Surface Functionalization

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Functionalization of Two-Dimensional MoS_2: On the Reaction Between MoS_2 and Organic Thiols

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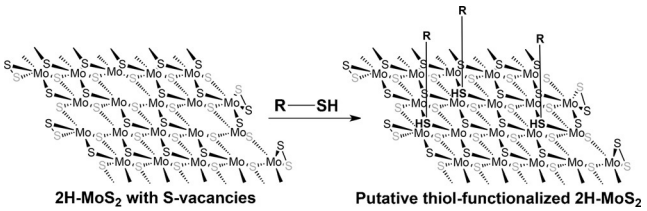
Abstract: *Two-dimensional layered transition metal dichalcogenides (TMDs) have attracted great interest owing to their unique properties and a wide array of potential applications. However, due to their inert nature, pristine TMDs are very challenging to functionalize. We demonstrate a general route to functionalize exfoliated 2H-MoS_2 with cysteine. Critically, MoS_2 was found to be facilitating the oxidation of the thiol cysteine to the disulfide cystine during functionalization. The resulting cystine was physisorbed on MoS_2 rather than coordinated as a thiol (cysteine) filling S-vacancies in the 2H-MoS_2 surface, as originally conceived. These observations were found to be true for other organic thiols and indeed other TMDs. Our findings suggest that functionalization of two-dimensional MoS_2 using organic thiols may not yield covalently or datively tethered functionalities, rather, in this instance, they yield physisorbed disulfides that are easily removed.*

In the rich family of two-dimensional (2D) layered nanomaterials, layered transition metal dichalcogenides (TMDs) have sparked increasing interest owing to their unique structures, wide range of chemical compositions, and a vast array of unique physical properties.[1–11] TMDs have potential applications in electronic devices, optoelectronics, sensing, energy storage, and catalysis.[1–14] A major focus of experimental research in recent years has concentrated on the development of synthetic routes to produce high-quality TMD nanosheets.[14–20] However, routes towards the efficient high-yield synthesis or exfoliation of TMDs remain lacking, hindering the production of large quantities of TMD nanosheets. Functionalization of such layered materials could facilitate the production of higher quantities of 2D TMDs, while also allowing for the tuning of their physical properties.

Molybdenum disulfide (MoS_2) is a prototypical TMD and acts as an excellent model system to explore the chemistry of 2D TMDs. 2D MoS_2 is most often isolated as one of two polymorphs:[14] in 2H-MoS_2 S-atoms coordinate to the Mo-atom in a trigonal prismatic fashion, whereas in 1T-MoS_2 the Mo-atom is octahedrally ligated. Importantly, thin layered 2H- and 1T-MoS_2 display different properties, 2H-MoS_2 is a semi-conductor (energy gap $\approx$1.2 eV) and a photoluminophore,[21,22] whereas 1T-MoS_2 is metallic and does not photoluminesce.[3] The covalent functionalization of 1T-MoS_2 has recently been reported,[23,24] employing a rather harsh chemical exfoliation (ce) procedure. No well-characterized examples of covalent functionalization of 2H-MoS_2 have been reported to date. We recently reported the mild functionalization of 2H-MoS_2 through ligation of surface S-atoms to coordination complexes,[25] our efforts are now focused on exploring routes towards the covalent functionalization of 2H-MoS_2.

Recent reports have claimed the functionalization of both ce-1T- and 2H-MoS_2 by reaction with organic thiols. In a seminal paper, Dravid and co-workers described the reaction between ce-1T-MoS_2 and organic thiols yielding functionalized ce-1T-MoS_2.[26] This was described as "ligand conjugation" to ce-1T-MoS_2, presumably meaning coordination of the thiol to Mo-atoms at S-vacancies (by forming a dative Mo–S bond). Later work has demonstrated further applications of this technique.[27–35] Unfortunately, in all of these reports, there remains little to no insight into the thiol ligand/MoS_2 interaction. At the inception of this work, we too postulated that 2H-MoS_2 could be functionalized using organic thiols by coordination of the thiol group to Mo-atoms at S-atom vacancies (Scheme 1). Herein, we present



Scheme 1. Proposed method to functionalize 2D 2H-MoS_2 at sulfur vacancies.

the one-step surface functionalization of 2H-MoS_2 nanosheets with an organic thiol (cysteine), resulting in functionalized 2H-MoS_2. We explore in detail the thiol/MoS_2 interaction and show that organic thiols may actually be physisorbed on MoS_2 as disulfides, rather than undergoing any bond-forming process with the MoS_2.

As we reported previously,[25] in the functionalization of 2H-MoS_2 it was necessary to disperse few-layer thick 2H-

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MoS_2 in 2-propanol (IPA), and not the standard (toxic) dispersion/exfoliating solvents *N*-methyl-2-pyrrolidone (NMP) or *N*-cyclohexyl-2-pyrrolidone (CHP).[3,15] The IPA dispersions of 2H-MoS_2 displayed a mean lateral dimension $\langle L \rangle$ of $\approx$260 nm and degree of exfoliation $\langle N \rangle$ of 9–10 layers. The IPA-exfoliated 2H-MoS_2 was thus an ideal 2D TMD dispersion for functionalization studies.

2H-MoS_2 normally displays S:Mo ratios of approximately 1.8:1($\pm$0.2), as suggested by X-ray photoelectron spectroscopy (XPS).[25,36] Transmission electron microscopy (TEM) analysis corroborated this, showing that basal-plane S-vacancies were common.[32,37,38] We postulated that thiol-containing organic molecules could fill these sulfur vacancies (Scheme 1). To test this hypothesis we reacted liquid-exfoliated 2H-MoS_2 with a thiol-containing organic molecule, cysteine. Cysteine was chosen because it is bio-relevant, commercially available, and contains functional groups (carboxylate and amine) that would allow for simple characterization and further derivatization. 2H-MoS_2 nanosheets (0.5 g L^{-1}) dispersed in IPA (20 mL) were reacted with the hydrochloride salt of L-cysteine dissolved in IPA (20 g L^{-1}, 10 mL) by combining the dispersion and solution and performing tip ultra-sonication on the mixture for 0.5 h at room temperature (Supporting Information). Following the ultra-sonication, the resulting dispersion was subjected to high-speed centrifugation to precipitate all dispersed materials. The resulting sediment was exhaustively washed with aqueous solutions, and then re-dispersed in IPA (10 mL) for further characterization.

The cysteine-functionalized re-dispersed 2H-MoS_2 (Cys-2H-MoS_2) displayed a markedly different dispersability in IPA compared to pristine 2H-MoS_2. The electronic extinction spectrum of Cys-2H-MoS_2 displayed a very high degree of nanosheet aggregation, as evidenced by the rather large baseline shift when comparing pristine 2H-MoS_2 to Cys-2H-MoS_2 (Figure 1a).[39] This difference was noticeable to the human eye (Figure 1b); Cys-2H-MoS_2 flocculated (formed clumpy materials) readily in IPA, whereas dispersions of pristine 2H-MoS_2 did not. Furthermore, Cys-2H-MoS_2 yielded dispersions that were black in color, whereas pristine 2H-MoS_2 dispersions tended to be yellowish green. These observations clearly indicate that the surface properties in the Cys-2H-MoS_2 had been altered dramatically compared to pristine 2H-MoS_2.

Importantly, functionalization appeared to have caused minimal changes to the relative intensities or energies of excitonic transitions attributed to exfoliated 2H-MoS_2 (Figure 1a). The transitions at λ_{max} = 459, 614, and 675 nm are typical of 2H-MoS_2. Cys-2H-MoS_2 displayed a similar set of features (λ_{max} = 496, 629, and 689 nm), displaying a small degree of red-shifting compared to the parent pristine 2H-MoS_2, which could be caused by the rather large baseline shift caused by flocculation. These observations are very important because they establish that functionalization yielded a slightly modified 2H-MoS_2 and, critically, did not yield the 1T-polytype (1T-MoS_2 has an extinction spectrum very different from 2H-MoS_2).[21] Most other covalent functionalization techniques to date have yielded 1T-MoS_2.

Comparison of the diffuse reflectance infrared Fourier transform (DRIFT) spectra of 2H-MoS_2 and Cys-2H-MoS_2 demonstrated a sharp feature at 384 cm^{-1} that is typical of 2H-MoS_2 (Figure 2),[40] indicating that the functionalization had not affected the vibrational properties or overall morphology

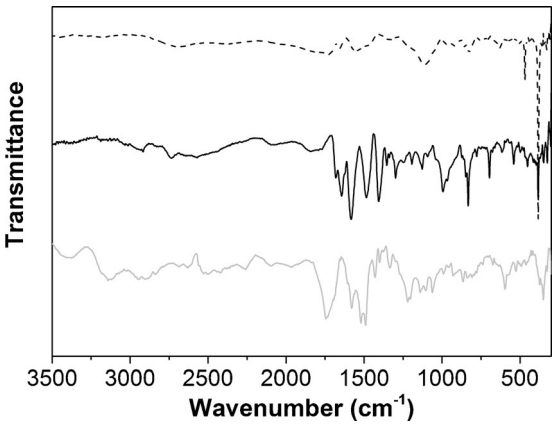


Figure 2. DRIFT spectra of pristine 2H-MoS_2 (dashed trace), Cys-2H-MoS_2 (solid trace) and cysteine (gray trace).

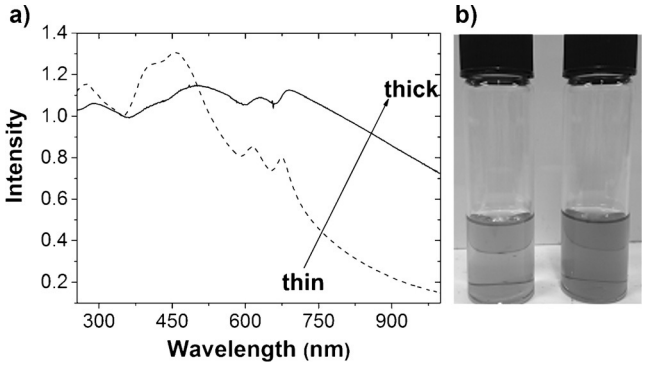


Figure 1. a) UV/Vis extinction spectra of 2H-MoS_2 (dashed trace) and Cys-2H-MoS_2 (solid trace) in IPA normalized to the local minimum at $\approx$350 nm. b) Photograph of diluted dispersions of 2H-MoS_2 (left) and Cys-2H-MoS_2 (right) in IPA.

in the Cys-2H-MoS_2. Importantly, the DRIFT spectrum for Cys-2H-MoS_2 showed a number of new features that we attributed to the introduction of a cysteine derivative to the surface of the nanomaterial. A comparison of the DRIFT spectra of cysteine with Cys-2H-MoS_2 showed that the vibrational properties of the cysteine on the 2H-MoS_2 surface have been altered considerably through reaction with 2H-MoS_2. Firstly, in cysteine a feature at 2532 cm^{-1} attributed to the ν_{S-H} was observed.[41] This feature was absent in Cys-2H-MoS_2, and there were no new features in this region of the DRIFT spectrum. This would suggest that the thiol group of cysteine had reacted in the presence of 2H-MoS_2. All previous reports on the reaction between organic thiols and MoS_2 showed a similar loss of the ν_{S-H} by IR spectroscopy, leading to the conclusion that the thiol had reacted with the MoS_2.[27–35] Secondly, cysteine displayed broad features at 1745 and 1377 cm^{-1} corresponding to stretches of its carbox-

ylate group.[41] In Cys-2H-MoS_2 these features had shifted to lower energy (1644 and 1354 cm^{-1}, respectively), presumably, again, as a result of a reaction between cysteine and 2H-MoS_2. In all, the DRIFT spectrum of Cys-2H-MoS_2 indicated that cysteine is coupled to the surface of the 2H-MoS_2. However, the clear and dramatic changes to the vibrational properties of the cysteine suggest that the cysteine had been chemically altered.

Raman spectroscopy also indicated that the reaction between cysteine and 2H-MoS_2 yielded a slightly altered 2H-MoS_2 surface. Minor changes to the relative intensities of resonantly enhanced features in the Raman spectrum (Supporting Information, Figures S1, S2) of Cys-2H-MoS_2 indicated organic functionalities were interacting with the 2H-MoS_2 surface.[36,38,42,43]

To examine the atomic-level 2H-MoS_2/cysteine interaction in Cys-2H-MoS_2, high-resolution X-ray photoelectron spectroscopy (XPS) analysis was performed. First, we observed that the Cys-2H-MoS_2 nanosheets preserved the semiconducting 2H polymorph after functionalization, and were not the 1T polymorph.[23,26,44] The XPS spectrum of cysteine (Figure 3b) exhibited a single doublet of S 2p peaks

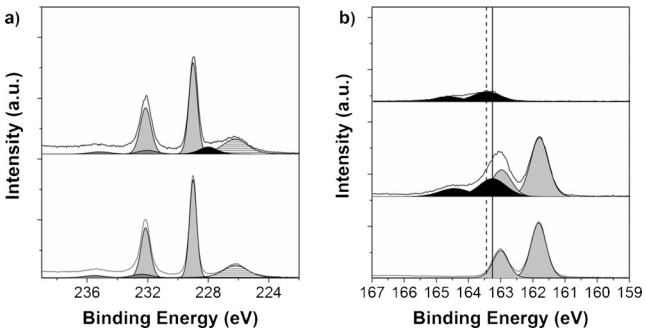


Figure 3. Fitted XPS spectra. a) Mo 3d core level spectra of Cys-2H-MoS_2 (top), and pristine 2H-MoS_2 (bottom). Fit components are attributed to 2H-MoS_2, MoO_3, S 2 s, and cysteine-like entities in both cases. b) S 2p core level spectra of cysteine salt (top), Cys-2H-MoS_2 (middle), and pristine 2H-MoS_2 (bottom). Fit components are attributed to 2H-MoS_2 (light gray), and cysteine-like entities (black).

with the S $2p_{3/2}$ binding energy at 163.5 eV. In contrast, peak fitting of the S 2p spectrum of Cys-2H-MoS_2 resulted in two doublets. The first doublet with S $2p_{3/2}$ binding energy at 161.8 eV made the largest contribution (68%) and was comparable to the S $2p_{3/2}$ peak of the pristine 2H-MoS_2. The smaller doublet with S $2p_{3/2}$ binding energy at 163.3 eV was attributed to the surface cysteine entities. A minor shift (0.2 eV) in the binding energy in this doublet relative to pure cysteine was observed, consistent with a chemical change to the cysteine molecule. The higher binding energy component represented 32% of the S-atoms on the sample surface, indicating a degree of functionalization of 32%. We note that thermo-gravimetric analysis (TGA, below) also suggested $\approx$30% loading of cysteine in Cys-2H-MoS_2.

Critically, the binding energy of the surface S-atoms in 2H-MoS_2 was not affected by the presence of a functional group on the nanosheet surface.[45] The S 2p XPS data was best fit with only two S-atom components: a cysteine-like component and a 2H-MoS_2 component. Furthermore, the Mo 3d XPS spectra displayed no differences between 2H-MoS_2 and Cys-2H-MoS_2, showing that the electronic environment around the Mo-atoms in Cys-2H-MoS_2 had not been altered upon functionalization. Previous reports showed that changes in the S 2p region of the XPS spectra of functionalized ce-1T-MoS_2 were indicative of the presence of functionality C- to MoS_2 S-bonds on the ce-1T-MoS_2 surface.[23,26] These observations suggest that chemical modification of the 2H-MoS_2 surface in Cys-2H-MoS_2 was unlikely to have occurred, while a chemical modification of cysteine had occurred.

TGA of Cys-2H-MoS_2 revealed a clear stepwise degradation (Figure S3). Pristine 2H-MoS_2 did not display any degradation below 500 °C. In Cys-2H-MoS_2, an approximately 30% weight loss took place between 215–265 °C. Because the thermal decomposition temperature of cysteine is 200–230 °C (Figure S3), we inferred that the significant weight loss was caused by the decomposition of cysteine-like molecules bound to the 2H-MoS_2 surface. According to TGA-coupled infra-red (TGA-IR) spectroscopy, the major gaseous product evolved from Cys-2H-MoS_2 was identified as CO_2 (Figure S4, 2349 cm^{-1}) which presumably derives from the decomposition of cysteine. The TGA thus indicated that an organic functionality, very similar to cysteine, was docked on 2H-MoS_2 in Cys-2H-MoS_2.

Having thoroughly characterized Cys-2H-MoS_2, we then probed the effect of the cysteine functionalities on the dispersability of the 2H-MoS_2. We found that Cys-2H-MoS_2 was readily re-dispersed in water (Figure S6). Pristine 2H-MoS_2 did not disperse in water (Figure S6), and few methods to effectively disperse 2H-MoS_2 in water by functionalization exist.[30,46] Importantly, the aqueous Cys-2H-MoS_2 dispersions were stable for at least one week. Furthermore, we could vary the pH of the aqueous dispersions, with no effect on the dispersability of the Cys-2H-MoS_2 (Figure S6). We previously identified methods to enhance TMD dispersability in acetone,[25] but the present water dispersion results are very important, potentially eliminating the use of organic solvents altogether for 2H-MoS_2.

We performed a number of experiments to verify the nature of the interaction between 2H-MoS_2 and cysteine. As stated earlier, XPS indicated that no change to the MoS_2 S- or Mo-atoms in Cys-2H-MoS_2 had occurred, with a very minor change to the surface cysteine. These observations indicated that the functionalization in Cys-2H-MoS_2 may not be covalent, and also suggested that cysteine S-atoms may not be filling S-atom vacancies. However, the surface properties of the 2H-MoS_2 in Cys-2H-MoS_2 had clearly been altered, as evidenced by UV/Vis spectroscopy and re-dispersion measurements. XPS, TGA, and Raman analyses confirmed the presence of surface functionalities in Cys-2H-MoS_2. However, these analyses provided no evidence for covalent or dative bond formation between the 2H-MoS_2 and functionality. Finally, the DRIFT measurements suggested a chemical change to the cysteine molecules on the surface, while the 2H-MoS_2 remained in a pristine state.

To probe the surface functional groups further, we removed them from the surface (de-functionalization). De-

functionalization was achieved by first dispersing the Cys-2H-MoS_2 in IPA and subsequently centrifuging this dispersion and decanting the IPA. Second, after multiple such washings, the resultant solids were re-dispersed in water, placed in a dialysis bag, and dialyzed for four days. After dialysis, the solvent was removed from the resulting dialysate under vacuum, and the obtained product (de-functionalized organic material) was analyzed by ^{1}H NMR, while the resulting 2H-MoS_2 was subjected to XPS. The ^{1}H NMR spectrum (Figure S8) of the diasylate product showed that the obtained material was not cysteine, but in fact was the oxidized (disulfide) derivative of cysteine, cystine. The identification of the disulfide product accounts for the disappearance of the ν_{S-H} resonance in the DRIFT spectrum of Cys-2H-MoS_2. XPS analysis of the post-dialysis 2H-MoS_2 showed that the de-functionalized nanomaterial was pristine 2H-MoS_2 (Figure S9, no organic S-features, confirming complete de-functionalization). Critically, when 2H-MoS_2 was reacted with cystine, we observed the same DRIFT and XPS features in the resulting functionalized material as we observed for Cys-2H-MoS_2 (Figure S17,18), showing physisorption of cystine on 2H-MoS_2. These observations demonstrate that the reaction between cysteine and 2H-MoS_2 caused the thiol to be converted to a new entity, but the 2H-MoS_2 was chemically unchanged.

We then compared the DRIFT spectrum of Cys-2H-MoS_2 with the DRIFT spectrum of cystine (Figure 4). The spectra showed an almost perfect overlap of resonances (of particular note is the S–S vibrational mode, $\nu_{S\text{-}S} = 540\ cm^{-1}$),[47] demonstrating that cystine (and not cysteine) was docked on the surface in Cys-2H-MoS_2. The lack of a chemical change to the 2H-MoS_2 in Cys-2H-MoS_2, and ease at which the cystine was de-functionalized from the surface, would suggest that cystine was simply physisorbed onto the 2H-MoS_2 surface. This is an important observation and probably accounts for the very high degree of loading of organic functionalities (Figure S5). Only through physisorption of multiple layers of organic functionality would such high levels of loading be achievable.

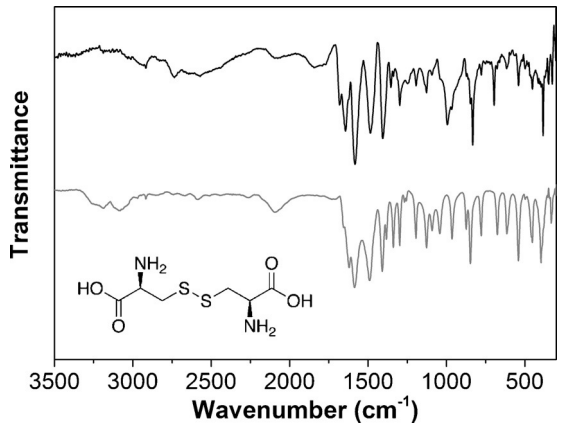
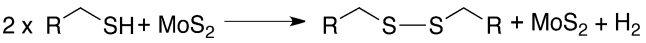


Figure 4. DRIFT spectra of Cys-2H-MoS_2 (black trace) and cystine (gray trace).

We were intrigued by the 2H-MoS_2 facilitated oxidation of cysteine to cystine yielding functionalization through physisorption of cystine. Earlier work demonstrated the functionalization of ce-1T-MoS_2 through ligand conjugation.[26] We explored the reaction of cysteine with ce-1T-MoS_2 (following the ligand conjugation methods) and obtained DRIFT and XPS spectra that showed cystine was docked onto the surface of ce-1T-MoS_2 (Figures S10 and S11), rather than cysteine. Thus, in both 2H- and 1T-polymorphs of MoS_2, their reaction with cysteine yielded cystine-functionalized MoS_2. We then performed the reaction between cysteine and 2H-MoS_2 under an inert atmosphere (N_2). Under these conditions, we obtained the same Cys-2H-MoS_2, containing the disulfide product cystine, as evidenced by DRIFT spectroscopy (Figure S12). This demonstrated that dioxygen was not facilitating the oxidation of cysteine to cystine, and that MoS_2 is likely the mediator of this transformation. To explore if oxidation was caused by the functionalization methods, we sonicated a solution of cysteine in IPA in the absence of MoS_2 (thus under the functionalization conditions). The ^{1}H-NMR spectrum (Figure S13) of the solids resulting from this experiment showed resonances typical of cysteine, and not cystine, verifying that the functionalization methods do not lead to the oxidation of cysteine. Finally, the analogous reaction between cysteine and liquid exfoliated 2H-WS_2 yielded similar results to 2H-MoS_2 (thus Cys-2H-WS_2, with cystine functionalities; Figure S16).

We also attempted the functionalization of liquid-exfoliated 2H-MoS_2 with other commercially available thiols (1-octanethiol, 3-mercaptopropionic acid) and identified oxidized disulfide products. The DRIFT spectrum of the products showed characteristic S–S vibrational features, suggesting the formation of disulfides (Figures S14, S15). The observation of $\nu_{C-S} = 615\ cm^{-1}$, as observed previously for dioctyl-disulfide-functionalized nanoparticles,[48] provided a very strong indication of disulfide formation when 1-octanethiol reacted with 2H-MoS_2. Furthermore, GC-MS analysis of the 2H-MoS_2/thiol reaction mixtures showed the presence of disulfide products (Figures S14, S15). It thus appears that TMDs facilitate the oxidation of organic thiols to disulfides. The formed disulfides appear to have physisorbed on the 2D TMD surface, presumably through electrostatic interactions.

The mechanism of disulfide formation is, at the moment, not clear to us. Because the oxidation of disulfides does not require O_2, we therefore propose that that MoS_2 is mediating the conversion of thiols to disulfide with the concomitant release of H_2 (Scheme 2). We think thiols donate a hydrogen atom to MoS_2, yielding a thiyl radical and a 1-electron-reduced product H[MoS_2]. The thiyl radical presumably reacts with another thiyl radical to yield disulfide. The H[MoS_2] possibly releases dihydrogen through the coupling of two H-atoms bound to the polymeric MoS_2 surface. This hypothesis requires extensive study to confirm the mechanism.



Scheme 2. MoS_2-mediated conversion of organic thiol to disulfide.

In conclusion, we have demonstrated a general route for the functionalization of 2H-MoS_2 nanosheets with cysteine. Functionalization was achieved by blending a dispersion of liquid-exfoliated 2H-MoS_2 with a solution of cysteine. The resulting Cys-2H-MoS_2 was fully characterized by UV/Vis, DRIFT, XPS, TGA, and Raman spectroscopy. We discovered that MoS_2 was facilitating the oxidation of cysteine to cystine during functionalization. Rather than coordinating as a thiol (cysteine) at S-vacancies in the 2H-MoS_2, as originally conceived, cystine was simply physisorbed on the nanosheet. These observations were found to be true for other organic thiols, and indeed other TMDs. Based on our findings, we urge caution with methods that employ organic thiols to chemically functionalize TMDs; the thiols may not be forming bonds with the surface. Present explorations in our lab are focused on alternative methods for the covalent functionalization of 2H-MoS_2.

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Keywords: 2D materials · liquid exfoliation · organic thiol · surface functionalization · transition metal dichalcogenides

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