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Site-selective functionalization of solution-processed transition metal dichalcogenides for vertical and lateral covalent networks and heterostructures

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Covalent chemistry provides a robust route to functionalize transition metal dichalcogenides (TMDs), endowing them with new properties and enabling control over their interfaces. This minireview surveys covalent functionalization strategies for TMDs, emphasising site-selectivity and preferential binding to the basal plane or at the edges. It also discusses how these reactions enable the formation of covalently interconnected vertical heterostructures and lateral percolated homo- and heteronetworks, which can be assembled directly from TMD inks. We highlight emerging examples of such covalent 2D–2D architectures and outline challenges and opportunities in scalable covalent homo- and heterostructures fabrication featuring solution-processed TMDs.

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Introduction

Two-dimensional transition metal dichalcogenides (2D TMDs, MX_2 , where M is a transition metal and X = S, Se, Te) have

attracted considerable attention due to their tunable electronic and optical properties, making them particularly attractive for (opto)electronics, energy storage, catalysis, and sensing.¹ To meet the growing demand for these materials, solution-processing of 2D TMDs is gaining momentum as a scalable and low-cost approach for large-area electronics and printed circuitry. Moreover, it enables direct low-temperature deposition on

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arbitrary substrates, compatibility with soft and organic materials, and straightforward integration into flexible and wearable electronics.²

A specific feature of the TMD chemistry is structural phase diversity or polymorphism.¹ For most Mo and W chalcogenides, the thermodynamically stable polytype is the semiconducting trigonal prismatic 2H phase, while the conductive 1T and distorted octahedral 1T' phases can be obtained either *via* direct synthesis or by (electro)chemical activation (e.g., *n*-butyllithium treatment).^{3,4} Metallic 1T/1T' phases are electron-rich, enhancing their reactivity towards certain electrophiles and enabling covalent functionalization routes that are inefficient on pristine 2H basal planes;⁵ accordingly, some reactions are strongly *phase-selective*. In addition to phase effects, reactivity in solution-processed TMDs can be considered intrinsically *site-selective*. The basal plane consists largely of fully coordinated chalcogen atoms and is comparatively inert, whereas edges, grain boundaries, and point chalcogen vacancies (further referred to as 'vacancies') are undercoordinated reactive sites with high affinity to sulfur-containing molecules.⁶ In solution-processed TMDs, the chalcogen vacancy fraction is generally higher at the edge.^{7,8} Therefore, by tuning the functional group to react with TMDs, we can also favour its *predominant* binding site. This can be used to control not only the molecular distribution and position of covalently attached molecules, but also to open up opportunities for controlled nanosheet assemblies or even site-selective functionalization.

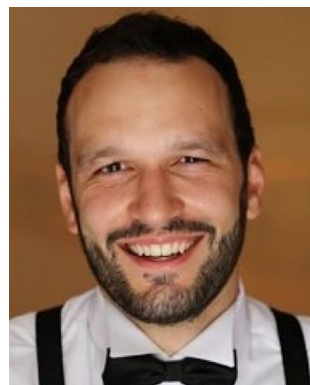
Beyond tuning the properties of individual nanosheets, covalent chemistry can be leveraged to build higher-order nanosheet assemblies, such as homo- and heteronetworks (edge-to-edge, lateral)/heterostructures (plane-to-plane, vertical). Unlike their van der Waals counterparts, covalently

bound assemblies offer access to controllable interlayer spacing through *ad hoc* molecular linkers and provide robust linkage between 2D building blocks.⁹ Moreover, the linkers themselves can impart functionality to the materials by incorporating doping or stimuli-responsive units.^{10,11} The design space therefore is vast.

This mini-review aims to showcase covalent functionalization of solution-processed TMDs with a special focus on site selectivity (preferential basal-plane *versus* edge/vacancy functionalization) and its emerging role in enabling covalent lateral and vertical 2D–2D networks and heterostructures (Fig. 1). We first summarise the main covalent reactions targeting basal planes and those preferentially resulting in binding to undercoordinated edge/vacancy sites. We then highlight how these reactions have enabled the early development of covalently interconnected vertical heterostructures and lateral percolated homo- and hetero-networks using TMD dispersions as the key building blocks. By organising the literature around site selectivity, we aim to clarify how molecular chemistry can be translated from nanosheet modification to scalable covalent 2D–2D assemblies.

Covalent functionalization strategies for TMDs

In general, the chemical functionalization of TMDs is particularly relevant for applications where surface chemistry and/or



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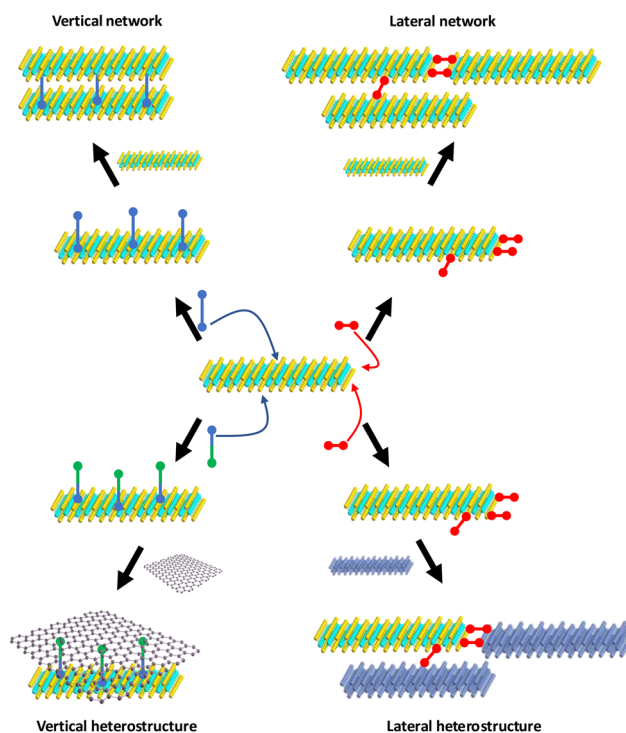


Fig. 1 Summary on the use of bidentate linkers for covalent vertical and lateral homo- and hetero-assemblies featuring 2D TMDs.



electronic properties play a significant role, *e.g.*, in sensing, electronics, energy storage, or catalysis.¹² Among the available molecular functionalization routes, covalent strategies are especially valuable because they are typically more robust and stable, and they tend to exert a stronger impact on the properties of the treated material.^{9,13} In this minireview, we present the most popular and enlightening approaches exploited to predominantly yield covalent bonds at TMD basal planes or edges by discussing opportunities and the challenges towards the realization of novel hybrid materials. The synthetic methods are organized by the reactive functional group, indicating the polymorph for which each approach is most effective. An overview of all strategies is provided in Table 1.

Basal plane functionalization

Grafting molecules on the basal planes of TMDs is highly sought after because it can enable precise tuning of key physical and chemical parameters, including doping level, work function, and wettability.⁶ However, since basal planes predominantly expose fully coordinated chalcogen atoms, they are intrinsically inert. As a result, covalent modification of basal planes typically requires the use of harsh chemistries or activation strategies.

Diazonium salts. Diazonium chemistry is one of the most widely studied methods of achieving high levels of basal-plane functionalization in both conductive and semiconductive MS₂ polymorphs.^{14,15} This approach relies on a radical-mediated reaction that results in covalent S–C bond formation. The proposed mechanism of the process comprises three main steps:

- (i) the diazonium salt derivative first approaches the surface of the TMD;
- (ii) charge rearrangement occurs, liberating the N₂ molecule and generating a reactive aryl radical;
- (iii) the newly formed radical reacts with the TMD surface to form a covalent S–C bond.¹⁵

In the semiconducting polymorph, diazonium functionalization is considered defect-initiated, with the first attachment occurring at a chalcogen vacancy, which then increases the reactivity of neighbouring lattice sites and enables propagation across the MoS₂ surface.¹⁵

This reaction is particularly practical for adjusting TMDs' electronic properties. For example, Benson *et al.* demonstrated

that attaching an electron-donating or electron-withdrawing group to the basal plane can finely tune the work function of covalently grafted MoS₂.¹⁶

Organic halides

This functionalization strategy is efficient for the electron-rich 1T/1T' phase of TMDs. It was first introduced in the literature as TMD functionalization by phase engineering.¹⁷ First, the process involves partially converting the semiconducting 2H phase to the metallic 1T phase *via n*-butyllithium treatment. Then, the nucleophilic attack of organic halides by the TMD occurs. It is now clear that, to serve as an effective nucleophile, the TMD must possess high electron density to facilitate the attack on the organic halide.¹⁷ This functionalization induces significant changes in the optoelectronic properties of the relevant TMDs. Notably, it partially converts the metallic 1T phase back to 2H, restoring photoluminescence and enabling gate modulation in field-effect transistors.¹⁷ Additionally, Ries *et al.* have shown that, by grafting functional groups of varying polarity *via* this route, MoS₂ membrane surfaces can be tuned for improved water desalination performance.¹⁸

Maleimide derivatives. Maleimides are well-known electrophiles with high affinity for soft nucleophiles such as sulfur, making them widely used in bioconjugation chemistry.¹⁹ Transition metal sulfides, with exposed sulfur atoms on their basal planes, have likewise been shown to react readily with maleimides to form covalent products featuring hypervalent S atoms.²⁰ The reaction can be carried out both in dispersion and on solid-supported MoS₂ films deposited on a substrate.²¹ The nature of the product depends strongly on the reaction conditions. In the presence of catalytic amounts of a base (*e.g.*, triethylamine), covalent grafting of a polymeric adlayer is typically observed, as the base not only activates the MoS₂ surface but also catalyses a competing opening of the maleimide C=C double bond followed by homopolymerisation.²² This leads to a significantly higher apparent functionalization degree. In the absence of a catalyst, maleimide homopolymerization is not promoted, and the reaction typically stops at (approximately) a molecular monolayer.²² Thus, the choice of experimental conditions depends on the desired application and whether a molecular layer or a polymeric coating is required.

The detailed mechanism of this reaction is still debated in the literature. While the pioneering study proposed a Michael addition reaction mechanism, as supported by the multiscale characterization of the product,²⁰ the follow-up studies have suggested a radical-based mechanism.²² Moreover, scanning probe studies on solid-supported samples report a non-uniform grafting pattern, with a higher local grafting density along line and point defects, alongside significant basal plane functionalization.²¹ Regardless of the exact pathway, this approach enables efficient basal-plane functionalization under mild conditions, preserving the structure and semiconducting character of the nanosheets.

Trifluoromethyl thianthrenium triflate (TTT). Another functionalization strategy was recently reported by Kerwin *et al.*: by treating TMDs with the TTT reagent under mild con-

Table 1 Covalent functionalization strategies for TMDs. Predominant site of covalent attachment reported under the stated conditions; contributions from basal planes, edges, grain boundaries and vacancy sites may coexist depending on defect density and processing of the material

Phase	Reagents	Predominant site	Ref.
1T, 2H	Diazonium salts	Basal plane	14–16
2H	Maleimides	Basal plane	20–22
1T	Organic halides	Basal plane	17 and 18
2H	TTT	Basal plane	23
2H, 1T	Thiols	Edge/basal plane	7, 29, 30, 32, 34, 35 and 38
2H	1,2-Dithiolane	Edge	36
1T, 2H	1,2-Dithiolene	Edge	37



ditions, they successfully achieved covalent decoration of the basal plane with $-\text{CF}_3$ groups, which introduced a strong p-doping effect.²³ While this approach is effective for the chemical doping of the nanosheets, it cannot be readily extended to covalent network or heterostructure formation because the $-\text{CF}_3$ group does not provide a bifunctional “linker” handle for interflake cross-linking.

Other reactions targeting the basal plane of TMDs have also been reported, such as treatments with $\text{M}(\text{OAc})_2$ salts,²⁴ carbenes,²⁵ *etc.*, yet these reactions have not been demonstrated to yield a covalent molecule–nanosheet bond and therefore fall outside of the scope of this minireview.

Edge functionalization

Defects, including point chalcogen vacancies, are ubiquitous in solution-processed 2D TMDs as they are generated during their exfoliation and subsequent processing.²⁶ In practice, solution processing tends to yield significantly higher vacancy densities at the flake edges: liquid-phase exfoliation commonly produces chalcogen-deficient edge terminations in TMDs due to severe flake fragmentation, and electrochemical/intercalation routes likewise increase the density of defect sites at the edges.^{7,8}

Alongside the key influence of defects on the optical and electrical properties, falling out of the scope of this minireview, defects are also highly reactive sites; their most relevant role here is as chemically addressable sites whose density and distribution largely determine the functionalization site-selectivity and the apparent grafting degree.²⁶

Organic thiols. Defect engineering is arguably the most straightforward and exploited approach for covalently attaching molecules to TMDs. This mild route takes advantage of naturally occurring or artificially introduced chalcogen vacancies, which are filled by organic thiols with chalcogen atoms.²⁷ This healing of vacancies can be performed in both the gas phase^{27,28} and in solution.^{7,29,30} Computational studies have also considered side reactions of the repair pathway involving the organic leaving group and dimerization (oxidation of thiol to form disulfide), depending on the experimental conditions.³¹ This reaction has been demonstrated not only on sulfides like MoS_2 and WS_2 ,⁷ but also on selenides and tellurides of transition metals.^{32,33}

So far, the detailed mechanism of this reaction remains unclear. Nonetheless, it is well established that thiols exhibit strong affinity for chalcogen vacancies and can effectively repair these sites. In this minireview, we therefore refer to it as covalent functionalization yielding a restored MoS_2 lattice with a covalently bound organic moiety (M-S-R). We also note that thiols have been reported to bind at basal-plane sulfur vacancies in mechanically exfoliated and CVD-grown TMDs where such vacancies are intrinsic or intentionally introduced within the basal plane,^{27,34,35} underscoring that thiol chemistry is not strictly site-selective and can yield mixed basal-plane and edge contributions. However, in solution-processed TMD dispersions, which are the focus of this mini-review, the

high density of accessible under coordinated sites at the edges often makes edge/vacancy attachment dominant.

1,2-Dithiolenes and 1,2-dithiolanes. Beyond thiols, dithiolanes and 1,2-dithiolenes are also known to heal chalcogen vacancies at the edges of the flakes and yield edge-functionalized nanosheets.^{36,37} According to DFT calculations, the mechanism of this reaction relies on the high affinity of S atoms in 1,2-dithiolenes toward S-vacancies in MoS_2 , resulting in edge S vacancies healing.³⁷

Overall, edge vacancy healing is a two-in-one approach as it repairs the defective structure of TMDs, improving their electronic properties, while simultaneously attaching functional molecules that can impart new properties or functions.

Characterization of covalently functionalized TMDs

Characterization of functionalized solution-processed TMDs, and especially assigning where binding occurs, is challenging primarily due to the intrinsic heterogeneity of the samples.⁹ Accordingly, convincing evidence typically relies on multiple complementary techniques and relevant controls.⁹ X-ray photoelectron spectroscopy (XPS) is usually the key starting point because it can (i) confirm heteroatom (carbon or other) incorporation into the material, and (ii) more critically, reveal new bonds to the chalcogen in its core level region (*e.g.*, components attributed to chalcogen-carbon bond formation for basal plane or vacancy healing for the edge/vacancy). Complementary vibrational/optical spectroscopies (Raman, infrared, UV-vis, photoluminescence) are most convincing when paired with identically processed controls. When feasible, scanning probe microscopy on solid-supported flakes can provide spatial evidence for whether functionalization is enriched at edges/vacancies *versus* basal planes.²¹ High-resolution transmission electron microscopy (HRTEM) can further inform on local defect density and on lattice restoration after vacancy-healing reactions,^{7,32} although direct visualization of attached organic functional groups is challenging. Characterization by thermogravimetric and/or elemental analysis is informative but often not precisely quantitative unless paired with evolved-gas analysis and relevant blanks, as residual solvent(s), surfactants and side reactions can inflate the apparent grafting density.^{9,22} Overall, reliable quantification and site assignment require converging evidence from multiple techniques, careful product purification, and appropriate controls. For a comprehensive discussion on characterization of functionalized 2D materials, including TMDs, we refer the reader to ref. 9.

From functionalized layers to interconnected architectures: covalent networks and heterostructures

The fact that different functional groups preferentially address distinct sites on TMD nanosheets (basal plane *versus* edge/vacancy) not only broadens the functionalization toolbox, but



also provides a means of programming how the flakes assemble into interconnected architectures.

One straightforward approach is to employ (hetero)bifunctional linkers that can react with two flakes to form covalent bridges. Depending on the location of the reactive sites and on how the assembly is processed, such linkers can yield either vertical 2D–2D structures (out-of-plane interlayer junctions) or lateral networks (in-plane edge-to-edge junctions). In vertical assemblies, covalent linkers can, in principle, define interlayer spacing,³⁹ while in lateral architectures they can improve interflake connectivity.³⁰ This general approach is modular and allows covalently bound 2D–2D in-plane and out-of-plane homo- and heterostructures to be assembled (Fig. 1).

Vertical networks and heterostructures

The covalent functionalization of the basal planes of 2D TMDs has led to early examples of plane-to-plane interconnected architectures, providing a conceptually distinct alternative to conventional van der Waals (vdW) stacking. Compared to vdW, covalent heterostructures offer greater control over interlayer distance, yield robust assemblies, and create a more chemically controlled interface where electronic coupling and stimuli-responsiveness can be tuned through the linker chemistry.^{9,11,13}

A representative example of vertical homostructures is the covalent cross-linking of liquid-phase-exfoliated MoS₂

nanosheets using maleimide chemistry reported by Vázquez Sulleiro and co-workers (Fig. 2a).⁴⁰ In this strategy, bifunctional organic linkers (bismaleimides) act as covalent bridges between adjacent basal planes, effectively creating MoS₂-linker-MoS₂ vertical architectures. This is a powerful route to control the interlayer spacing in homostructures of MoS₂ and opens opportunities for interconnecting other sulfides in a similar fashion. Building on this concept, increasing the linker length and rigidity offers a route to further adjust interlayer spacing and porosity. For instance, porous, vertically interconnected MoS₂–MoS₂ architectures have been produced by incorporating longer conjugated linkers through organic halide chemistry and Sonogashira coupling, as demonstrated by Pramoda *et al.*³⁹ Beyond simple assemblies, introducing stimuli-responsive linkers is particularly appealing because it can add functionality at the interface itself. A notable direction is the integration of photoswitchable molecular components to make the assembly responsive to light stimuli.¹¹

As for heterostructures, only a limited number of examples have been reported where two distinct 2D materials are covalently interconnected using heterobifunctional molecular linkers. A prominent case is the graphene (Gr)–MoS₂ heterostructure demonstrated by Vázquez Sulleiro *et al.*, comprising CVD-grown graphene and LPE MoS₂ (Fig. 2b).⁴¹ More recently, Chen, Hou and Prato provided a systematic study of fully solution-processed covalent MoS₂–Gr stacks using different organic

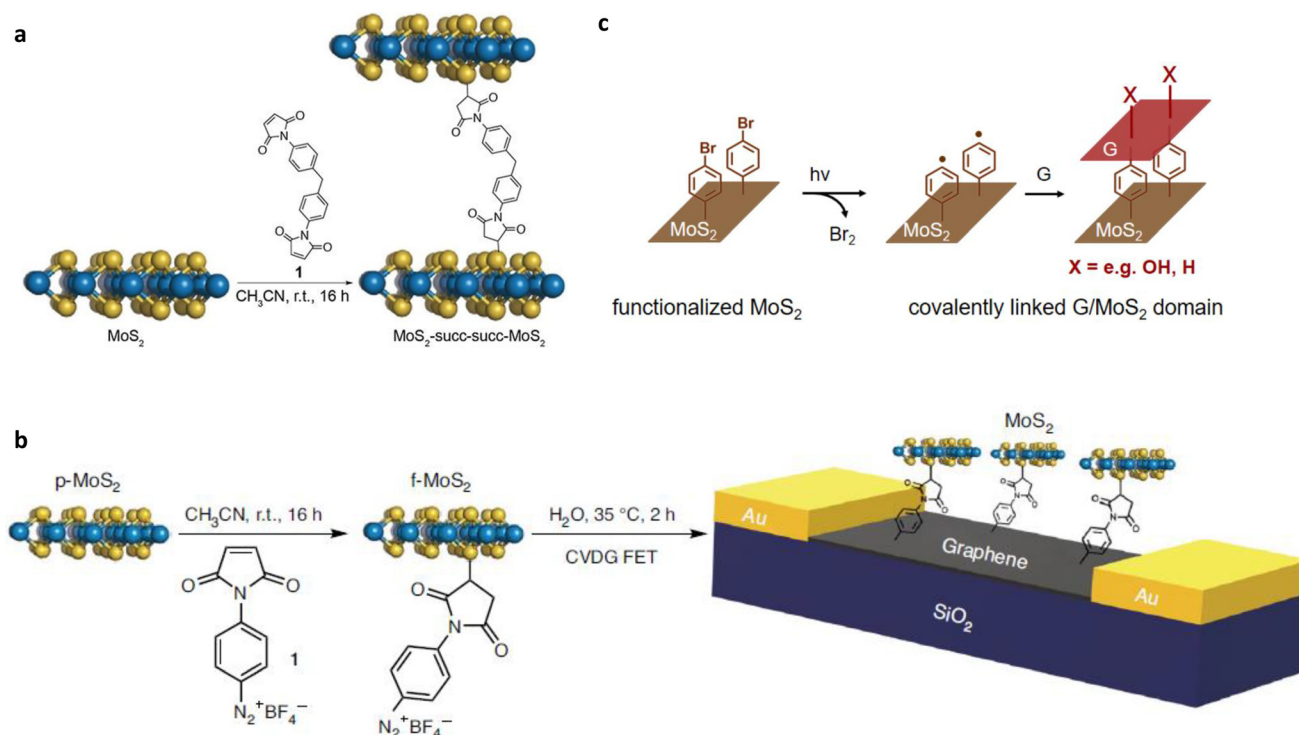


Fig. 2 Examples of covalent vertical homo- and hetero-structures. (a) MoS₂–MoS₂ tethered by bismaleimide difunctional linker. Reproduced from ref. 40 with permission from Wiley-VCH GmbH, copyright 2021. (b) On-device MoS₂ heterostructure formation. Reproduced from ref. 41 with permission from Springer Nature, copyright 2022. (c) Mechanism of the laser-triggered Gr–MoS₂ covalent cross-linking for spatially defined covalent heterostructures. Reproduced from ref. 42 licensed under an Attribution-NonCommercial-NoDerivatives 4.0 International Licence (CC BY-NC-ND 4.0).



linkers and complementary anchoring strategies, where they prepared two types of covalent MoS₂-Gr stack: one with diazonium salt and halide, another with maleimide and diazonium salt.¹³ In parallel, Chen and co-workers reported strategies enabling spatially defined covalent patterning within MoS₂-Gr heterostructures by laser-activated cross-linking⁴² and further demonstrated its applicability to solution-processed TMDs (Fig. 2c).⁴³ This direction is particularly relevant for device integration, where the controlled placement of covalent junctions can allow local tuning of charge transport, charge separation, or chemical response without functionalizing the entire film. Finally, vertical heterostructures are also emerging as practical platforms for materials immobilization and integration, for example, enabling one 2D material to be robustly anchored onto another (e.g., screen-printed Gr electrode decorated by LPE MoS₂) for biomarker detection.⁴⁴ While such applications are still at an early stage, they emphasize a prag-

matic advantage of covalent vertical assemblies: increased robustness and interface stability in-device.

Lateral networks and heterostructures

Due to the high density of reactive edge/vacancy sites in solution-processed TMDs, initial demonstrations revealed that thiol chemistry could facilitate network formation in micro-metre-thick films. For instance, a thiol-interconnected TMD networks were achieved in drop-cast and spray-coated films by Ippolito *et al.*^{7,30} Network formation not only contributed to the robustness and stability of the system but also improved the electronic characteristics of the films. In principle, the same concept can be translated to other deposition routes used for 2D-material inks (e.g., vacuum filtration, spin coating, inkjet printing). However, in standard wet-deposited films, the interflake contact geometry is less tightly controlled; disorganized flake overlapping, partial restacking, and uncontrolled interfaces in

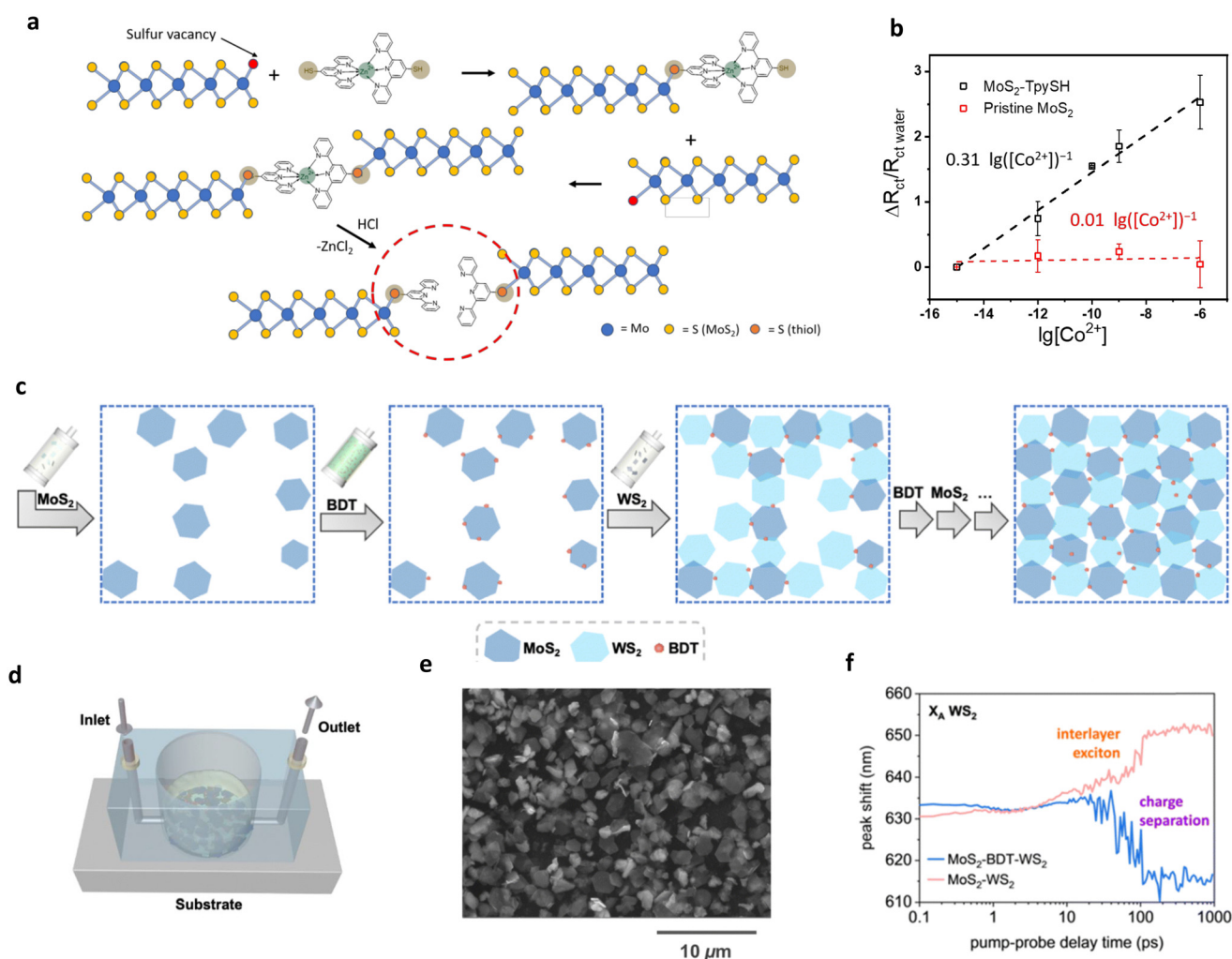


Fig. 3 Lateral covalent heterostructures *via* a microfluidic-assisted deposition approach. (a) MoS₂-TerpySH hybrid for sensitive and selective chemical sensing of Co²⁺, (b) calibration curve of the sensor as compared to pristine MoS₂ film. Reproduced from ref. 10 licensed under a Creative Commons Attribution 4.0 International Licence (CC BY 4.0). (c) MoS₂-WS₂ lateral heterostructure formation. (d) Scheme of the microfluidic chamber. (e) SEM image of the solution-deposited heterostructure. (f) Evidence of the improved charge separation in the covalent lateral heterostructure as compared to the MoS₂-WS₂ blend. Reproduced from ref. 47 licensed under a Creative Commons Attribution 3.0 Unported Licence (CC-BY 3.0).



multicomponent films can make the relative contributions of lateral and vertical covalent junction formation more difficult to resolve.⁴⁵ In addition, stabilizers, surfactants and binders used in 2D ink formulations can remain trapped in the deposited film, partially covering reactive sites and thereby affecting the apparent grafting degree and effective site selectivity.⁴⁶

To address these limitations, strategies that enforce an additional degree of film growth control during deposition are emerging. For example, microfluidic-assisted deposition has emerged as a method to assemble nearly one-flake-thick films from the TMD inks.^{10,47} It is a modular, stepwise approach to assembling thin films from 2D inks, offering exceptional control over the structure, composition, and connectivity of the resulting network. The process involves the sequential injection of the dispersion of a nanomaterial and a bifunctional linker targeting the edge (*e.g.*, dithiol for TMDs) into a microfluidic chamber under controlled laminar flow conditions and for pre-defined time intervals. The presence of a bifunctional linker is crucial for promoting lateral interflake stitching: in its absence, deposition does not yield a laterally percolating network. We therefore consider the linker as a “molecular glue” that drives lateral growth and mechanically reinforces the film by covalently bridging neighbouring nanosheets. Using this approach in combination with sulfur-vacancy chemistry, we recently demonstrated functional networks that respond to external stimuli such as heavy-metal ions, enabling high-performance chemical sensing (Fig. 3a and b).¹⁰

Our group also recently reported an edge-to-edge in-plane heterostructure assembly *via* a microfluidic-assisted approach to generate covalent networks of two distinct semiconducting TMDs (namely, LPE n-type MoS₂ and ambipolar WS₂) directly from the corresponding inks (Fig. 3c–e).⁴⁷ Such covalent hetero-networks provide facilitated pathways for charge transfer and charge separation than corresponding vdW-contacted blends (Fig. 3f), while retaining the scalability of ink-based assembly. Despite the inherent heterogeneity of solution-processed nanosheets (for example, broad size/thickness distributions), this remains one of the few examples of a solution-assembled, covalently stitched lateral TMD–TMD heterostructure constructed directly from inks.⁴⁷

Overall, lateral networks and heterostructures highlight the central role of edge/vacancy reactivity in solution-processed TMDs: covalent linkers can act simultaneously as vacancy healers, junction bridges, and functional elements that impart chemical recognition or responsiveness.

Conclusions and perspectives

Covalent chemistry provides an increasingly powerful toolbox for solution-processed TMDs to engineer interfaces and interflake junctions. Here, we discuss how basal plane functionalization was exploited to modify not only the 2D nanosheets but also to enable vertical covalent 2D–2D structures. Complementarily, we illustrate how the lateral covalent interconnection of TMDs *via* edge/vacancy chemistry can be enhanced and exploited, and how

covalent hetero-networks can be assembled directly from dispersions. These examples expand the vision from solely functionalized flakes toward chemically programmed 2D building blocks for scalable (multi)functional devices.

In our opinion, several challenges must be addressed for the emerging field of covalent 2D–2D assemblies to mature and flourish. First, the assignment of the functionalization sites (basal plane *versus* edge/vacancy) and degree is not a trivial task in solution-processed nanosheets, requiring thorough multiscale characterization of the product/deposited film. Second, achieving structural control and uniformity remains a key bottleneck that depends on the precision of the chemistry involved, the quality of the starting materials, and the deposition method of choice. Progress will likely require tighter control over phase purity, flake size/thickness distributions, and defect densities in TMD inks, as well as deposition protocols that yield better-controlled geometries. Third, the functional objectives of covalent homo- and hetero-structures should be articulated more explicitly. Beyond demonstrating covalent linkage, future studies should leverage it to engineer a specific property or parameter, such as interlayer distance, junction resistance, charge-transfer efficiency, or stimuli responsiveness, and benchmark the resulting performance against appropriate controls. Such benchmarking will be essential in identifying instances where covalent linkage provides a true advantage, as well as in guiding the rational design of scalable 2D–2D assemblies.

In perspective, several research directions appear especially enticing: (i) expanding the library of covalent synthetic approaches to functionalize TMDs, particularly for semiconducting 2H polymorph; (ii) the rational design of (bi)functional linkers that not only tune interflake and interlayer spacing but also introduce additional functions such as redox activity, photoresponsiveness, or molecular recognition; and (iii) establishing processing strategies that guide the assembly pathway and geometry, such as stepwise deposition protocols.

Overall, the site-selective covalent chemistry of TMDs provides a unique opportunity to assemble complex and controlled structures directly from 2D inks. Continued progress in functionalization strategies, characterization, and cross-linking control, not only through chemistry but also *via* deposition methods, is expected to expand the palette of 2D–2D vertical and lateral assemblies and accelerate their integration into scalable functional materials and devices.

Conflicts of interest

The authors declare no conflicts of interest.

Data availability

Data sharing not applicable – no new data generated. Data sharing is not applicable to this article (*Minireview*) as no new data were created or analyzed in this study.



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