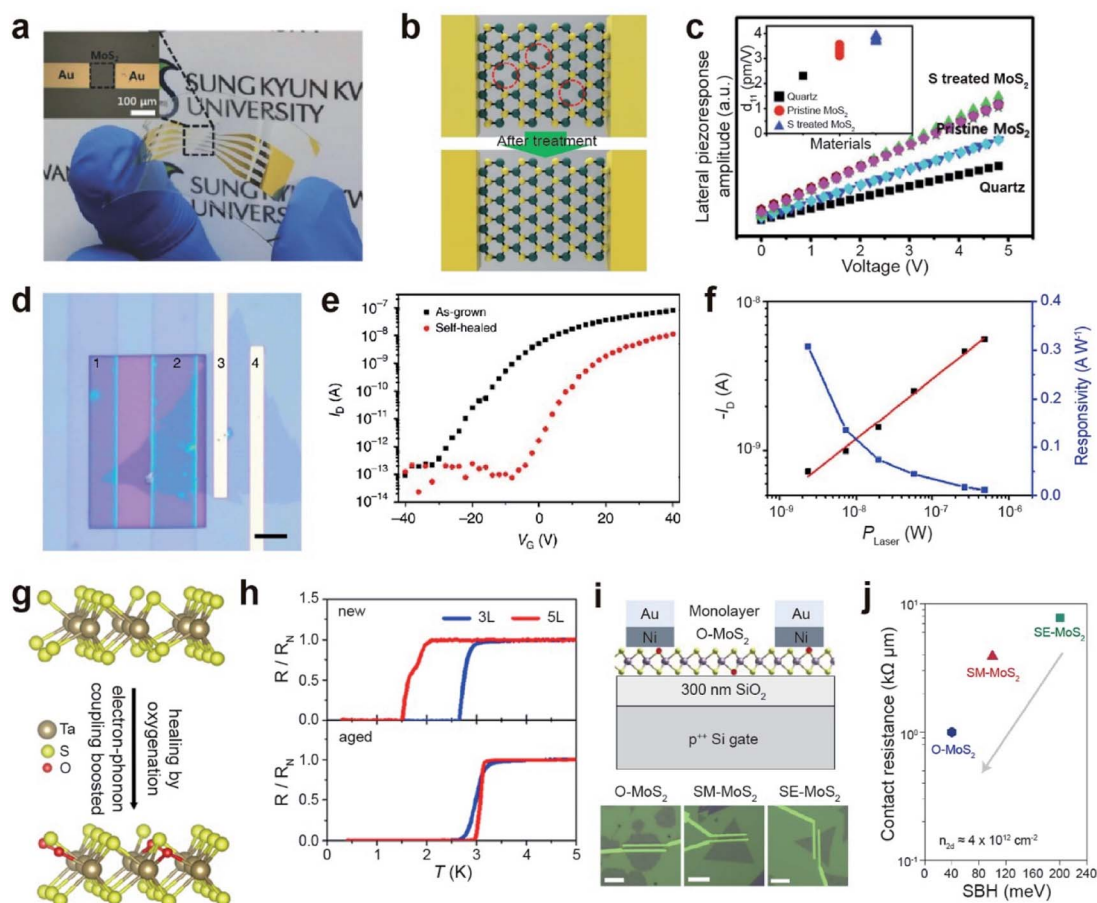


Fig. 11 Repair-based various applications: PENG, photodiode, superconductors, and contact resistance in FETs. **PENG:** (a) photograph of a flexible PENG device on a PET substrate. (b) Schematic of S_V healing in MoS_2 via H_2S treatment. (c) Lateral piezoelectric effect of quartz, S_V - MoS_2 , and S_V -treated MoS_2 samples. **Photodiode:** (d) optical image of (1–2) a selectively self-healed (PEDOT:PSS) MoS_2 FET, (2–3) a self-healed MoS_2 /as-grown MoS_2 homojunction, and (3–4) as-grown MoS_2 FET devices (scale bar: 5 μm). (e) I – V transfer curve of as-grown MoS_2 (black) and self-healed MoS_2 (red). (f) Photocurrent and responsivity on the (2–3) MoS_2 homojunction device. **Superconductors:** (g) schematic of oxygen passivated TaS_2 . (h) Normalized resistance as a function of temperature for new and aged (after 3 weeks) devices. **Contact resistance in FETs:** (i) schematic of the as-fabricated oxygen-rich MoS_2 (O- MoS_2) FET on SiO_2/Si and the corresponding optical images of O- MoS_2 , SM- MoS_2 and SE- MoS_2 with a 1 μm channel length. (j) Contact resistance (R_C) versus Schottky barrier height (SBH) for the three devices. (a–c) Adapted with permission.¹⁹³ Copyright 2018, Wiley-VCH. (d–f) Adapted with permission under a Creative Commons CC-BY License.¹⁹⁴ Copyright 2017, Springer Nature Limited. (g and h) Adapted with permission.¹⁹⁸ Copyright 2020, American Chemical Society. (i and j) Adapted with permission.¹⁸⁶ Copyright 2022, Springer Nature Limited.

and the free energy between the phases differ, depending on the material. For example, 2H- MoS_2 is more stable than 1T'- MoS_2 under ambient conditions and the free energy difference between the two phases is very large ($\Delta E > 0.8$ eV). In contrast, MoTe_2 exhibits a small free energy difference ($\Delta E < 50$ meV) between the 2H and 1T' phases.^{200,201} Therefore, techniques for phase transition are unique for each material. Metallic phase accelerates the electron transport to obtain low contact resistance of FETs and enhances their performance in electrocatalysis, supercapacitors, and batteries.

Li intercalation effectively reduces the energy barrier of the phase transition from 2H- MoS_2 to 1T- MoS_2 and stabilizes the metallic phase.²⁰² *n*-Butyllithium in hexane was employed for Li intercalation in MoS_2 and it induced a phase transition from 2H to 1T. This was followed by sonication of LiMoS_2 to exfoliate 1T MoS_2 (~ 1 –3 nm film) in water (Fig. 12a).²⁰³ The 1T- MoS_2 thin

films, prepared by drop-casting on a DVD disc, were reverted to the 2H phase by IR laser irradiation, as confirmed by XRD (Fig. 12b). The characteristic (002) peaks for 2H- MoS_2 disappeared after 60 min, and new diffraction peaks (indicated by stars) appeared, which correspond to the 1T phase. Furthermore, electrochemical lithiation has been proposed to replace the flammable and dangerous *n*-butyllithium. Li foil and MoS_2 were used as anodes and cathodes, respectively.^{204,205} Alternatively, alkali metals (lithium, potassium, or sodium) and naphthalene can be used for phase transitions.^{206–209}

A low free energy difference (< 50 meV) between the 2H and 1T' phases in MoTe_2 enables a reversible phase transition. For example, electrostatic doping with an ionic liquid (*N,N*-diethyl-*N*-(2-methoxyethyl)-*N*-methylammoniumbis(trifluoromethylsulfonyl-imide) and DEME-TFSI) gating in a FET triggers a reversible phase transition (Fig. 12c).^{210,211} The Raman spectra

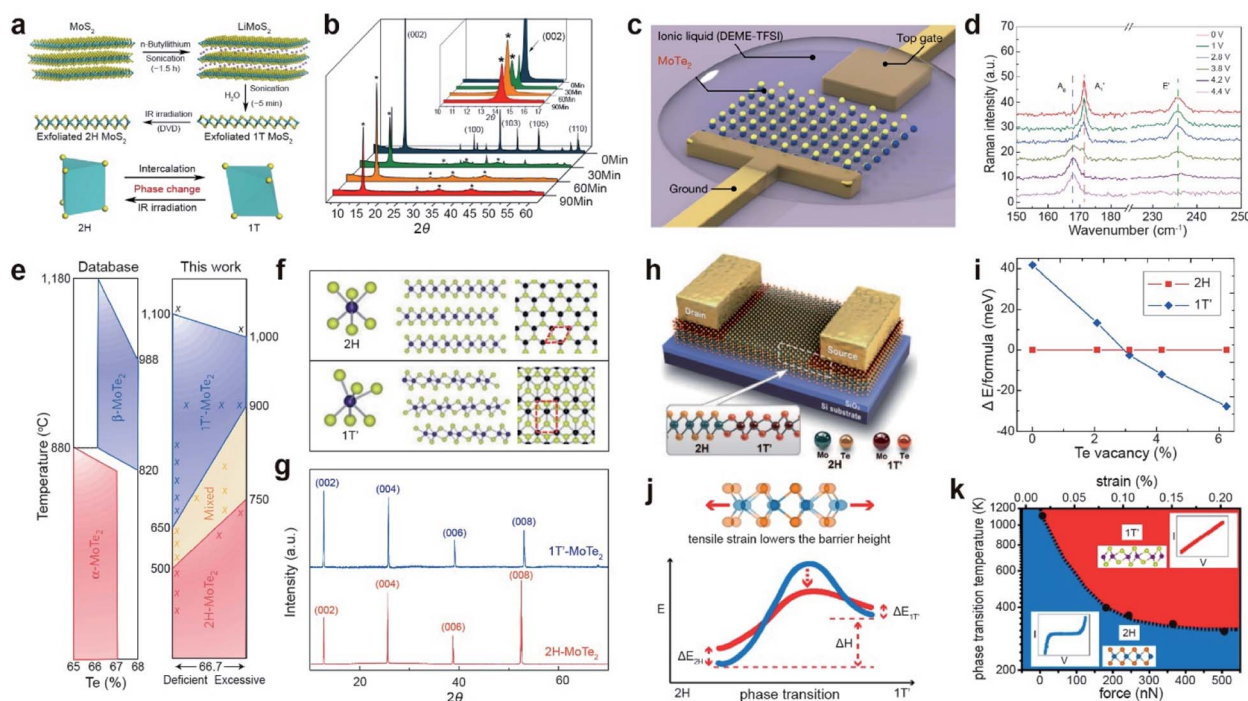


Fig. 12 Phase transition of 2D TMDs with Li intercalation, electrostatic doping, thermal annealing, laser, and tensile strain. **Li intercalation:** (a) schematic illustration of Li intercalation into MoS₂. (b) XRD patterns obtained during the sonication-assisted lithium intercalation of MoS₂ for different times. **Electrostatic doping:** (c) schematic of a monolayer MoTe₂ FET. (d) Raman spectra of phase transition from the 2H to the 1T' phase with bias changed from 0 V to 4.4 V. **Thermal annealing:** (e) phase diagram of MoTe₂ from the ASM alloy phase diagram database (left) and the new phase diagram based on experiment (right). (f) Ball-and-stick models for 2H- and 1T'-MoTe₂. (g) XRD patterns of 1T'-MoTe₂ (blue) and 2H-MoTe₂ (red) single crystals. **Laser treatment:** (h) schematic of a 1T'/2H MoTe₂ homojunction device. (i) DFT-calculated energy difference between the 2H and 1T' phases as a function of Te_v concentration. **Tensile strain:** (j) schematic of the strain-dependent phase transition barrier. (k) Temperature- and force-dependent phase diagram of semiconducting 2H and metallic 1T' MoTe₂. (a and b) Adapted with permission.²⁰³ Copyright 2011, American Chemical Society. (c and d) Adapted with permission.²¹⁰ Copyright 2017, Springer Nature Limited. (e–g) Adapted with permission.²¹⁶ Copyright 2015, Springer Nature Limited. (h and i) Adapted with permission.²²² Copyright 2015, American Association for the Advancement of Science. (j and k) Adapted with permission.²²⁴ Copyright 2016, American Chemical Society.

of MoTe₂ exhibit the gradual disappearance of the A'₁ mode (171.5 cm⁻¹) and E' mode (236 cm⁻¹) of 2H MoTe₂ with increasing gate voltage from 0 V to 4.4 V, in addition to the appearance of the A_g mode (165.5 cm⁻¹) of 1T' MoTe₂ (Fig. 12d). A fully reversible phase transition of MoTe₂ can be achieved by increasing or decreasing the gate voltage. Similarly, the electrochemical phase transition of MoTe₂ (from a monolayer to a 73 nm thick sample) was achieved using ionic liquid gating at room temperature in air.²¹² The phase transition of T-TaS₂ (from T to H) and NbSe₂ (from 2H to 1T) was achieved by applying a high bias voltage under a scanning tunneling microscope (STM) tip at low temperatures.^{213,214} The high density of electron doping from the 2D electrode [Ca₂N]⁺·e⁻ drives the phase transition from the 2H to the 1T' phase in a long MoTe₂ (up to ~100 nm) sample.²¹⁵

In addition, the phase diagram of MoTe₂ indicates that the phase stability of 2H and 1T' strongly depends on temperature and Te deficiency (Fig. 12e). Only the 1T' phase was obtained by rapid cooling at 900 °C during the flux synthesis process, whereas the 2H phase was obtained by slow cooling to room temperature, as confirmed by XRD patterns (Fig. 12f and g).²¹⁶ On the other hand, a phase transition from 1T' to 2H MoTe₂ has

been demonstrated with thermal annealing at 650 °C under a Te rich atmosphere.²¹⁷ Recently, single-crystal multilayer 2H MoTe₂ films were successfully synthesized *via* a phase transition from a polycrystalline multilayer 1T' MoTe₂ film initiated from single-crystal 2H MoTe₂ seeds.²¹⁸ The phase transitions of other TMDs, such as TaS₂, PtSe₂, and PdSe₂, were also demonstrated with thermal annealing processes.^{219–221}

A homojunction between the 2H and 1T' phases in the MoTe₂ FET was realized by a laser-driven phase transition (Fig. 12h). The metallic 1T' phase was induced by selective laser irradiation of the 2H region to introduce Te vacancies (Fig. 12i). This homojunction in MoTe₂ FET devices significantly reduces the contact resistance by forming an ohmic contact between the 1T' and 2H regions.²²² Similarly, the metastable 1T/1T phase of MoS₂ is changed to a stable 2H phase *via* continuous-wave laser and femtosecond pulsed laser radiation.²²³

The introduction of strain is another strategy for inducing a phase transition. The tensile strain lowered the barrier height for the phase transition from 2H-MoTe₂ to 1T'-MoTe₂ (Fig. 12j). The temperature is further required to overcome the energy barrier for the phase transition under tensile strain (Fig. 12k). Experimentally, the reversible phase transition between 2H and



1T' of MoTe₂ was confirmed using an atomic force microscope (AFM) tip.²²⁴ Supercritical CO₂ treatment can also induce a phase transition in TMDs *via* the formation of local strain in MoS₂.^{225,226} A chalcogen vacancy is also used to induce local strain, resulting in the spatial phase transition of MoS₂ and PdSe₂.^{227,228}

Phase transitions in TMDs can be achieved by alkali metal intercalation, electrostatic doping, electron transfer, thermal treatment, external irradiation, and strain. A summary of the phase transitions of the TMDs is listed in Table 2. Reversible phase transition between 2H and 1T (1T') can be induced by Li intercalation/annealing as well as ionic liquid gating. However, Li intercalation, plasma treatment, and supercritical CO₂ can't reach 100% yield of metallic phase TMDs.

Application. The phase-transition of TMDs can be used in various applications, including wireless energy harvesting, solar cells, Li-ion batteries, resistive memory devices, and electrocatalytic applications.

For wireless energy harvesting from the Wi-Fi band (2.45 and 5.9 GHz), a rectifier device is fabricated using MoS₂ on a flexible Kapton substrate. Fig. 13a illustrates a lateral MoS₂ semi-conducting-metallic (2H-1T/1T') Schottky diode with palladium and gold layers forming Schottky and ohmic contacts, respectively. Nonlinear *I-V* characteristics were observed for a given input radio frequency (RF) power owing to the presence of a Schottky junction between Pd and 2H-MoS₂, which is attributed to the rectification behavior. For an input RF power of 5 mW, the device exhibited a cutoff frequency of 10 GHz and an output voltage of 3.5 V, because of the rectified voltage increase (*V*_{out}) (Fig. 13b). Hence, a high cut-off frequency is sufficient to cover both Wi-Fi bands.²²⁹ A flexible Wi-Fi band antenna integrated with a MoS₂ phase junction (2H-1T/1T')

Schottky diode can achieve wireless energy harvesting of electromagnetic radiation, which is efficiently used for self-powered systems.

A perovskite solar cell was fabricated with 1T-MoS₂ as the hole transport layer (HTL) in the device architecture of FTO/c-TiO₂/SnO₂QD/Cs_{0.1}FAPbI₃(0.81)MAPbBr₃(0.09)/MoS₂/PTAA/Au (Fig. 13c). 1T-MoS₂ reduced the mismatch between the energy-band alignment and trap density of perovskite, which increased the carrier concentration and improved the fill factor. The power conversion efficiency (PCE) of 1T-MoS₂ increased from 15.05% to 18.54% (Fig. 13d).²³⁰ In other work, a single-layer MoS₂_xSe₂(1-x) nanosheet with the 1T phase (≈ 66%) was synthesized by electrochemical Li intercalation and exfoliation. The metallic 1T MoS₂_xSe₂(1-x) phase facilitates electron transport to the counter electrode surface in dye-sensitized solar cells (DSSCs).²³¹ A higher PCE of 8.94% with 1T-MoS₂@HCS (hollow carbon sphere) was attained compared to those of 2H-MoS₂@HCS (8.16%) and Pt (8.87%).²³²

Metallic-phase TMDs are promising electrodes for metal-ion batteries. Electrochemical cycling for the phase transition from bulk 2H-MoS₂ to 1T'-Li_xMoS₂ *via* Li intercalation/deintercalation induced the formation of reformable nanodomains (Fig. 13e). Li_{1.0}MoS₂ showed a high specific capacity of 636 mA h g⁻¹ at 1 A g⁻¹ with a capacity retention of 80% and coulombic efficiency of 100%, whereas the capacity of bulk MoS₂ collapsed very sharply (Fig. 13f). The domain boundaries between nanodomains facilitate the mass transport of Li⁺ ions and charge/discharge reaction: S + 2Li⁺ + 2e⁻ ↔ Li₂S.²³³ Another example is the TiO-1T-MoS₂ nanoflower composite for Na-ion batteries, which exhibits a high reversible capacity, attributed to the well-distributed conductive TiO with 1T-MoS₂. This improves the electrical conductivity and stability.^{234,235} In Li-S

Table 2 Summary of representative phase transition methods of TMDs

Materials	Phase	Methods	Application	References
MoS ₂	2H → 1T	Li intercalation	—	203
MoS ₂	2H → 1T	Na and naphthalenide intercalation	—	206
MoS ₂	2H → 1T'	Li intercalation	—	207
MoS ₂	2H → 1T	Electrochemical Li	HER	208
MoS ₂	2H → 1T/1T'	K intercalation	—	209
MoTe ₂	2H → 1T'	Electrostatic doping	—	211
NbSe ₂	2H → 1T	Electrostatic doping	—	214
MoTe ₂	2H → 1T'	Electron transfer ([Ca ₂ N] ⁺ ·e ⁻)	—	215
MoTe ₂	2H → 1T'	Thermal treatment	—	216
TaS ₂	1T → 2H	Thermal treatment	—	219
PtSe ₂	1T ↔ 1H	Thermal treatment	—	220
MoTe ₂	2H → 1T'	Laser irradiation	FET	222
MoS ₂	1T/1T' → 2H	Laser irradiation	—	223
MoTe ₂	2H → 1T'	Tensile strain (AFM tip)	—	224
MoS ₂	2H → 1T'	Supercritical CO ₂	HER	225
MoS ₂	2H → 1T	Ar plasma	FET	227
MoS ₂ _x Se ₂ (1-x)	2H → 1T	Electrochemical Li	Solar cell	231
MoS ₂	2H → 1T	Li intercalation	Supercapacitor	238
WS ₂ /Gr	2H → 1T	Li intercalation	Supercapacitor	239
MoS ₂	2H → 1T'	Li intercalation	Neuromorphic computing	241
WS ₂	2H → 1T	Li intercalation	HER	243
ReS ₂ _x Se ₂ (1-x)	2H → 1T'	Li intercalation	HER	248
MoSe ₂	2H → 1T	Li intercalation	HER	249



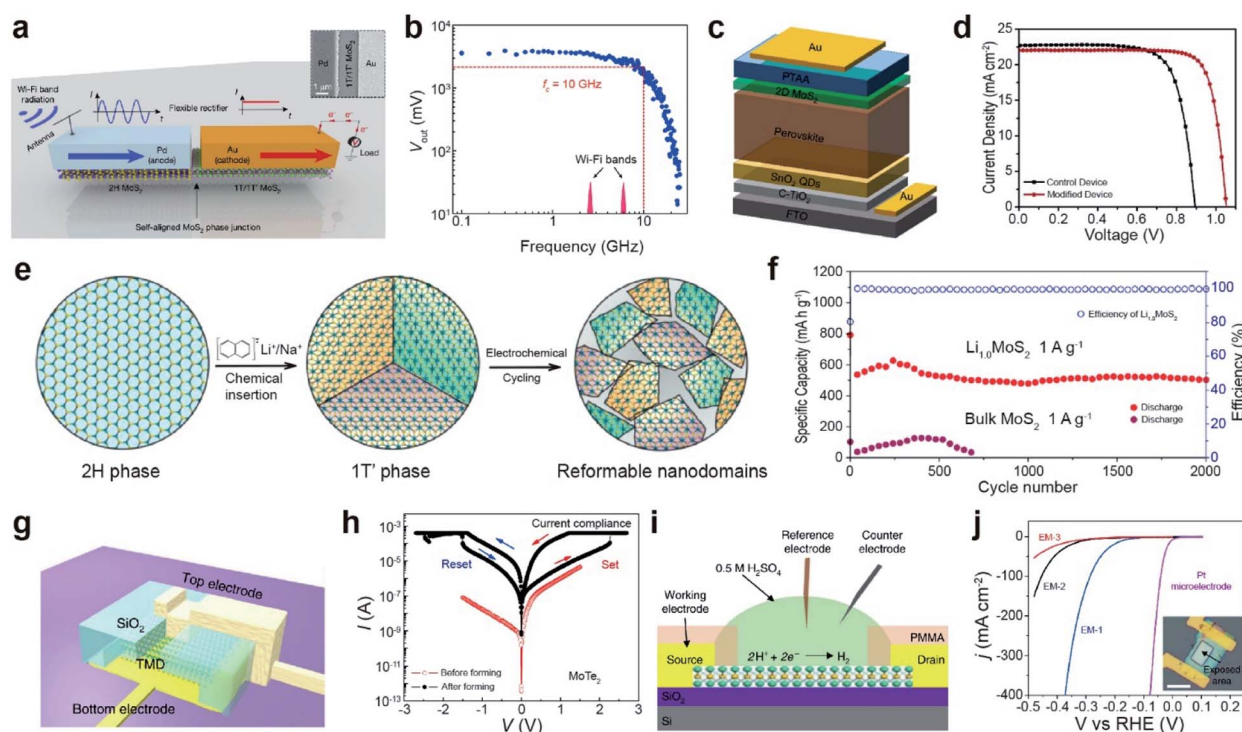


Fig. 13 Phase transition for various applications: wireless energy harvesting, solar cell, Li-ion battery, resistive memory, and electrocatalytic applications. **Wireless energy harvesting:** (a) schematic of a lateral MoS₂ semiconducting–metallic (2H–1T/1T') Schottky diode with palladium and gold layers forming a Schottky and an ohmic contact, respectively. The antenna receives a Wi-Fi signal and converts it into an AC signal. The Schottky MoS₂ diode rectifies the AC signal to the DC one. (b) Device output voltage as a function of frequency. **Solar cell:** (c) scheme of a solar cell architecture. (d) *J*–*V* curves of CsFAMA devices. **Li-ion battery:** (e) schematic of crystalline domain formation after chemical lithiation of bulk 2H–MoS₂. (f) The cycling performance of Li₁₀MoS₂ and bulk MoS₂ at 1 A g^{−1} for 2000 cycles, respectively. **Resistive memory:** (g) schematic of a vertical MoTe₂ resistive random access memory (RRAM) device. (h) *I*–*V* curves of a MoTe₂ RRAM device with a flake thickness of 24 nm and an area of (520 nm × 330 nm). Bipolar resistive switching behavior of MoTe₂ before (red) and after (black) formation. Arrows indicate the sweep direction. **HER electrocatalyst:** (i) schematic of the electrochemical microcell for HER measurements. (j) Polarization curves of the current density obtained with EM-1, EM-2 and EM-3. (a and b) Adapted with permission.²²⁹ Copyright 2019, Springer Nature Limited. (c and d) Adapted with permission.²³⁰ Copyright 2020, Elsevier B.V. (e and f) Adapted with permission under a Creative Commons CC-BY License.²³³ Copyright 2016, American Chemical Society. (g and h) Adapted with permission.²⁴⁰ Copyright 2019, Springer Nature Limited. (i and j) Adapted with permission.²⁴⁵ Copyright 2018, Springer Nature Limited.

batteries, metallic 1T–MoS₂ nanodots suppressed the diffusion of polysulfides and accelerated redox kinetics, which was confirmed by *in situ* XRD and EIS characterization.²³⁶ In supercapacitors, metallic 1T–MoS₂ displays an intrinsic capacitance of 14.9 μF cm^{−2}, which is 10-fold higher than that of 2H–MoS₂ in an aqueous electrolyte (1 M NaF).²³⁷ Metallic 1T–MoS₂ nanosheets contributed to the efficient absorption/desorption of various aqueous electrolyte ions (H⁺, Na⁺, K⁺, and Li⁺), which resulted in a high capacitance (~400 to 700 F cm^{−3}).²³⁸ 1T–WS₂/GO shows high performance in supercapacitors owing to the fast reversible reaction of W with proton insertion.²³⁹

A resistive random access memory (RRAM) device was fabricated by sandwiching TMD materials between top (Ti/Ni) and bottom (Ti/Au) electrodes on a SiO₂ isolation layer, which ensured vertical transport (Fig. 13g).²⁴⁰ The switching behavior of MoTe₂ was attributed to the formation of a conductive filament by the gradual phase transition from a 2H phase to a distorted transient (2H_d; intermediate state) and T_d conductive orthorhombic (1T) phase with an applied electrical field. The *I*–*V* curves of a MoTe₂ device (~24 nm thick) demonstrate

a resistive switching behavior after forming the conductive filament over 2.3 V (Fig. 13h). The device exhibited highly reproducible resistive switching within 10 ns between a low and a high resistive state. The thickness of MoTe₂ varied with the set voltage of the device. In the case of the Mo_{1−x}W_xTe₂ alloy, the set voltage can be reduced by increasing the concentration of W, as a result of the reduction in the energy barrier for the phase transition. The Au/Li_xMoS₂/Au device shows typical memristive behavior due to the reversible phase transition between 2H and 1T'–MoS₂ films, which is controlled by the redistribution of Li⁺ ions under an electric field.²⁴¹

Phase transitions are also useful for electrocatalytic applications. The basal planes of 2H–MoS₂ and 2H–WS₂ are effectively activated for the HER *via* a phase transition to the 1T phase.^{242–244} An electrochemical microcell was used to study the HER mechanism (Fig. 13i).²⁴⁵ The HER activity of 1T' (EM-1) and a mixture of 1T'–2H (EM-2) and 2H (EM-3) phases was tested in an acidic medium. The LSV curves of EM-1 exhibited the highest HER activity, with a low onset potential of 200 mV and a high current density of 607 mA cm^{−2} at 400 mV compared to other



samples (Fig. 13j). Another study demonstrated that the grain boundary between 2H and 1T phases acted as an active site for the HER.²⁴⁶ Furthermore, mesoporous 1T-MoS₂ nanosheets with many edge sites and S vacancies provided superior HER activity owing to their high conductivity and abundant catalytically active sites.²⁴⁷ 1T-phase ReS₂xSe₂(1-x) nanodots outperformed ReS₂ and ReSe₂ in terms of the HER performance.²⁴⁸ Superior HER performance was also observed for molybdenum dichalcogenides (MoSe₂) over their tungsten counterparts (WS₂ and WSe₂) after BuLi exfoliation.²⁴⁹ In photocatalytic H₂ evolution, the lateral 1T@2H-MoS₂ heterostructure demonstrates an improved photocatalytic efficiency because the 1T phase serves as an electron acceptor and transporter to suppress a charge recombination process.²²⁵ During the HER, the 1T phase in the hybrid TiO₂@1T-MoS₂ is irreversibly converted into a more active 1T' phase, providing more active sites and improving the HER activities.²⁵⁰

3.2. Heterostructures

Heterostructures are essential elements in the modern semiconductor industry and play a crucial role in high-speed electronics and optoelectronic devices.^{251–256} This wide range of applications stem from the tunable band alignment which enables electron and hole transfer across the heterojunction. TMD-based heterostructures consist of vertical van der Waals and lateral heterostructures.^{257–261} The former is constructed by the layer-by-layer stacking of 2D TMD materials, and the latter is formed by the lateral growth of another TMD at the edge of an initial TMD. The construction of a vertical heterostructure by applying the “pick-up” and “drop-down” methods with the mechanical exfoliation approach has been described in another study.^{262–267} The direct growth of heterostructures on pristine TMDs by employing CVD is focused on in this review.

Vertical heterostructures. To grow vertical heterostructures directly, a nucleation site is required to initiate an overlayer growth on top of a pristine TMD. With the aid of focused laser irradiation combined with raster scanning, a periodic array of defects on pristine WSe₂ is created to serve as nucleation sites (Fig. 14a).^{268,269} Direct laser patterning enables the creation of local defects at specific sites without contaminating other areas of the underlying WSe₂. The pre-patterned WSe₂ was placed in a separate furnace to synthesize an overlayer of metallic VSe₂. The growth temperature of VSe₂ was 600 °C (much lower than that of WSe₂ at 850 °C), to prevent thermal damage to WSe₂. The metallic VSe₂/WSe₂ heterostructure significantly reduced the contact resistance between electrodes and WSe₂ by forming an atomically clean vdW interface, resulting in a high on/off ratio of 10⁷ and a high “on” current (Fig. 14b). These studies demonstrated that synthetic VSe₂/WSe₂ vdW contacts offer considerable advantages over typical lithographically developed electrodes with low contact resistance.²⁶⁸

Furthermore, unstable edges or vertices of the TMD flakes can be utilized as nucleation seed sites. As an example, epitaxial growth of the SnS₂ overlayer from a vertex of a triangular WSe₂ via a two-step CVD process flake was observed in the optical image, forming vdW WSe₂/SnS₂ vertical bilayer heterostructures

(Fig. 14c and d).²⁷⁰ A type-III heterojunction between WSe₂ and SnS₂ was established (Fig. 14e). Therefore, photo-excited electrons and holes in WSe₂ prefer to transfer to low-energy states in SnS₂, rather than forming excitons in WSe₂, resulting in significant PL quenching of WSe₂.

Lateral heterostructures. Two-step lateral heterostructure growth of pre-synthesized VS₂ nanosheets, followed by stitching with MoS₂ monolayers at its edges, is shown in Fig. 14f and g.²⁷¹ To uncover the nature of the proposed epitaxial growth behavior of lateral VS₂/MoS₂ stitching, second harmonic generation (SHG) imaging was employed. The orientation distribution of the surrounding MoS₂ domains reveals the polycrystalline nature of MoS₂ domains (Fig. 14h (top)). Nucleation arises from the vertices of VS₂, instead of lateral epitaxial growth from the VS₂ edges (Fig. 14h (bottom)). In FET devices with lateral heterostructures, *I*_{DS} with VS₂ contact is six times higher than that of the counterpart with the Ni contact (for the same *V*_G and *V*_{DS}), implying that this approach is a promising way to reduce contact resistance (Fig. 14i).

Overall, this section consolidates recent advances in post-processing techniques for the synthesis of lateral and vertical heterostructures. By considering the respective thermal decomposition temperatures of TMDs, a vast number of vdW heterostructures can be synthesized. A summary of the growth of these heterostructures is given in Table 3. vdW heterostructures grown in a one-step process using mixed precursors have been reported; however, there is a high probability of forming alloys or mixed heterostructures with this method, degrading the unique physical and chemical properties of heterostructures.

Application. Heterostructures are desirable in a broad range of fields, including field-effect transistors, biosensors, light-emitting diodes, photodetectors, photovoltaic devices, and energy storage.

MoS₂/WS₂ and WS₂/MoS₂ vertical heterostructures (type-II heterojunctions) were explored as photocatalysts for hydrogen evolution (Fig. 15a).²⁷² For MoS₂/WS₂/Au, the photoexcited electrons in WS₂ were injected into the conduction band of MoS₂ via stepwise band alignment and contributed to the reduction of H⁺ to evolve H₂, whereas the holes in the monolayer WS₂ were neutralized by electrons from the electrode. Such effective separation of the photo-excited electron-hole pairs in the MoS₂/WS₂ stacks greatly promoted H₂ evolution, leading to the highest H₂ evolution content after 6 h (Fig. 15b).

A vertically stacked vdW GaSe/MoSe₂ heterostructure was constructed to create a p-n junction for photodetector and solar-cell applications (Fig. 15c).²⁷³ To test the photovoltaic response of vdW GaSe/MoSe₂, a FET was fabricated. The *I*-*V* transfer characteristics reveal diode behavior, which is ascribed to p-type GaSe and n-type MoSe₂. Furthermore, the photovoltaic characteristics of the heterostructure under white light illumination were investigated. While negligible photoresponse (black solid curve) is observed in the dark, the output current (red solid curve) under light shows an open-circuit voltage (*V*_{oc}) of ~0.57 V and a short circuit current density (*J*_{sc}) of ~0.35 mA cm⁻² at *V*_{bg} = 0 V (Fig. 15d). Ultimately, the resulting solar energy conversion performances, such as photo-to-electron conversion efficiency,



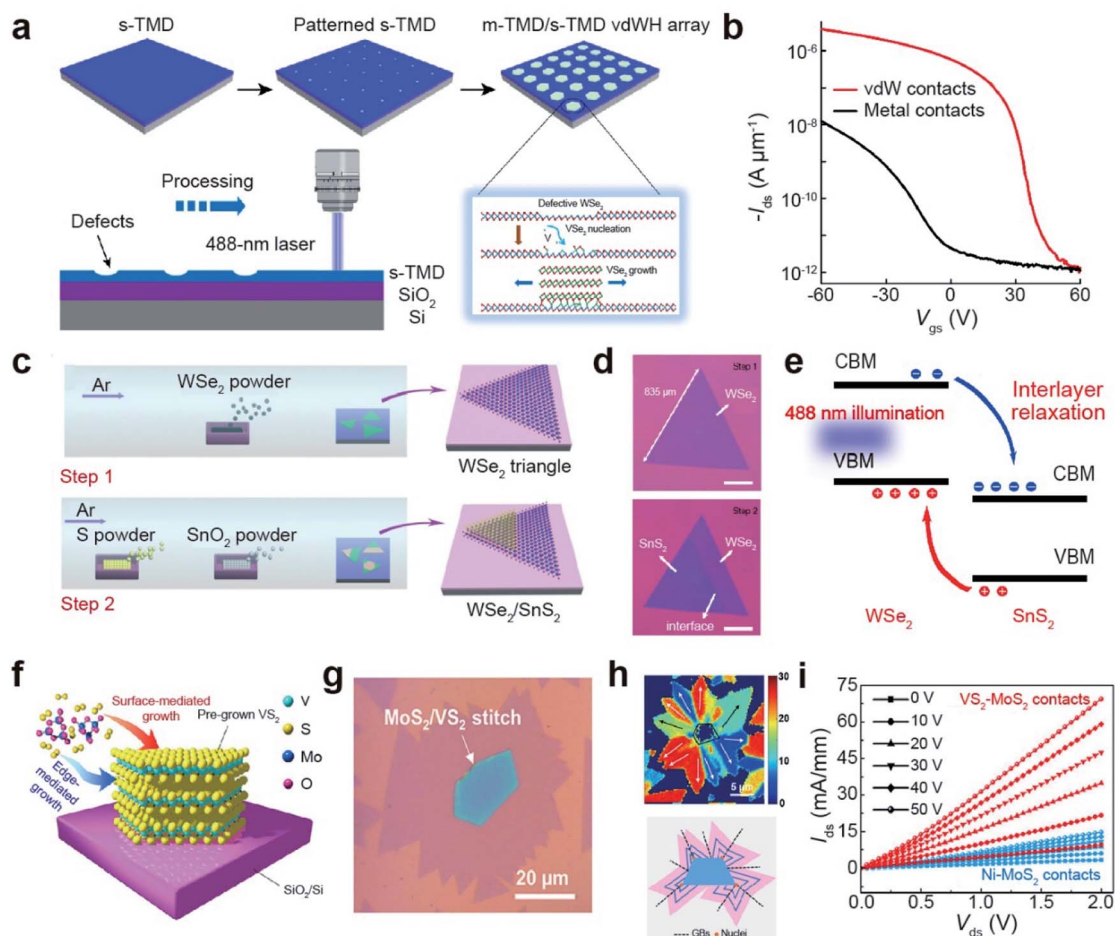


Fig. 14 Defect and edge mediated growth for vertical van der Waals heterostructures (vdWH) and lateral heterostructures. **Vertical van der Waals heterostructures:** (a) schematic demonstration of large-area WSe₂ selectively patterned to create periodic defect arrays as nucleation sites for site-specific growth of VSe₂ to form VSe₂/WSe₂ vdWH arrays. (b) I - V transfer curves of VSe₂/WSe₂ vdWH compared with a WSe₂ FET, obtained at $V_{DS} = -0.1$ V. (c) Schematics of a two-step epitaxy growth of the WSe₂/SnS₂ heterostructure. (d) Corresponding optical image of as-grown monolayer WSe₂ obtained after step 1 and the as-grown WSe₂/SnS₂ vertical heterostructure after the second step by using the same WSe₂ flake. (e) Schematic illustrations of the band structure and photoexcitation processes at the type-III WSe₂/SnS₂ heterojunction. **Lateral heterostructures:** (f) schematics of MoS₂ growth at the edge or surface of the pre-synthesized VS₂ nanosheets. (g) Optical images of the VS₂/MoS₂ stitching. (h) SHG imaging showing the distribution of MoS₂ domains surrounding VS₂ nanosheets (top) and proposed illustration of the stitching growth mechanism of MoS₂ at the vertices of VS₂ flakes (bottom) (blue lines indicate the growth pattern of MoS₂). (i) I_{DS} - V_{DS} characteristics of the VS₂/MoS₂ device compared with the Ni-MoS₂ contact, at varying V_G (0 to 50 V). (a and b) Reproduced with permission.²⁶⁸ Copyright 2020, Springer Nature Limited. (c-e) Reproduced with permission under a Creative Commons CC-BY License.²⁷⁰ Copyright 2017, Springer Nature Limited. (f-i) Reproduced with permission.²⁷¹ Copyright 2018, American Chemical Society.

fill factor, and photoresponsivity, are estimated to be 0.12%, 0.38 and 5.5 mA W⁻¹, respectively, at $V_{bg} = 0$ V.

The poor stability of TMDs under ambient conditions is often a bottleneck for scalable device applications. Recent studies have shown that 2D TMD heterostructures can significantly improve their air stability through interlayer coupling. 2D CrSe₂ nanosheets, with varying thicknesses (down to a monolayer), were grown on a dangling bond-free WSe₂ monolayer *via* a two-step CVD process.²⁷⁴ Atomic force microscopy images of the heterostructures revealed that monolayer CrSe₂ exhibited an outstanding air stability for up to 45 days (Fig. 15e), with no apparent change in the surface roughness or magnetic properties. Theoretical calculations suggested that charge transfer for the WSe₂ substrate and interlayer coupling within CrSe₂ play

a critical role in the magnetic order of few-layered CrSe₂ nanosheets. Notably, magnetotransport measurements revealed that the layer thickness of CrSe₂ exhibits differential magnetic properties. A thickness of up to three layers exhibits weak magnetic characteristics, whereas an increase in ferromagnetic (FM) properties was observed for four layers.²⁷⁴ Fig. 15f shows that the remnant anomalous Hall resistance (R_{AHE}^r) of the layer thickness of CrSe₂ decreases with increasing temperature and vanishes at around the Curie temperature (T_C). The T_C values of the 7 and 13 L devices were found to be significantly higher than those of the 4 L device, indicating that the FM properties increased significantly with layer thickness.

Finally, the interlayer coupling of post-deposited Bi₂Se₃ on MoS₂ heterostructures can be modulated by regulating the



Table 3 Summary of the growth heterostructures by applying CVD

Host	Incorporated material	Processing temperature	Heterostructure type	Reference
WS ₂	NbS ₂	750–800 °C	Vertical and lateral	251
WS ₂	CuI nanosheets	450 °C	Vertical	252
WS ₂	Sb ₂ Se ₃ nanowires	600 °C	Vertical	253
WS ₂	FAPBI ₃ (2D perovskite)	360 °C	Vertical	254
WSe ₂	CoSe	535 °C	Lateral	255
WS ₂	CdI ₂	315–325 °C	Vertical	256
WS ₂ (1–x)Se _{2x}	SnS ₂	550 °C	Vertical	257
MoS ₂	Sb ₂ Te ₃	600 °C	Vertical	258
MoS ₂	MoSe ₂	600 °C	Vertical	259
MoS ₂	NiTe ₂	550 °C	Vertical	260
MoSe ₂	InSe ₂	660 °C	Vertical	261
MoSe ₂	GaSe	710 °C	Vertical and lateral	273

presence of oxygen with controlled thermal energy.²⁷⁵ Fig. 15g shows an AFM image of a Bi₂Se₃/MoS₂ heterostructure with a height of 3.5 nm. While the PL intensity is significantly quenched under a N₂ atmosphere, it increases in air (Fig. 15h), indicating that intercalated oxygen interrupts the interlayer coupling between Bi₂Se₃ and MoS₂. This characteristic can be applied to gas sensors.

4. Summary and prospects

We reviewed the recent developments and state-of-the-art atomic and structural modifications of TMDs with their unique physical/chemical properties. High performance device applications were discussed for post-treated TMDs, such as electronics, catalysis, energy storage, wearable biosensors, piezoelectricity, CoVID-19 sensors, TENGs, flexible PNGs,

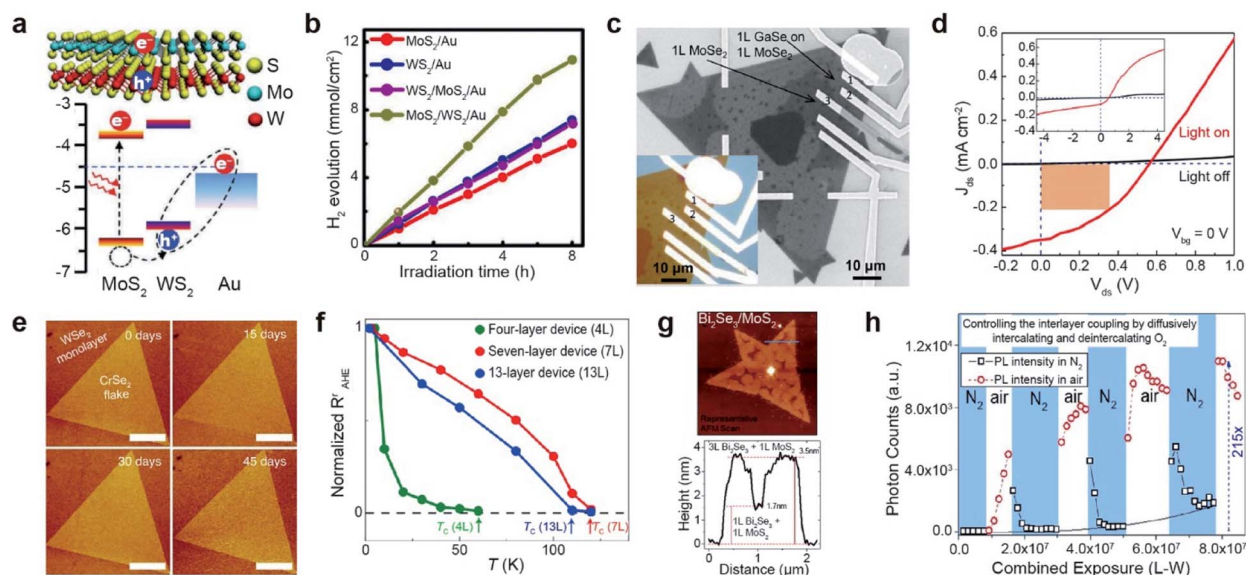


Fig. 15 Applications of heterostructures: photocatalysis, solar cell, magnetism, and sensors. **Photocatalysis:** (a) effective electron transfer mechanism for enhanced photocatalytic H₂ evolution in MoS₂/WS₂ vertical heterostructures under light irradiation. (b) Photocatalytic H₂ evolution curves of MoS₂, WS₂, MoS₂/WS₂, and WS₂/MoS₂ under an irradiation time of 6 h. **Solar cell:** (c) SEM image of a device consisting of a 1 L GaSe/MoSe₂ heterostructure. Marked positions 1 and 2 indicate GaSe/MoSe₂, while position 3 is for MoSe₂. Inset shows the corresponding optical image. (d) J_{DS} - V_{DS} curves ($V_{bg} = 0$ V) with (red solid curve) and without (black solid curve) white light illumination across the hetero-junction. The area with orange shading indicates P_{max} . The inset shows the I_{DS} - V_{DS} curves on a larger scale. **Magnetism:** (e) atomic force microscopy images of monolayer CrSe₂ on WS₂ after exposure in air up to 45 days (scale bars: 3 μ m). (f) Remnant anomalous Hall resistance (R_{AHE}) as a function of temperature with 4, 7, and 13 layers of CrSe₂. **Sensors:** (g) AFM image of the Bi₂Se₃/MoS₂ 2D heterostructure and corresponding line profile, demonstrating the growth of Bi₂Se₃ on MoS₂ crystals. (h) Variation of PL intensity under alternating air and nitrogen environments while a focused laser is applied, demonstrating that a nitrogen environment restores the interlayer coupling. (a and b) Reproduced with permission.²⁷² Copyright 2016, Wiley-VCH. (c and d) Reproduced with permission.²⁷³ Copyright 2016, American Association for Advancement of Science. (e and f) Reproduced with permission.²⁷⁴ Copyright 2021, Springer Nature Limited. (g and h) Reproduced with permission.²⁷⁵ Copyright 2019, American Chemical Society.



superconductor devices, wireless energy harvesting, solar cells, and memory and neuromorphic devices. The outlook for each topic is as follows.

4.1. Selectivity and scalability of vacancy generation

Expansion from a laboratory to an industrial scale is critical. Therefore, homogeneous vacancy generation by using a cost-effective process over a large area of TMDs should be considered. During post-treatment of TMDs, unintended defects such as the coexistence of metal and chalcogen vacancies, line defects and degradation can be generated under high power or temperature. Selective vacancy engineering plays a critical role in the research of the effect of chalcogen vacancies on the properties of TMDs. More research is needed to improve selective vacancy generation (S_V or TM_V).

4.2. Unclear catalytic mechanism by spontaneous oxygen passivation at vacancy sites

Several studies have been conducted to enhance the electrocatalytic performance owing to chalcogen vacancies in TMDs. However, STEM analysis of chalcogen vacancies has revealed that oxygen passivation at the vacancies is unavoidable due to spontaneous incorporation of oxygen. The actual active sites for catalytic reactions are still ambiguous. DFT calculations have been successfully used to analyze the Gibbs free energy of the HER and adsorption of metal ions on the vacancies. Most structural models are monolayers, whereas synthesized energy conversion and storage materials are multilayers. Therefore, a comparison of experimental results with theoretical ones shows apparent differences. A precise model that is consistent with multilayer materials is required. Moreover, *in situ/operando* characterization and advanced techniques are needed to understand the intermediate reactions and electrochemical reactions on vacancies for more diverse applications.

4.3. Dopant's homogeneity and its position

Studies on achieving substitutional impurity doping in TMDs have progressed considerably over the past year. Several innovative techniques for incorporating dopants have been studied; however, a few challenges remain. Efforts to modulate and control the homogeneous distribution of dopants are still daunting. As the homogeneity of dopants varies from the basal planes to the edges, the physical and chemical properties of the doped TMD tend not to be uniform. Therefore, a critical look is required during the generation of defects to ensure the uniformity of the defect distribution, as they will serve as nucleation sites for dopants. Furthermore, the control of the dopant position is very important for some applications, such as single-photon emission and diluted magnetic 2D semiconductors, but it has not yet been resolved.

4.4. Broader research for Janus 2D materials

The progress is still in its infancy. Although several theoretical predictions have been performed for numerous Janus structures, only MoSSe and WSSe have been experimentally

investigated. Furthermore, the uniqueness of the Janus structures should trigger new breakthrough applications in the field of science. Therefore, efforts should be made to improve the fabrication skills and applications of Janus 2D TMDs in the future.

4.5. Hybrid and asymmetric functionalization

In covalent functionalization approaches, the high coverage and uniform distribution of functional molecules on TMDs are limited, and hence, they deserve special attention. A special focus on the functionalization of Janus or heterostructure TMDs with organic molecules is needed, which will eventually offer some interesting physical and chemical properties based on the functional molecules. In addition, hybrid and asymmetric/Janus functionalization of TMDs have recently provided enriched electronic and optical properties of pristine TMDs.²⁷⁶ Therefore, this will facilitate the fabrication of next-generation multi-storage memory devices.

4.6. Optimization of functionalization techniques

Conventional techniques (drop-casting, dip-coating or soaking, spin-coating, and thermal evaporation) are predominantly used for organic functionalization of TMDs.^{277–280} These techniques consist of some disadvantages such as thick coatings, non-uniformity, aggregation, solvent evaporation dynamics, uncontrollable surface dewetting, and material accumulation at drop edges (coffee ring effect). Spin-coating has many adjustable parameters (concentration of organic molecules, boiling point of the solvent, and rotation speed) to optimize.^{281–283} In the future, direct printing can be applied to overcome many issues found in other techniques. Currently, functional organic molecules are dispersed in solvents to form the desired functional ink. As a result, the integration of organic molecule printing techniques with TMDs can be effectively used for large-scale fabrication at low-cost, lightweight wearable biosensors, flexible photodetectors, micro-energy storage devices, and memory elements.^{284–287} Therefore, it will provide a pathway for developing next-generation electronic technologies.

4.7. Unclear repair mechanism

Currently, few methods are employed to repair atomic chalcogen vacancies in TMD materials. The repair mechanism for healing TMDs with organic molecules (*i.e.* thiol molecules and bis(trifluoromethane) sulfonamide (TFSI)) are still unclear.¹⁸⁷ Therefore, more research, using advanced techniques such as STEM and *in situ* TEM, is required.

4.8. Quantum application for oxygen passivation

Furthermore, passivating TMDs with oxygen atoms showed promising applications in electronic devices. Similarly, oxygen passivation offers some interesting quantum phenomena such as elevated electron–phonon interaction, breaking structural symmetry and anisotropy, Rashba spin–orbit interaction, enhanced piezoelectricity, and improved Ising superconductivity.¹⁹⁸



4.9. Stability and scalability of phase transition

Phase engineering has been studied to prepare metallic (1T or 1T') phases from semiconducting (2H) phases. In the field of energy applications, the most widely studied technique for phase transition is Li intercalation through Li or organolithium reagents, which are highly corrosive and flammable, hindering industrial scalability. Furthermore, long lithiation times at high temperatures result in excess lithium and organic residues. The thermodynamic instability of the synthesized 1T/1T' phase is a major drawback that hinders its further application. Thus, the yield and stability of the 1T/1T' phase are important challenges that need to be overcome. Finally, it is necessary to develop a different phase-selective route to prepare metallic TMDs with a high phase purity.

4.10. Large scale synthesis of vertical heterostructures

The scalable growth of heterostructures has been a challenge, restricting extensive applications. At present, high-quality vdW heterostructures with sizes of only a few micrometers are achievable. The fabrication of large-area 2D heterostructures has been reported by sequential atomic layer deposition, molecular beam epitaxy, and exfoliation transfer techniques. However, clean and sharp interfaces were not obtained using these fabrication methods. Hence, continuous research on the realization of high-quality vdW heterostructures is necessary for the development of novel optoelectronic, electronic, and solar-cell devices. CVD is one of the most promising methods for producing high-quality, large-size TMDs. This is because of the ease in designing the growth parameters and revamping home-built CVD systems.²⁸⁸ In the future, further advances are required to improve the synthesis of wafer-scale high-quality vdW heterostructures for manufacturing lines in the semiconducting industry.

Author contributions

B. K., L. A. A., S. M. K. and K. K. K. designed the scope of the review. B. K., Y. S. W., L. A. A. and S. H. C. collected the references, organized the images and wrote the initial manuscript. Y. S. W. and S. H. C. modified and arranged the figures. S. M. K. and K. K. K. supervised and revised the manuscript. All the authors participated in the revision of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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