

Two-dimensional MoS₂ catalyzed oxidation of organic thiols

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ABSTRACT: Thiol-chemistry directed techniques have been extensively employed to modify the properties of two-dimensional (2D) MoS₂ nanosheets, aiming to heal or functionalize sulfur vacancies (SVs). However, the exact nature of the organic thiol/exfoliated MoS₂ interaction remains under dispute. Herein, the reactions between 2H-MoS₂ and organic thiols are explored in detail. We quantitatively monitor the consumption of 1-octanethiol in the presence of exfoliated 2H-MoS₂ nanosheets using ¹H nuclear magnetic resonance (NMR) spectroscopy. The generation of dioctyl-disulfide product was detected as the only product of the 2H-MoS₂/1-octanethiol reaction. Furthermore, it was found that this reaction was catalytic, and was not caused by atmospheric dioxygen. In addition, we found that the following affected the kinetics of the reaction: the thickness of the exfoliated 2H-MoS₂ nanosheets; the use of deuterated substrate (kinetic isotope effect = 2); and the electron donating nature of the thiol substrate. The disulfide product was postulated to be formed via the intermolecular exchange between free thiols and either adsorbed thiolate (or thiyl radicals) or desorbed thiyl radicals. Our studies demonstrate that the ‘functionalization’ of 2H-MoS₂ nanosheets with organic thiols is likely simply 2H-MoS₂-catalyzed oxidation of the thiol, with no evidence for any bond-forming (covalent or dative) interaction between the thiols and MoS₂.

Introduction: Thin layered transition metal dichalcogenide (TMD, *e.g.* MoS₂) nanosheets have been stimulating increasing interest in a wide array of applications owing to their unique electronic, optoelectronic, and catalytic properties.^[1-3] The significant progress in the synthesis of MoS₂ nanosheets has enabled the production of thin layered and large-area MoS₂ nanosheets on the lab scale.^[2, 4] Nevertheless, the obtained MoS₂ nanosheets, with randomly distributed sulfur vacancies (SVs), are normally not perfect lattices.^[5, 6] These SVs have been found to be a double-edged sword, they can either serve as active sites for various catalytic reactions^[7, 8] or act as trap states affecting the intralayer charge transport.^[9, 10] From the perspective of fabrication of electronic devices, defect-free MoS₂ nanosheets are highly desired. To this end, thiol chemistry based techniques have been applied widely in recent years aiming to either repair the SVs^[11] via uptake of S atoms from thiols to SVs sites or to passivate/functionalize the SVs of MoS₂ nanosheets through binding of thiol ligands to the unsaturated Mo atoms in SV sites.^[12] While the repair of SVs (S-atom uptake) by reacting thiols with MoS₂ has been exhaustively proven, the exact nature of the initial thiol/MoS₂ interaction remains under dispute, particularly in the cases of thiol-functionalization of MoS₂.^[13-17]

In a previous study, we demonstrated a general route to functionalize 2H-MoS₂ with cysteine (an organic thiol).^[14] Critically, 2H-MoS₂ was found to be facilitating the oxidation of the thiol, cysteine, to the disulfide, cystine during the functionalization process. The resulting cystine was simply physisorbed on the MoS₂ nanosheets rather than

any bond-forming process between the thiol or disulfide and the 2H-MoS₂ surface having occurred.^[14] Subsequently, theoretical research by Tománek and co-workers also predicted that thiols may form disulfides on the MoS₂ surface. However, this proposal required the presence of additional adsorbed dangling sulfur atoms which form a hydro-disulfide, which then reacts with a second thiol to form the dialkyldisulfide.^[17] Another theoretical study by Wang and co-workers also suggested the possibility of formation of disulfide product by reaction of MoS₂ with organic thiols, although they predicted that a relatively high energy barrier and steric hindrance might limit this process.^[16] To further understand the mechanism of MoS₂ mediated thiol oxidation, herein we present a detailed reactivity and kinetic study into the reaction between 2H-MoS₂ and organic thiols.

Results and Discussion: For this study, 1-octanethiol was used as a model thiol substrate. The reason for this was that 1-octanethiol is a representative organic alkylthiol of the cohort that have been used to functionalize TMDs through ‘ligand conjugation’.^[11, 15, 18] Furthermore, 1-octanethiol and the oxidized product dioctyl disulfide have easily distinguished features that can be probed by ¹H nuclear magnetic resonance (¹H NMR) spectroscopy. Thin-layered 2H-MoS₂ nanosheets were prepared by ultrasonication of bulk MoS₂ in 2-propanol (IPA) as illustrated previously (see supporting information for details),^[5, 14] yielding the exfoliated 2H-MoS₂ nanosheets with 9-10 layer thickness. MoS₂ is either found with the Mo ion in a trigo-

nal prismatic environment (1T) or an octahedral environment (2H). We have used the 2H polymorph because it is relatively chemically inert and has not undergone any redox reactions for its synthesis (unlike the 1T polymorph), making it less likely to influence the exploration of thiol oxidation reactivity.

In a typical reaction, a molar excess of 1-octanethiol was mixed with the liquid exfoliated 2H-MoS₂ powder in CD₃OD (unless otherwise stated) followed by bath sonication for 10 min and refluxing the resulting dispersion in the presence or absence of air. The mixture was heated to reflux only to accelerate the reaction, we observed the same outcomes over longer time periods without heating. The reaction progress was monitored using ¹H NMR spectroscopy, where 1-octanethiol displayed a characteristic triplet signal at $\delta = 2.49$ ppm corresponding to the protons bonded to the α -carbon (-CH₂-SH). This triplet was shifted to the lower field region in dioctyl disulfide due to the deshielding effect of the disulfide entity, giving rise to a new triplet resonance at $\delta = 2.68$ ppm (Figure 1).

Control reaction of 1-octanethiol in the presence of air but in the absence of 2H-MoS₂: The oxidation of 1-octanethiol in the absence of 2H-MoS₂ was investigated by refluxing 1-octanethiol (200 μ L, 1.15 mmol) in CD₃OD (1 mL) at 100 °C under an air atmosphere for 24 hrs. The ¹H NMR spectrum of the resulting solution showed no change when compared to pure 1-octanethiol and no detectable dioctyl disulfide signals were observed (Figure 1). This suggested that there was negligible oxidation of 1-octanethiol to dioctyl disulfide under an air atmosphere in the absence of 2H-MoS₂.

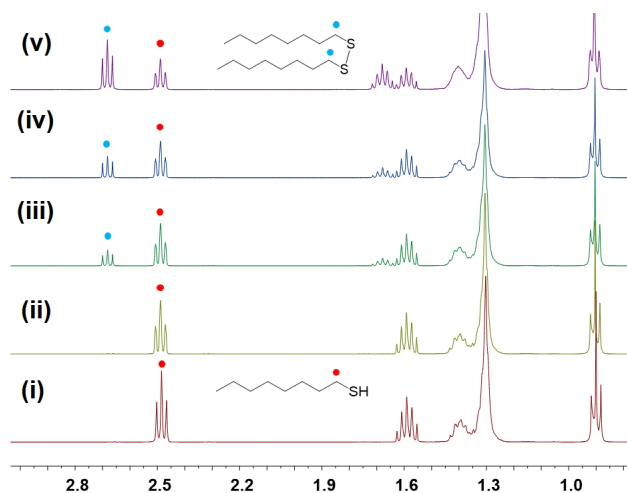


Figure 1. ¹H-NMR (400 MHz, CD₃OD) spectra of (i) pure 1-octanethiol; (ii) after heating 1-octanethiol in CD₃OD under reflux (in air) for 24 h; (iii) 1-octanethiol/exfoliated 2H-MoS₂ reaction mixture (in air) after 4 h, (iv) 6 h, and (v) 24 h. Highlighted triplet resonances: 1-octanethiol, $\delta = 2.49$ ppm, red dot; dioctyl disulfide, $\delta = 2.68$ ppm, blue dot. Other signals are associated with either the 1-octanethiol or disulfide derivative thereof.

Oxidation of 1-octanethiol in the presence of air and 2H-MoS₂: Liquid-exfoliated 2H-MoS₂ powder (10 mg, 52

mM) was added to the above solution after it had refluxed for 24 h. The resulting reaction dispersion was heated at 100 °C under an air atmosphere for 24 h and the reaction progress was monitored by ¹H NMR (Figure 1). The concentration of 1-octanethiol decreased by ~20%, 25%, and 55% with respect to the starting concentration after refluxing for 4 h, 6 h, and 24 h, respectively. We assessed a rather large error in this kinetic measurement, along with others reported below of $\pm 20\%$. Critically, however, consistent trends were ascertained in the kinetic analysis, allowing us to draw conclusions into the mechanism of thiol oxidation. The yield of dioctyl disulfide was thus 55% after 24 h. The increase of dioctyl disulfide accompanied by the decrease of 1-octanethiol indicated that the oxidation of 1-octanethiol to dioctyl disulfide was mediated by the 2H-MoS₂ nano-sheets. Dioctyl disulfide was found to be the only product of the 2H-MoS₂/1-octanethiol reaction by ¹H NMR (Figure 1) and gas chromatography coupled to mass spectrometry (GC-MS) analysis of the post-reaction mixture (Figure S1). It can thus be deduced that 2H-MoS₂ was required for the oxidation of thiol to disulfide. This result was also consistent with our previous observations during functionalization of liquid exfoliated 2H-MoS₂ with cysteine, where the majority of cysteine was converted to cystine.^[14]

Oxidation of 1-octanethiol in the presence of 2H-MoS₂ but in the absence of air: To understand the influence of air and gain more insight into the role of 2H-MoS₂ nano-sheets in the oxidation of 1-octanethiol, the reaction of 1-octanethiol with 2H-MoS₂ in an air-free atmosphere was performed. 1-octanethiol (200 μ L, 960 mM) was mixed with liquid exfoliated 2H-MoS₂ (10 mg, 52 mM) in completely de-aerated CD₃OD (1 mL). The dispersion was heated at 100 °C under an Ar atmosphere. ¹H NMR analysis showed two sets of signals corresponding to 1-octanethiol and the oxidised product dioctyl disulfide (Figure S2), indicating that significant quantities of dioctyl disulfide formed in the absence of air. The yield of dioctyl disulfide after 24 h was 30%. The turnover number (TON, the number of moles of 1-octanethiol consumed versus the number of moles of 2H-MoS₂) after 24 h for this air-free reaction was 3.2, whereas the TON for the same reaction performed under an air atmosphere (Figure 1) over 24 h was found to be 10.2. We assume the differences between aerated and de-aerated solutions are as a result of O₂ accelerating the oxidation reaction in the aerated solution.

These observations demonstrate that 2H-MoS₂ was facilitating the oxidation of a thiol to a disulfide, and that this was not an O₂-mediated process but was accelerated by the presence of O₂. The obtained large TONs indicated that 2H-MoS₂ nano-sheets *catalyzed* the oxidation of 1-octanethiol to dioctyl disulfide.

Kinetic study of anaerobic 1-octanethiol oxidation in the presence of 2H-MoS₂: For the reaction between 1-octanethiol and 2H-MoS₂, we determined the reaction rates and explored the effect of 1-octanethiol and 2H-MoS₂ concentrations on these rates. To simplify this reaction

mechanism study, all kinetic measurements were performed under an inert (de-aerated) atmosphere.

Fixed [1-octanethiol] and varied [2H-MoS₂]: We first fixed the concentration of 1-octanethiol (524 mM) and varied the concentrations of the dispersions of liquid exfoliated 2H-MoS₂ (28, 57, 114, 170, 227 mM). The reaction progress was monitored using ¹H NMR spectroscopy. In the first 8 h of the reaction, the concentration of 1-octanethiol ([1-octanethiol]) decreased against time (Figures 2, S₃), and this decrease was accelerated at higher concentrations of 2H-MoS₂ ([2H-MoS₂]). A plot of [1-octanethiol] changes against time displayed a linear relationship (Figures 2, S₃), which is suggestive of a *pseudo-zero-order* reaction in 1-octanethiol.

Between 8 h and 24 h the reaction appeared to slow at all [2H-MoS₂], but particularly at higher [2H-MoS₂] (Figure S₃). The rates of 1-octanethiol consumption ($-d[\text{RSH}]/dt$) between 0-8 h were plotted against [2H-MoS₂] to investigate the effect of 2H-MoS₂ concentration on the reaction rate (Figure 2). Up to concentrations of 170 mM 2H-MoS₂ (the ratio of [2H-MoS₂] to [1-octanethiol] = 0.32), the more 2H-MoS₂ nanosheets employed in the reaction, the faster the 1-octanethiol consumption. The slope of this plot gave a rate constant for this reaction of $k = 0.26 \text{ h}^{-1}$. Interestingly, the 227 mM dispersion reaction mixture displayed evidence for aggregated and precipitated 2H-MoS₂ (floculation). This re-aggregation phenomenon was also observed in the reactions using lower concentrations of 2H-MoS₂ after extended periods of stirring, which was evidenced by the decreased 1-octanethiol consumption rate after 8 h (Figure S₃).

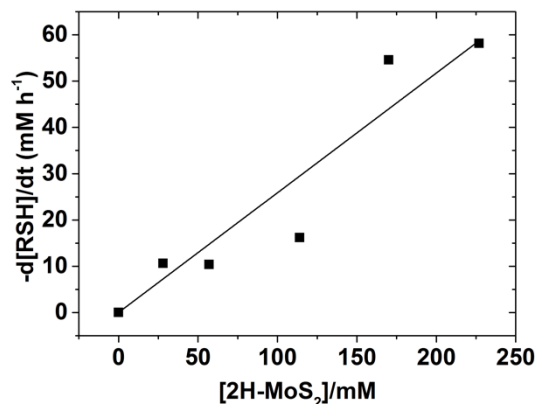


Figure 2. Plot of rate of [1-octanethiol] ([RSH]) consumption ($-d[\text{RSH}]/dt$) versus [2H-MoS₂].

Effect of re-aggregation of nano-sheets: We believe the lower rate for high [2H-MoS₂] and after longer reaction times are related. We expect high degrees of aggregation of the 2H-MoS₂ nano-sheets at higher [2H-MoS₂] and over longer reaction times. The probability of re-aggregation increases both a high [2H-MoS₂] and after long periods in dispersion without continuous sonication.^{19, 20} To test the

effect of the degree of aggregation on the rate of the 1-octanethiol oxidation reaction, instead of using liquid exfoliated 2H-MoS₂ nanosheets (9-10 layers),¹⁴ bulk (not exfoliated) 2H-MoS₂ (57 mM) was reacted with 1-octanethiol (100 μl, 524 mM) in CD₃OD under the same reaction conditions described above (Figure S₄). Approximately 6% of 1-octanethiol was consumed and converted to dioctyl disulfide. In comparison, under the same reaction conditions liquid-exfoliated 2H-MoS₂ nanosheets (57 mM) led to a ~30% conversion of 1-octanethiol. Overall, the bulk material oxidized 1-octanethiol at a rate that was an order of magnitude smaller than the exfoliated materials. Furthermore, we monitored the re-aggregation of 2H-MoS₂ by electronic absorption spectroscopy (Figure S₅). In the first 4 h of the reaction minimal re-aggregation was apparent, whereas after 24h almost complete re-aggregation was observed. We postulate that the increase in the conversion efficiency using liquid-exfoliated 2H-MoS₂ can be attributed to the increased number of accessible active sites in the exfoliated 2H-MoS₂ versus the bulk 2H-MoS₂.

Fixed [2H-MoS₂] and varied [1-octanethiol]: Reactions with a fixed amount of liquid exfoliated 2H-MoS₂ (57 mM) and varied concentrations of 1-octanethiol (274, 524, 960, 1330, 1640 and 1921 mM) were performed and monitored using ¹H NMR spectroscopy. Plots of the change in [1-octanethiol] against time revealed a linear decay of [1-octanethiol] with time was observed at all concentrations of 1-octanethiol (Figure S₆). To study the influence of [1-octanethiol] on the reaction rate, the rates of 1-octanethiol depletion ($-d[\text{RSH}]/dt$) were plotted against the initial [1-octanethiol] (Figure 3). This yielded a linear fit confirming that the rate of thiol oxidation was *pseudo-zero-order* in 1-octanethiol. The slope of this plot gave a rate constant for this reaction of $k = 0.018 \text{ h}^{-1}$.

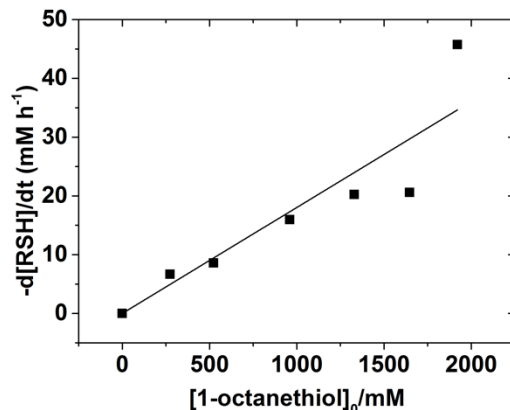


Figure 3. Plots of observed zero-order rates (1 - 8 h) of 1-octanethiol oxidation ($-d[\text{RSH}]/dt$) versus initial [1-octanethiol].

The kinetic studies suggest a dependence of the rate of [1-octanethiol] depletion on both [2H-MoS₂] and [1-octanethiol]. This indicates the involvement of these two species in or prior to the rate-limiting step (RDS).

Other factors that could affect the rate of the 2H-MoS₂/1-octanethiol reaction:

Kinetic Isotope Effect: The possibility of a kinetic isotope effect to the 2H-MoS₂-mediated 1-octanethiol oxidation was studied by performing the parallel reactions between exfoliated 2H-MoS₂ (52 mM) and 1-octanethiol (960 mM) in CH₃OH or CD₃OD (1 mL, Figure S7). We expect facile H⁺/D⁺ exchange between the methanol solvent and 1-octanethiol, allowing for the in-situ generation of H- or D-1-octanethiol in CH₃OH or CD₃OD, respectively. A kinetic isotope effect (KIE) of 2 was measured where the reaction was faster in CH₃OH than in CD₃OD. This observation suggested that H⁺ or H-atom transfer was involved in or occurred prior to the rate-limiting step of the 1-octanethiol oxidation reaction.

Light effect: Benefiting from its semiconducting nature, 2H-MoS₂ has previously been investigated as a photocatalyst.^[21] To check the effect of light in the catalytic 2H-MoS₂ mediated oxidation, the oxidation reaction between 2H-MoS₂ (57 mM) and 1-octanethiol (960 mM) was performed in both the dark and under ambient light conditions (Figure S8). The measured reaction rate was almost the same, indicating that ambient light irradiation was not involved in the 1-octanethiol oxidation by 2H-MoS₂.

Nature of the thiol substrate: To probe the effect of the nature of the thiol substrate on the oxidation reaction kinetics, the oxidation reactivity of 2H-MoS₂ nano-sheets towards L-cysteine and thiophenol were also studied using ¹H NMR spectroscopy. Both substrates were readily oxidized to their disulfide products (Figure S9) in the presence of 2H-MoS₂. In both cases the turnover number was 3 – 5, indicating that the oxidation was catalytic. The rates of oxidation of thiol to disulfide in the presence of the same concentration of 2H-MoS₂ nano-sheets (57 mM) followed the sequence: L-cysteine > thiophenol > 1-octanethiol (Figures 4, S10-S11). The oxidation reaction rate of L-cysteine was four-fold greater than that of 1-octanethiol oxidation, and was approximately two-fold greater than the rate of oxidation of thiophenol. This significant change in the reaction rate of thiol oxidation using different thiol substrates indicated that the 2H-MoS₂ catalyzed thiol oxidation process was affected by the electron donating ability of functionalities on the organic thiols. A comparison of the pK_a (S-H) of the three thiols revealed that the highest thiol oxidation rate was achieved when the pK_a (S-H) was smallest (L-cysteine). The thiol oxidation rate decreased with the increase of pK_a of thiol substrates (Figure 4). Alongside the KIE result, this observation suggests that the S-H functionality is involved in the rate limiting step in the oxidation of the thiol to disulfide.

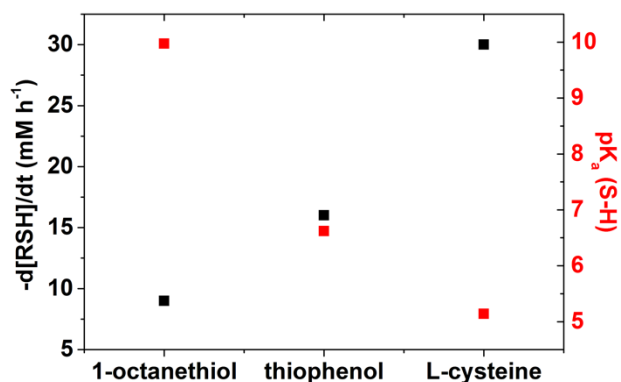


Figure 4. The rate of oxidation of thiols (black) and the pK_a of S-H group (red) of the thiol substrates.

At this point it is worth recalling that in our previous work, and all other studies on thiol functionalization of MoS₂ the disappearance of the thiol S-H vibrational mode ($\nu = 2500 \text{ cm}^{-1}$) in the infra-red spectra of the ‘functionalized’ material had occurred.^[12, 13, 14] This led some to conclude the formation of a bond between the thiol and MoS₂. Moreover, the XPS spectra of the same ‘functionalized’ MoS₂ samples displayed a chemically unchanged MoS₂ surface, confirming that the thiol/MoS₂ reaction product was likely simply physisorbed on the MoS₂ surface (as confirmed by both XPS and infra-red spectroscopies).^[12, 13, 14]

Postulation of a mechanism of 2H-MoS₂ catalyzed anaerobic thiol oxidation: Two computational studies by Wang and co-workers and Tománek and co-workers have addressed the mechanism of thiol oxidation by MoS₂.^[16, 17] In both reports, it was postulated that the organic thiol binds at a sulfur vacancy in the MoS₂ and subsequent homolytic thiol S-H bond cleavage results in formation of a Mo-S bond and either a Mo-H or a S_{MoS₂}-H bond. Wang predicted that a second thiol molecule then reacted with the formed Mo-S/Mo-H entity to yield disulfide and two Mo-H species. Tománek predicted the formation of an RSSH species and conversion of this to disulfide RSSR in subsequent steps.

We postulate that the incoming thiol coordinates at SVs on the 2H-MoS₂ surface. We postulate subsequent proton transfer to an S atom in the vicinity of the SV, leaving the thiolate group (RS⁻) bound to a Mo (Figure 5).^[16] This would represent *heterolytic* S-H bond breakage, in contrast to the mechanisms proposed by Tománek and Wang. Thiol proton transfer at the surface of an MoS₂ catalyst has been demonstrated in previous MoS₂ catalyzed hydrodesulfurization studies.^[22, 23] The proposed proton transfer is supported by our experimental results which clearly demonstrate rate-limiting proton transfer (KIE = 2 and the pK_a (S-H) of the thiol influenced the rate of thiol oxidation).

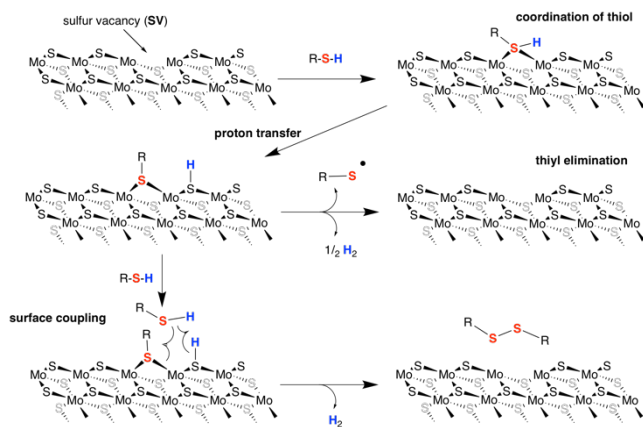


Figure 5. Proposed mechanisms for MoS₂ nanosheets catalyzed thiol oxidation.

Following proton transfer, we postulate that there are two pathways that can result in disulfide formation and H₂ evolution (Figure 5): 1) a thiyl radical (RS•) would be released from the thiolato-MoS₂-H surface and subsequently react with another thiyl radical or a solution phase thiol to yield disulfide and ½H₂; or 2) radical coupling on the surface could occur between an incoming second thiol molecule and the de-protonated thiolate group resulting in disulfide and H₂ formation. Unfortunately, our kinetic data do not allow us to differentiate between these pathways.

The kinetic data do demonstrate that both the [1-octanethiol] and [2H-MoS₂] influence the rate of the reaction. Critically, however, the associated rate constants (0.018 h⁻¹ and 0.26 h⁻¹, respectively) suggest that the influence of [2H-MoS₂] on the reaction is 15-fold greater than the influence of [1-octanethiol]. This would suggest that access to SVs is the limiting factor in this catalytic reaction. It is worth recalling that bulk 2H-MoS₂ mediated the oxidation of 1-octanethiol at a far inferior rate than the exfoliated 2H-MoS₂ (Figure S4). Furthermore, the rate of the oxidation reaction continued to increase at high [1-octanethiol] (thus was not inhibited), suggesting that the thiol does not block SV sites, and that the product of the reaction, either thiyl radical or disulfide, reacts further easily (*i.e.* through thiyl radical release or reaction with an incoming thiol molecule). Combined, these results suggest that SVs on the 2H-MoS₂ surface are the location at which thiol oxidation occurs. This oxidation is more likely to occur with high degree of SVs, thus in exfoliated materials.

In conclusion, in the presence of 2H-MoS₂ nanosheets, 1-octanethiol and other organic thiols, can be catalytically oxidized to dioctyl disulfide and other disulfides, respectively, even in the absence of dioxygen. The degree of exfoliation of the 2H-MoS₂ nanosheets played a significant role in the catalytic activity for 1-octanethiol oxidation, suggesting that edges or vacancies on 2H-MoS₂ nanosheets were likely the catalytically active sites. The dioctyl disulfide was postulated to be formed either via thiyl radical-radical coupling or intermolecular exchange between the free thiols and adsorbed thiolate species. Overall, our findings clearly demonstrate that organic thiols do not react with TMDs yielding covalently functionalized TMDs. Rather, in all

cases tested in our laboratory, they result in thiol oxidation to disulfide and chemically unchanged TMDs. We continue to urge caution with methods that employ organic thiols to chemically functionalize TMDs.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available free of charge on the ACS Publications website. The following are available: experimental details including sample preparation procedures, characterization and instrumentation, ¹H NMR and GC-MS spectra, and kinetic measurements and plots. (PDF)

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