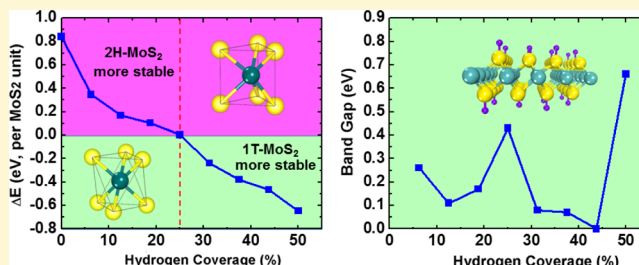


Stabilization and Band-Gap Tuning of the 1T-MoS₂ Monolayer by Covalent Functionalization

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ABSTRACT: The MoS₂ monolayer is the second most studied two-dimensional material after graphene. However, the covalent chemistry through the S layers has not been fully explored for controlling the properties of the MoS₂ monolayer. Herein we probe the potential of chemical functionalization of monolayer MoS₂ in tuning its electronic properties by first-principles density functional theory. We find that the chemical bonding of the functional groups (H, CH₃, CF₃, OCH₃, NH₂) is anomalously strong (4–5 eV) on the 1T phase (in low-coverage regimes) but very weak on the 2H phase. This strong affinity of 1T-MoS₂ for functional groups is closely related to its metallicity and partially filled Mo 4d states. More interestingly, 1T-MoS₂, which is metastable when unfunctionalized, becomes the stable phase after a crossover coverage of functionalization. Surface functionalization also results in dramatic changes to the electronic properties of 1T-MoS₂. We find that the band gap of the 1T-MoS₂ monolayer strongly depends on the functional group type and its coverage and can be tuned from zero to ~1 eV. This work demonstrates the great potential of controlling monolayer MoS₂'s phase stability and electronic properties by covalent functionalization.



INTRODUCTION

Molybdenum disulfide (MoS₂) is a typical example of quasi-two-dimensional (2D) layered transition metal dichalcogenides (TMDCs).¹ The closed packed planes of Mo atoms are sandwiched between two layers of S atoms. The bonding within each S–Mo–S sandwich layer is covalent and strong, while the individual S–Mo–S slabs are loosely stacked upon each other via van der Waals interaction. As a result, bulk MoS₂ can be easily exfoliated to form single to few layer sheets. The interlayer spacing in bulk MoS₂ also enables the intercalation of various guest species. As one of the most well-known and studied TMDCs, MoS₂ is a versatile material used for decades as a lubrication agent and a hydrodesulfurization catalyst and, recently, for hydrogen evolution reaction^{2,3} and as a material for photovoltaics⁴ and battery electrodes.⁵ Lately, research has shifted the focus to MoS₂ nanosheets of a single layer to a few layers for their unique electronic, catalytic, and optical properties.^{6–13}

The two commonly found crystal phases for bulk MoS₂ are the thermodynamically stable 2H phase (space group, *P6₃/mmc*)¹⁴ and the metastable 1T phase (space group, *P3m1*);¹⁵ H and T represent hexagonal and trigonal symmetry of the crystal structure, respectively. As shown in Figure 1, each Mo center of the 2H phase is prismatically coordinated by six surrounding S atoms, with the S atoms in the upper layer lying directly above those of the lower layer, whereas in the 1T phase the Mo atom is octahedrally coordinated to six neighboring S atoms and the two S layers stack in the A-B packing mode. The 2H and 1T phases of MoS₂ have substantially different electronic properties due to the difference in crystal symmetry.^{16–19} Bulk 2H-MoS₂ is a semiconductor with an indirect band gap of ~1.2 eV,

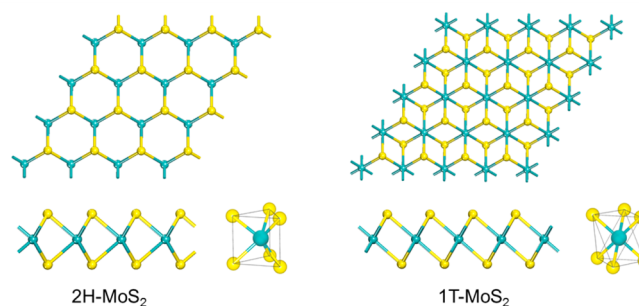


Figure 1. Top and side views of the 2H (left) and 1T (right) structures for the MoS₂ monolayer. The trigonal prism coordination for the Mo atom in 2H-MoS₂ and the octahedral coordination for the Mo atom in 1T-MoS₂ are also shown. Mo, cyan; S, yellow.

and the nature of the band gap changes from indirect to direct when thickness is reduced to be a single layer (~1.8 eV).²⁰ The 1T-MoS₂ phase, however, is metallic.²¹

2D nanosheets of 2H-MoS₂ can be obtained by micro-mechanical,^{22,23} liquid-phase chemical²⁴ or electrochemical exfoliation²⁵ in common solvents starting from the bulk 2H-MoS₂ precursors, or by direct chemical vapor deposition (CVD) growth.^{26–29} The 1T-MoS₂ phase has not been found in nature but can be made via intercalation of the 2H-MoS₂ lattice with alkali metals. For example, lithium³⁰ or lithium compound intercalation (butyllithium,³¹ lithium borohy-

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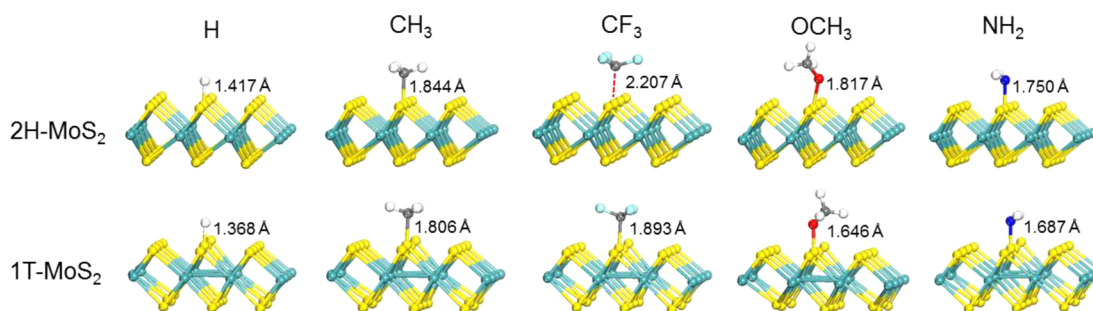


Figure 2. Optimized structures of functionalized 2H-MoS₂ and 1T-MoS₂ phases with different R-groups: from left to right, -H, -CH₃, -CF₃, -OCH₃, and -NH₂. S-R bond lengths are given.

drude^{32,33}) could induce phase transformation of the 2H phase to the 1T phase. Subsequent exfoliation and reduction of these intercalates leads to the release of free 1T-MoS₂ nanosheets. The structural change is suggested to be triggered by the charge transfer from lithium or the lithium compound to the MoS₂ host.^{34,35} The mechanism of the phase transition was recently revealed by in situ scanning transmission electron microscopy with atomic resolution.^{19,36}

Much less explored than the 2H phase, the 1T-MoS₂ nanosheets exhibit interesting properties. Several recent experimental studies have demonstrated that the exfoliated 1T-MoS₂ nanosheets show extraordinary hydrogen evolution reaction (HER) catalytic activity, much more efficient (about 600 times higher) than the few-layer 2H-MoS₂.^{33,37,38} Covalent functionalization is a commonly used approach to modify the properties of 2D materials but has been rarely applied to 1T-MoS₂ (two computational studies examined functionalization of the 2H phase^{39,40}). This situation changed in late 2014 when surface covalent functionalization by organic groups such as -CH₃ and -CH₂CONH₂ was found to significantly alter the optical properties of the 1T phase of transition metal dichalcogenide nanosheets (such as MoS₂, WS₂, and MoSe₂), which renders the metallic 1T phase semiconducting and gives it strong and tunable photoluminescence.⁴¹ However, the mechanism responsible for the dramatic changes in electronic and optical behaviors is unknown. This interesting experimental advance calls for a theoretical perspective of how the covalent functionalization changes the electronic properties of MoS₂ monolayer. Another issue is the stability of the 1T-MoS₂ phase: it could undergo phase transition back to the 2H-MoS₂ structure upon thermal annealing around 100 °C.³² Thus, how to stabilize the 1T-MoS₂ is also a challenge. Previous studies showed that 1T-MoS₂ can be stabilized by rhenium doping,⁴² but chemical modifications via functional groups may provide a new and more versatile way for stabilization as the recent experiment demonstrated. In this paper, we show from density functional theory (DFT) calculations that chemical functionalization of the 1T-MoS₂ monolayer leads to much higher stability and tunable band gaps with different functional groups at different coverages, thereby opening the door to further experimental verification and exploration of the 1T-MoS₂ phase.

METHOD

The DFT computations were performed by using the Vienna *ab initio* simulation package.⁴³ The ion-electron interaction is described with the projector augmented wave (PAW) method.⁴⁴ Electron exchange-correlation is represented by the functional of Perdew, Burke, and Ernzerhof (PBE) of generalized gradient approximation (GGA).⁴⁵ A

cutoff energy of 450 eV was used for the plane-wave basis set. The convergence threshold for structural optimization was set to be 0.02 eV/Å in force. The Brillouin zone was sampled by Monkhorst-Pack *k*-point mesh. The adsorption energy of the functional groups on MoS₂ is defined as $E_{\text{ad}} = E_{\text{total}} - (E_{\text{MoS}_2} + E_{\text{adsorbate}})$, where E_{total} , E_{MoS_2} , and $E_{\text{adsorbate}}$ correspond to the energies of functionalized MoS₂, unfunctionalized MoS₂, and isolated functional group, respectively. A negative value of E_{ad} suggests favorable interaction.

RESULTS AND DISCUSSION

We examined the surface functionalization of monolayer 2H-MoS₂ and 1T-MoS₂ by various functional groups, including -H, -CH₃, -CF₃, -OCH₃, and -NH₂, to determine the favorable adsorption sites and their adsorption energies. We started with a low surface coverage on only one side of the MoS₂ layer (0.06 per S atom). The optimized structures for different functional groups are shown in Figure 2. We probed different surface adsorption sites and found that all the examined functional groups (R-) prefer to adsorb on top of the S atoms to form S-R covalent bonds, as expected. Table 1

Table 1. Adsorption Energy (E_{ad} , eV per Group) of Different Functional Groups on 2H- and 1T-MoS₂ Single-Layer at a Surface Coverage of 0.06 per S Atom

functional groups	-H	-CH ₃	-CF ₃	-OCH ₃	-NH ₂
E_{ad} (eV) on 2H-MoS ₂	-0.39	-0.15	0.01	-0.08	-0.09
E_{ad} (eV) on 1T-MoS ₂	-5.03	-4.85	-4.21	-4.31	-4.65

shows the adsorption energies of the functional groups on MoS₂. One can see that the functional groups are only weakly bonded to the 2H-MoS₂ surface with a small adsorption energy in the range of -0.08 to -0.39 eV. The CF₃ group is even repelled from the surface with a positive E_{ad} . By contrast, all the functional groups are strongly bonded to the 1T-MoS₂ surface, with E_{ad} varying from -4.2 eV to -5.0 eV, which is reflected in the shorter surface S-R bonding distance on 1T-MoS₂ as compared with that on the 2H-MoS₂ surface (Figure 2). Among the functional groups examined, hydrogen has the strongest interaction with the 1T-MoS₂ surface, suggesting that hydrogenation could be a simple way to functionalize the 1T phase. The overall interaction energy of functional groups on 1T-MoS₂ is anomalously strong; for comparison, the computed S-R bonding energy in the CH₃S-R molecule is 3.79, 3.13, 3.11, 3.17, and 3.15 eV for R = H, CH₃, CF₃, OCH₃, and NH₂, respectively. This implies that the S-R bonding interaction is significantly strengthened when the -R group is adsorbed on the 1T-MoS₂ surface.

Why is there anomalously strong bonding of functional groups on 1T-MoS₂, whereas their bonding to 2H-MoS₂ is so weak? To address this question, we computed the electronic density of states (DOS) of unfunctionalized 2H- and 1T-MoS₂ (Figure 3). One can see that 2H-MoS₂ is semiconducting with a

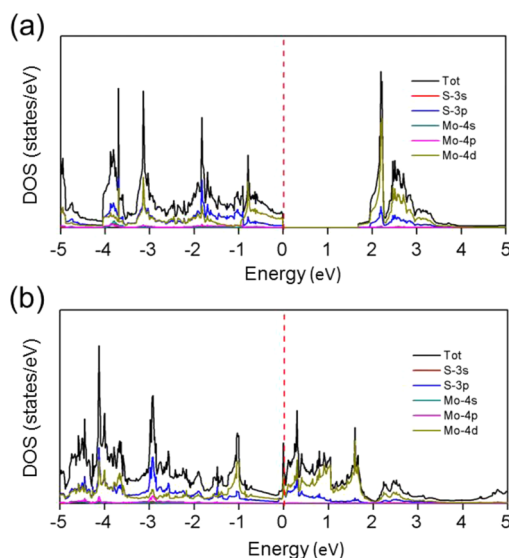


Figure 3. Total and orbital-projected density of states (DOS) of unfunctionalized 2H-MoS₂ (a) and 1T-MoS₂ (b). The Fermi level (dashed line) is set as zero.

band gap of 1.67 eV. Both valence band (VB) and conduction band (CB) comprise mainly the Mo 4d states and slightly the S 3p states. The key reason that the chemical functionalization is weak on the 2H-MoS₂ surface is because the electrons in each band of the 2H-MoS₂ phase are all well paired. Any functional group on the surface would cause an unwanted perturbation to the otherwise well-separated CB and VB states. Unlike the semiconducting 2H-MoS₂, the 1T-MoS₂ monolayer is metallic (Figure 3b), and the electronic states around the Fermi level are mainly composed of the Mo 4d and S 3p states which are only partially filled. These states provide the unpaired electrons to pair up with the chemical groups, leading to a strong covalent interaction. In other words, the chemical groups are interacting with the whole metallic 2D layer via the S atom. Hence, the drastic difference in chemical reactivity of 2H- and 1T-MoS₂ is intimately related to their very different electronic structures.

Due to the much more favored interaction between functional groups and the 1T phase, surface covalent functionalization increases the stability of 1T-MoS₂ against 2H-MoS₂. As a result, functionalization could make the 1T-MoS₂ phase become more stable than the 2H phase and the question is at what coverage. To test this idea, we compare the relative stability of the two phases after functionalization: Figure 4 shows how the energy difference of 1T-MoS₂ versus 2H-MoS₂ changes with the functional group coverage for both H and CH₃ groups (the trend is similar for the other functional groups). Before functionalization, the 2H phase is more stable than the 1T phase by 0.84 eV per MoS₂ unit. After functionalization, the relative stability of the 1T phase increases dramatically with the coverage of the H or the CH₃ group. The stability order reverses, and the 1T phase becomes more stable when the coverage exceeds 25%. Further, when the coverage

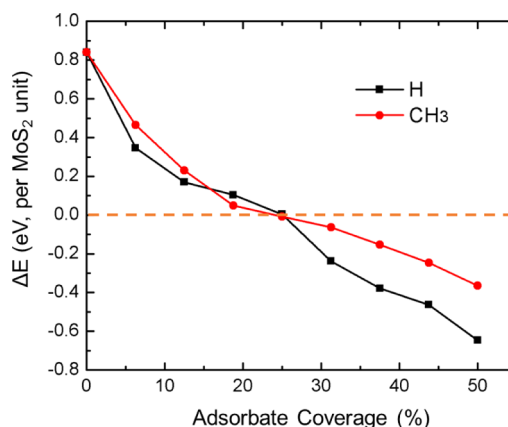


Figure 4. Energy difference between 1T- and 2H-MoS₂ phases (ΔE , eV per MoS₂ unit) as a function of the adsorbate coverage (functional groups are adsorbed on both surfaces of the MoS₂ monolayer; coverage is measured by relative occupancy of the S sites). Here $\Delta E = E_{(1T)} - E_{(2H)}$; positive ΔE (above the dashed line) indicates that 2H phase is more stable, and negative ΔE (below the dashed line) indicates that 1T phase is more stable.

reaches 50%, ΔE is enlarged to be -0.65 and -0.37 eV for H- and CH₃-functionalized MoS₂, respectively. Therefore, the metastable 1T-MoS₂ phase before functionalization can be transformed to the more stable phase after covalent functionalization. This important conclusion is consistent with the experimental finding that the functionalized 1T-MoS₂ can sustain up to 300 °C before transforming to the 2H phase;⁴¹ in addition, it suggests that hydrogenation is as effective as the organic groups in stabilizing the 1T phase.

To interrogate the effect of chemical functionalization in tuning the electronic properties of the 1T phase, we further explored how the electronic structure of the 1T phase changes with the coverage (Figure 5). One can see that the band gap of

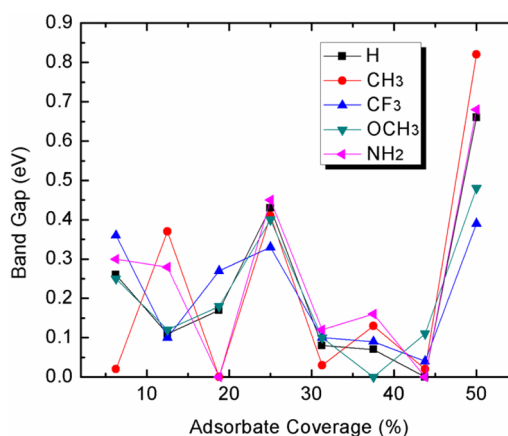


Figure 5. Computed band gaps of covalently functionalized 1T-MoS₂ by different functional groups at different surface coverages.

the 1T phase shows a strong, oscillatory dependence on the coverage of a functional group. At the low coverages (<25%), the band gap also displays a strong dependence on the functional groups for a given coverage. Both behaviors are very interesting and intriguing. The overall variation in the band gap spans from 0 to ~ 0.82 eV, but given the underestimate of the band gap by the PBE functional we employed here,^{46,47} we expect that the true range will be over 1 eV.

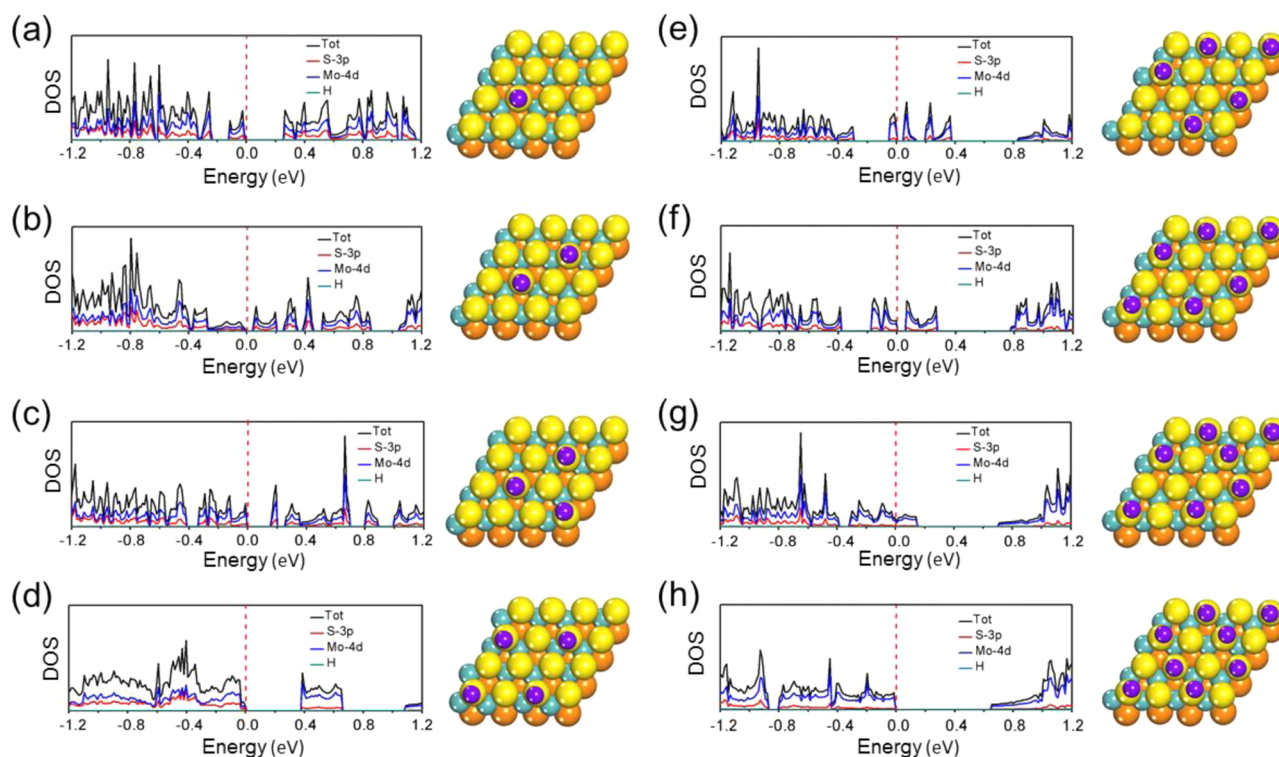


Figure 6. Geometric and electronic structures of H-functionalized 1T-MoS₂ at different coverages: (a) 6.25%; (b) 12.5%; (c) 18.75%; (d) 25%; (e) 31.25%; (f) 37.5%; (g) 43.75%; (h) 50%. H, purple; Mo, cyan; front S layer, yellow; back S layer, orange.

To understand the variation of the band gap with the coverage, we plot in Figure 6 the geometric structures as well as the corresponding DOS of H-functionalized 1T-MoS₂ at different coverages. One can see that the valence band and conduction band near the Fermi level mainly consist of the Mo 4d states. In other words, although the functional groups are attached to the S atoms, the modulation on the electronic structure mainly happens to the Mo 4d states. At H coverages of 6.25%, 25%, and 50% (Figure 6a,d,h), the whole systems have higher symmetry and relatively large band gaps develop at 0.26, 0.43, and 0.66 eV, respectively. In between these coverages and structures, symmetry is lower and gap states are present around the Fermi level, leading to small band gaps and metallic states. Figure 6 suggests a strong dependence of the band gap on both the adsorption coverage and the superstructure of adsorbates.

Some recent experiments have demonstrated that chemically exfoliated MoS₂ and WS₂ nanosheets can be functionalized by thiol ligands, which is presumably achieved by coordination of thiolate groups at the S vacancy sites.^{48,49} We tested this suggestion by functionalizing 1T and 2H MoS₂ by a model thiolate group, -SCH₃, at a surface coverage of 0.06 per S atom. We found that -SCH₃ is strongly bonded to the S atom via the S-S bond with a large adsorption energy of -4.83 eV on the perfect 1T MoS₂ surface but repelled away from the perfect 2H MoS₂ surface. This indicates that the 1T phase can be favorably functionalized by thiolate groups, while the defect-free 2H phase cannot. We found that when a surface S vacancy exists, the 2H-phase MoS₂ becomes amenable to thiolate functionalization with an adsorption energy of -2.41 eV per SCH₃ group. The defect-induced reactivity for the 2H-phase is in good agreement with the experimental finding.⁴⁸

The great tunability of the electronic properties of 1T-MoS₂ by covalent functionalization, as demonstrated in this work,

suggests a novel way to realize the full potential of this 2D material in nanoelectronic and optoelectronic applications.^{6,50} The recent experimental finding of strong photoluminescence of chemically functionalized 1T-MoS₂ at ~1.6 eV⁴¹ is such an example and is supported by the present first-principles simulation. We show that the band gap of functionalized 1T-MoS₂ can vary up to 1 eV. As mentioned earlier, this is a lower bound, given the well-known underestimation of the band gap by the DFT method employed here.⁴⁷ Accurate prediction of the band gap and optical properties of functionalized 1T-MoS₂ is warranted and will be pursued in the near future.

The phase selectivity in the chemical functionalization of MoS₂ may offer a useful approach to separate the 1T phase from the 2H phase, which usually coexist in chemically exfoliated MoS₂.⁴⁹ For example, considering the high reactivity of the 1T phase, it may be possible to control its solubility by choosing functional groups with different hydrophilic or hydrophobic effects, and one can then transfer the 1T MoS₂ from the water phase into an organic phase to make an effective separation from the 2H MoS₂ phase.

SUMMARY AND CONCLUSIONS

In summary, we have investigated covalent functionalization of the MoS₂ monolayer by density functional theory. We found that adsorption of functional groups (H, CH₃, CF₃, OCH₃, SCH₃, and NH₂) are very weak on the 2H phase of MoS₂ but very strong on the 1T phase due to its metallic character. As surface coverage increases, the 1T phase is dramatically stabilized and becomes more stable than the 2H phase after a crossover coverage (~25%). More interestingly, the band gap of 1T-MoS₂ shows a strong, nonmonotonic dependence on the functional-group type and its coverage. The present work shows that covalent functionalization has the power to fully

unleash the potential of monolayers of MoS₂ and other transition metal dichalcogenides.

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Notes

The authors declare no competing financial interest.

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