

Engineering optoelectronic properties of two-dimensional transition metal dichalcogenides via acid treatment: defect manipulation mechanisms and the optical–electrical trade-off

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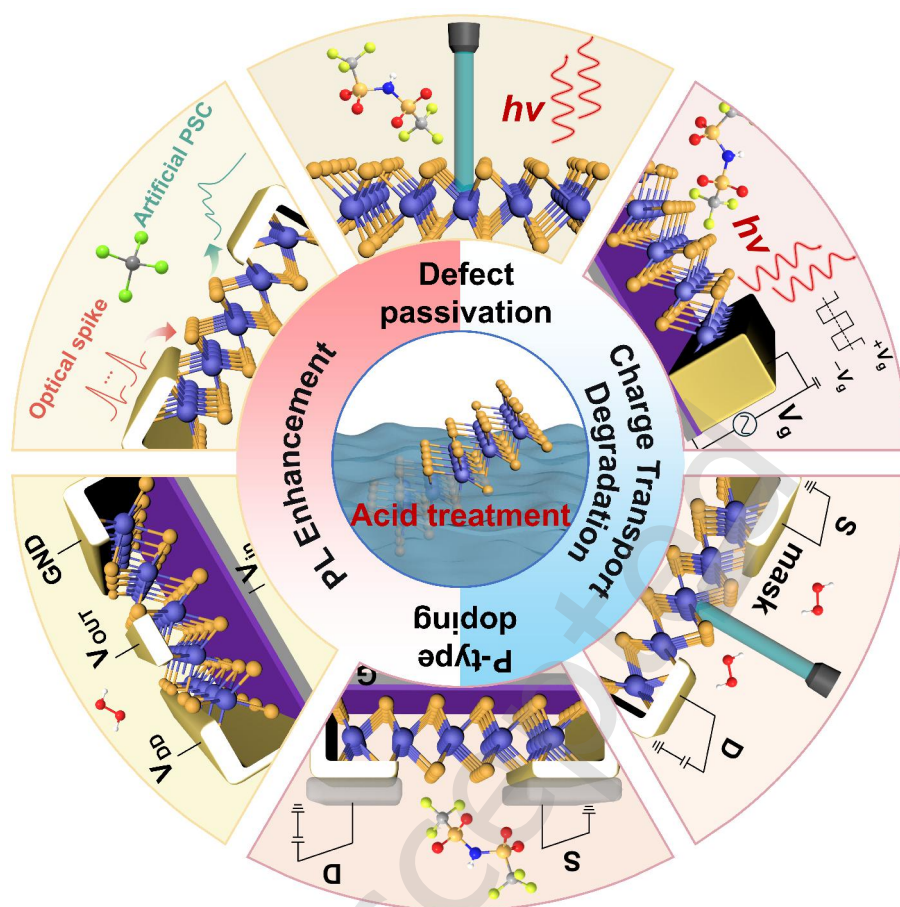
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This review elucidates the competing mechanisms between defect passivation and p-type doping during acid treatment, and rationalizes the counterintuitive degradation of charge transport via a hopping model. In addition to Brønsted acids, the discussion also incorporates emerging Lewis acids, collectively advancing the development of high-performance optoelectronic devices.

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ABSTRACT: Two-dimensional transition metal dichalcogenides (TMDs) are promising candidates for next-generation optoelectronics, but their performance is often constrained by intrinsic defects. Acid treatment has emerged as a powerful defect engineering strategy, dramatically boosting the photoluminescence (PL) quantum yield of these atomically thin semiconductors. This review systematically examines progress in acid-induced PL enhancement of TMDs over the past decade and distills the underlying mechanisms and ongoing controversies. A central theme is the ubiquitous trade-off: optical properties improve markedly, whereas electrical transport in field-effect transistors frequently degrades after treatment. This counterintuitive behavior is rationalized through a sulfur vacancy-mediated hopping transport model, which shows that the trade-off is an inherent consequence of defect manipulation rather than a side effect. Moving beyond this compromise, synergistic design rules for decoupling optical and electronic responses are critically assessed, with particular emphasis on the emerging use of Lewis acids for targeted property modulation. Finally, future research directions are outlined, including integrating machine learning with atomic-scale defect characterization, testing the generality of defect-selective passivation across diverse defects, and advancing these strategies toward practical device applications.

KEYWORDS: transition-metal dichalcogenide, acid treatment, defect passivation, p-type doping, quantum yield, charge transport

1 Introduction

Atomically thin transition metal dichalcogenides (TMDs) represent a frontier platform for next-generation optoelectronics, where strong Coulomb interactions and lightwave-driven control enable the stabilization of exotic quantum phases such as exciton crystals and pseudospin switches[1,2]. Recent advances have demonstrated in-sensor wireless computing[3], in-pixel display processing[4], neuromorphic spiking vision[5], volitional hyperspectral imaging[6], and spaceborne communication[7], together pointing toward a paradigm shift in low-latency, energy-efficient, and extreme-environment optoelectronics. Underpinning these advances, large-scale monolayer TMDs, obtained via Au-assisted mechanical exfoliation (ME) or direct chemical vapor deposition (CVD), have profoundly facilitated the lab-to-fab transition[8-10]. However, owing to mechanical or thermal strain and the volatility of chalcogen atoms, sulfur vacancies at densities of 10^{12} – 10^{13} cm⁻² are inevitably generated in monolayer TMDs[11-13]. These defects give rise to detrimental effects that severely compromise device performance: (i) extremely low room-temperature photoluminescence quantum yields (PL QYs, 0.01%–6%)[14,15]; (ii) a pronounced discrepancy between theoretically predicted room-temperature electron mobility (μ_e ,

410–1100 cm² V⁻¹ s⁻¹) and experimentally measured values (0.1–20 cm² V⁻¹ s⁻¹)[16,17]; and (iii) a prolongation of photodetector response times by several orders of magnitude[18,19]. Thus, the path to high-performance TMD-based optoelectronics hinges on effective defect passivation.

The concept of “defect engineering” has recently emerged as a strategic framework for rationally manipulating the physicochemical properties of two-dimensional (2D) TMDs through fundamental understanding of defect characteristics[12,13,20,21]. Two primary approaches have been developed to mitigate the detrimental effect of defects: introduction of dopants (e.g., NaBr, Fe₂O₃, B₂O₃) during synthesis[22-25], and various post-growth treatments including chemical functionalization (e.g., thiols, acids, electroactive molecules)[26-29], gas-phase doping (e.g., S, O₂, H₂S)[30-33], and laser irradiation[34-38]. Among these, wet-chemical treatments using thiols or acids strike an optimal balance between facile processing, chemical versatility, and robust outcomes (Fig. 1a). Thiol- based surface treatments have been extensively explored for passivating TMDs, offering the distinct advantage of enhancing electrical properties while providing moderate PL enhancement. For instance, (3-mercaptopropyl)trimethoxysilane (MPS) enables a room-temperature μ_e of ~ 150 cm² V⁻¹ s⁻¹ in MoS₂ field-effect

transistors (FETs)[39-41]. However, the improvement in transport performance is accompanied by only modest optical enhancement (typically <10-fold)[42-44]. In stark contrast, organic superacid treatments, such as those employing bis(trifluoromethane)sulfonimide ((CF₃SO₂)₂NH, TFSI), have emerged as a far more powerful strategy for optical engineering. These superacids boost the PLQY of monolayer MoS₂ or WS₂ to near-unity, but often at the cost of carrier mobility[14,45-47]. Nevertheless, the microscopic origin of this trade-off remains inadequately understood, motivating the mechanistic analysis that follows.

Thiol-based treatments, which serve as a key reference for interpreting acid-TMD interactions, have been proposed to operate through three mechanisms: vacancy repair via S-C bond cleavage[39,48], covalent grafting at sulfur vacancies[44,49-51], and radical dimerization yielding physisorbed disulfides[52-54]. While these thiol-based mechanisms provide a basic framework, they may not fully account for the extraordinary optical enhancement achieved with superacids. The distinct behaviors of thiols and superacids originate from their fundamentally different chemical interactions with TMD surfaces, namely physisorption versus chemisorption, and electron donation versus protonation. In particular, the role of dissociated protons (H⁺) in the PL enhancement of acid-treated TMDs remains actively debated and has not been systematically reviewed to date[55]. Addressing this gap through a focused analysis is therefore essential to clarify the underlying chemical and physical processes involved in acid-mediated defect passivation.

Alongside mechanistic investigations, recent studies have also identified a variety of acid families capable of modulating the optoelectronic properties of TMDs (Fig. 1b). Despite these advances, existing reviews have largely treated optical and electrical properties in isolation. Samori *et al.* provided a comprehensive survey of molecular chemistry approaches (thiols, polymers, self-assembled monolayers, etc.), yet their broad scope did not focus on acids or the interplay between optical and electrical performance[11]. Rao *et al.* reviewed chemical passivation strategies primarily for PL enhancement, with limited discussion of electrical transport degradation[27]. Kiriya and Lien focused on TFSI superacid alone, without extending to other acid families or addressing FET performance[55]. Notably, none of these works have systematically dissected the origin of the optical-electrical trade-off or established a comparative framework to rationalize why different acids produce divergent optical and electronic responses.

In response to these open questions, this review provides a comparative mechanistic analysis of acid-TMD interactions across three key fronts: the competing passivation and doping pathways and their historical evolution are first examined; the degradation of electrical transport is then rationalized through a sulfur vacancy-mediated hopping model; mitigation strategies and the emerging role of Lewis acids in decoupling optical and electronic performance are finally critically assessed.

2 Fundamental Defects and Characterization in TMDs

2.1 Defect Types and Electronic Signatures

Defect formation in monolayer TMDs is fundamentally

governed by the sulfur chemical potential ($\Delta\mu_S$), which dictates the dominant defect pathway and reconciles discrepancies across preparation methods[56-59]. This parameter directly determines the stability ordering of zero-dimensional point defects, with representative structures illustrated in Fig. 2a-2o. Of these, the mono-sulfur vacancy (V_S) stands out as the most common intrinsic defect in ME and CVD-grown monolayer TMDs, owing to its relatively low formation energy (E_{form})[24,59,60]. Density functional theory (DFT) calculations show that the E_{form} of V_S in monolayer MoS₂ is highly sensitive to $\Delta\mu_S$, ranging from 2.57 eV under S-rich conditions (0 K) to 1.56 eV under Mo-rich conditions at typical growth temperatures (~1000 K)[56,61,62]. This wide variation reflects differences in exchange-correlation functionals, supercell size, electrostatic correction schemes, and chemical potential references, which should be carefully specified when comparing defect energetics across studies.

Notably, sulfur adatoms (S_{ad} (B-site)) exhibit the lowest formation energy among all defects (~0.99 eV), and have been observed via scanning transmission electron microscopy (STEM), though their high mobility makes them difficult to routinely capture[63,64]. In contrast, the di-sulfur vacancy (V_{S2}) exhibits the second-highest concentration among sulfur-related defects, as its E_{form} (~4.14-5.15 eV) is approximately twice that of V_S[57,61]. Although V_S is often considered the reference defect, it is not invariably the most abundant under all growth conditions. When $\Delta\mu_S$ is sufficiently low (Mo-rich conditions), antisite defects such as Mo_S and MoS₂ can compete with or even surpass V_S in concentration, with E_{form} as low as ~1.9 eV, explaining their dominance in physical vapour deposition and pulsed laser deposition samples[57, 65]. By contrast, the E_{form} of metal-vacancy-related defects (V_{Mo}, V_{MoS3}, and V_{MoS6}) and Mo adatoms are relatively high (>5 eV), rendering them thermodynamically unfavorable and thus rarely observed[62].

Beyond point defects, intrinsic one-dimensional defects in monolayer TMDs mainly include grain boundaries (GBs) and edges[66]. In CVD-grown polycrystalline films, GBs arise from the coalescence of misoriented crystalline grains and are classified according to their constituent ring structures. Specifically, tilt boundaries consisting of 5|7, 6|8, or 4|6 ring arrays, and mirror twin boundaries composed of 4|4 or 4|8 rings[67]. Notably, GBs exhibit distinct electronic and optical behaviors depending on their atomic configurations: mirror twin boundaries (Mo-rich) induce n-type doping and PL quenching due to enhanced trion formation, whereas tilt boundaries (S-rich) introduce deep-level trap states and PL enhancement via exciton-trion conversion[68]. By contrast, edges are categorized as zigzag (Mo- or S-terminated) or armchair types[66]. Zigzag edges exhibit metallic character, whereas armchair edges remain semiconducting. Notably, edges with 50% S vacancies can inherit the metallic nature through bond reconstruction, making them critical catalytic sites.

Among these, V_S are the most common point defects in ME/CVD TMDs and primary targets for defect engineering. DFT calculations on monolayer MoS₂ reveal that a V_S introduces unoccupied deep levels located ~0.46 eV below the conduction band minimum (CBM). These levels act as compensation centers in n-type TMDs by trapping free electrons and pinning the Fermi level (E_F), with the associated electron density spatially confined within ~3 Å of the vacancy

(Fig. 2p and 2q)[69]. Direct experimental visualization via scanning tunneling spectroscopy (STS) further corroborates this picture, showing a sharp peak in the local density of states at the vacancy site, which decays exponentially over a few angstroms (Fig. 2r)[70].

These observations collectively establish the V_S as the predominant intrinsic defect in monolayer TMDs, owing to its low formation energy across a wide range of chemical potentials. Its deep donor level and strong wavefunction localization, both theoretically predicted and experimentally visualized, introduce discrete gap states that localize electrons below the mobility edge and drive a crossover from band-like to hopping transport at low carrier densities. This hopping mechanism, which governs the charge transport properties of TMDs in the low-density regime, will be elaborated in Section 5.2.

2.2 Characterization Techniques for Defects

STEM is the most common tool for directly visualizing individual defects. Among these techniques, high-angle annular dark-field STEM (HAADF-STEM) provides image intensity proportional to the square of the atomic number (Z^2), enabling the differentiation and identification of different atomic species. As shown in Fig. 3a, only V_S and V_{S_2} defects are observed in CVD-grown monolayer MoS_2 , appearing as regions of reduced contrast[71]. By statistically analyzing at least 10 ADF-STEM images, Kim *et al.* quantified the densities of V_S and V_{S_2} as $\sim 8.57 \times 10^{13}$ and $\sim 0.89 \times 10^{13} \text{ cm}^{-2}$, respectively[72]. Scanning tunneling microscopy/spectroscopy (STM/STS) provides complementary atomic-scale imaging and electronic characterization of defects in MoS_2 . The apparent defect morphology in Fig. 3b is strongly bias-dependent: V_S appears as depressions under both bias polarities, whereas V_{Mo} appears as depressions under positive bias but exhibits three-lobed protrusions under negative bias, which serves as a key fingerprint for defect identification[73]. Quantitative analysis reveals that the density of V_S is approximately 8.5 times that of V_{Mo} , consistent with the E_{form} calculations[73]. Separately, STS resolves a V_S -induced mid-gap state at $\sim 0.65 \text{ eV}$ below the CBM, in agreement with DFT calculations[74]. Nevertheless, STEM and STM have limited imaging areas, making it difficult to quantify low-density defects over macroscopic sample regions with statistical significance. Moreover, STEM necessitates the use of relatively low acceleration voltages during measurements to avoid introducing additional defects, whereas STM is a time-consuming technique that is most commonly operated under ultrahigh vacuum conditions.

To address these limitations, Rosenberger and co-workers have successively proposed conductive atomic force microscopy (CAFM) and lateral force microscopy (LFM) as two techniques enabling rapid, nondestructive characterization and quantitative analysis of defects[75-78]. As shown in Fig. 3c, CAFM offers multiscale imaging capability on WSe_2 flakes ranging from nanometer to micrometer scales[76]. Additionally, the team assigned the bright CAFM spots to V_S for the first time, consistent with the enhanced local conductivity expected from V_S -induced mid-gap states[75]. This finding further revealed a macroscopic inhomogeneity in defect density: within a single WS_2 triangle, the edge density is approximately one order of magnitude higher than near the center. In contrast to CAFM and STM, which require a conductive pathway, LFM is a purely

mechanical technique that operates under ambient conditions and is sensitive only to the topmost atomic layer. As shown in Fig. 3d, the effectiveness of LFM is validated by the direct coincidence of LFM-detected defects (green circles) with the more conductive (dark) defects observed by CAFM on the same region of bulk $MoSe_2$ [77]. Furthermore, LFM has been demonstrated as a versatile tool for direct defect characterization on insulating growth substrates, *in situ* device channels, and even suspended or polymer-supported monolayers[78]. Notably, it achieves a detection limit below $2 \times 10^{13} \text{ cm}^{-2}$, a regime where conventional Raman spectroscopy loses sensitivity.

Beyond instrumental advances, machine learning (ML) has recently emerged as a powerful tool for addressing the bottlenecks of traditional analysis, particularly its largely qualitative nature, reliance on pre-established physical models, and poor scalability. For example, Kalinin *et al.* applied a fully convolutional network (FCN) to perform pixel-wise classification of atomically resolved STEM images, extracting coordinates of all atomic species[79]. These coordinates were subsequently used in a weakly supervised framework to identify defect types beyond those in the initial training set. Following this direction, Kim *et al.* adopted a U-Net model based on the FCN algorithm, combined with a convolutional neural networks-based denoiser[80]. This model enables high-throughput quantification of five distinct atomic site types, reducing analysis time from approximately one hour to seconds per image. Extending deep learning-based analysis to STM, Smalley *et al.* trained an ensemble of U-Net models to automatically detect atomic-scale defects in WSe_2 STM images, extracting their coordinates and reducing analysis time from 30 min per image to seconds[81]. The same models also demonstrated generalization to CAFM. Yet, image-driven deep learning models remain constrained by fixed-size patches and struggle with complex, non-periodic structures such as aggregated vacancy lines with flexible lattice distortion. To overcome this limitation, Wang *et al.* introduced a few-shot learning framework based on an equivariant graph neural network, which represents atomic structures as graphs of nodes (atoms) and edges (bonds)[82]. This approach enables flexible and robust identification of diverse configurations, including vacancies, GBs, and stacking faults, with three orders of magnitude fewer parameters than image-based models.

Overall, while STEM and STM remain indispensable for defect characterization, their limited throughput and imaging areas have prompted the development of complementary techniques such as CAFM, LFM, and ML-assisted analysis. Deep learning enables automated, efficient defect detection across multiple microscopy modalities, and emerging graph neural networks further overcome the limitations of image-driven models by flexibly encoding complex atomic configurations. This offers a powerful path forward for comprehensive defect exploration.

3 Acid-Mediated Optical Property Modulation

3.1 Advances in Acid-Enhanced PL

TFSI was initially employed as a p-type chemical dopant for carbon nanotubes and graphene, owing to its strong electron-withdrawing groups[83,84]. Its high transmittance, environmental stability, and strong electron-withdrawing ability make it an ideal dopant for graphene anodes in organic

optoelectronics[85,86]. The potential of TFSI for TMD passivation was further demonstrated in 2015, when Javey *et al.* reported a 190-fold PL enhancement in ME monolayer MoS₂, achieving near-unity PL QY at low excitation power (Fig. 4a)[14]. This enhancement was accompanied by a significant prolongation of the PL lifetime from 0.3 ns to 10.8 ns. For PL behavior under high excitation power, readers are referred to the recent work by Teng *et al.*[87]. The following year, Javey *et al.* further reported that TFSI served as an effective passivator for sulfur-based TMDs (MoS₂, WS₂), but was considerably less effective for their selenium-based counterparts (MoSe₂, WSe₂)[45]. The STM study revealed that this contrasting behavior originated from the distinct defect types (acceptor or donor) in these materials. As shown in Fig. 4b, the donor impurities (red circles) in sulfur-based TMDs correspond to sulfur vacancies, which promote passivation reactions with TFSI[45]. Conversely, a high density of acceptor impurities (dark circles) adsorbed on the surface of selenium-based TMDs do not react with TFSI, instead leading to deeper doping[88].

Beyond exfoliated flakes, the versatility of TFSI passivation was extended to CVD-grown monolayers. In the same year, Javey *et al.* demonstrated that the same acid treatment was also effective for CVD-grown monolayer MoS₂[89]. Owing to inherently higher sulfur vacancy concentrations, as-grown CVD samples exhibited a substantially lower PL QY (~0.1%) than exfoliated samples (~0.6%)[14,57,89]. Following strain release by wet-etching transfer, subsequent TFSI treatment boosted the PL QY of MoS₂ to ~30% (Fig. 4c)[89]. Despite these advances, the ambient stability of TFSI-treated samples remained a concern. In 2017, Javey *et al.* addressed this issue by encapsulating monolayer MoS₂ and WS₂ with an amorphous fluoropolymer (CYTOP) prior to TFSI treatment, thereby protecting the superacid-induced modification from deactivation by water or organic solvents (top panel of Fig. 4d)[90]. This approach allowed TFSI to diffuse through the encapsulation layer, achieving near-unity PL QYs that remained stable against subsequent rinsing. Following patterning, the CYTOP-encapsulated monolayer MoS₂ maintained a high and uniform PL QY, paving the way for the fabrication of high-performance 2D optoelectronic devices (bottom panel of Fig. 4d)[90].

Inspired by this strategy, extensive investigations into acid molecules for modulating PL emission have been undertaken. In 2015, Su *et al.* achieved an ~8-fold PL enhancement in monolayer MoS₂ by exfoliating it onto an H₂O₂-precleaned SiO₂/Si substrate (Fig. 4e)[91]. Introducing a spin-coated toluene layer on top of the treated sample further amplified the enhancement to ~27-fold, forming a toluene/MoS₂/H₂O₂ sandwich structure. The substantial increase upon toluene capping suggested that the chemical environment at the TMD interface, rather than purely the acid molecule itself, plays a significant role in modulating the PL response. In 2016, Shi *et al.* revealed that among hydrogen halide vapors, only HBr was effective for monolayer MoSe₂, despite similar acidities of HCl, HBr, and HI (Fig. 4f)[92]. HBr treatment not only imposed p-type doping but also removed SeO₂ impurities and partially repaired Se vacancies, establishing a mechanism beyond mere proton donation. In 2017, Zhang *et al.* demonstrated that poly(4-styrenesulfonate) (PSS), which is the acidic polyelectrolyte component in poly(3,4-ethylenedioxythiophene):poly(4-

styrenesulfonate) (PEDOT:PSS), was responsible for an ~2-fold PL enhancement in monolayer MoS₂ (Fig. 4g)[64]. They provided the first direct STEM evidence for vacancy repair, establishing the sulfur vacancy self-healing (SVSH) mechanism that would later inform the interpretation of superacid effects. In 2018, Kiriya *et al.* compared TFSI and H₂SO₄ treatments on monolayer MoS₂ in aqueous environment and found that both acids yielded comparable PL enhancement (~4–8 fold) under identical deprotonation conditions[93]. This result was pivotal because it demonstrated that the enhancement does not require the TFSI anion, a finding that challenged the emerging anion-repair models and redirected attention to the role of H⁺. Between 2019 and 2021, oleic acid (OA), a long-chain carboxylic acid, emerged as a distinct passivating agent (PA) for monolayer TMDs[15,94,95]. Unlike TFSI, OA is a weak acid incapable of effective proton donation. Instead, it acts as a Lewis base, coordinating to chalcogen vacancies through its electron-rich carboxylate group (Fig. 4h, left)[15]. This ligand passivation mechanism, analogous to that established in colloidal quantum dots, significantly enhances PL emission (Fig. 4h, right) while improving electrical transport[15]. Such behavior contrasts with the proton-donation paradigm of superacid treatments (see Section 5.1).

Since 2021, studies have extended to TFSI analogues. As depicted in Fig. 4i, the superacid trifluoromethanesulfonic acid (CF₃SO₃H, TFMS) shares the trifluoromethanesulfonyl moiety with TFSI[28]. Xu *et al.* demonstrated that TFMS treatment yields substantial PL enhancement in monolayer MoS₂ and WS₂, with PL QYs reaching 14.1% and 56.7%, respectively, which were among the highest values reported for CVD-grown TMDs at the time. Beyond these results, they further identified the respective roles of [CF₃SO₃]⁻ and H⁺: the anion repairs sulfur vacancies, while both contribute to p-type doping, synergistically enhancing PL emission. In addition to TFSI (abbreviated as TFSA in their work), Murphy *et al.* reported five other analogues capable of enhancing PL in monolayer/few-layer MoS₂ or monolayer WS₂[96]. These include trifluoromethanesulfonamide (CF₃SO₂NH₂), bistrifluoroacetamide ((CF₃CO)₂NH, BTFA), 2,2,2-trifluoroacetamide (CF₃CONH₂, TFA), 2,2,2-trifluoroethylamine (CF₃CH₂NH₂, TFEA), and methanesulfonamide (CH₃SO₂NH₂, MSA). To avoid confusion with TFMS (trifluoromethanesulfonic acid) defined earlier in this review, we refer to CF₃SO₂NH₂ as TfNH₂ (originally abbreviated as TFMS in Ref. [96]). All five analogues enhanced PL, with particularly notable enhancement from TFEA. Although TFEA is completely non-acidic and devoid of both sulfonyl and carbonyl groups, it still considerably enhanced the PL of all three TMDs examined (Fig. 4j)[96]. This finding challenges the prevailing mechanistic models: the absence of a clear correlation between PL enhancement and any specific chemical functionality (acidity, sulfonyl groups, or sulfur content) suggests that the proposed proton-passivation and anion-repair mechanisms may not be universal. The functional groups responsible for these effects therefore remain unclear and will be discussed in detail in Section 4.1.

Taken together, the landscape of acid-enhanced PL in TMDs has evolved from TFSI-induced near-unity QY to encompass superacids (TFSI, TFMS), strong acids (HBr, H₂SO₄), weak acids (OA), polymer acids (PSS), and less acidic

or non-acidic analogues (TfNH₂, BTFA, TFA, TFEA, MSA), alongside oxidizing agents such as H₂O₂. Whether the enhancement originates from molecular structure, H⁺ donation, anion-mediated passivation, or charge-transfer doping remains an open question, setting the stage for the mechanistic debates examined in Section 4.

3.2 Estimation of PL QY

For quantitative assessment of material quality, PL QY is a more reliable metric than the PL enhancement factor, as it provides an absolute measure of emission efficiency independent of excitation conditions[97]. Direct measurement of PL QY via integrating sphere spectroscopy is challenging for TMDs due to their inherently weak luminescence. Hence, two indirect approaches are commonly employed.

3.2.1 Steady-state and Transient PL Analysis

PL QY is defined as the ratio of emitted to absorbed photons[98]. To quantitatively determine QY, Javey *et al.* derived it from the external quantum efficiency (EQE) by correcting for the photon escape fraction from the emissive layer (approximated as $1/4n^2$, where n is the refractive index of the medium)[14]. They then developed a kinetic model to analyze the recombination pathways governing QY, based on both steady-state and time-resolved PL measurements. The model distinguishes three competing processes: radiative recombination (rate $\tau_r^{-1}\langle N \rangle$), defect-mediated recombination ($B_{nr}n^2$), and biexciton-induced nonradiative recombination ($C_{bx}\langle N \rangle^2$). The steady-state QY is expressed as[14]:

$$QY = \tau_r^{-1}\langle N \rangle / (\tau_r^{-1}\langle N \rangle + B_{nr}n^2 + C_{bx}\langle N \rangle^2) \quad (1)$$

where τ_r is the exciton radiative lifetime, $\langle N \rangle$ is the exciton concentration, n is the carrier concentration, B_{nr} is the defect-mediated recombination rate, and C_{bx} is the biexciton recombination coefficient. The model assumes that excitons formed from free carriers are consumed either radiatively or via biexciton annihilation, while defects act as additional nonradiative centers. By analyzing the single-exponential decay kinetics of the TFISI-treated sample at the lowest pump fluence, the radiative lifetime $\tau_r = 10.8$ ns was directly obtained. With this τ_r fixed and assuming $B_{nr} \approx 0$ for the TFISI-treated sample, the $C_{bx} = 2.8$ cm² s⁻¹ was extracted by fitting the steady-state QY curve. Keeping C_{bx} constant, further fitting of the experimental data from the as-exfoliated sample, yielded the $B_{nr} = 1.5 \times 10^6$ cm² s⁻¹. With these parameters, the model (dashed line in Fig. 5a) showed reasonable agreement with the steady-state measurements for the TFISI-treated sample[14].

This model has since been applied across multiple material systems, revealing a recurring trend: TFISI treatment effectively eliminates B_{nr} in exfoliated MoS₂, WS₂ (Fig. 5b), and CYTOP-MoS₂ (Fig. 5c), yielding near-unity QY[45,90], while CVD-grown MoS₂ retains a residual B_{nr} of 2×10^4 cm² s⁻¹, limiting QY to ~30% (Fig. 5d)[89]. Substrate decoupling via solvent evaporation reduces B_{nr} in CVD-grown WSe₂, achieving a QY of ~60%[29]. Altogether, these analyses establish B_{nr} as the primary figure of merit for defect density, underscoring the material- and treatment-dependent nature of nonradiative suppression.

3.2.2 Standard Reference Dye

In this method, the QY of a TMD is determined relative to

a reference standard with known QY, such as a fluorescent organic dye. The evolution of reference materials has progressed through several stages. Rhodamine 6G (C₂₈H₃₁ClN₂O₃, R6G) in dilute methanol solution exhibits near-unity PL QY and was initially used as a thin-film reference after spin-coating[23,24,99-101]. However, R6G fluorescence is severely quenched in the solid state due to molecular aggregation. To overcome this limitation, Matsuda *et al.* developed a 3-borylbithiophene derivative (C₅₈H₄₉BN₂S₄) embedded in a poly(methyl methacrylate) (PMMA) matrix, achieving a solid-state PL QY of ~36% (Fig. 5e(i))[102]. Using this material as a reference, the PL QY of ME monolayer TMDs, including MoS₂, MoSe₂, WS₂, and WSe₂, was determined to be on the order of 10⁻² to 10⁻³[102,103]. In contrast, ReS₂ exhibited a consistently low PL QY on the order of 10⁻⁴, regardless of layer thickness from monolayer to seven layers[104]. Subsequently, Kim *et al.* refined this approach by embedding R6G in PMMA, yielding spatially uniform reference films with tunable QY depending on film thickness and dye concentration (Fig. 5f(i-iii))[105]. The QY of TMDs (QY_{TMDs}) is calculated as[105]:

$$QY_{TMDs} = QY_{Ref} \times (I_{TMDs}/A_{TMDs}) / (I_{Ref}/A_{Ref}) \times F_{sp} \quad (2)$$

where QY_{Ref} is the QY of the reference sample measured with an integrating sphere; I_{TMDs} and I_{Ref} are the PL intensities of the TMD and the reference samples, respectively; A_{TMDs} and A_{Ref} are their corresponding absorptions; and F_{sp} is a calibration factor that corrects for the wavelength-dependent instrument response of the microscope and spectrometer. Using this approach, the QY of mechanically exfoliated monolayer MoSe₂, WS₂, and WSe₂ was determined to be on the order of 10⁻² to 10⁻³. This method has been widely adopted to assess PL QY enhancements achieved through various strategies, including chemical treatments (e.g. TFISI, TFMS) and substrate engineering[28,106-108]. A key consideration regarding the reference dye is spectral matching: it should be selected based on its emission wavelength relative to the target TMD. The 3-borylbithiophene derivative emits at ~640 nm, whereas R6G peaks at ~553 nm (Fig. 5e(ii) and Fig. 5f(iv))[102,105]; closer spectral overlap minimizes systematic errors.

Collectively, two indirect methods are used for PL QY estimation: the former extracts radiative and nonradiative recombination rates; the latter compares PL intensity and absorption against calibrated dye-polymer films (R6G or 3-borylbithiophene). While both have enabled valuable cross-study comparisons, the extracted QY values can vary by nearly an order of magnitude depending on excitation, substrate, and calibration, which underscores the need for standardized reporting protocols.

4 Mechanism of Optical Property Modulation by Acid

4.1 The Competing Mechanisms

As discussed in Section 3.1, acid treatment effectively suppresses multiple nonradiative loss channels in TMDs, including defect-mediated nonradiative recombination, trion formation, and exciton-exciton annihilation, thereby significantly enhancing PL QY[95]. However, the precise microscopic mechanism remains debated. TFISI, the most extensively studied superacid in this context, is generally believed to function through a combination of defect passivation

and p-type doping (Fig. 6). Since TFSI dissociates completely into protons (H^+) and bulky anions ($[(CF_3SO_2)_2N]^-$) in solution, a critical question arises: which species, or both, is responsible for the observed enhancement? We address this question by examining the roles of protons and anions in the following subsections.

4.1.1 The Role of H^+ in Defect Passivation

To elucidate the role of protons in defect passivation, Kiriya *et al.* (2018) systematically compared the PL response of monolayer MoS_2 treated with Brønsted acids (TFSI and H_2SO_4) [93]. They found that the efficacy of TFSI in enhancing PL was strongly influenced by solvent acidity: 1,2-dichloroethane (DCE), the most acidic solvent among those tested, yielded the strongest PL enhancement (Fig. 7a) [93]. When TFSI and H_2SO_4 were compared at identical proton concentrations in H_2O , comparable PL enhancement (4–8 fold) was observed, suggesting that the anion plays a secondary role. To isolate the cation effect, a non-protonated salt (Li_2SO_4) was introduced as a control. Unlike H_2SO_4 , it did not significantly alter the PL emission (Fig. 7b) [93]. Given that H_2SO_4 and Li_2SO_4 differ only by the substitution of protons with lithium ions, this confirmed that H^+ is essential for PL enhancement. These findings established a foundation for subsequent pH-dependent PL studies and pointed toward a possible mechanism involving proton-mediated suppression of non-radiative recombination, rather than mere cationic surface adsorption [109–111].

A complementary theoretical perspective was provided by Robertson *et al.* (2018), who used DFT calculations to explore the atomistic origin of proton-induced passivation [112]. They first ruled out direct passivation by TFSI anions, noting that these large molecules are only physisorbed on the MoS_2 surface. Instead, they modeled the interaction of one, two, or three hydrogen atoms with a sulfur vacancy (see schematic illustration in Fig. 7c) [112]. Their key finding was that mid-gap trap states are fully eliminated only when three hydrogen atoms bonded symmetrically at the vacancy in a -1 charge state (Fig. 7d) [112]. In this configuration, the C_{3v} symmetry maximizes the Mo–H bonding–antibonding splitting of the e states, pushing them out of the bandgap. However, the $3H^-$ configuration carries a formation energy slightly higher than that of the H^+ and $2H^0$ configurations, and as previously noted by Javey *et al.*, protonation of the three dangling bonds at the sulfur vacancy is energetically unfavorable [14], raising questions about its practical feasibility.

Given the kinetic infeasibility of direct defect protonation, Javey *et al.* proposed an alternative mechanism in which H^+ participates in a two-step process: it initially forms a thiol-like bond with a sulfur adatom on the surface, followed by reductive elimination at the vacancy to yield a stable S–Mo bond and released hydrogen [14]. This hypothesis was later validated by Zhang *et al.* (2017), who demonstrated a SVSH mechanism using the nonoxidizing acid PSS, as illustrated schematically in Fig. 7e [64]. STEM imaging directly confirmed the presence of sulfur adatoms on as-grown MoS_2 (Fig. 7f, left), which serve as the sulfur source for vacancy repair [64]. After PSS treatment, STEM revealed restored lattice symmetry (Fig. 7f, right) [64], and X-ray photoelectron spectroscopy (XPS) data showed an increase in the S/Mo ratio from ~ 1.67 to ~ 1.86 , confirming

vacancy filling. This mechanism relies on the initial presence of sulfur adatoms, but it is unclear whether passivation can occur in samples lacking such surface clusters.

The mechanistic role of the ambient environment in PL enhancement was further elucidated through a series of studies, which progressively extended the understanding of H^+ -mediated defect passivation beyond the simple protonation model. Kiriya *et al.* (2020) demonstrated that ultraviolet (UV) irradiation following TFSI treatment dramatically enhance PL emission of monolayer MoS_2 , whereas UV irradiation alone produced no significant effect, pointing to the necessity of both the superacid and photoactivation [113]. In their proposed scheme (Fig. 7g), photogenerated carriers react with H_2O to generate reactive species (O_2 , H_2O_2 , and OH radicals), which passivate defect sites in the acidic environment provided by the superacid [113]. This H_2O -dependent mechanism was further supported by control experiments: PL enhancement degraded under vacuum or prolonged air exposure (Fig. 7h), and TFSI treatment in an inert N_2 environment failed to produce enhancement even with subsequent UV photoactivation (Fig. 7i) [113]. These observations were attributed to desorption of hygroscopic TFSI molecules and associated H_2O [113].

The mechanistic picture was reinforced by subsequent morphological and theoretical evidence from the same group. Atomic force microscopy (AFM) imaging revealed a punctate TFSI/ H_2O film selectively formed on the UV-treated MoS_2 surface, and NaCl immersion experiments confirmed that UV irradiation significantly enhanced surface hydrophilicity [114]. DFT calculations further showed that H_2O molecules bind most favorably to OH-modified defect sites on the MoS_2 surface (Fig. 7j) [114]. This explains why UV-induced OH modification promotes co-adsorption of H_2O and TFSI, thereby facilitating subsequent proton-mediated defect passivation. Based on this mechanism, PMMA encapsulation stabilized the PL enhancement of superacid-treated MoS_2 for over 30 days in ambient air. The role of UV-induced surface modification was further corroborated in bilayer MoS_2 , where the UV-TFSI process yielded a ~ 700 -fold PL enhancement only in twisted bilayers. Such bilayers possess weakened interlayer coupling, which allows UV-induced separation into a monolayer-like state prior to TFSI passivation [115]. This photo-mediated mechanism was subsequently confirmed by Knobel *et al.* (2024) using 532 nm laser activation [116].

4.1.2 The Role of H^+ or Anions in P-type Doping

H^+ -mediated charge transfer doping has also been proposed as a mechanism for PL enhancement, distinct from the defect passivation discussed above. Cao *et al.* (2017) attributed this effect to the intercalation of H^+ at the monolayer–substrate interface, rather than adsorption on the top surface (Fig. 8a(i)) [117]. This assignment was supported by AFM measurements showing a height increase from ~ 0.70 nm to ~ 1.1 nm after TFSI treatment (Fig. 8a(ii)), consistent with layer separation induced by cation intercalation [117]. To differentiate these two scenarios, a suspended-membrane experiment was performed: after TFSI treatment, the substrate-supported region exhibited substantial PL enhancement, whereas the suspended area showed only a mild increase (Fig. 8a(iii)) [117]. If top-surface adsorption were the dominant mechanism, one would expect a spatially uniform enhancement. The observed contrast

thus indicates an interfacial origin. This intercalation-induced separation is believed to mitigate substrate-mediated non-radiative recombination, thereby contributing to PL enhancement alongside the doping effect.

Further mechanistic insight was gained from control experiments using cation-TFSI salts with varying ionic radii (Li^+ , Na^+ , K^+). Significant PL enhancement occurred exclusively with Li^+ , suggesting that smaller cations are more readily intercalated. DFT calculations confirmed p-type doping via negative charge transfer (ΔQ) for both H^+ and Li^+ adsorbates on MoS_2 (Fig. 8b), establishing that the cation itself serves as the electron acceptor[117]. This p-type doping is expected to enhance PL in intrinsically n-type monolayers (MoS_2 , MoSe_2 , WS_2) by promoting neutral exciton emission, while suppressing it in p-type WSe_2 .

Critically, this assignment is corroborated by an independent, purely electronic approach. Javey *et al.* (2019) demonstrated that electrostatic gating can reproduce the similar PL enhancement without any chemical treatment: applying a negative bias to deplete background electrons in n-type MoS_2 suppresses trion formation and promotes neutral exciton recombination (Fig. 8c)[118]. The convergence of chemical and electrostatic carrier-density modulation underscores the exciton-trion equilibrium as the central determinant of PL efficiency.

Further mechanistic refinement came from Rao *et al.* (2021), who systematically compared a series of cation donors and molecular p-dopants to distinguish the roles of cation versus anion (Fig. 8d)[119]. Among TFSI-based salts, Li-TFSI produced twice the PL enhancement of H-TFSI (Fig. 8e)[119]. Raman spectroscopy provided direct evidence for cation adsorption: both H-TFSI and Li-TFSI treatments activated a previously silent A_{2u} mode at $\sim 468\text{ cm}^{-1}$, indicating lattice perturbation by adsorbed cations. DFT calculations further showed that Li adsorbs much more favorably at the abundant surface sites than H , leading to substantially higher Li^+ coverage on the MoS_2 surface and thus more effective suppression of trion formation and subgap trap states (Fig. 8f)[119]. This cation-adsorption mechanism explains the superior performance of Li-TFSI over H-TFSI . The anion also plays a critical role: triflate (Tf) anions coordinate with surface Mo/W sites and act as n-dopant, promoting trion formation and counteracting the cation benefit, which is consistent with the minimal improvement from Li-Tf and PL quenching from Na-Tf . By contrast, the bulky, non-coordinating TFSI anion with two strong electron-withdrawing groups ($-\text{CF}_3\text{SO}_2$) suppresses such competitive n-doping. Together, these results establish two selection rules for effective PL enhancement: stable cation adsorption and a non-coordinating counter anion. The superior performance of Li-TFSI over H-TFSI will be further addressed in Section 4.2.2 through transient PL dynamics.

4.1.3 Synergistic Effect of H^+ and Anions

In contrast to models that attribute PL enhancement solely to H^+ or assume anions are merely non-coordinating spectators, an alternative framework proposes a synergistic effect between the two species. This perspective is supported by complementary studies that collectively point toward a unified picture of chemical passivation in monolayer TMDs, with atomic-scale evidence reported shortly thereafter.

Kim *et al.* (2017) investigated the effects of TFSI and

benzyl viologen (BV) on CVD-grown monolayer WS_2 and found that these molecules produced opposite PL responses and doping characteristics: p-type for TFSI and n-type for BV[120]. Spatially resolved PL mapping under TFSI treatment (Fig. 9a) revealed that the enhancement was markedly stronger at the edge region than in the inner region of the triangular WS_2 grains[120]. Through spectral decomposition of exciton contributions, the authors attributed this heterogeneous behavior to a dual mechanism: p-type doping arising from the electron-withdrawing fluorine atoms in TFSI extended across the entire grain. Meanwhile, pronounced PL enhancement, particularly at the edges originated from defect passivation, presumably targeting sulfur vacancies. Although the precise chemical nature of this passivation remained unresolved, the spatial correlation with edge sites suggested the involvement of anions as PAs.

In parallel, Zhu *et al.* provided mechanistic insight using an ionic liquid (IL) on monolayer MoS_2 [121]. Contacting the sample with an IL and electrically grounding it allows electron extraction from the intrinsically n-type material. This process yielded PL enhancement comparable to that from TFSI treatment (Fig. 9b)[121]. The proposed mechanism involves reduction of H^+ from the IL to H_2 by the extracted electrons, which release TFSI anions that electrostatically screen and passivate defects such as sulfur vacancies. This IL-induced enhancement was reversible and correlated positively with initial defect density, implying the coexistence of charged and neutral nonradiative recombination centers.

From a different perspective centered on anion composition, Kim *et al.* (2018) employed DFT calculations to demonstrate that formation of a $\text{CF}_3\text{-SO}_2\text{-N-CF}_3$ species and an SO_2 molecule is energetically favorable by 0.73 eV, suggesting that released TFSI anions may readily dissociate[72]. STEM analysis quantitatively established that the dominant defects in pristine MoS_2 were V_S and V_{S_2} . No obvious sulfur adatoms were detected in the pristine samples, ruling out the possibility that passivation merely involves mobilization of pre-existing surface species. After TFSI treatment, the sulfur vacancy concentration decreased dramatically, with $\sim 90\%$ of total vacancies repaired. Based on these observations, the authors concluded that the passivating sulfur atoms originated from the TFSI anions, a mechanism further corroborated by DFT calculations. These calculations revealed that reactive SO_2 molecules dissociated from TFSI can be reduced at sulfur vacancy sites, depositing S atoms that form strong S-Mo bonds while releasing O_2 . The overall repair process is exothermic, with an exothermicity of $\sim 0.34\text{ eV}$ (Fig. 9c)[72].

This repair mechanism was also observed with other superacids. Xu *et al.* (2021) demonstrated that TFMS, which shares comparably high acidity with TFSI, significantly boosted the PL QY of monolayer MoS_2 and WS_2 when treated in aqueous solution[28]. STEM analysis confirmed that TFMS treatment effectively repaired V_S in pristine MoS_2 , restoring the perfect configuration (Fig. 9d); no sulfur adatoms were present in the pristine sample[28]. DFT calculations further revealed that the most energetically favorable configuration involved the TFMS anion occupying the vacancy, which eliminated mid-gap trap states (Fig. 9e(i-iv))[28]. In this configuration, the highly electronegative fluorine and oxygen atoms attract electrons near the defect sites (Fig. 9e(v,vi))[28]. Control experiments with $\text{CF}_3\text{SO}_3\text{K}$, which provides the same anion but lacks a proton,

produced only a modest ~ 20 -fold enhancement, whereas TFMS (containing H^+) yielded a ~ 200 -fold enhancement. This contrast suggested that vacancy repair is primarily mediated by the anion, while the pronounced p-type doping effect derives predominantly from H^+ .

Subsequent work by Murphy *et al.* (2022) systematically examined the generality of this mechanism by comparing a series of TFSI analogues on MoS_2 and WS_2 (molecular structures in Fig. 9f)[96]. Using the Gutmann–Beckett method to quantify Lewis acidity via acceptor numbers, they found that only TFSI exhibited superacidity, while the other analogues were markedly less acidic (Fig. 9g)[96]. Crucially, effective PL enhancement was achieved with analogues lacking sulfonyl groups, sulfur, or oxygen. For example, TFA and TFEA performed comparably to TFSI in several cases, despite possessing very low acidity (with TFEA being completely nonacidic) (Fig. 9h)[96]. These observations suggest that neither high acidity nor the presence of specific functional groups is essential for effective PL enhancement. The absence of a consistent chemical origin across these effective treatments suggests that the theoretically proposed defect passivation mechanism may not be universal, or at least requires more precise techniques for identification. To facilitate such a comparison and to provide an overview of the reported results, the key PL parameters and proposed mechanisms for each acid treatment are summarized in Table 1.

Overall, three competing mechanistic models have been proposed for superacid-induced PL enhancement: (i) H^+ -mediated passivation, (ii) cation-induced p-type doping, and (iii) synergistic H^+ /anion effects. Each is supported by distinct evidence: pH dependence, spatial mapping, and STEM/DFT, respectively. However, non-acidic analogues TFEA challenges all three models by producing significant PL enhancement without acidity or the proposed functional groups, suggesting the true mechanism may be system-dependent or multifactorial.

4.2 The Trap-Limited PL Dynamics

4.2.1 Low-Temperature Defect Luminescence

Defect-related luminescence becomes pronounced at low temperatures, giving rise to distinct low-energy PL peaks that serve as key signatures for probing defect states[122–125]. As shown in Fig. 10a(i), the localized exciton (X^L) in monolayer MoS_2 emerges prominently under low-temperature and low-excitation-power conditions but quenches completely above ~ 150 K[126]. The critical temperature varies across samples owing to differences in defect density and material type[127–130]. This temperature-dependent luminescence is well described by a three-state model (Fig. 10a(ii)): upon excitation, band-edge excitons are rapidly captured into trap states; below ~ 150 K, they decay radiatively to the ground state; above ~ 150 K, thermal energy enables detrapping to the band edge, followed by radiative recombination[126]. This thermally activated pathway accounts for the quenching of X^L emission at room temperature and explains the concurrent PL enhancement and prolonged lifetime in acid-treated samples.

However, Liu *et al.* (2020) reported a counterintuitive result[131]. As shown in Fig. 10b, the pristine MoS_2 monolayer at 8 K exhibits a broad peak comprising neutral excitons (X_A) and charged trions (X_T)[131]. After TFSI treatment, this peak blue-shifts and narrows, accompanied by the emergence of a

new low-energy peak (X_D) whose presence is reversible upon adsorption and removal. This observation is counterintuitive: the same treatment that eliminates nonradiative recombination at room temperature (thereby enhancing PL) simultaneously gives rise to a defect-related emission peak at cryogenic temperatures. To account for this, Liu *et al.* proposed a modified three-state model (Fig. 10c): at 8 K, trapped excitons in pristine MoS_2 decay predominantly via nonradiative pathways due to insufficient thermal energy for detrapping; after TFSI treatment, the suppression of nonradiative recombination promotes radiative recombination from trap states, enhancing X_D emission[131].

Using circularly polarized PL spectroscopy, Liu *et al.* further found that the valley polarization degree P remained nearly unchanged ($\sim 53\%$ before versus $\sim 54\%$ after TFSI treatment at 8 K)[131]. According to the conventional relation $P = 1/(1 + 2\tau/\tau_s)$, where τ is the exciton lifetime and τ_s is the valley depolarization time, the prolonged exciton lifetime after TFSI treatment would be expected to reduce P [132]. This counterintuitive absence of reduction was explained by the same three-state model: the prolonged lifetime is dominated by trapped excitons ($>95\%$), whereas the intrinsic band-edge exciton lifetime is not extended by the treatment. Valley depolarization is governed by band-edge exciton dynamics and thus remains unaffected[133]. This finding demonstrates that superacid treatment can simultaneously enhance PL efficiency and preserve valley polarization, which is a desirable combination for valleytronic applications. This counterintuitive modulation of exciton dynamics was further elucidated by transient spectroscopic studies, as detailed below.

4.2.2 Ultrafast Dynamics in Subgap Defect States

Beyond dramatically enhancing PL emission, acid treatment also substantially prolongs the fluorescence lifetime of TMDs at room temperature. This extended lifetime was initially attributed to the suppression of defect-mediated nonradiative recombination following TFSI treatment, which promotes band-edge exciton emission[14,45,89,90]. Subsequent studies using other acids, such as OA and TFMS, have reinforced this interpretation[15,28,94].

A critical conceptual distinction was made by Tisdale *et al.* (2017), who clarified that the ultralong lifetimes (several to tens of nanoseconds) observed after TFSI treatment are an artifact of trap-mediated dynamics, not an indication of enhanced intrinsic radiative recombination[133]. Using spectrally resolved transient PL spectroscopy, they showed that excitons spend $>95\%$ of their lifetime in trap states below the band edge, thereby obscuring the much shorter true radiative lifetime (tens to hundreds of picoseconds) at room temperature. This distinction reconciles the seemingly contradictory observations: TFSI treatment suppresses nonradiative recombination (shortening the true radiative lifetime), while the presence of residual trap states prolongs the apparent PL lifetime through trapping–detrapping processes.

Building on this framework, Rao *et al.* (2019) performed ultrafast pump–probe measurements to directly probe how TFSI modifies exciton dynamics[134]. As shown in Fig. 10d, both untreated and TFSI-treated monolayer MoS_2 exhibited two pronounced ground-state bleaching (GSB) signals corresponding to the A (~ 1.88 eV) and B (~ 2.03 eV) excitonic transitions[134].

Strikingly, an additional subgap defect-state bleach emerged at ~ 1.70 eV only in the TFSI-treated sample. Normalized kinetics revealed a critical insight: the decay of the A exciton GSB coincided precisely with the rise of the subgap defect bleach, directly confirming population transfer from band-edge A excitons to defect states (Fig. 10d, middle, inset)[134]. Even more compellingly, the TFSI-treated sample exhibited identical emission at 1.88 eV whether excited above the bandgap or resonantly via defect-state absorption at 1.70 eV (Fig. 10d, bottom)[134]. A key implication of this work is that TFSI primarily functions to lower the E_F rather than directly repairing sulfur vacancies, thereby rendering subgap defect states optically accessible while leaving their physical structure intact.

Rao *et al.* further developed a two-step passivation strategy combining a PA (such as a thiol or sulfide) with TFSI. This approach achieved significantly enhanced PL (~ 275 -fold), more than double that of TFSI alone, while simultaneously shortening the PL lifetime. The disappearance of the subgap feature at ~ 1.70 eV in pump-probe spectra (Fig. 10d, middle) confirms that the PA effectively eliminates the sulfur-vacancy-related subgap trap states, while TFSI lowers the E_F to suppress trion formation[134]. Thus, the two-step strategy separately addresses two distinct loss channels: defect trapping and excessive n-doping.

The same group further explored the role of cation donors in a subsequent study[119]. Time-resolved PL measurements revealed that Li-TFSI-treated MoS₂ exhibited a shorter average lifetime compared to H-TFSI-treated samples, and pump-probe spectroscopy confirmed the absence of subgap defect-state bleaching in Li-TFSI-treated samples, allowing excitons to recombine more efficiently via the radiative channel (Fig. 10e)[119]. These observations are consistent with the cation-adsorption mechanism discussed in Section 4.1.2. Conversely, Knobel *et al.* (2024) further demonstrated that under continuous light exposure following TFSI treatment, the increase in PL intensity is accompanied by a corresponding rise in PL lifetime, consistent with the suppression of nonradiative pathways (Fig. 10f)[116].

Taken together, it is now well established that acid treatment alters exciton dynamics by modifying defect-state distribution and occupancy. Different treatments can extend the apparent PL lifetime (by suppressing nonradiative recombination) or shorten the true radiative lifetime (by effective passivation). These observations are not contradictory but rather reflect whether the apparent or true radiative pathway is probed. Nevertheless, the precise role of TFSI, whether it directly repairs defects or primarily modulates the Fermi level, remains an open question.

5 Acid-Mediated Electrical Property Modulation

5.1 Frontiers in Device Applications

Beyond PL enhancement, acid treatment constitutes a versatile strategy for modulating the functional properties of TMDs. In electronic devices, the impact of acid treatment on TMD-based FET performance depends critically on the molecular structure of the acid employed. Strong acids or oxidizing agents, such as TFSI (Fig. 11a)[46], PSS, or H₂O₂, typically degrade device performance, as evidenced by a

positive shift in threshold voltage (V_{th}) and reduced source-drain current (I_{ds}) in back-gated MoS₂ FETs[14,47,64,123]. This degradation underscores the need for optimizing charge transport, a challenge addressed in Section 6.1. Conversely, weak acids including OA and α -lipoic acid (ALA) improve device performance[15,135]. Unlike TFSI, these weak acids neither protonate the TMD lattice nor induce significant charge transfer doping[15,136]. In the case of OA, the electron-rich carboxylate group forms a dative covalent bond with electrophilic W atoms at sulfur vacancy sites, effectively passivating defects. Concurrently, its hydrophobic alkyl chain suppresses ambient O₂ and H₂O adsorption[15]. These combined effects enhance μ_e and I_{ds} in WS₂ FET. Similarly, ALA with its cyclic disulfide group enables effective sulfur vacancy passivation, while its terminal carboxylic acid moiety leaves the doping level largely unaltered, as evidenced by a negligible shift in V_{th} [135]. The resultant reduction in charge impurity scattering translates to improved μ_e .

Extending beyond individual transistor performance, acid-induced doping effects have been harnessed to fabricate functional homojunctions. A representative study by Zhang *et al.* (2017) demonstrated a lateral MoS₂ homojunction diode by selectively treating one half of the channel with PSS while leaving the other half pristine (Fig. 11b)[64]. The work function difference of ~ 150 meV between the treated and pristine regions creates a built-in electric field that efficiently separates photocarriers, enabling a low ideality factor of ~ 1.6 and a photoresponsivity of ~ 308 mA/W (Fig. 11c)[64]. The same group later employed H₂O₂ treatment to fabricate a similar MoS₂ homojunction, achieving a rectification ratio of ~ 100 and an ideality factor of ~ 1.9 (Fig. 11d and 11e)[123]. This result further confirms that defect-mediated work function modulation is a viable route for constructing homojunctions in monolayer TMDs.

Beyond MoS₂, acid treatment has proven effective in enhancing photodetectors based on other TMDs. Park *et al.* (2017) reported that HCl treatment significantly improved the photocurrent and photoresponsivity of multilayer WSe₂ photodetectors (Fig. 11f)[137]. The enhancement arises from p-type doping via charge transfer from adsorbed Cl molecules, which reduces the effective hole barrier height at the WSe₂/Pt interface and facilitates carrier collection. Extending this strategy, the same group (2019) applied selective HCl doping to multilayer ReSe₂[138]. Unlike full-channel doping, selective doping creates a lateral p⁺-p homojunction that enhances photocarrier separation, while Cl passivation reduces recombination, simultaneously improving both photoresponsivity (1.93×10^3 A/W) and response speed (millisecond scale).

While the aforementioned approaches rely on PMMA masks for selective patterning, Riedo *et al.* (2020) developed a mask-free strategy integrating thermochemical scanning probe lithography (tc-SPL) with reactive gas exposure (Fig. 11g)[139]. This approach enables spatially controlled p- or n-type doping in monolayer MoS₂: heating in HCl/H₂O induces the rearrangement of sulfur atoms and the formation of protruding S-S bonds for p-type character, whereas heating in N₂ creates sulfur vacancies for n-type doping. Using this method, a lateral p-n junction was fabricated in a single step without masks or alignment marks, achieving a rectification ratio of 1.2×10^4 .

The acid-induced doping strategy has also been extended to logic applications, where the key mechanistic principle lies in creating spatially resolved work function differences to enable multi-state channel activation. Zhang *et al.* (2019) employed H_2O_2 treatment to introduce V_S that act as shallow trapping centers, modulating the local work function and creating an n^+-n homojunction[123]. This defect-engineered MoS_2 junction served as the active component in a logic inverter with a voltage gain of ~ 4 (Fig. 11h and 11i)[123]. For multi-valued logic applications, Joo *et al.* (2020) demonstrated a ternary inverter with stable logic states (“1”, “1/2”, and “0”) based on a cross-type $\text{WSe}_2/\text{MoS}_2$ heterojunction treated with poly(methyl methacrylate-co-methacrylic acid) (PMMA-co-PMAA) (Fig. 11j and 11k)[140]. The carboxyl acid groups in PMAA coordinate with metal atoms at Se or S vacancies, inducing charge transfer that modulates the doping level of the respective layers. This modulation broadens the anti-ambipolar transistor characteristics and enables the intermediate logic state. Similarly, Kang *et al.* (2022) fabricated a pseudo-heterojunction by selectively doping multilayer MoS_2 with TFSI (Fig. 11l)[47]. The TFSI treatment reduces sulfur vacancy density, decreasing the electron concentration and increasing the work function of the treated regions. The resulting energy-band misalignment between MoS_2 and chemically modified MoS_2 (c- MoS_2) leads to sequential channel activation under gate bias, generating a stable intermediate state for ternary logic gates (Fig. 11m)[47].

Acid treatment has also enabled TMD-based light-emitting devices. Javey *et al.* (2018) demonstrated a transient-electroluminescence (t-EL) device where an alternating-current (AC) voltage drives light emission from monolayer TMDs (Fig. 11n)[141]. In this architecture, carrier injection is governed by transient tunneling currents that are largely independent of the Schottky barrier height. For a WSe_2 device, the internal and external efficiencies were $\sim 0.06\%$ and $\sim 0.01\%$, respectively, whereas TFSI treatment on a WS_2 device improved them to $\sim 1.2\%$ and $\sim 0.2\%$, though the efficiency remained limited by biexciton-induced PL QY droop at high injection levels ($\sim 3.4\%$) (Fig. 11o)[141]. Ferrari *et al.* (2024) further developed a metal-insulator-semiconductor (MIS) light-emitting diode (LED) based on monolayer WS_2 (Fig. 11p)[142]. TFSI treatment enhanced the EQE by nearly an order of magnitude (from $\sim 0.025\%$ to $\sim 0.195\%$) by suppressing n-type doping and shifting the dominant emission from trions to neutral excitons, while the MIS structure enables hole injection through a thin hBN tunnel barrier. In both cases, the acid-induced suppression of nonradiative recombination and excess electron density serves as the common mechanistic thread for improving EL efficiency.

Overall, acid treatment is a versatile strategy for tuning TMD properties: while strong acids like TFSI degrade FET performance, weak acids such as OA and ALA enhance mobility by passivating defects. Beyond individual transistors, acid-induced doping enables diverse devices, including homojunctions, photodetectors, logic inverters, and LEDs. To realize these, strategies range from selective patterning to mask-free lithography and multi-valued logic, all relying on mechanisms like work-function modulation, defect healing, and carrier optimization, which collectively underscore the broad applicability of acid treatment.

5.2 Defect-Induced Hopping Transport

The conventional view that sulfur vacancies degrade charge transport primarily via carrier scattering requires revision. A more comprehensive framework is provided by the mobility edge model, which distinguishes extended state (responsible for band-like conduction) from localized tail states, where transport proceeds via thermally activated hopping (Fig. 12a)[143]. Within this paradigm, sulfur vacancies generate a population of localized mid-gap states that serve as hopping sites. The competition between these channels can be diagnosed through the temperature dependence of conductivity (σ), which characteristically follows $\ln \sigma \propto T^{-n}$ [144]. The exponent n serves as a characteristic fingerprint: $n = 1$ indicates transport governed by a well-defined energy barrier, corresponding to nearest-neighbor hopping (NNH) or thermally activated (TA) conduction. For $n < 1$, the transport mechanism corresponds to variable-range hopping (VRH), which is further classified by its dimensional dependence: Mott VRH with $n = 1/3$ for 2D systems and $n = 1/4$ for 3D systems, and Efros-Shklovskii (ES) VRH with $n = 1/2$, where the latter arises from a Coulomb gap induced by electron-electron interactions.

Direct evidence identifies sulfur vacancies as the microscopic origin of these localized states. Temperature-dependent measurements on back-gated few-layer MoS_2 FET reveal NNH conduction above ~ 100 K and a crossover to 2D Mott VRH below, as carriers increasingly tunnel to more distant yet energetically accessible sites at low temperatures (Fig. 12b)[69]. This signature was subsequently confirmed in monolayer WS_2 and MoS_2 devices, where the characteristic energy T_0 decreased with increasing V_g , indicating progressive suppression of hopping at higher carrier densities (Fig. 12c and 12d)[145,146].

With this diagnostic framework, a set of counterintuitive observations becomes explicable: targeted passivation of sulfur vacancies (via TFSI or PSS) has been consistently reported to degrade, rather than enhance, FET performance[14,46,47,64]. The paradox is resolved by recognizing that passivation removes the very defects that create localized hopping sites, thereby eliminating the primary conduction pathway where hopping prevails. A similar interpretation was earlier invoked for hexadecanethiol (HDT)-treated few-layer MoS_2 [147]. Collectively, these findings suggest that the net effect of defect engineering is regime-dependent: passivation is counterproductive where hopping prevails, but may restore mobility by reducing scattering in systems closer to the band-like regime.

The converse perspective is equally revealing: introducing moderate vacancy densities can be beneficial. Zhang *et al.* systematically introduced sulfur vacancies on MoS_2 via controlled H_2 annealing and achieved an optimal defect concentration of 4.7%, yielding a record room-temperature μ_e of $115 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [148]. Variable-temperature four-probe measurements confirmed Arrhenius-type NNH dependence ($\sigma \propto \exp(-\Delta E/k_\text{B}T)$) with an activation energy ΔE of 20–80 meV (Fig. 12e and 12f)[148]. This energy range is characteristic of hopping between localized states, whereas TA excitation to the band edge typically requires $\Delta E > 100$ meV[149]. Critically, the extracted average hopping distance matched the inter-defect spacing (Fig. 12g), confirming sulfur vacancies themselves as the hopping sites[148].

The hopping mechanism can also be tailored by chemically

engineering inter-flake connectivity, a strategy particularly relevant for printed polycrystalline networks. Samori *et al.* extracted the hopping exponent α from the reduced activation energy of printed covalent MoS₂ networks (Fig. 12h)[150]. Pristine MoS₂ films exhibited ES-VRH ($\alpha \sim 0.5$), dominated by scattering from charged defects. Aliphatic 1,3-propanedithiol (PDT) reduced α to ~ 0.25 (3D Mott VRH) by passivating sulfur vacancies, whereas π -conjugated 1,4-benzenedithiol (BDT) treatment increased α to ~ 1 (NNH) as the aromatic ring bridged adjacent flakes, establishing effective inter-flake pathways. The latter is evidenced by the average hopping distance decreasing to ~ 0.7 nm, which matches the molecular bridge length (Fig. 12i)[150]. This comparison demonstrates that molecular engineering offers a route to tailor both the connectivity and the type of hopping transport in TMDs devices.

Taken together, the mobility edge framework redefines sulfur vacancies not merely as scattering centers but as hopping sites in the low-density regime. This paradigm explains the counterintuitive observation that vacancy passivation can degrade transport where hopping prevails, while moderate vacancy densities can optimize mobility. Molecular engineering further enables tunable hopping dimensionality, underscoring that defect effects are regime-dependent rather than universally detrimental.

6 Strategies for Electrical Property Modulation via Acid

6.1 Mitigating TFSI Side Effects

Charge transport in monolayer TMDs is governed by multiple factors beyond surface defects[17,143], including metal contacts[151], surface adsorption[152], and dielectric interfaces[153]. While thiols and weak acids (e.g., HDT, PSS) primarily affect the channel itself, superacids such as TFSI introduce an additional complication: electrode corrosion, which cannot be fully explained by the hopping transport model alone. Early work by Javey *et al.* (2015) identified this issue using back-gated MoS₂ transistors with Ni/Au contacts on SiO₂/Si substrates[14]. Despite the presence of an Au capping layer, the underlying Ni was severely corroded after TFSI treatment, leading to poor contacts and degraded device performance. This corrosion effect was circumvented by depositing a 20 nm ZrO₂ protective layer over the contact regions (Fig. 13a, inset)[14]. Following TFSI treatment, the transfer characteristics exhibited a positive shift in V_{th} and reduced I_{ds} , consistent with a decrease in n-type doping, while the improved subthreshold swing (SS) pointed to a reduction in interface trap states (Fig. 13a)[14].

Subsequent work extended this strategy to top-gated architecture and explored electrode materials resistant to acid corrosion. Shahrjerdi *et al.* (2017) demonstrated that Ag contacts withstood TFSI treatment without corrosion, eliminating the need for a protective capping layer[154]. In devices with Ag/Au electrodes and a 20 nm HfO₂ gate dielectric, TFSI treatment induced a positive V_{th} shift, enhanced ON/OFF ratio, and improved SS relative to the untreated device, confirming effective passivation of channel defects and interface traps (Fig. 13b)[154].

Despite these advances, a critical mechanistic question remained unresolved. Using ultrafast pump-probe spectroscopy, Rao *et al.* (2021) showed that TFSI treatment alone does not

eliminate sulfur vacancies but merely reduces the electron concentration[134]. Such distinction is critical because the E_F shift away from the conduction band can make the carrier density comparable to the trap density, leading to severe carrier localization and a two-order-of-magnitude reduction in μ_e [134]. This insight proposed a two-step strategy: a PA, such as a thiol or sulfide, is first applied to chemically passivate vacancies, followed by TFSI to remove excess electrons (Fig. 13c)[134]. Compared with TFSI alone, this combined approach preserved near-pristine μ_e while maintaining the positive V_{th} shift. However, the mechanistic complexity of thiol-TMD interactions highlights the need for further study.

In parallel, efforts were directed toward simplifying the passivation procedure. Lim *et al.* (2023) demonstrated a one-step approach in which a back-gate bias (-90 V, 60 min) was applied during TFSI treatment of multilayer MoS₂ transistors (Fig. 13d, inset)[155]. The applied bias drove H⁺ into the MoS₂ lattice, enabling concurrent passivation of sulfur vacancies and SiO₂ interface dangling bonds, resulting in a μ_e enhancement exceeding 2200% at low temperatures (Fig. 13d)[155]. However, this strategy proved thickness-dependent: in monolayer MoS₂ devices, the positive V_{th} shift was accompanied by decreased I_{ds} . The authors attributed this to the dominance of physically adsorbed TFSI anions on the channel surface, which outweigh the beneficial effects of H⁺ passivation[156]. In contrast, this adverse effect was significantly mitigated in thicker channels (~ 10 nm).

Collectively, mitigating TFSI side effects has evolved through three stages: contact protection (ZrO₂ capping, Ag electrodes), mechanistic clarification (electron removal rather than vacancy repair), and developing combined or bias-assisted strategies. While these advances have improved device performance, the thickness-dependent competition between passivation and surface adsorption remains an open challenge.

6.2 Exploration of Novel Lewis Acids

To circumvent corrosion issues inherent to Brønsted acids, Lewis acids have emerged as effective p-type dopants for TMDs, leveraging the strong electron-accepting capability of their central metal ions. Unlike Brønsted acids, which act through surface protonation and charge transfer, Lewis acids can serve as substitutional dopants. This distinction has profound implications for both doping stability and device functionality.

Zhou *et al.* (2022) systematically investigated the p-type doping of few-layer PdSe₂ using SnCl₄ treatment[157]. Sn substitution introduces acceptor states that shift the E_F toward the valence band, enabling continuous polarity modulation from n-type to bipolar and ultimately p-type as the SnCl₄ concentration increases (Fig. 14a)[157]. This substitutional doping strategy proved universal across WSe₂, WS₂, ReSe₂, MoSe₂, MoTe₂, and PtSe₂. Javey *et al.* (2024) further advanced the contact engineering aspect by employing PtCl₄ to degenerately doped few-layer WSe₂ FET, achieving a contact resistance of 0.23 k $\Omega \cdot \mu\text{m}$, which is among the lowest reported for p-type TMD FETs[158]. The Pt⁴⁺ ions withdraw electrons from WSe₂, thinning the Schottky barrier width and facilitating hole injection. Crucially, devices retained degenerate doping after 86 days in air and withstood spike annealing up to 400 °C when capped with ZrO₂, distinguishing PtCl₄ from less robust dopants. To facilitate direct comparison of the acid effects and

mechanisms, Table 2 summarizes the key electrical parameters along with the corresponding optimization strategies.

Temperature has also emerged as a critical parameter for enhancing Lewis acid incorporation. For SnCl_4 -treated few-layer WS_2 , elevated temperatures enhance p-type doping through activated chemical adsorption[159]. Similarly, Xiao *et al.* achieved substitutional doping in few-layer PtSe_2 by immersion in FeCl_3 solution at 120 °C (Fig. 14b and 14c), with direct visualization of Fe atoms occupying Pd sites via STEM[160]. In both cases, elevated temperatures facilitate the doping process by promoting chemical adsorption in the former and overcoming kinetic barriers to substitution in the latter, which is also effective for WS_2 , MoSe_2 , WSe_2 , and MoTe_2 .

The spatial selectivity of solution-phase doping enables lateral p–n homojunctions through selective masking. Zhou *et al.* used PMMA to mask half of a PdSe_2 channel during SnCl_4 treatment, achieving a rectification ratio of $\sim 10^2$ and a photoresponse $\theta = 0.6$ (Fig. 14d–14f)[157]. Xiao *et al.* adopted HfO_2 as a more robust mask, achieving a rectification ratio of $\sim 10^4$ and $\theta = 0.72$ (Fig. 14g–14i)[160]. The sublinear photoresponse in both cases ($\theta < 1$) indicates that photogenerated carrier recombination is not fully suppressed, consistent with the relatively weak built-in electric field arising from the work function difference between the doped and pristine regions. The improved performance with HfO_2 arises from more effective spatial confinement of doping, which preserves a sharper junction interface for more efficient photocarrier separation.

The Lewis acid doping strategy has also been extended to neuromorphic synaptic devices. Xiao *et al.* (2024) demonstrated a photoelectric synaptic device based on SnCl_4 -doped WSe_2 , featuring with an ultralow energy consumption of ~ 0.1 fJ per synaptic event (Fig. 14j)[161]. Unlike conventional Brønsted acids that mainly induce surface charge transfer, SnCl_4 treatment enables substitutional doping of Sn^{4+} at W sites. This introduces acceptor states near the valence band maximum that act as shallow trapping centers, inducing a persistent photoconductivity (PPC) effect that provides the physical basis for synaptic weight modulation. Beyond emulating fundamental synaptic behaviors, including excitatory postsynaptic current (EPSC), paired-pulse facilitation, and short-term to long-term memory transition, the Sn-WSe_2 device also exhibits high-pass filtering for image sharpening (Fig. 14k). This filtering suppresses low-frequency signals and enhances high-frequency components through trap-mediated PPC accumulation[161]. Photoelectric synergistic modulation, with p-type doping setting the electrical baseline and PPC providing optical tunability, enables reconfigurable Boolean logic gates (AND, OR) in a single device (Fig. 14l–14n)[161]. Together, these advances highlight a promising pathway for next-generation neuromorphic devices in the post-Moore era.

Overall, Lewis acids offer a complementary paradigm to Brønsted acids through substitutional doping, enabling precise polarity modulation, ultralow contact resistance, and spatial-selective p–n homojunctions. Temperature-assisted processing further enhances doping efficiency. Beyond conventional electronics, this approach has been extended to neuromorphic devices featuring PPC-based synapses and reconfigurable logic, establishing Lewis acid doping as a versatile platform spanning both conventional FETs and emerging optoelectronic

applications.

7 Summary and Outlook

This review systematically summarizes the past decade of research on acid treatment as a means to modulate the optoelectronic properties of 2D TMDs. Superacid treatment (e.g., with TFSI) enhances the PL QY to near-unity values through two competing mechanisms (defect passivation and p-type doping), which are mediated by introduced H^+ , anions, or a combination thereof. Two counterintuitive effects arising from TFSI treatment are identified: (i) enhanced low-temperature defect emission and (ii) degraded room-temperature FET performance, with the latter rationalized by a sulfur vacancy-mediated hopping transport model. The critical trade-off between optical enhancement and electrical degradation underscores the need for strategic mitigation, with the two-step thiol–acid passivation approach emerging as a particularly promising solution. Beyond conventional Brønsted acids, Lewis acids (e.g., SnCl_4 , PtCl_4 , FeCl_3) are increasingly explored for precise p-type doping, enabling high-performance homojunction photodetectors and ultralow-power artificial synapses.

Despite these advances, three critical challenges persist: (i) the mechanistic origin is debated, as the non-acidic analogue TFEA also induces strong PL enhancement, challenging existing models; (ii) the efficacy for other defect types is poorly understood, as most studies focus only on sulfur vacancies; and (iii) the practical barriers to initial market application are largely unexplored. To tackle these, three complementary directions are proposed as follows.

(1) From indirect inference to direct visualization: ML as a bridge. The mechanistic debate stems largely from the inability to directly observe acid–defect interactions at the atomic scale. To date, passivation effects have been inferred from *ex situ* STEM defect counts and spectroscopic shifts (e.g., XPS, Raman, low-temperature PL). However, these indirect signatures cannot definitively distinguish between true vacancy repair, surface adsorption, charge transfer, or their combinations. ML offers concrete solutions: deep learning enables high-throughput defect detection in STEM images[80,162]. When combined with ML-enhanced DFT calculations, these experimental data can be dynamically integrated to construct the definitive mechanism, encompassing the adsorption, dissociation, and bonding of acid molecules at defect sites. Specifically, ML accelerates such calculations by efficiently sampling vast configurational spaces and reducing computational cost. This could help disentangle the roles of H^+ and anions, thereby resolving the mechanistic ambiguity.

(2) From vacancy-centric to defect-diverse: systematic survey of defect reactivity. Other defect species, such as metal vacancies, antisites, adatoms, or GBs, may exhibit distinct reactivities toward acid treatment. Indeed, Javey *et al.* showed that TFSI treatment is highly effective only under sulfur-deficient conditions (V_S -dominant), but ineffective under sulfur-rich conditions where cation-related defects prevail[89]. Future work should systematically investigate acid–defect interactions across a broad range of defect types. Combined with high-throughput DFT[163,164], ML can accelerate prediction of defect reactivity trends, guiding rational acid selection without exhaustive experimentation. This would also reveal whether the success of TFSI on sulfur vacancies represents a special case or a general principle.

(3) Addressing practical limitations: from lab demonstration to real-world application. Environmental stability is a primary concern: TFSI-treated samples degrade upon ambient exposure[90,113]. Thermal stability is another limiting factor. Although TFSI-based passivation has been reported to be thermally stable up to at least 300 °C[154], standard semiconductor processing often involves temperatures exceeding 400 °C[165], raising compatibility concerns. Device reliability is compromised by acid-induced electrode corrosion, particularly for Ni contacts, necessitating protective capping layers such as ZrO₂[14]. Scalability remains a formidable hurdle, as defect density and treatment efficacy differ significantly between growth methods[89]. Reproducibility is equally concerning. Even for the same acid (TFSI) on the same material, reported PL enhancement spans over two orders of magnitude across studies[14,93], underscoring that critical experimental parameters are not yet fully controlled. To overcome these limitations, future work should prioritize systematic studies that quantify degradation mechanisms under relevant operating conditions, develop industry-compatible encapsulation and contact protection strategies, establish standardized reporting protocols for reproducibility, and demonstrate acid treatment on wafer-scale TMD films.

In summary, addressing these challenges and pursuing the directions outlined above holds significance beyond optimizing a single process. It aims to construct a knowledge framework that bridges atomic-scale mechanisms with macroscopic device functionality, ultimately enabling a transition from passive defect passivation to active functionality design.

Data availability

Not applicable.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Q. S. F.: Writing – original draft, investigation. Y. Z. L.: Writing – review & editing, funding acquisition, conceptualization. W. Z. L.: Funding acquisition, supervision, project administration. All the authors have approved the final manuscript.

Informed consent

Not applicable.

Ethics statement

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Use of AI statement

None.

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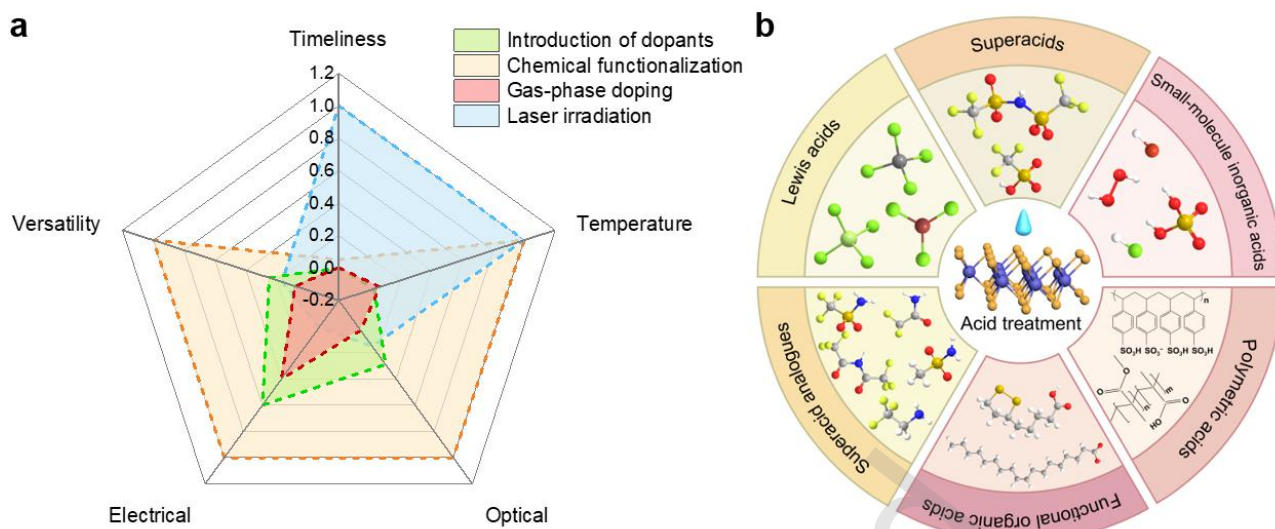


Figure 1 (a) Multi-dimensional performance comparison of defect engineering strategies for TMDs. (b) Schematic illustration of acid-based functionalization for optoelectronic tuning of TMDs.

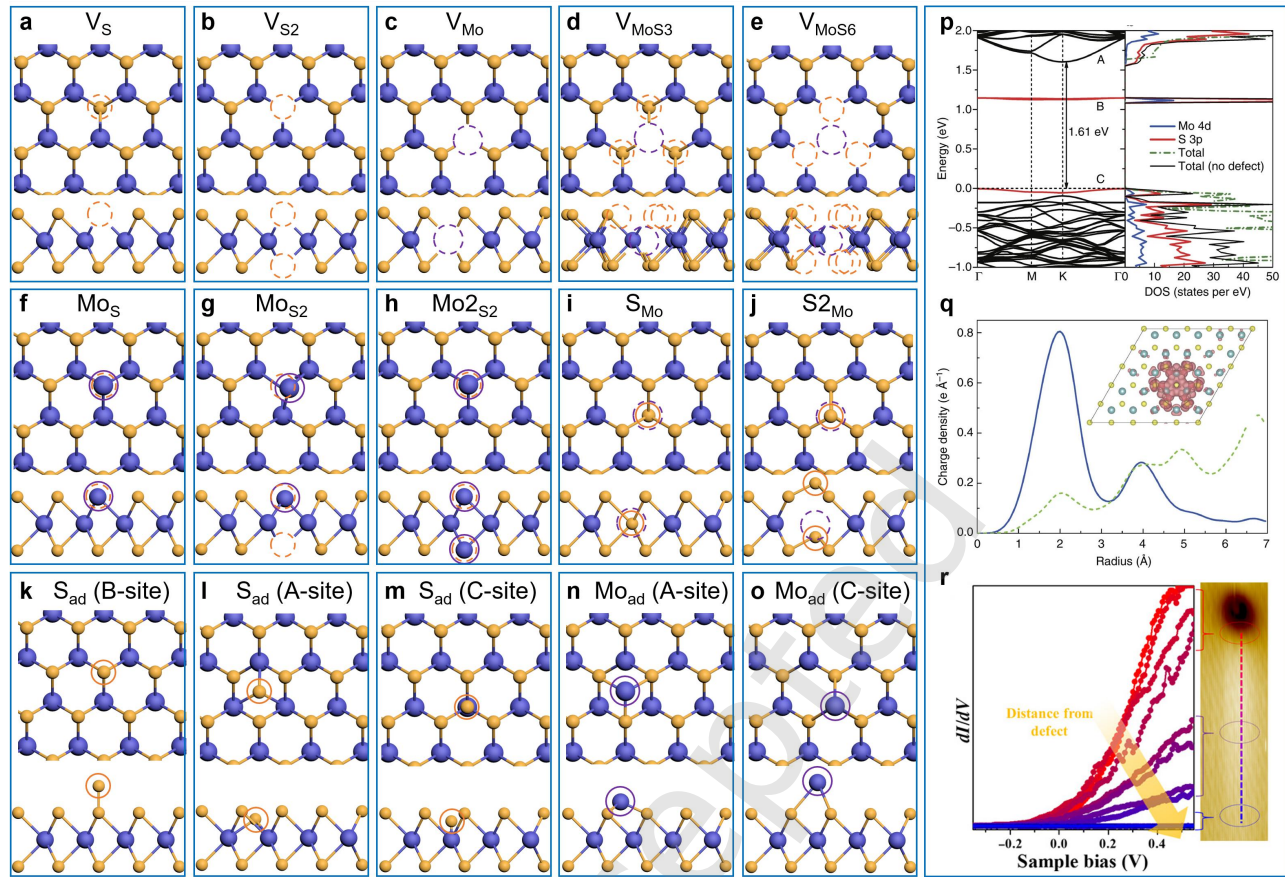


Figure 2 (a-o) Top and side views of representative point defects in monolayer MoS₂. Dashed and solid circles denote missing and added atoms, respectively. Purple, Mo atoms; orange, S atoms. (p) Band structure and partial density of states, and (q) charge density of the mid-gap state localized at a V_S, for a monolayer MoS₂ 5 × 5 supercell. (p,q) Reproduced with permission from Ref. [69]. Copyright 2013, Springer Nature Limited. (r) Spatial STS near the conduct band edge as a function of the distance from the defect. Reproduced with permission from Ref. [70]. Copyright 2017, The American Association for the Advancement of Science.

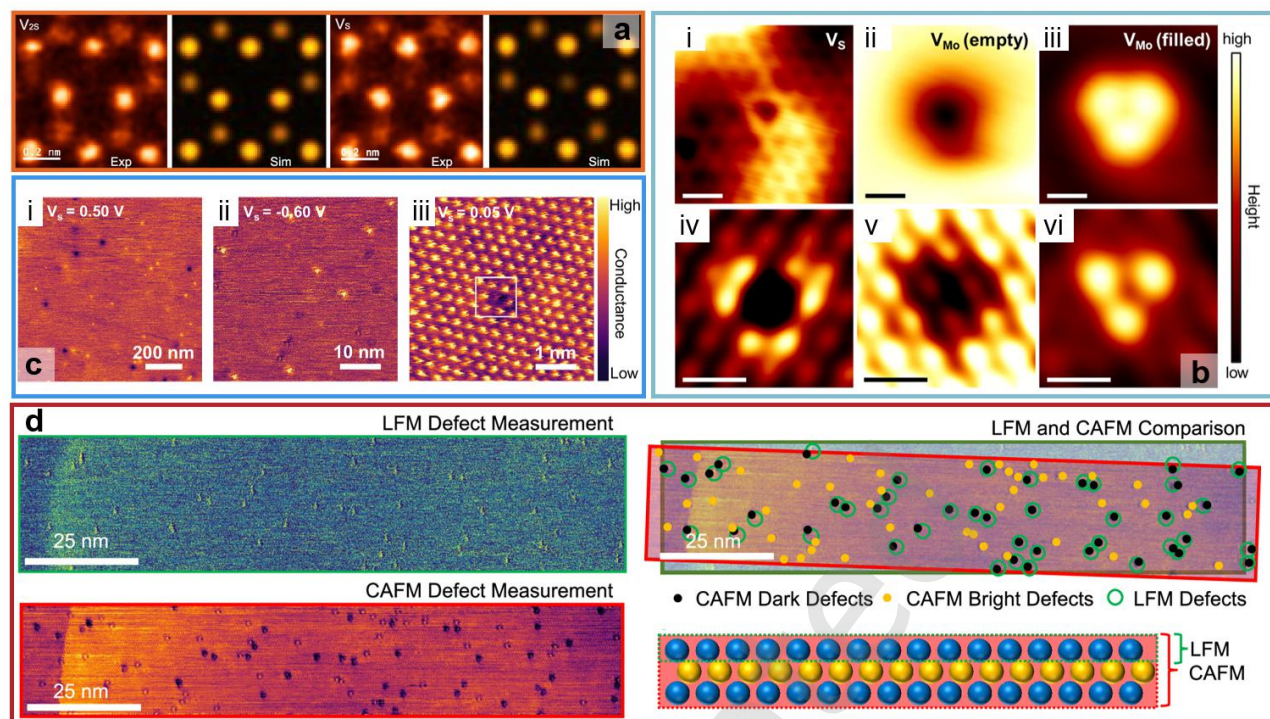


Figure 3 (a) Atomic-resolution STEM-ADF images of 1H-MoS₂ monolayer with V_S and V_{S2} defects. Reproduced with permission from Ref. [71]. Copyright 2020, American Chemical Society. (b) Top: atomic-resolution STM topography of V_S and V_{Mo} under empty-state and filled-state biases, respectively; bottom: corresponding constant-current STM topography simulations of the defects. Scale bars: 0.5 nm. Reproduced under terms of the CC-BY license from Ref. [73]. Copyright 2022, The Authors, published by Springer Nature. (c) Multiscale CAFM imaging of WSe₂: large defects on a thick flake (1 μm), atomic-scale defects on thick flake (10 nm), and atomic-resolution defect on monolayer/Au (nanoscale). Reproduced with permission from Ref. [76]. Copyright 2023, American Chemical Society. (d) Comparison of LFM and CAFM for defect detection. Left column, top: LFM image of defects; bottom: CAFM image of the same region. Right column, top: overlay of LFM (green) and CAFM (black: high conductivity, yellow: low conductivity) defect locations; bottom: schematic illustrating measurement depth, where CAFM probes multiple layers whereas LFM is sensitive only to the topmost atomic layer. Reproduced with permission from Ref. [77]. Copyright 2024, American Chemical Society.

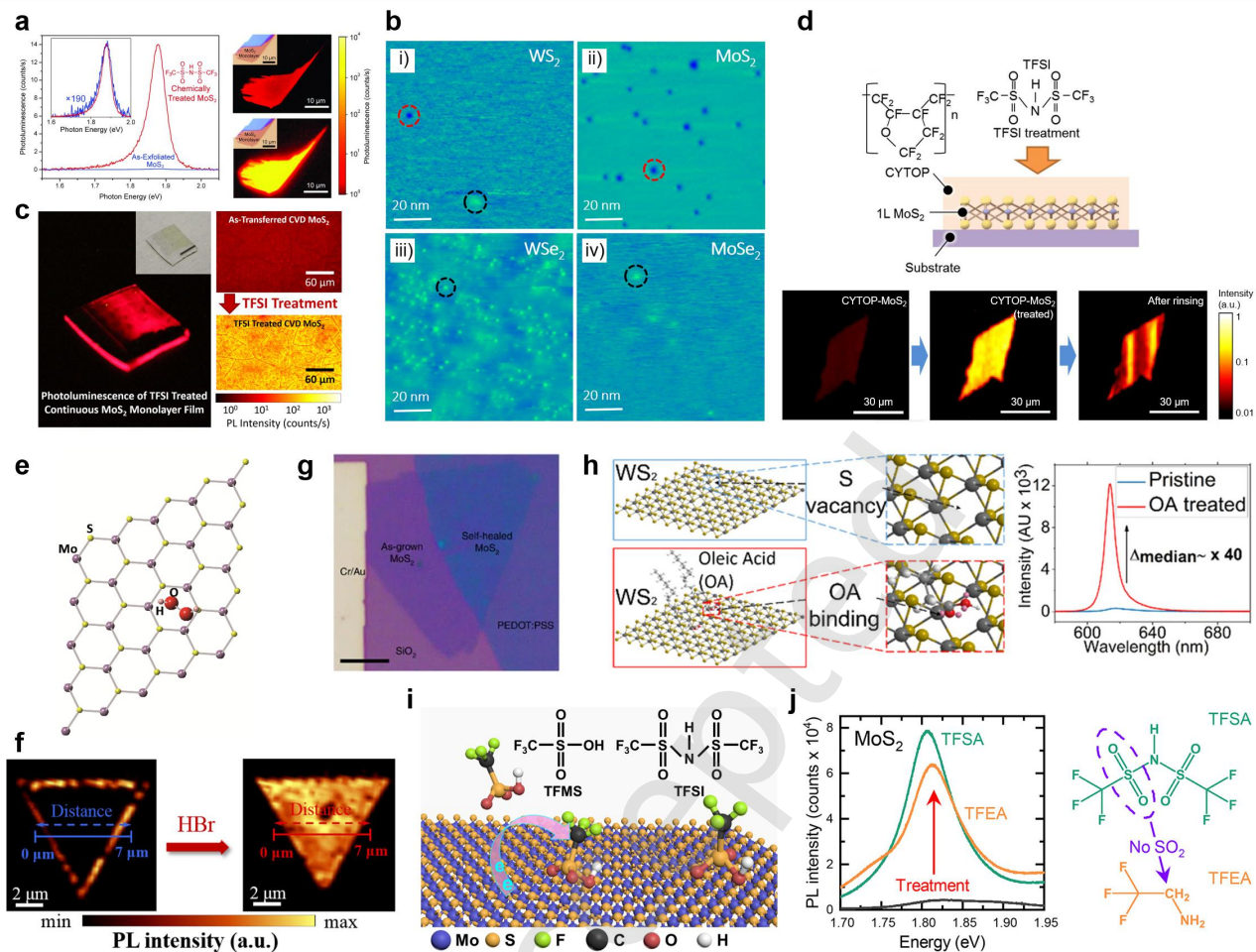


Figure 4 Tuning the PL emission in monolayer TMDs via acid treatment. (a) PL spectra and PL images of as-exfoliated MoS₂ monolayers before and after TFSI treatment. Reproduced with permission from Ref. [14]. Copyright 2015, The American Association for the Advancement of Science. (b) STM images of bulk WS₂, MoS₂, WSe₂, and MoSe₂ flakes; red and black circles indicate donor and acceptor impurities, respectively. Reproduced with permission from Ref. [45]. Copyright 2016, American Chemical Society. (c) Photograph and log-scale PL images of a CVD-grown MoS₂ film transferred onto a quartz substrate, acquired before and after TFSI treatment. Reproduced with permission from Ref. [89]. Copyright 2016, American Chemical Society. (d) Schematic illustration of a CYTOP-encapsulated monolayer MoS₂ treated with TFSI (top) and corresponding PL images before treatment, after TFSI, and after water rinsing (bottom). Reproduced with permission from Ref. [90]. Copyright 2017, American Chemical Society. (e) Top view of MoS₂ supercell with adsorbed H₂O₂ molecule. Reproduced with permission from Ref. [91]. Copyright 2015, Royal Society of Chemistry. (f) PL intensity maps of a MoSe₂ flake before and after HBr treatment. Reproduced with permission from Ref. [92]. Copyright 2016, American Chemical Society. (g) Optical microscopy (OM) image of a lateral MoS₂ homojunction device. Scale bar: 5 μm. Reproduced under terms of the CC-BY license from Ref. [64]. Copyright 2017, The Authors, published by Springer Nature. (h) Schematic illustration of OA bonding at a sulfur vacancy site in monolayer WS₂ (left) and representative PL spectra before and after OA treatment (right). Reproduced under terms of the CC-BY license from Ref. [15]. Copyright 2019, American Chemical Society. (i) Molecular structures of TFMS and TFSI (top) and schematic illustration of TFMS repairing sulfur vacancies and extracting electrons in monolayer MoS₂ (bottom). Reproduced with permission from Ref. [28]. Copyright 2021, Wiley-VCH GmbH. (j) PL spectra of few-layer MoS₂ flakes treated with TFSI and TFEA (left) and corresponding chemical structures (right). Reproduced under terms of the CC-BY license from Ref. [96]. Copyright 2022, The Authors, published by American Chemical Society.

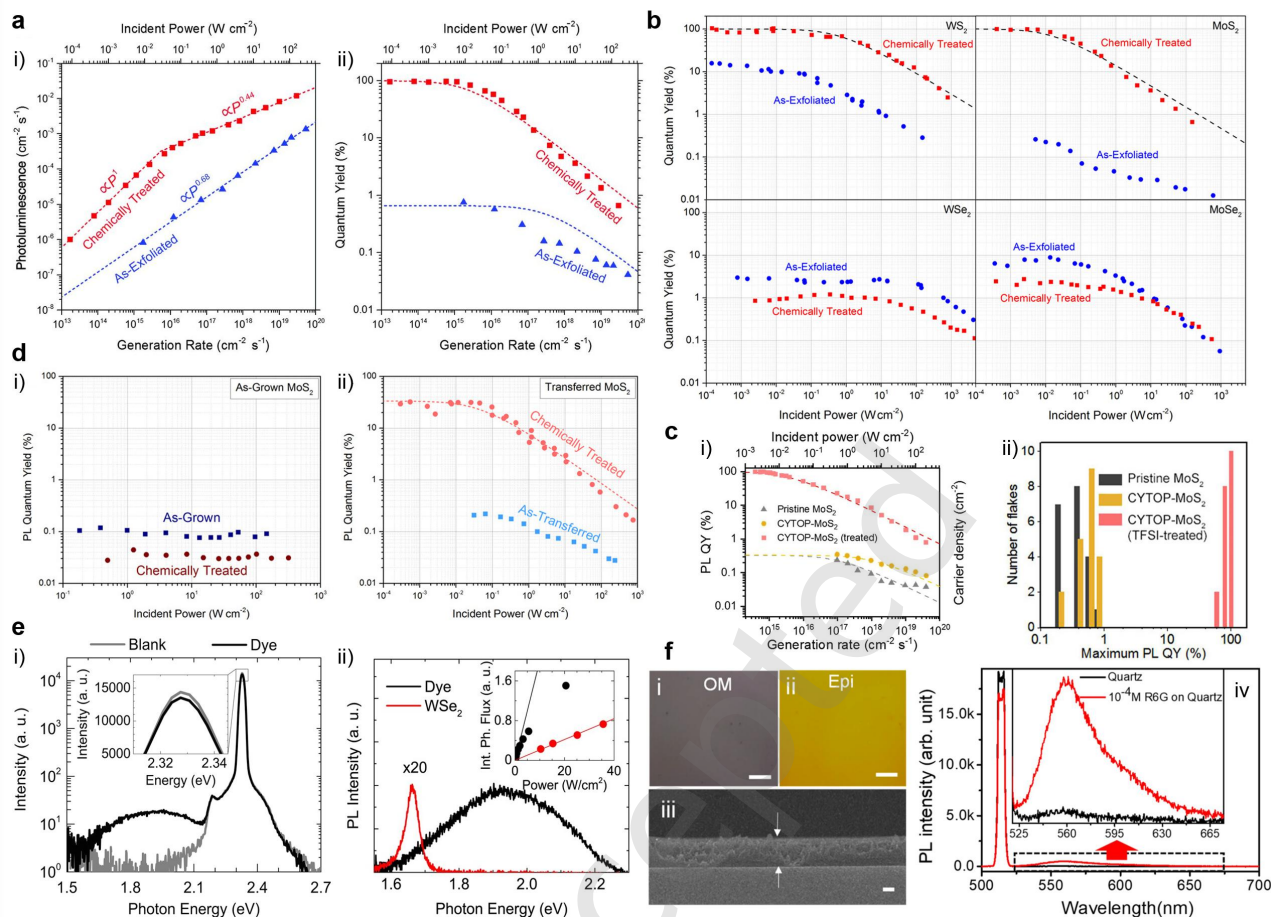


Figure 5 Two methods for determining the PL QY of TMDs. (a) Pump-power dependence of the integrated PL intensity and QY for as-exfoliated and treated MoS₂. Reproduced with permission from Ref. [14]. Copyright 2015, The American Association for the Advancement of Science. (b) Pump-power dependence of QY for as-exfoliated and chemically treated WS₂, MoS₂, WSe₂, and MoSe₂. Reproduced with permission from Ref. [45]. Copyright 2016, American Chemical Society. (c) Left: Pump-power dependence of PL QY for an as-exfoliated MoS₂ monolayer in three different states: as-exfoliated, CYTOP-coated, and TFSI-treated. Right: Corresponding PL QY histogram for 20 individual flakes measured at an incident power density of $1 \times 10^{-2} \text{ W cm}^{-2}$ after each treatment. Reproduced with permission from Ref. [90]. Copyright 2017, American Chemical Society. (d) Pump-power dependence of QY for a CVD-grown MoS₂ single domain, comparing (i) as-grown (non-transferred) and (ii) transferred samples, both after TFSI treatment. Reproduced with permission from Ref. [89]. Copyright 2016, American Chemical Society. (e) 3-Borylbithiophene reference dye embedded in PMMA: (i) PL spectrum with excitation light for absolute QY measurement; (ii) comparison of PL spectra of the reference dye and monolayer WSe₂ on a glass substrate, acquired at 1.3 and 36 W cm⁻², respectively. Reproduced with permission from Ref. [102]. Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (f) R6G reference: (i) OM and (ii) epi-fluorescence images (scale bars: 5 μm); (iii) scanning electron microscopy image (scale bar: 100 nm) of a 300 nm thin film; (iv) PL spectra of the film and bare quartz substrate measured with an integrating sphere. Reproduced under terms of the CC-BY license from Ref. [105]. Copyright 2020, The Authors, published by Multidisciplinary Digital Publishing Institute.

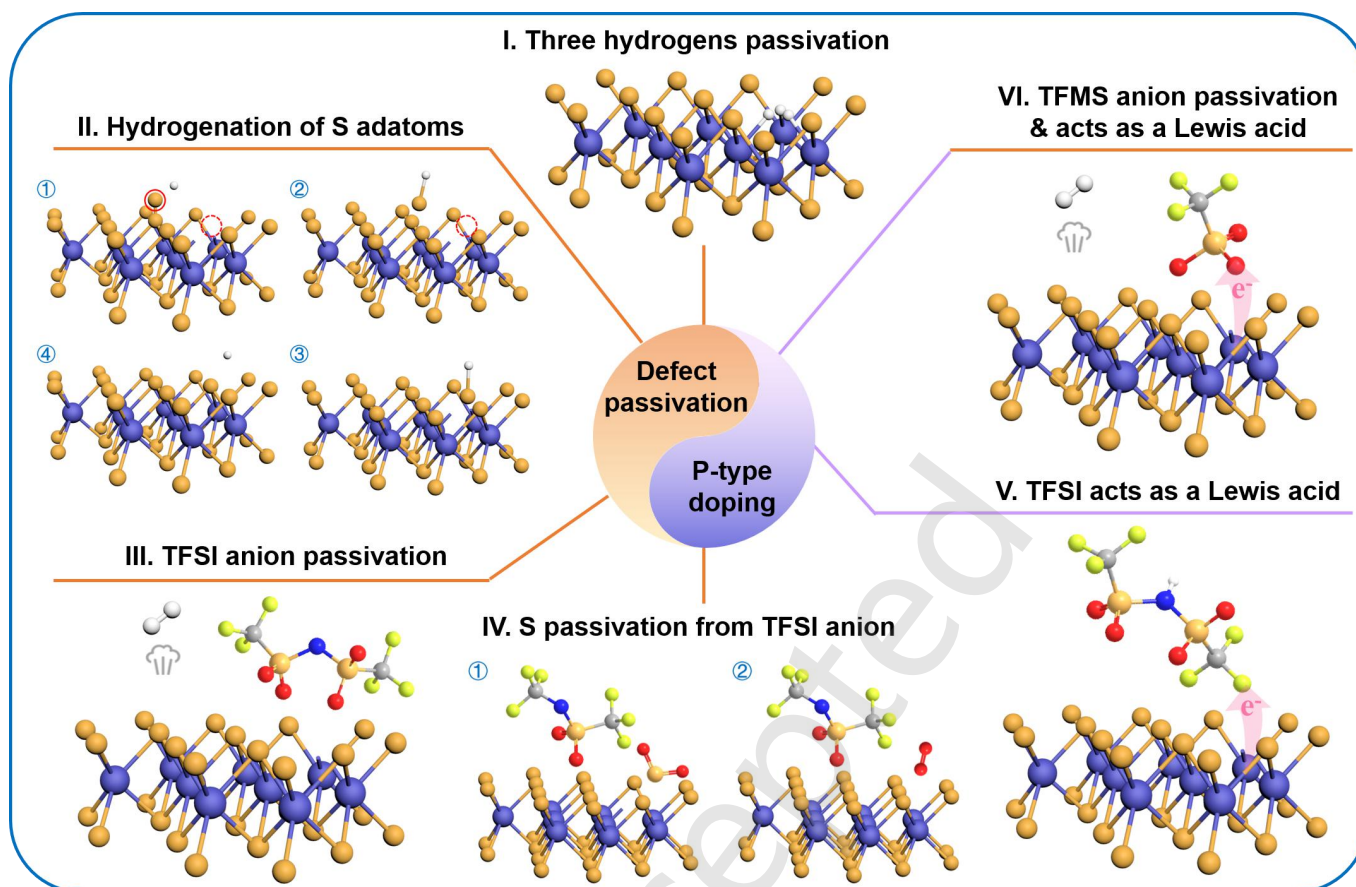


Figure 6 Possible mechanisms of superacid-induced PL enhancement in TMDs.

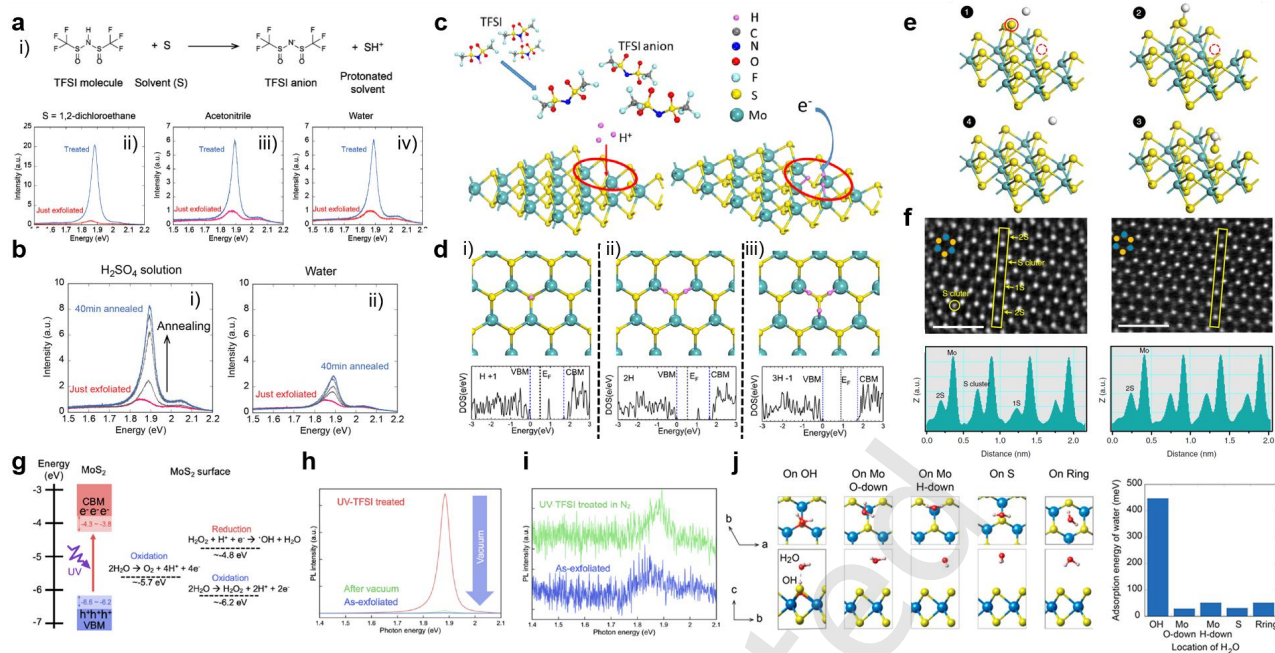


Figure 7 Proton-mediated defect passivation for enhanced PL emission in monolayer MoS₂. (a) Top: Schematic illustration of TFSI deprotonation in a solvent. Bottom: PL spectra of monolayer MoS₂ after TFSI treatment in DCE, acetonitrile, and water. (b) PL spectra of H₂SO₄-treated and Li₂SO₄-treated monolayer MoS₂. (a,b) Reproduced with permission from Ref. [93]. Copyright 2018, American Chemical Society. (c) Schematic illustration of defect passivation by TFSI. (d) Geometries and PDOS for one, two, and three hydrogen atoms at a sulfur vacancy, corresponding to H⁺, 2H⁰, and 3H⁻ configurations, respectively. (c,d) Reproduced under terms of the CC-BY license from Ref. [112]. Copyright 2018, The Authors, published by AIP Publishing. (e) Schematic illustration of the structural evolution induced by PSS, illustrating the SVSH mechanism. (f) HAADF-STEM images of monolayer MoS₂ before and after PSS treatment, with corresponding Z-contrast line profiles below. Scale bar: 1 nm. (e,f) Reproduced under terms of the CC-BY license from Ref. [64]. Copyright 2017, The Authors, published by Springer Nature. (g) Proposed reaction pathways between photogenerated carriers and surface species on monolayer MoS₂. (h) PL spectra measured in air for as-exfoliated, UV-TFSI-treated, and post-vacuum-treated samples. (i) PL spectra measured in N₂ for as-exfoliated and UV-TFSI-treated samples. (g-i) Reproduced with permission from Ref. [113]. Copyright 2020, American Chemical Society. (j) Optimized configurations and calculated adsorption energies of H₂O on monolayer MoS₂. Reproduced with permission from Ref. [114]. Copyright 2021, American Chemical Society.

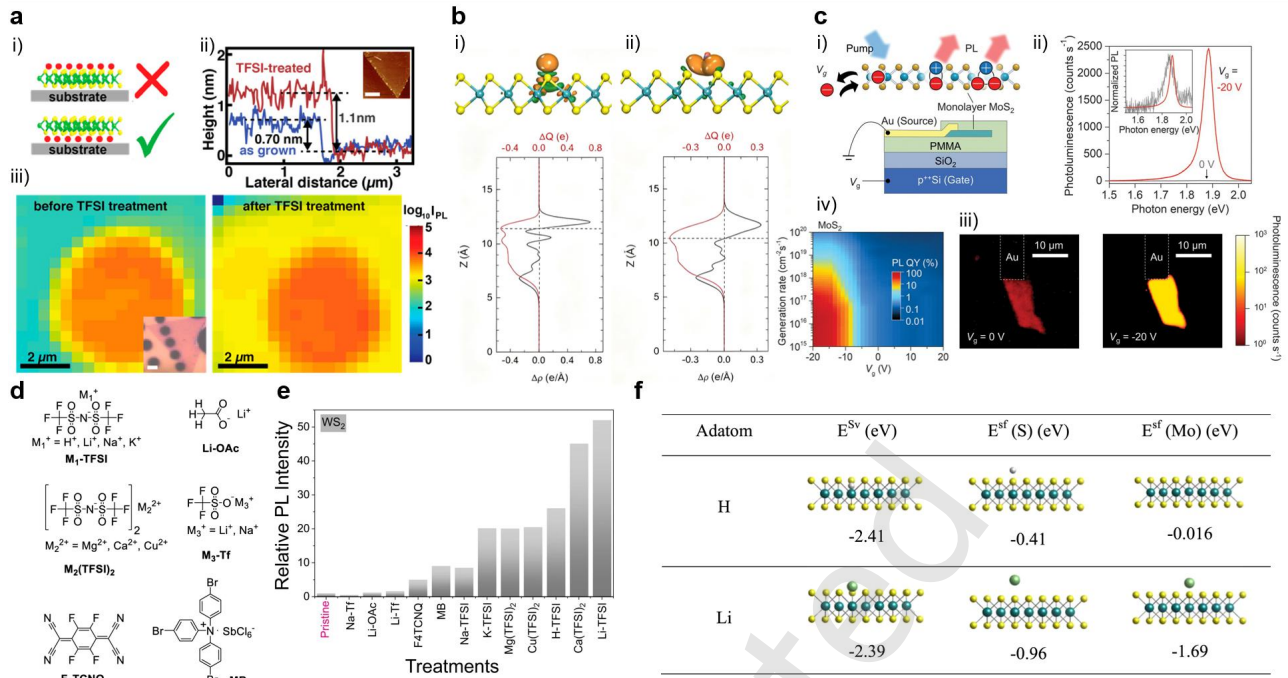
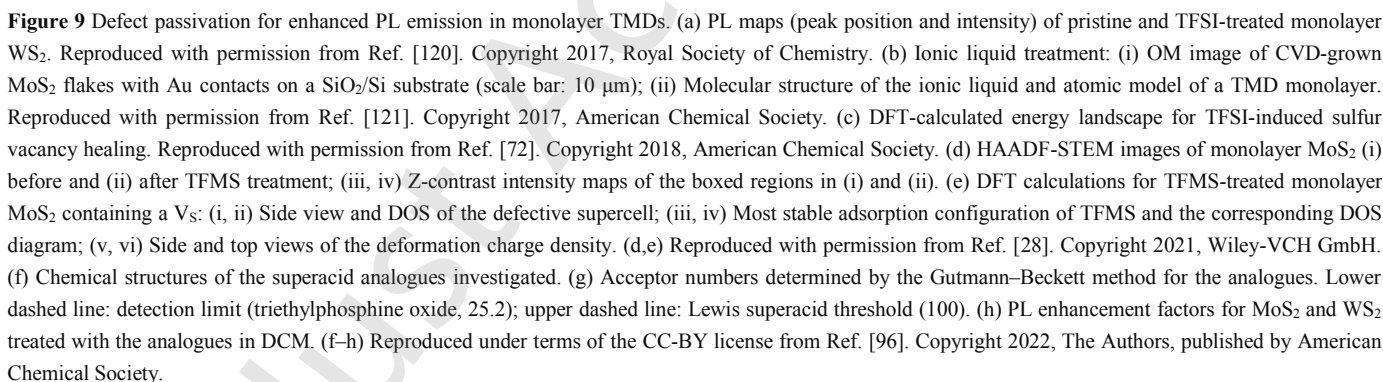


Figure 8 Acid-induced p-type doping for enhanced PL emission in monolayer TMDs. (a) Cation intercalation: (i) Schematic illustration; (ii) AFM height profiles of as-grown monolayer WS₂ before and after TFSI treatment; (iii) PL intensity map of a monolayer on a prepatterned SiO₂/Si substrate with holes. (b) Calculated differential charge density $\Delta\rho$ (black line) and cumulative transferred charge ΔQ (red line) for monolayer MoS₂ with H⁺ (left) and Li⁺ (right). Side views of the corresponding DFT models are shown above. (a,b) Reproduced with permission from Ref. [117]. Copyright 2017, American Chemical Society. (c) Near-unity PL QY in MoS₂ achieved via electrostatic doping: (i) Device schematic and gate-dependent PL spectra; (ii) PL spectra acquired at $V_g = -20$ V and 0 V at a generation rate $G = 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$; (iii) PL images acquired at $V_g = 0$ V (left) and -20 V (right); (iv) Color plot of PL QY as a function of G and V_g . Reproduced with permission from Ref. [118]. Copyright 2019, The American Association for the Advancement of Science. (d) Molecular structures of the chemicals used. (e) PL intensity enhancement factors for WS₂ under different treatments, normalized to the pristine sample. (f) DFT simulation of H and Li adatoms formation energies and the configurations on the different positions of monolayer MoS₂. (d–f) Reproduced under terms of the CC-BY license from Ref. [119]. Copyright 2021, The Authors, published by Springer Nature.



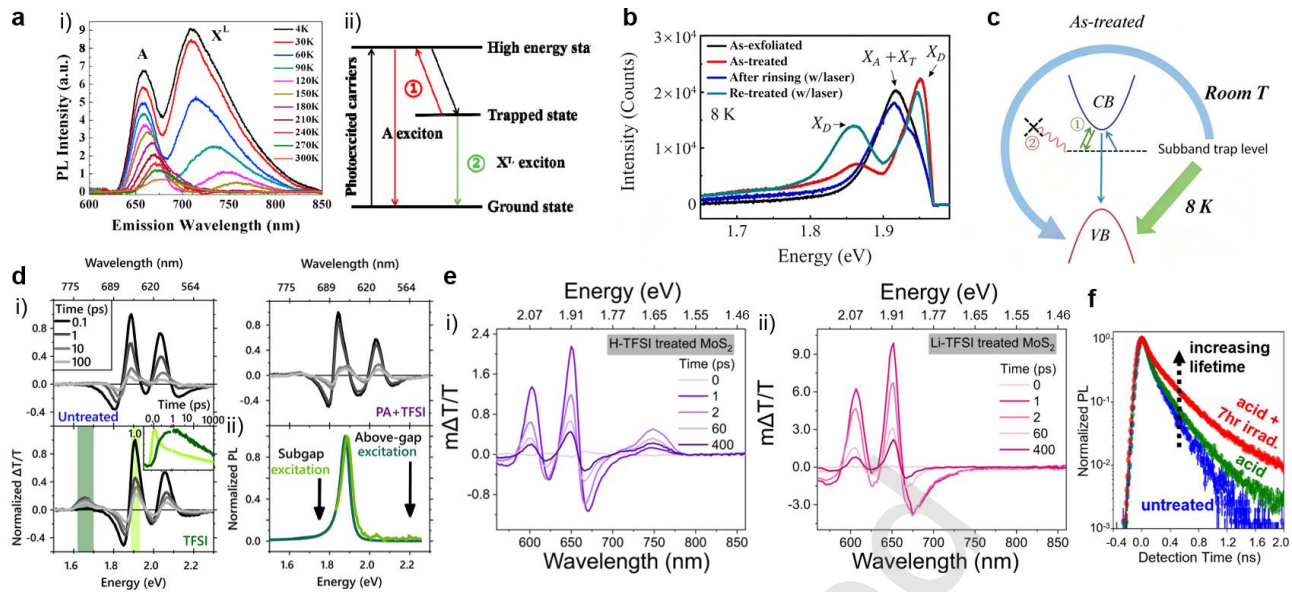


Figure 10 Trap-limited PL dynamics in monolayer MoS₂. (a) Temperature-dependent PL spectra (i) and the corresponding three-state model (ii). Reproduced with permission from Ref. [126]. Copyright 2020, Elsevier B. V. (b) Low-temperature PL spectra acquired after various treatments, revealing defect-related emission upon superacid treatment. (c) Proposed exciton decay pathways involving defect-induced levels in TFSI-treated monolayers. (b,c) Reproduced with permission from Ref. [131]. Copyright 2020, American Chemical Society. (d) Pump-probe measurements on treated MoS₂: (i) Kinetic traces for different treatment conditions; (ii) Comparison of PL emission energy under subgap and above-bandgap excitation, showing identical emission. Reproduced under terms of the CC-BY license from Ref. [134]. Copyright 2021, The Authors, published by American Chemical Society. (e) Pump-probe kinetics of (i) H-TFSI-treated and (ii) Li-TFSI-treated MoS₂. Reproduced under terms of the CC-BY license from Ref. [119]. Copyright 2021, The Authors, published by Springer Nature. (f) Ultrafast single-photon counting lifetime measurements for untreated and TFSI-treated MoS₂ after 0 and 7 hours of 550 nm pulsed laser exposure. Reproduced with permission from Ref. [116]. Copyright 2024, American Chemical Society.

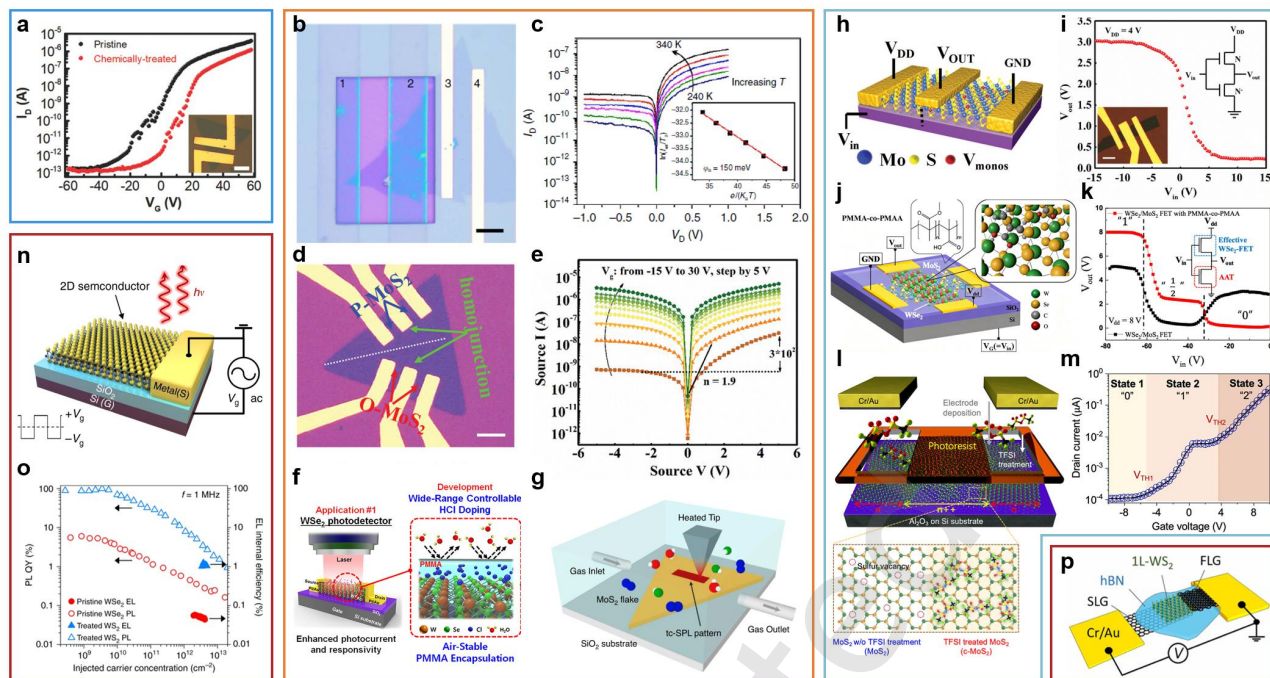


Figure 11 Functionalization of TMDs via acid treatment. (a) Transfer characteristics of a monolayer MoS₂ FET before and after TFSI treatment. Reproduced with permission from Ref. [46]. Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) OM image of homojunction defined by electrodes 2–3 between self-healed (electrodes 1–2) and as-grown (electrodes 3–4) MoS₂ FET regions. Scale bar: 5 μm. (c) Temperature-dependent output characteristics. (b,c) Reproduced under terms of the CC-BY license from Ref. [64]. Copyright 2017, The Authors, published by Springer Nature. (d) OM image of MoS₂ FETs featuring original, processed, and homojunction regions. Scale bar: 10 μm. (e) Gate-dependent rectification behavior. (d,e) Reproduced with permission from Ref. [123]. Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (f) Schematic illustration of an HCl-doped WSe₂ photodetector. Reproduced with permission from Ref. [137]. Copyright 2017, American Chemical Society. (g) Schematic illustration of the tc-SPL setup. Reproduced under terms of the CC-BY license from Ref. [139]. Copyright 2020, The Authors, published by Springer Nature. (h) Schematic illustration of a MoS₂-based logic inverter. (i) Voltage transfer characteristic. (h,i) Reproduced with permission from Ref. [123]. Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (j) Cross-type WSe₂/MoS₂ heterojunction following PMMA-co-PMAA treatment. (k) Ternary inverter characteristics before and after treatment. (j,k) Reproduced with permission from Ref. [140]. Copyright 2020, American Chemical Society. (l) Schematic illustration of a pseudo-heterostructure MoS₂ device. (m) Transfer characteristics measured at $V_D = 5$ V. (l,m) Reproduced with permission from Ref. [47]. Copyright 2022, American Chemical Society. (n) Schematic illustration of a t-EL device, wherein an AC voltage applied between gate and source induces emission near the source contact edge. (o) PL QY and η_{int} as a function of injected carrier concentration for a pristine WSe₂ device and a superacid-treated WS₂ device. (n,o) Reproduced under terms of the CC-BY license from Ref. [141]. Copyright 2018, The Authors, published by Springer Nature. (p) Schematic illustration of the LED structure. Reproduced under terms of the CC-BY license from Ref. [142]. Copyright 2024, The Authors, published by IOP Publishing Ltd.

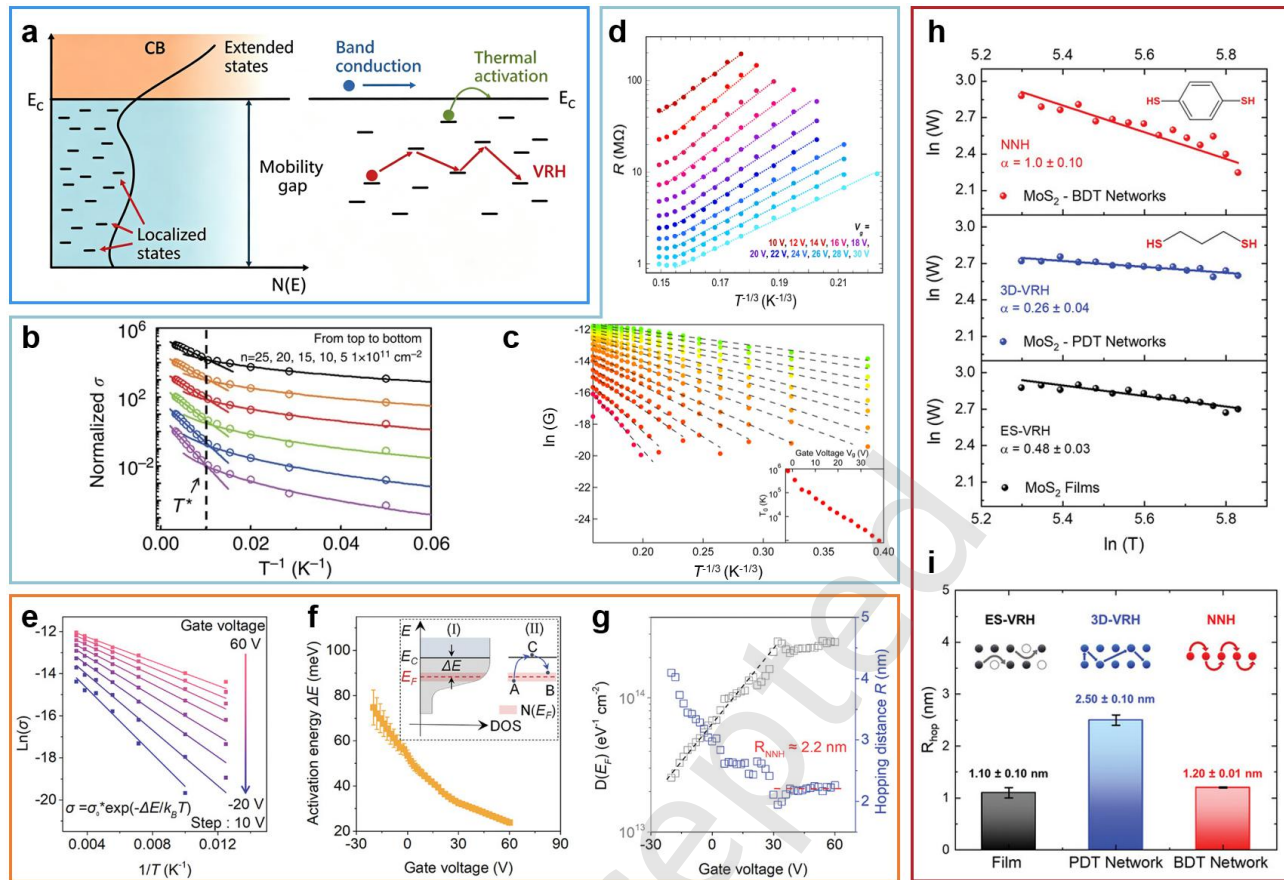


Figure 12 Charge transport mechanisms in TMDs. (a) Schematic illustration of the mobility edge concept. Reproduced with permission from Ref. [143]. Copyright 2018, Royal Society of Chemistry. (b) Arrhenius plot of the normalized conductivity (symbols) for a back-gated monolayer MoS₂ FET, with fits to a hopping model (solid lines). Reproduced with permission from Ref. [69]. Copyright 2013, Springer Nature. (c) Logarithmic sheet conductivity plotted as a function of $T^{-1/3}$ for various gate voltages. Reproduced with permission from Ref. [145]. Copyright 2014, American Chemical Society. (d) Temperature-dependent resistance of device measured at $V_d = 1$ V, revealing VRH behavior. Reproduced with permission from Ref. [146]. Copyright 2015, American Chemical Society. (e) Four-probe Arrhenius plots of sheet conductance σ for a MoS₂ FET over the temperature range of 300-80 K. (f) Activation energy (ΔE) as a function of gate voltage. (g) Average inter-defect distance and minimum hopping distance plotted against defect density. (e-g) Reproduced with permission from Ref. [148]. Copyright 2021, Wiley-VCH GmbH. (h) $\ln(W)$ versus $\ln(T)$ plots for pristine MoS₂ films, MoS₂-PDT networks, and MoS₂-BDT networks. All α values were extracted at $V = 1$ V. (i) Extrapolated R_{hop} for the three systems, along with schematics of the corresponding hopping pathways. (h,i) Reproduced under terms of the CC-BY license from Ref. [150]. Copyright 2023, The Authors, published by Wiley-VCH GmbH.

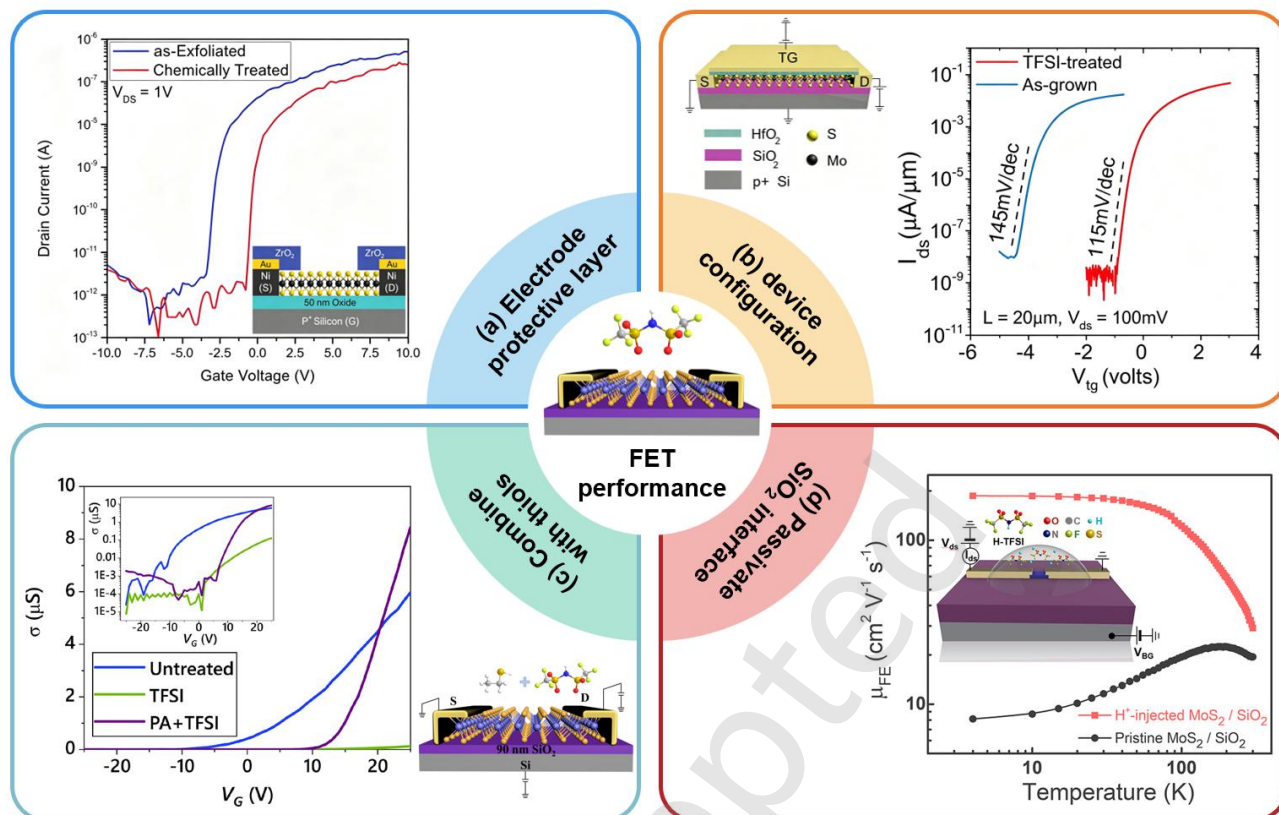


Figure 13 Strategies for enhancing the performance of TFSI-treated MoS₂ FETs. (a) Transfer characteristics of a monolayer MoS₂ FET before and after treatment. Reproduced with permission from Ref. [14]. Copyright 2015, The American Association for the Advancement of Science. (b) Schematic illustration of a top-gated MoS₂ FET (left) and corresponding transfer characteristics of CVD-grown devices before and after treatment (right). Reproduced with permission from Ref. [154]. Copyright 2017, AIP Publishing. (c) Mobility plotted against gate voltage for different treatment steps (left) and schematic of a MoS₂ FET sequentially treated with a PA followed by TFSI (right). Reproduced under terms of the CC-BY license from Ref. [134]. Copyright 2021, The Authors, published by American Chemical Society. (d) $\log(\mu_{FE})$ versus $\log(T)$ for pristine and H⁺-injected MoS₂ devices on SiO₂ substrate. Reproduced with permission from Ref. [155]. Copyright 2023, American Chemical Society.

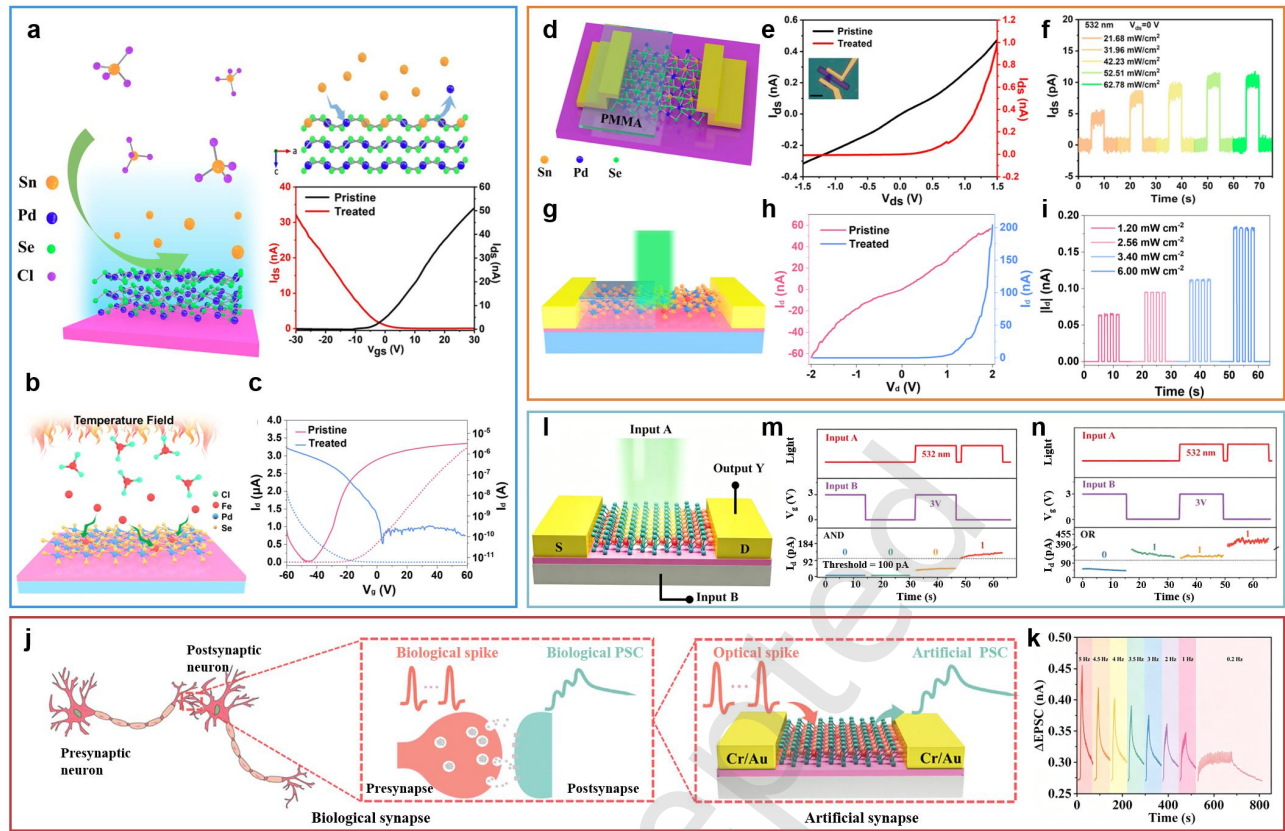


Figure 14 Functionalization of TMDs via Lewis acid treatment. (a) Left: schematic of the Sn doping process in PdSe₂ using SnCl₄ treatment. Right (top): side-view atomic configuration of Sn-doped PdSe₂. Right (bottom): transfer curves of the PdSe₂ FET measured before and after Sn doping. Reproduced with permission from Ref. [157]. Copyright 2022, American Chemical Society. (b) Schematic illustration of Fe atom doping in PdSe₂ via FeCl₃ treatment. (c) Transfer characteristics of a PdSe₂ FET before and after FeCl₃ treatment. (b,c) Reproduced with permission from Ref. [160]. Copyright 2025, Wiley-VCH GmbH. (d) Schematic illustration of a PdSe₂ p-n homojunction. (e) I - V curves of a pristine and Sn-doped p-n junction. (f) Photoresponse under 532 nm illumination at various intensities. (d-f) Reproduced with permission from Ref. [157]. Copyright 2022, American Chemical Society. (g) Schematic illustration of another PdSe₂ p-n homojunction. (h) I - V curves of a pristine and Fe-doped junction. (i) Photoresponse under 532 nm illumination at various intensities. (g-i) Reproduced with permission from Ref. [160]. Copyright 2025, Wiley-VCH GmbH. (j) Analogy between a biological synapse and a Sn-doped WSe₂ artificial synapse. (k) Δ EPSC responses triggered by 30 optical pulses at various frequencies. (l) Schematic of the logic gate device architecture. (m) AND and (n) OR logic functions under optical input. (j-n) Reproduced with permission from Ref. [161]. Copyright 2024, Wiley-VCH GmbH.

Table 1 Summary of room-temperature PL characteristics of acid-treated monolayer TMDs.

Acid	TMD	Preparation	Treatment conditions	Key PL parameters				Proposed mechanism	Ref.
				Peak shift (meV)	Enhancement factor ^{a)}	QY (%)	Lifetime (ns)		
TFSI	MoS ₂	ME	0.2 mg/mL TFSI in DCE/DCB, immersion	0	190	~100 ^{b)} 0.6 ^{b)}	~10.8 0.3	H ⁺ -induced SVSH	[14]
TFSI	MoS ₂	ME	0.2 mg/mL TFSI in DCE/DCB, immersion	0	423	↑ ^{b)}	↑	S vacancy passivation	[45]
	WS ₂	ME	TFSI in DCE/DCB, immersion	0	11	↑ ^{b)}	↑		
	MoSe ₂	ME	TFSI in DCE/DCB, immersion	0	0.39	↓ ^{b)}	↓	Ineffective	
	WSe ₂	ME	TFSI in DCE/DCB, immersion	0	0.43	↓ ^{b)}	↓		
TFSI	MoS ₂	CVD ^{c)}	2 mg/mL TFSI in acetonitrile, immersion	0	↑	30 ^{b)} 0.1 ^{b)}	4.2 0.19	Strain release & S vacancy passivation	[89]
TFSI + UV	MoS ₂	ME	TFSI treatment (2 mg/mL in acetonitrile, immersion) + UV illumination	+30	230	–	1.35 <0.04	Photo-driven defect passivation via H ₂ O/O ₂ reactions and TFSI acidity	[113]
TFSI + UV (order-independent)	MoS ₂	ME	TFSI immersion (2 mg/mL in dehydrated acetonitrile) + UV illumination, order-independent	+50	Two orders of magnitude	–	–	UV-induced OH modification promoting TFSI nanolayer with S vacancy passivation by H ⁺	[114]
PA + TFSI	MoS ₂	ME	PA treatment (0.1 M ethanethiol in acetonitrile, spin-coating) + TFSI treatment (5 mg/mL TFSI in DCE, immersion)	+30	275	–	2.5 3.5	PA-induced S vacancy passivation and TFSI-induced n-doping reduction	[134]
H ₂ O ₂	MoS ₂	ME	30% H ₂ O ₂ , ultrasonication	blue-shift	~8	–	–	P-type doping & S vacancy passivation	[91]
HBr	MoSe ₂	CVD	49% HBr in H ₂ O, spray	blue-shift	30	–	–	P-type doping, Se vacancy repair, and impurity removal	[92]
PSS	MoS ₂	CVD	1 wt% PEDOT:PSS, immersion	+22	2	–	–	H ⁺ -induced SVSH	[64]
H ₂ SO ₄	MoS ₂	ME	3.55 × 10 ^{−4} M H ₂ SO ₄ in H ₂ O, immersion	blue-shift	4~8	–	–	H ⁺ governs PL enhancement	[93]
OA	WS ₂	ME	Degassed OA, submersion	blue-shift	27	–	↑	Coordination passivation of W dangling bonds	[15]
OA	MoSe ₂	ME	Pure degassed OA, drop-casting	blue-shift	58	–	↑	Coordination passivation of Mo dangling bonds	[94]
OA	WS ₂	CVD	OA	blue-shift	~20	–	↑	Defect passivation	[95]
TFMS	MoS ₂	CVD	30 wt% TFMS in H ₂ O, spin-	blue-shift	206	14.1 ^{d)} 0.2 ^{d)}	0.05 0.011	S vacancy repair by anion; p-type doping	[28]

	WS ₂	CVD	coating	blue-shift	48	56.7 ^{d)} 2.7 ^{d)}	0.036 0.008	by both anion and H ⁺
	MoSe ₂	CVD		blue-shift	12	—	—	
	WSe ₂	CVD		blue-shift	2	—	—	P-type doping
TFSI	MoS ₂	CVD		blue-shift	~43	—	—	Mechanism unclear;
TfNH ₂	MoS ₂	CVD	2 mg/mL	blue-shift	~43	—	—	not due to S-vacancy
BTFA	MoS ₂	CVD	superacid and	blue-shift	~14	—	—	repair, Brønsted
TFA	MoS ₂	CVD	its analogues in	blue-shift	~43	—	—	acidity, or the [96]
TFEA	MoS ₂	CVD	DCM,	blue-shift	~14	—	—	presence of
MSA	MoS ₂	CVD	immersion	blue-shift	↑	—	—	sulfonyl/sulfur/oxygen species

^{a)}PL intensity enhancement factor, defined as the ratio of PL intensity of acid-treated samples to that of as-prepared samples; ^{b)}QY calculated from the measured EQE after correction for the fraction of light within the escape cone; ^{c)}Sample transferred from the growth substrate to the target substrate prior to TFSI treatment; ^{d)}QY estimated using an R6G thin film as a reference. Note: Values before and after the vertical line (|) correspond to treated and as-prepared samples, respectively. Arrows (↑/↓) indicate an increase or decrease relative to the as-prepared sample. Abbreviation: DCB = 1,2-dichlorobenzene; DCM = dichloromethane.

Table 2 Summary of acid treatments for electrical transport in TMD-based FETs.

Acid	TMD	Channel	Contact electrode	Key FET parameters				Reported effect	Ref.
				I_{ds} (nA)	V_{th} shift (V)	SS (V/dec)	μ_e (cm ² V ⁻¹ s ⁻¹)		
TFSI	MoS ₂	monolayer	Ni/Au (ZrO ₂ cap)	↓	Positive	Improved (↓)	–	N-doping removal and interface trap reduction	[14]
TFSI	MoS ₂	monolayer	Cr/Au	↓	Positive	–	–	Defects and free carrier concentration reduction	[46]
TFSI	MoS ₂	monolayer	Cr/Au	↓	Positive	–	~1.8 8.1	S vacancy healing-induced n-doping reduction	[47]
TFSI	MoS ₂	monolayer	Ag/Au	No significant change	Positive	0.115 0.145	~12 (similar before/after)	S vacancy passivation induced trap density reduction	[154]
PA + TFSI	MoS ₂	monolayer	Au	No significant change	Positive	–	No change	Both carrier density and charge trap density reduced	[134]
TFSI + back-gate bias	MoS ₂	multilayer	Graphene (Cr/Au pads)	–	Positive	–	↑	Gate-bias-driven H ⁺ injection simultaneously passivates sulfur vacancies and SiO ₂ interface traps	[155]
TFSI + back-gate bias	MoS ₂	multilayer	Cr/Au	↑	20.6 –17.3	–	128.3 40.5	Layer-dependent: surface adsorption (monolayer, degradation) vs H ⁺ passivation (multilayer, enhancement)	[156]
OA	WS ₂	monolayer	In/Au	290 11	–	8 16	$1 \times 10^{-2} 5 \times 10^{-4}$	S vacancy passivation induced trap density reduction	[15]
OA	MoSe ₂	monolayer	Pd/Au	↑	1.3 4.8	~1 ~4	–	Se vacancy passivation induced trap density reduction	[94]
ALA	MoS ₂	monolayer	Cr/Au	↑	Slight negative or no shift	–	↑ ~100%	S vacancy filling induced charge impurity scattering reduction	[135]
PSS	MoS ₂	monolayer	Au (pristine); PEDOT:PSS (self-healed)	↓	Positive	Improved (↓)	–	PSS-induced SVSH	[64]
H ₂ O ₂	MoS ₂	monolayer	Cr/Au	unchanged or slight ↓	Positive	–	↓	H ₂ O ₂ -induced V _s : electron trapping + scattering centers	[123]
PtCl ₄	WSe ₂	few-layer	Au	↑	Positive	0.155 (after)	–	P-type doping induced contact resistance reduction	[158]