

Functionalization of Two-Dimensional MoS₂: On the Reaction Between MoS₂ and Organic Thiols

Xin Chen,^{a,b} Nina C. Berner,^{a,b} Claudia Backes,^{a,c} Georg S. Duesberg,^{a,b} Aidan R. McDonald*^{a,b}

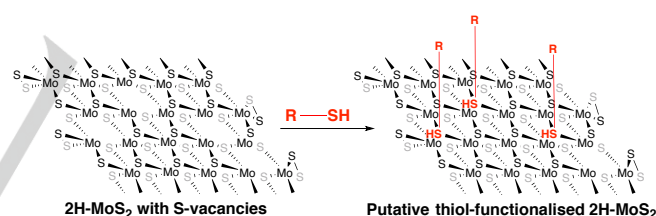
Abstract: Two-dimensional layered transition metal dichalcogenides (TMDs) have attracted great interest due to their unique properties and a wide array of potential applications. However, due to their inert nature, pristine TMDs are very challenging to functionalize. We demonstrate a general route to functionalize exfoliated 2H-MoS₂ with cysteine. Critically, MoS₂ was found to be facilitating the oxidation of the thiol cysteine to the disulfide cystine during functionalization. The resulting cystine was physisorbed on MoS₂ rather than coordinating as a thiol (cysteine) filling S-vacancies in the 2H-MoS₂ 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 MoS₂ using organic thiols does not yield covalently or datively tethered functionalities, rather it yields 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 due 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. A major focus of experimental research in recent years has concentrated on the development of synthetic routes to produce high-quality TMD nanosheets.^[12-17] However, as of yet, routes towards the efficient high-yield synthesis or exfoliation of TMDs are 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 (MoS₂) is a prototypical TMD and acts as an excellent model system to explore the chemistry of 2D TMDs. 2D MoS₂ is most often isolated as one of two polymorphs:^[15] in 2H-MoS₂ S-atoms coordinate to the Mo-atom in a trigonal planar fashion; whereas in 1T-MoS₂ the Mo-atom is octahedrally ligated. Importantly, thin layered 2H- and 1T-MoS₂ display different properties, 2H-MoS₂ is a semi-conductor (energy gap ~1.2 eV) and a photoluminophore,^[18-19] whereas 1T-MoS₂ is metallic and does not photoluminesce.^[3] The covalent functionalization of 1T-MoS₂ has recently been reported,^[20-21] employing an extremely harsh chemical exfoliation (ce) procedure. No well-characterized examples of covalent functionalization of 2H-MoS₂ have been reported to date. We recently reported the mild functionalization

of 2H-MoS₂ through ligation of surface S-atoms to coordination complexes,^[22] our efforts are now focused on exploring routes towards the covalent functionalization of 2H-MoS₂.

Recent reports have shown the functionalization of both ce-1T- and 2H-MoS₂ by reaction with organic thiols. In a seminal paper, Dravid and co-workers described the reaction between ce-1T-MoS₂ and organic thiols yielding functionalized ce-1T-MoS₂.^[23] This was described as 'ligand conjugation' to ce-1T-MoS₂ presumably meaning coordination of the thiol to Mo-atoms at S-vacancies (a dative Mo-S bond formed). Later work has demonstrated further applications of this technique.^[24-32] Unfortunately, in all of these reports, there remains little to no insight into the thiol ligand/MoS₂ interaction. At the inception of this work, we too postulated that 2H-MoS₂ could be functionalized using organic thiols by coordination of the thiol group to Mo-atoms at S-atom vacancies (Scheme 1). Herein, we present the one-step surface functionalization of 2H-MoS₂ nanosheets with an organic thiol (cysteine), resulting in functionalized 2H-MoS₂. We explore in detail the thiol/MoS₂ interaction and show that organic thiols may actually be physisorbed on MoS₂ as disulfides, rather than undergoing any bond-forming process with the MoS₂.



Scheme 1. Postulated method to functionalize 2D 2H-MoS₂ at sulfur vacancies.

As we reported previously,^[22] in the functionalization of 2H-MoS₂ it was necessary to disperse few-layer thick 2H-MoS₂ in 2-propanol (IPA), and not the standard (toxic) dispersion/exfoliating solvents N-Methyl-2-pyrrolidone (NMP) or N-Cyclohexyl-2-pyrrolidone (CHP).^[3, 12] The IPA dispersions of 2H-MoS₂ displayed mean lateral dimension <L> of ~260 nm and degree of exfoliation <N> of 9-10 layers. The IPA-exfoliated 2H-MoS₂ was thus an ideal 2D TMD for functionalization studies.

2H-MoS₂ normally displays S:Mo ratios of approximately 1.8:1 (± 0.2) as suggested by X-ray photoelectron spectroscopy (XPS).^[22, 33] Transmission electron microscopy (TEM) analysis corroborates this, showing that basal-plane S-vacancies are common.^[29, 34-35] We postulated that thiol-containing organic molecules could fill these sulfur vacancies (Scheme 1). To test this postulate we reacted liquid exfoliated 2H-MoS₂ with a thiol-containing organic molecule, cysteine. Cysteine was chosen because it is bio-relevant, commercially available, and contains

[a] X. Chen, Dr. N. C. Berner, Dr. C. Backes, Prof. Dr. G. S. Duesberg, Dr. A. R. McDonald
CRANN/AMBER Nanoscience Institute
Trinity College Dublin, The University of Dublin
College Green, Dublin 2 (Ireland)
E-mail: aidan.mcdonald@tcd.ie

[b] School of Chemistry
[c] School of Physics

functional groups (carboxylate and amine) that would allow for simple characterization and also further derivatization. 2H-MoS₂ nanosheets (0.5 g/L) dispersed in IPA (20 mL) were reacted with the hydrochloride salt of L-cysteine dissolved in IPA (20 g/L, 10 mL) by combining the dispersion and solution and performing tip ultra-sonication on the mixture for 0.5 h at room temperature (see supporting information for full experimental details). Following the ultra-sonication, the resulting dispersion was subjected to high-speed centrifugation to precipitate all dispersed materials. The resulting sediment was subsequently exhaustively washed with aqueous solutions, and then re-dispersed in IPA (10 mL) for further characterization.

The cysteine-functionalized re-dispersed 2H-MoS₂ (Cys-2H-MoS₂) displayed a markedly different dispersability in IPA compared to pristine 2H-MoS₂. The electronic extinction spectrum of Cys-2H-MoS₂ displayed very high degrees of nanosheet aggregation as evidenced by the rather large baseline shift when comparing pristine 2H-MoS₂ to Cys-2H-MoS₂ (Figure 1(a)).^[36] This difference was noticeable to the human eye - Cys-2H-MoS₂ flocculated (formed clumpy materials) readily in IPA, whereas dispersions of pristine 2H-MoS₂ did not. Furthermore, Cys-2H-MoS₂ yielded dispersions that were black in color, whereas pristine 2H-MoS₂ dispersions tended to be yellowish-greenish (Figure 1(b)). These observations are a clear indication that the surface properties in the Cys-2H-MoS₂ had been altered dramatically compared to pristine 2H-MoS₂.

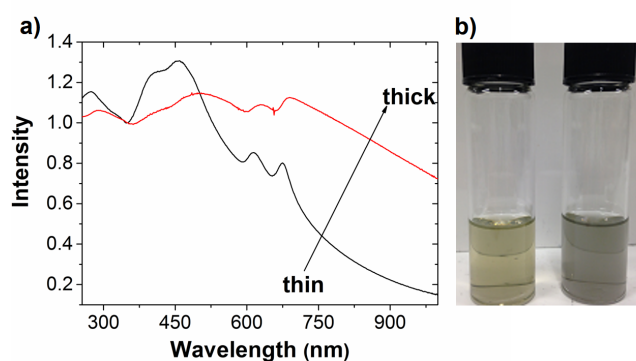


Figure 1. a) UV-Vis extinction spectra of 2H-MoS₂ (black trace) and Cys-2H-MoS₂ (red trace) in IPA normalized to the local minimum at ~350 nm. b) Color photograph of diluted dispersions of 2H-MoS₂ (left) and Cys-2H-MoS₂ (right) in IPA.

Importantly, functionalization appeared to have caused minimal changes to the relative intensities or energies of excitonic transitions attributed to exfoliated 2H-MoS₂ (Figure 1(a)). The transitions at $\lambda_{\text{max}} = 459, 614$ and 675 nm are typical of 2H-MoS₂. Cys-2H-MoS₂ displayed a similar set of features ($\lambda_{\text{max}} = 496, 629$ and 689 nm), displaying a small degree of red-shifting compared to the parent pristine 2H-MoS₂, which we postulate is as a result of the rather large baseline shift caused by flocculation. These observations are very important, because they establish that functionalization yielded a slightly modified 2H-MoS₂ and, critically, did not yield the 1T-polytype (1T-MoS₂ has an extinction spectrum very distinct from 2H-MoS₂).^[18] Most other covalent functionalization techniques to date have yielded 1T-MoS₂.

Comparison of the diffuse reflectance infrared Fourier transform (DRIFT) spectra of 2H-MoS₂ and Cys-2H-MoS₂ demonstrated a sharp feature at 384 cm⁻¹ that is typical of 2H-MoS₂ (Figure 2),^[37] indicating that the functionalization had not affected the vibrational properties or overall morphology in the Cys-2H-MoS₂. Importantly, the DRIFT spectrum for Cys-2H-MoS₂ 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-MoS₂ showed that the vibrational properties of the cysteine on the 2H-MoS₂ surface have been altered considerably through reaction with 2H-MoS₂. Firstly, in cysteine a feature at 2532 cm⁻¹ attributed to the $\nu_{\text{S-H}}$ was observed.^[38] This feature was absent in Cys-2H-MoS₂, and there were no new features in this region of the DRIFT spectrum. This would suggest that the thiol group of cysteine has reacted in the presence of 2H-MoS₂. All previous reports on the reaction between organic thiols and MoS₂ showed a similar loss of the $\nu_{\text{S-H}}$ by infra-red spectroscopy, leading to the conclusion that the thiol had reacted with the MoS₂.^[24-32] Secondly, cysteine displayed broad features at 1745 cm⁻¹ and 1377 cm⁻¹ corresponding to stretches of its carboxylate group.^[38] In Cys-2H-MoS₂ 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-MoS₂. In all, the DRIFT spectrum of Cys-2H-MoS₂ indicates that cysteine is coupled to the surface of the 2H-MoS₂. However, the clear and dramatic changes to the vibrational properties of the cysteine suggest that the cysteine had been chemically altered.

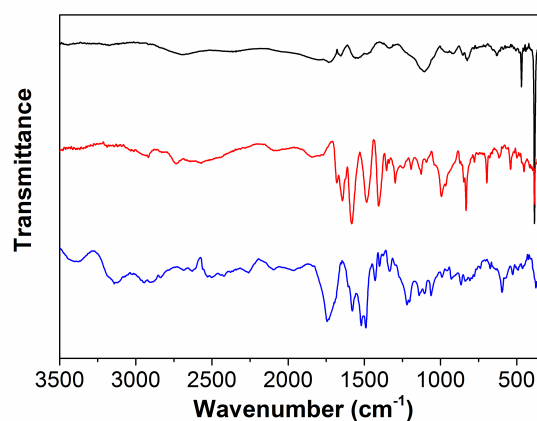


Figure 2. DRIFT spectra of pristine 2H-MoS₂ (black trace), cysteine (blue trace) and Cys-2H-MoS₂ (red trace).

Raman spectroscopy also indicated that the reaction between cysteine and 2H-MoS₂ yielded a slightly altered 2H-MoS₂ surface. Minor changes to the relative intensities of resonantly enhanced features in the Raman spectrum (Figures S1, S2) of Cys-2H-MoS₂ indicate organic functionalities were interacting with the 2H-MoS₂ surface.^[33, 35, 39-40]

To examine the atomic-level 2H-MoS₂/cysteine interaction in Cys-2H-MoS₂, high-resolution X-ray photoelectron spectroscopy (XPS) analysis was performed. Firstly, we observed that the Cys-2H-MoS₂ nanosheets preserved the semiconducting 2H polymorph after functionalization, and are not the 1T polymorph.^[20, 23, 41] The XPS spectrum of cysteine (Figure 3(b))

exhibited a single doublet of S 2p peaks with the S 2p_{3/2} binding energy at 163.5 eV. In contrast, peak fitting of the S 2p spectrum of Cys-2H-MoS₂ results 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-MoS₂. The other smaller doublet with S 2p_{3/2} binding energy at 163.3 eV can be 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 suggests ~30% loading of cysteine in Cys-2H-MoS₂.

Critically, the binding energy of the surface S-atoms in 2H-MoS₂ was not affected by the presence of a functional group on the nanosheet surface.^[42] The S 2p XPS data was best fit with only two S-atom components - a cysteine-like component and a 2H-MoS₂ component. Furthermore, the Mo 3d XPS spectra displayed no differences between 2H-MoS₂ and Cys-2H-MoS₂, showing that the electronic environment around the Mo-atoms in Cys-2H-MoS₂ had not been altered upon functionalization. Previous reports showed that changes in the S 2p region of the XPS spectra of functionalized ce-1T-MoS₂ were indicative of the presence of functionality C- to MoS₂ S-bonds on the ce-1T-MoS₂ surface.^[20, 23] These observations suggest that chemical modification of the 2H-MoS₂ surface in Cys-2H-MoS₂ was unlikely to have occurred, while a chemical modification of cysteine had occurred.

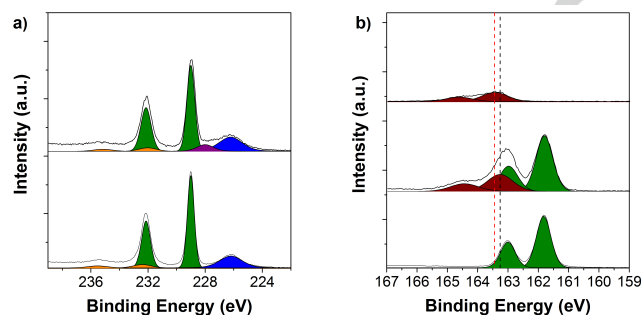


Figure 3. Fitted XPS spectra. a) Mo 3d core level spectra of Cys-2H-MoS₂ (top), and pristine 2H-MoS₂ (bottom). Fit components are attributed to 2H-MoS₂ (green), MoO₃ (orange), S 2s (blue) and cysteine-like entities (purple) in both cases. b) S 2p core level spectra of cysteine salt (top), Cys-2H-MoS₂ (middle), and pristine 2H-MoS₂ (bottom). Fit components are attributed to 2H-MoS₂ (green), and cysteine-like entities (red).

TGA of Cys-2H-MoS₂ revealed a clear stepwise degradation (Figure S3). Pristine 2H-MoS₂ did not display any degradation below 500 °C. In Cys-2H-MoS₂, an approximately 30% weight loss took place between 215–265 °C. The thermal decomposition temperature of cysteine is from 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-MoS₂ surface. According to TGA-coupled infra-red (TGA-IR) spectroscopy, the major gaseous product evolved from Cys-2H-MoS₂ was identified as CO₂ (Figure S4, 2349 cm⁻¹) which presumably derives from the decomposition of cysteine. TGA

thus indicates that an organic functionality, very similar to cysteine, is tethered to 2H-MoS₂ in Cys-2H-MoS₂.

Having thoroughly characterized Cys-2H-MoS₂ we then probed the effect of the cysteine functionalities on the dispersability of the 2H-MoS₂. We found that Cys-2H-MoS₂ was readily re-dispersed in water (Figure S5). Pristine 2H-MoS₂ did not disperse in water (Figure S5), and few methods to effectively disperse 2H-MoS₂ in water by functionalization exist.^[27, 43] Importantly, the aqueous Cys-2H-MoS₂ 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 2H-MoS₂ (Figure S6). We previously identified methods to enhance TMD dispersability in acetone,^[22] but the present water dispersion results are very important, potentially eliminating the use of organic solvents altogether.

We performed a number of experiments to verify further the nature of the interaction between 2H-MoS₂ and cysteine. As earlier stated, XPS indicated that no change to the MoS₂ S- or Mo-atoms in Cys-2H-MoS₂ had occurred, with a very minor change to the surface cysteine. These observations indicate that the functionalization in Cys-2H-MoS₂ was not covalent and also suggested that cysteine S-atoms were not filling S-atom vacancies. However, the surface properties of the 2H-MoS₂ in Cys-2H-MoS₂ 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-MoS₂, however, these analyses provided no evidence for covalent or dative bonding formation between the 2H-MoS₂ and functionality. Finally, the DRIFT measurements suggested a chemical change to the cysteine molecules on the surface, while the 2H-MoS₂ remained in a pristine state.

In order to probe the surface functional groups further, we removed them from the surface (de-functionalization). De-functionalization was achieved by firstly dispersing the Cys-2H-MoS₂ in IPA and subsequently centrifuging this dispersion and decanting the IPA (repeated numerous times). Secondly, after the multiple 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 ¹H NMR, while the resulting 2H-MoS₂ was subjected to XPS. The ¹H NMR spectrum (Figure S7) showed the obtained product 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-MoS₂. XPS analysis of the post-dialysis 2H-MoS₂ showed that the de-functionalized nano-material was *pristine* 2H-MoS₂ (Figure S8, no organic S-features, confirming complete de-functionalization). As postulated, these observations confirm that the reaction between the organic thiol and 2H-MoS₂ caused the thiol to be converted to a new entity, but the 2H-MoS₂ was chemically unchanged.

We then compared the DRIFT spectrum of Cys-2H-MoS₂ 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 (ν_{S-S} = 540 cm⁻¹)^[44] demonstrating that in fact cystine (and not cysteine) was docked on the surface in

Cys-2H-MoS₂. The lack of a chemical change to the 2H-MoS₂ in Cys-2H-MoS₂ and ease at which the cystine was defunctionalized from the surface, would suggest that cystine was simply physisorbed to the 2H-MoS₂ surface.

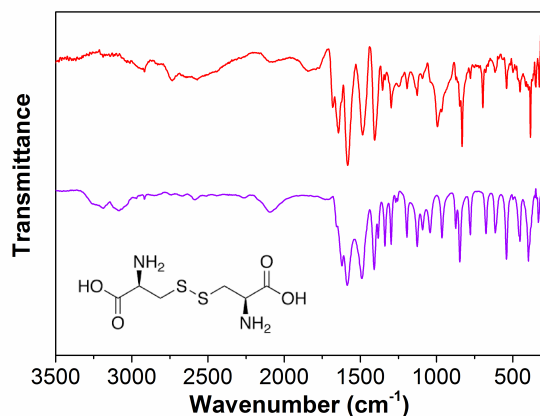


Figure 4. DRIFT spectra of Cys-2H-MoS₂ (red trace) and cystine (purple trace).

We were intrigued by the 2H-MoS₂ facilitated oxidation of cysteine to cystine yielding 'functionalization' through physisorption of cystine. Earlier work demonstrated the functionalization of ce-1T-MoS₂ through 'ligand conjugation'.^[23] We explored the reaction of cysteine with ce-1T-MoS₂ (following the 'ligand conjugation' methods) and obtained DRIFT spectra that showed cystine was tethered to the surface of ce-1T-MoS₂ (Figure S9), rather than cysteine. Thus in both 2H- and 1T-polymorphs of MoS₂, their reaction with cysteine yields cystine-functionalized MoS₂. We then performed the reaction between cysteine and 2H-MoS₂ under an inert atmosphere (N₂, thus in the absence of air (an oxidant)). Under these inert conditions, we obtained the same Cys-2H-MoS₂, containing the disulfide product cystine, as evidenced by DRIFT spectroscopy (Figure S10). This demonstrated that dioxygen was not facilitating the oxidation of cysteine to cystine, and that MoS₂ is likely the mediator of this transformation. In order to explore if oxidation was caused by the functionalization methods, we sonicated a solution of cysteine in IPA in the absence of MoS₂ (thus under the functionalization conditions). The ¹H-NMR spectrum (Figure S11) 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-WS₂ yielded similar results to 2H-MoS₂ (thus Cys-2H-WS₂, with cystine functionalities, Figure S13).

We also attempted the functionalization of liquid exfoliated 2H-MoS₂ with another commercially available thiol (1-octanethiol) and identified oxidized disulfide products. The DRIFT spectrum of the 1-octanethiol/2H-MoS₂ product showed a characteristic S-S vibrational peak at $\nu_{S-S} = 540 \text{ cm}^{-1}$ (Figure S12(a)) suggesting the formation of the disulfide H₁₇C₈-S-S-C₈H₁₇. Furthermore, the observation of $\nu_{C-S} = 615 \text{ cm}^{-1}$, as observed previously for dioctyl-disulfide functionalized nanoparticles,^[45] provided a very strong indication of disulfide formation when 1-octanethiol reacted with 2H-MoS₂. Furthermore, GC-MS analysis of the 2H-

MoS₂/1-octanethiol reaction mixture showed the presence of the disulfide product (C₁₆H₃₄S₂, Figure S12(b)). It thus appears that TMDs facilitate the oxidation of organic thiols to disulfides (Scheme 2). The formed disulfides appear to have physisorbed on the 2D TMD surface presumably through electrostatic interactions.



Scheme 2. MoS₂-mediated conversion of organic thiol to disulfide.

In conclusion, we have demonstrated a general route for the functionalization of 2H-MoS₂ nanosheets with cysteine. Functionalization was achieved by blending a dispersion of liquid exfoliated 2H-MoS₂ with a solution of cysteine. The resulting Cys-2H-MoS₂ was fully characterized by UV-Vis, DRIFT, XPS, TGA, and Raman. We discovered that MoS₂ was facilitating the oxidation of cysteine to cystine during functionalization. Rather than coordinating as a thiol (cysteine) at S-vacancies in the 2H-MoS₂, 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-MoS₂.

Acknowledgements

This publication has emanated from research supported in part by the European Union (FP7-333948, AMcD) and a research grant from Science Foundation Ireland (SFI/12/RC/2278). CB acknowledges the German research foundation DFG (BA 4856/1-1). GSD acknowledges SFI (PI_10/IN.1/I3030).

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

References

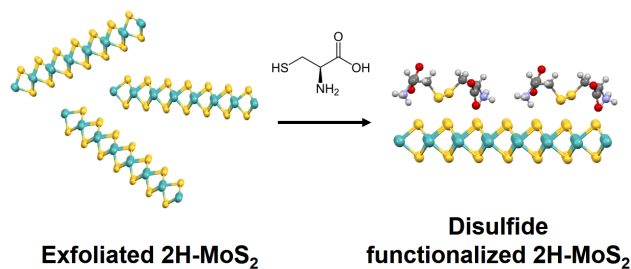
- [1] H. Zhang, K. P. Loh, C. H. Sow, H. Gu, X. Su, C. Huang, Z. K. Chen, *Langmuir* **2004**, *20*, 6914-6920.
- [2] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nat. Nano.* **2011**, *6*, 147-150.
- [3] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, M. Chhowalla, *Nano Lett.* **2011**, *11*, 5111-5116.
- [4] Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai, *J. Am. Chem. Soc.* **2011**, *133*, 7296-7299.
- [5] K.-K. Liu, W. Zhang, Y.-H. Lee, Y.-C. Lin, M.-T. Chang, C.-Y. Su, C.-S. Chang, H. Li, Y. Shi, H. Zhang, C.-S. Lai, L.-J. Li, *Nano Lett.* **2012**, *12*, 1538-1544.
- [6] T. Cao, G. Wang, W. Han, H. Ye, C. Zhu, J. Shi, Q. Niu, P. Tan, E. Wang, B. Liu, J. Feng, *Nat. Comm.* **2012**, *3*, 887.
- [7] K. F. Mak, K. He, J. Shan, T. F. Heinz, *Nat. Nano.* **2012**, *7*, 494-498.
- [8] H. Zeng, J. Dai, W. Yao, D. Xiao, X. Cui, *Nat. Nano.* **2012**, *7*, 490-493.
- [9] H. J. Conley, B. Wang, J. I. Ziegler, R. F. Haglund, S. T. Pantelides, K. I. Bolotin, *Nano Lett.* **2013**, *13*, 3626-3630.
- [10] K. Lee, R. Gatensby, N. McEvoy, T. Hallam, G. S. Duesberg, *Adv. Mater.* **2013**, *25*, 6699-6702.

- [11] V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano, J. N. Coleman, *Science* **2013**, *340*, 1420.
- [12] J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grieveson, K. Theuvsen, D. W. McComb, P. D. Nellist, V. Nicolosi, *Science* **2011**, *331*, 568-571.
- [13] H. Li, Z. Yin, Q. He, H. Li, X. Huang, G. Lu, D. W. H. Fam, A. I. Y. Tok, Q. Zhang, H. Zhang, *Small* **2012**, *8*, 63-67.
- [14] Y. Zhan, Z. Liu, S. Najmaei, P. M. Ajayan, J. Lou, *Small* **2012**, *8*, 966-971.
- [15] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, H. Zhang, *Nat. Chem.* **2013**, *5*, 263-275.
- [16] M. O'Brien, N. McEvoy, T. Hallam, H.-Y. Kim, N. C. Berner, D. Hanlon, K. Lee, J. N. Coleman, G. S. Duesberg, *Sci. Rep.* **2014**, *4*, 7374.
- [17] C. Yim, M. O'Brien, N. McEvoy, S. Riazimehr, H. Schäfer-Eberwein, A. Bablich, R. Pawar, G. Iannaccone, C. Downing, G. Fiori, M. C. Lemme, G. S. Duesberg, *Sci. Rep.* **2014**, *4*, 5458.
- [18] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Gallii, F. Wang, *Nano Lett.* **2010**, *10*, 1271-1275.
- [19] K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, *Phys. Rev. Lett.* **2010**, *105*, 136805.
- [20] K. C. Knirsch, N. C. Berner, H. C. Nerl, C. S. Cucinotta, Z. Gholamvand, N. McEvoy, Z. Wang, I. Abramovic, P. Vecera, M. Halik, S. Sanvito, G. S. Duesberg, V. Nicolosi, F. Hauke, A. Hirsch, J. N. Coleman, C. Backes, *ACS Nano* **2015**, *9*, 6018-6030.
- [21] D. Voiry, A. Goswami, R. Kappera, C. d. C. C. e. Silva, D. Kaplan, T. Fujita, M. Chen, T. Asefa, M. Chhowalla, *Nat. Chem.* **2015**, *7*, 45-49.
- [22] C. Backes, N. C. Berner, X. Chen, P. Lafargue, P. LaPlace, M. Freeley, G. S. Duesberg, J. N. Coleman, A. R. McDonald, *Angew. Chem. Int. Ed.* **2015**, *54*, 2638-2642.
- [23] S. S. Chou, M. De, J. Kim, S. Byun, C. Dykstra, J. Yu, J. Huang, V. P. Dravid, *J. Am. Chem. Soc.* **2013**, *135*, 4584-4587.
- [24] M. Makarova, Y. Okawa, M. Aono, *J. Phys. Chem. C* **2012**, *116*, 22411-22416.
- [25] S.-D. Jiang, G. Tang, Z.-M. Bai, Y.-Y. Wang, Y. Hu, L. Song, *RSC Adv.* **2014**, *4*, 3253-3262.
- [26] L. Zhou, B. He, Y. Yang, Y. He, *RSC Adv.* **2014**, *4*, 32570-32578.
- [27] R. Anbazhagan, H.-J. Wang, H.-C. Tsai, R.-J. Jeng, *RSC Adv.* **2014**, *4*, 42936-42941.
- [28] J.-S. Kim, H.-W. Yoo, H. O. Choi, H.-T. Jung, *Nano Lett.* **2014**, *14*, 5941-5947.
- [29] Z. Yu, Y. Pan, Y. Shen, Z. Wang, Z.-Y. Ong, T. Xu, R. Xin, L. Pan, B. Wang, L. Sun, J. Wang, G. Zhang, Y. W. Zhang, Y. Shi, X. Wang, *Nat. Commun.* **2014**, *5*, 5290.
- [30] T. Liu, S. Shi, C. Liang, S. Shen, L. Cheng, C. Wang, X. Song, S. Goel, T. E. Barnhart, W. Cai, Z. Liu, *ACS Nano* **2015**, *9*, 950-960.
- [31] E. P. Nguyen, B. J. Carey, J. Z. Ou, J. van Embden, E. D. Gaspera, A. F. Chrimes, M. J. S. Spencer, S. Zhuikov, K. Kalantar-zadeh, T. Daeneke, *Adv. Mater.* **2015**, *27*, 6224-6229.
- [32] K. Cho, M. Min, T.-Y. Kim, H. Jeong, J. Pak, J.-K. Kim, J. Jang, S. J. Yun, Y. H. Lee, W.-K. Hong, T. Lee, *ACS Nano* **2015**, *9*, 8044-8053.
- [33] M. Donarelli, F. Bisti, F. Perrozzi, L. Ottaviano, *Chem. Phys. Lett.* **2013**, *588*, 198-202.
- [34] H. Qiu, T. Xu, Z. Wang, W. Ren, H. Nan, Z. Ni, Q. Chen, S. Yuan, F. Miao, F. Song, G. Long, Y. Shi, L. Sun, J. Wang, X. Wang, *Nat. Commun.* **2013**, *4*, 2642.
- [35] H.-P. Komsa, S. Kurasch, O. Lehtinen, U. Kaiser, A. V. Krasheninnikov, *Phys. Rev. B* **2013**, *88*, 035301.
- [36] C. Backes, R. J. Smith, N. McEvoy, N. C. Berner, D. McCloskey, H. C. Nerl, A. O'Neill, P. J. King, T. Higgins, D. Hanlon, N. Scheuschner, J. Maultzsch, L. Houben, G. S. Duesberg, J. F. Donegan, V. Nicolosi, J. N. Coleman, *Nat. Commun.* **2014**, *5*, 4576.
- [37] G. Berhault, L. Cota Araiza, A. Duarte Moller, A. Mehta, R. Chianelli, *Catal. Lett.* **2002**, *78*, 81-90.
- [38] A. Pawlukoć, J. Leciejewicz, A. J. Ramirez-Cuesta, J. Nowicka-Scheibe, *Spect. Chim. Acta A* **2005**, *61*, 2474-2481.
- [39] X. Zhang, X.-F. Qiao, W. Shi, J.-B. Wu, D.-S. Jiang, P.-H. Tan, *Chem. Soc. Rev.* **2015**, *44*, 2757-2785.
- [40] M. A. Pimenta, E. del Corro, B. R. Carvalho, C. Fantini, L. M. Malard, *Acc. Chem. Res.* **2015**, *48*, 41-47.
- [41] This is evident in features in the Mo 3d core level spectra identified at 229.0 and 232.1 eV for Mo 3d_{5/2} and Mo 3d_{3/2} respectively (Figure 3(a)). If it were 1T-MoS₂, features at 228.6 and 231.7 ± 0.15 eV would be expected, supporting our UV-vis observations.
- [42] A mild broadening of the S 2p component attributed to 2H-MoS₂ (161.8 eV) is not significant enough to suggest chemical modification.
- [43] W. Zhang, Y. Wang, D. Zhang, S. Yu, W. Zhu, J. Wang, F. Zheng, S. Wang, J. Wang, *Nanoscale* **2015**, *7*, 10210-10217.
- [44] E. J. Bastian, R. B. Martin, *J. Phys. Chem.* **1973**, *77*, 1129-1133.
- [45] B. S. Zelakiewicz, G. C. Lica, M. L. Deacon, Tong, *J. Am. Chem. Soc.* **2004**, *126*, 10053-10058.

Entry for the Table of Contents

COMMUNICATION

In the functionalization of 2D MoS₂ with organic thiols, thiols were oxidized to disulfides, rather than coordinating at S-vacancies in the MoS₂ surface, as originally conceived. The oxidation was facilitated by MoS₂, resulting in a high density of organic disulfides docked on the MoS₂ surface.



*Xin Chen, Nina C. Berner, Claudia Backes, Georg S. Duesberg, Aidan R. McDonald**

Page No. – Page No.

Functionalization of Two-Dimensional MoS₂: On the Reaction Between MoS₂ and Organic Thiols